THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN THE UNIVERSITY OF OXFORD

ABSTRACT

of

LEAD ISOTOPE AND AGE STUDIES OF URANIUM AND LEAD MINERALS FROM THE BRITISH ISLES AND FRANCE

by

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ABSTRACT

This thesis is concerned with investigations of two largely dissimilar problems, which are treated in separate Parts. In Part I, uranium-lead studies of five pitchblende specimens from four localities in Cornwall are described.

Chemical analysis for uranium in the pitchblendes was effected by chromatographic separation on a cellulose column, followed by gravimetric finish as the oxide. For lead, a dithizone separation was used, followed by gravimetric finish as the sulphate. Dithizone-separated lead was precipitated as lead sulphide for mass spectrometric analysis.

The mass spectrometer used throughout this work was a Metropolitan-Vickers Type MS 5 instrument with 12 in. radius, 90° analyser tube, using volatilization of solid lead sulphide from a heated tungsten triple filament as ion source. The isotopic measurements of Moorbath of seven galenas from S. W. England were used to correct for the presence of common lead which was relatively high in all specimens.

The 206/238 and 207/235 ages obtained are concordant within experimental errors for all specimens (207/206 ages are unreliable in this age range). The 206/238 ages are considered the most significant, and these fall into three groups of values - 225 m.y., 124 m.y., 60 m.y. - which are markedly different from the only other concordant U/Pb age of 290 m.y. reported for Cornwall, and from the mean K/Ar and Rb/Sr age of 280 m.y. determined for the Dartmoor granite.

X-ray powder diffraction photos were taken of all pitchblende specimens analysed for age determination. Calculation of cell sizes show that these decrease with decreasing age. Decreasing cell sizes are due to increasing

degrees of oxidation of uranium in the pitchblendes. Autoradiograph and polished section studies show that recent weathering has not affected the specimens, that radon loss is unlikely, and that uranium is present as coffinite as well as pitchblende in all specimens.

A unique interpretation of the data cannot yet be made. The following main possibilities are discussed in detail:-

(a) The ages represent periods of primary mineralisation.

(b) Lead loss has made the ages apparently low.

(c) The specimens have all been mineralised at the same period, but have been remobilised at one or more later periods.

The third hypothesis is considered the most likely. The observation of an abnormal radiogenic component in a galena specimen from the same deposit as a pitchblende specimen would be good evidence for remobilisation. However, galena from the South Terras lode has normal isotopic composition. No other galena from the same deposit as a pitchblende specimen studied was available for isotopic analysis.

The following conclusions are consistent with the evidence available, but are necessarily tentative:-

(1) The 60 m.y. age represents a period of local remobilisation of pitchblendes - and possibly also of other hydrothermal minerals - in Cornwall in early Tertiary times.

(2) The 124 m.y. age may represent a similar period of remobilisation in early Cretaceous times.

(3) The 225 m.y. age may represent a primary mineralisation.

(4) Alternatively, only a 60 m.y. event may have occurred, which partially reduced the ages of original 225 m.y. or 280 m.y. old pitchblende to give intermediate values.

Many more pitchblende specimens must be studied by all the techniques applied in this work before these problems can be conclusively solved.

In Part II, the results of isotope analyses of 74 galena specimens (63 from Ireland and 11 from France) are reported. Each specimen was analysed at least twice. The agreement generally obtained between replicate results indicates that the precision of the percentage Pb^{204} figures quoted is within 0.4%, and of the percentage Pb^{206}, Pb^{207}, and Pb^{208} figures is within 0.2%. The isotopic analysis of two inter-laboratory lead reference samples gave close agreement with other results obtained using the solid source volatilization technique; agreement was not so close with results obtained using gas sources.

Lead sulphide precipitates were chemically prepared from all galena specimens for use as samples for isotopic analysis. An alternative sample form for isotopic analysis of fine crushed galena, separated on the micro-panner from contaminating minerals in the specimen, was also found to be most satisfactory.

The digital computer was applied throughout this work to:-

(i) the correction for non-linearity in the recorder of the mass spectrometer.

(ii) the calculation of lead isotope and model parameter results from the raw data of each mass spectrometer run.

(iii) the calculation of tables for solving the Holmes-Houtermans equation accurately; copies of these tables are included inside the back cover.

(iv) the calculation of lead model ages and geochemical ratios from lead isotope ratios and abundances.

Copies of these programmes and specimen series of data and results are included at the end of this thesis.

Moorbath's isotope data for 17 galenas from Ireland have also been

included, so that all the 80 galenas, which have been isotopically analysed from Ireland so far, are discussed in this thesis. The Holmes-Houtermans model was used for the interpretation of all the lead isotope data. Lead model ages are very sensitive to small changes in the physical constants and parameters used in their calculation. The exact effect involved is shown by some sample calculations.

The models of Russell and associates were found to be inapplicable for the interpretation of these lead isotope data from Ireland and France.

The Irish galenas have yielded results broadly similar to those found by Moorbath for galenas from England, Scotland and Wales. Four anomalously old galenas have been definitely identified, all from near Oughterard, Co. Galway. In addition, four Irish galenas with anomalously young (negative) model ages have been measured, the first of this type recognized in the British Isles. These latter specimens come from isolated lead occurrences at Knockybrin, Co. Donegal, Tankardstown, Co. Waterford and Slieve Binian, Co. Down. The major lead mineralisation in Ireland occurred from Ordovician to Triassic times, the most frequent mineralisation occurring between the Devonian and the Permian. Individual deposits and areas are discussed in detail.

The model ages of the eleven galenas from Bretagne and Normandie, France, also range from Ordovician to Triassic values, although the few data available render these limits tentative only. A critical assessment is made of the only other isotopic measurements reported for galenas from France.

Moorbath's definition of 'periods' of lead mineralisation for the British Isles has been re-examined from the distributions of the combined data of Moorbath and the author (83 galenas from England, Scotland and Wales, and 80 galenas from Ireland). It is concluded that 'periods' of mineralisation should

now be defined less precisely than by Moorbath. Successive groups of model ages cannot be distinguished positively unless they are at least 80 m.y. apart.

The geochemical ratios U^{238}/Pb^{204} and Th^{232}/U^{238} are found to exhibit significant small regional variations in Ireland, the values for both these ratios being somewhat higher in the East and South-East than in the rest of the island. The values of these geochemical ratios for the French galenas are remarkably constant despite the wide variations in their geographical and geological settings and in their model ages.

One of the Appendices comprises a report of a preliminary trace element investigation into the silver, thallium and gold contents of some British galenas by neutron activation analysis. Four galenas from each of the Northern and Southern Pennines mineralised areas were analysed. The thallium content of all galenas is close to 1 p.p.m.. The four Northern Pennines galenas have a higher silver content than the four Southern Pennines galenas.

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PART I

URANIUM-LEAD AGES OF PITCHBLENDES FROM CORNWALL

C H A P T E R I

INTRODUCTION

1. (1) REVIEW OF THE URANIUM-THORIUM-LEAD AGE METHOD.

The radioactive decay of uranium and thorium to lead was used for the first estimations of the absolute age of uranium minerals by Boltwood (1907). The applicability and accuracy of this chemical method were limited until Nier (1938, 1939, 1941) developed mass spectrographic methods for the accurate determination of the isotopic composition of lead.

Lead consists of four isotopes of masses 204, 207 and 208. All except the first are the end products (daughters) of a specific parent isotope after a long series of disintegration processes, for which the overall equations are:-

$$U^{238} \longrightarrow Pb^{206} + 8\alpha$$

$$U^{235} \longrightarrow Pb^{207} + 7\alpha$$

$$Th^{232} \longrightarrow Pb^{208} + 6\alpha$$

Each decay chain possesses a known overall rate of decay. By measurement of each parent and daughter isotope present in a sample, ages can be calculated from the daughter:parent ratios, Pb^{206}/U^{238}, Pb^{207}/U^{235} and Pb^{208}/Th^{232}. The ratio Pb^{206}/Pb^{207} is also sensitive to time owing to the different half-lives of the uranium parent isotopes - ($U^{238} = 4.51 \times 10^9$ yr., $U^{235} = 7.13 \times 10^8$ yr.; also $Th^{232} = 1.42 \times 10^{10}$ yr.)

The calculation of all four ages requires a chemical analysis to obtain weight percentage of total uranium, thorium and lead. Isotope weights of lead are obtained from the isotope abundances determined by mass spectrometry. Uranium need not be isotopically analysed as the present-day

ratio of its two isotopes U^{238}/U^{235} is accurately known (137.7). Thorium does not require isotope analysis as it consists of Th^{232} only.

Most uranium and thorium minerals have crystallised with some ordinary (or "common") lead in their lattice structures. In these cases, the total lead measured chemically represents radiogenic lead plus common lead. The amount of common lead can be accurately estimated by also measuring the isotope abundances of a uranium-free lead mineral, such as galena, which exists in association with the uranium mineral. This amount is given by the proportion of the non-radiogenic isotope Pb^{204} present in the uranium mineral, relative to that in the lead mineral.

For uranium and thorium minerals, wet methods of chemical analysis are the most satisfactory. When the three or four different isotopic ages for a single sample agree within their experimental errors, the age of mineralisation of the sample can be confidently defined. But such agreement is infrequent, in spite of the greatly increased accuracy and sensitivity of analytical methods in recent years. This remains a major problem with the U-Th-Pb method.

Although the isotopic ages are frequently in disagreement, they generally exhibit one of two distributions. The more common distribution (for convenience dubbed here the "majority distribution") is -

$$\frac{207}{206}\,(\text{age}) > \frac{207}{235} > \frac{206}{238} \quad \left(> \frac{208}{232}\right)$$

The less common distribution (the "minority distribution") is -

$$\frac{206}{238} > \frac{207}{235} > \frac{207}{206}$$

$\frac{208}{232}$ ages have not been determined for many samples because of low thorium

contents, and so cannot yet be considered in detail.

Various processes have been studied as the causes of these internal disagreements. Gain or loss of parent or daughter isotope in the mineral are the general processes involved. Thus, Wickman (1942) suggested that some gaseous members of the decay chains of uranium and thorium may be lost by diffusion out of the mineral. Of the several components of emanation from uranium-thorium minerals, only Rn^{222} (in the U^{238} decay chain) has a half-life sufficiently long (3.825 days) to allow any gaseous diffusion out of the mineral before complete decay has occurred to the next (solid) member of the chain. This suggestion was studied by Kulp and associates (Kulp et al., 1953; Giletti and Kulp, 1955), who found that radon loss depended on mineral type. For example, pitchblendes showed radon loss varying from 0.064 to 16.6%, but uraninites from 0.58 to only 0.80%. These and other authors (e.g. Louw, 1955) recommended the 207/235 age as the most reliable, because that decay chain does not have Rn^{222} as an intermediate member. The 206/238 age would be decreased and the 207/206 age increased by radon loss. This would account for the majority distribution.

Holmes (1948) showed that loss of daughter isotopes, (i.e. the three radiogenic lead isotopes 206, 207, 208) would also lead to the majority distribution in the calculated ages. This process was suggested by Ahrens (1955 a, b) to explain the pattern of age distributions for specimens from Rhodesia. He concluded that for all except young specimens, for which experimental errors become greatly magnified (Kohman and Saito, 1954), the 207/206 age is the most reliable estimate. This opinion was shared by Kulp and Eckelmann (1955; also Eckelmann and Kulp, 1956) after an exhaustive

study of a suite of pitchblendes from the Lake Athabasca uranium province, Canada. Radon loss was insufficient to explain the age discrepancies observed. This was also found by Horne and Davidson (1955) for samples from Witwatersrand, South Africa.

The mechanism of such lead loss has been explained by two main processes. Ahrens (1955 a, b) argued from the highly ordered nature of the Rhodesian age pattern that lead deficiency was controlled by some physical process at a uniform rate ever since the minerals were formed. However, Wetherill favoured loss of lead by leaching or re-working of the minerals, i.e., controlled by chemical processes. Wetherill (1956 a) developed a graphical procedure for calculation of the effect of multiple episodes of U-Pb fractionation on calculated ages. Wetherill (1956 b) applied this to Ahrens' Rhodesian age data. He concluded that the latter's concept of "convergent age" had little meaning, and that chemical leaching or alteration at a single time could explain the observed ages.

Tilton (1956, Tilton and Nicolaysen, 1957) submitted powdered samples of monazites, zircons and uraninites, for which isotopic age determinations had been made, to mild acid washes. Correlations were found between the age distributions of the samples and the lead isotope compositions of the acid washes. These results, and the supporting work of Starik (1956), favour the chemical leaching hypothesis.

The largely theoretical investigations of Nicolaysen (1957) showed that diffusion of lead from the radioactive mineral in the solid state could also explain the observed age distribution. Russell and Ahrens (1957) showed a further regularity in the Rhodesian isotope data, rejected Wetherill's explanation, and suggested another possible physical process controlling lead

deficiency in the recoil of atoms following alpha-particle emission. This and solid diffusion are the sort of physical processes for which Ahrens was searching, but as yet little experimental evidence has been adduced to confirm these suggestions.

While the nature of the mechanism of lead loss remains doubtful(and it is quite likely that it is controlled by both chemical and physical processes), there is now fairly general agreement that it is the major cause of the majority age distribution. Nevertheless, although radon loss is not now generally considered to be a major cause of age discrepancies (e.g. Jacobs et al., 1959, p.182), it is still occasionally suggested. For example, Greenhalgh and Jeffery (1959) explained the age distributions obtained for a suite of sixteen Australian Precambrian uranium minerals by radon loss, although they did not experimentally determine radon loss from their samples.

The minority age distribution is found for about one in every four or five samples of uranium minerals analysed. It can be explained as being caused by relatively recent loss of uranium from the mineral (Holmes, 1948). This elevates the 206/238 age and also the 207/235 age to a lesser extent. The 207/206 age is insensitive to the loss (or gain) of uranium, and so should represent the age of mineralisation, provided this has not been so recent as to make this age inaccurate due to experimental error. Tilton and Nicolaysen (1957) have shown by acid washing experiments that, in two monazites which showed this age distribution, there were excessive solubilities of uranium relative to thorium and Pb^{206} relative to Pb^{208} in the acid washes. Ahrens (1955 c) suggested that incomplete precipitation of uranium in gravimetric analyses of samples with low uranium concentrations, would cause an apparent minority age distribution. However, this is not applicable where

analyses are reliable, or when instrumental techniques have been used. It is generally considered that loss of uranium has been caused by simple chemical leaching.

Kulp and Eckelmann (1957) summarised all U-Th-Pb age results to date and found that each mineral type appeared to possess a characteristic discordant age pattern. The main value of this work lies in the comparison of Th-Pb ages with U-Pb and Pb-Pb age distributions. The generalisations for such minerals as sphene, samarskite and euxenite were based on very few measurements.

Another cause of age discrepancy is the presence of original radiogenic lead in the uranium mineral on crystallisation. This has been suggested by Stern et al. (1960) to have caused the apparently high ages obtained from Carbon County, Pennsylvania. A graphical procedure, modified from Wetherill (1956 a), was applied to obtain the age of the mineralisation.

The difficulty of interpreting some discordant age data is shown in a study of some Colorado Plateau ores by Miller and Kulp (1958), in which all the following processes are considered necessary to account for the discrepancies:-

(a) local sources with high U/Th and U/Pb ratios;

(b) variable radon leakage;

(c) suitable ground-water movement;

(d) deposition at the site of H_2S production (in the vicinity of organic debris where sulphate-reducing bacteria were active) at low temperature.

Similar problems of interpretation are posed by the U-Pb ages obtained in the present study for pitchblendes from Cornwall. These ages provide the first concrete evidence to support the suggestion of Davidson (1960) that extensive remobilisation has affected Hercynian ore deposits in Europe.

1. (2) AIMS OF THIS STUDY.

This study was undertaken as an investigation of the age (or ages) of mineralisation in S. W. England, as part of the general study of calibrating the geological time-scale being made by the Geological Age and Isotope Research Group in this laboratory. At the start of this work there was considerable evidence for the extension of the geological time-scale, the last construction of which had been made by Holmes in 1947 - his "B" scale. The publication by Mayne, Lambert and York (1959) of extensions to the time-scale initiated much other work on this problem until Holmes (1960) and Kulp (1961) were able to construct acceptable revisions of Holmes' "B" scale. The significance of ages from S. W. England to this problem is outlined in Section 1. (3).

The only other isotopically controlled U-Th-Pb age determination to be reported for S. W. England prior to the present work was that of Darnley et al. (1960) on a uraninite from Geevor. The age obtained was a useful confirmation of the Permian-Carboniferous boundary on the time-scale, and it was originally hoped that this study might provide similar results. Samples were scarce, as uranium production from Cornish mines had long ceased, and this study was limited to the only five samples available (from four localities).

The results of this study have not fulfilled the original hopes with regard to the time-scale. But the discovery of ages younger than Hercynian have proved unexpectedly interesting in revealing a more complex pattern of mineralisation in S. W. England than previously understood.

The techniques of X-ray powder diffraction photography and ore microscopy were also applied to the samples, with the aims of obtaining further evidence to explain the age results.

1. (3) OTHER AGE MEASUREMENTS FROM S. W. ENGLAND.

S. W. England has been the subject of considerable geochronological study recently because of the particular importance of the age of the granitic intrusions for geological time-scale calibration. The connection at depth of the five major granite bosses (of which only the Dartmoor granite is out of the area of Figure 1), has been demonstrated by the gravity measurements of Bott et al. (1958). Also, the petrological and field relationships are similar for all the granites, indicating a common period of intrusion.

Stratigraphically, the Dartmoor granite was probably emplaced in the highest Carboniferous or early Permian times (Groves, 1931; Dewey, 1948; Butcher, 1961). Accordingly, the age of this granite has been taken as indicating the Carboniferous-Permian boundary (e.g. Lambert and Mills, 1961). Table I summarises all isotopic age determinations made to date on the Dartmoor and Land's End granites. Neglecting the total volume determinations of York, a mean age of 277$\pm$ 9 m.y. is obtained for the Dartmoor granite.

The data for the Land's End granite are too few to distinguish any real difference between the time of its crystallisation and that of the Dartmoor granite. The suggestion has been made (Long, 1961), that the K-Ar age of the Land's End granite is lower than its Rb-Sr age because of small loss of argon during a later re-heating. The possibility of this having occurred is, in fact, increased by the age data presented in this thesis. Age data are not yet available for the other granites of S. W. England.

The close connection between the zoned mineralisation in S. W. England and the intrusion of the granite has long been recognised (e.g. Dunham, 1952). Dines (1956) has identified "emanative centres" from which the mineralising

TABLE 1.

Age Measurements of Granites from S.W. England*

K-Ar Age (m.y.)		Source	Rb-Sr Age (m.y.)	Source
Dartmoor granite, Haytor Rocks, Dartmoor, Devon.				
279		(1)	267	(2)
263		(1)	284	(2)
271		(1)	279	(2)
288		(3)		
292		(3)		
280		(4)		
260	(t.v.)	(4)		
265	(t.v.)	(4)		

Average age from isotope dilution measurements: 277 ± 9 m.y.

Land's End granite, Botallack Cove, Land's End, Cornwall.

250		(1)	270	(5)
250		(4)		
255		(4)		

References

(1) Kulp et al. (1960) : Analyses at Lamont

(2) Kulp et al. (1960) : Analyses at Oxford

(3) Faul, quoted in Davidson (1960) : Analyses at U.S. Geol. Surv., Washington

(4) York (1960) : Analyses at Oxford

(5) Lambert and Mills (1961) : Analyses at Oxford

(Note - No.9437 should be at Botallack Cove, not at Lamorna Cove as marked in Figure 8 of this paper.)

(t.v.) - total volume measurement; all others by isotope dilution.

* This table taken from Long (1961) with kind permission.

fluids evolved from the still molten core of the granite. The mineralised zone marked in Figure 1 obliquely cuts across the fold structures and follows the underground ridges of granite defined by Bott et al. (1958). The primary mineralisation is thus younger than the intrusion but it is unlikely that the age difference would be great. This primary mineralisation occurred in lodes with a general E-W trend. Lodes with N-S trend, generally containing a lower temperature suite of minerals, post-date the E-W lodes, and have also caused some peripheral mineralisation along the latter.

The uraninite from Geevor whose U-Th-Pb ages were determined by Darnley et al. (1960) came from an E-W tin lode, two miles N. of, and in a similar geological setting to, the Owles mine from which comes pitchblende No. 3 of this thesis. The concordant age of 290 m.y. for the Geevor sample is 20 m.y. higher than the Rb-Sr age determination of the Land's End granite, but it is possible that the latter is a little lower than the actual age of the intrusion, and that experimental errors could account for the difference. Darnley and his associates have been investigating more uranium minerals from S. W. England but the results are not yet released.

The only other isotopic determinations made in S. W. England are those of Moorbath (1959 a, b) on seven galenas, which were used for the common lead corrections in this work. Holmes-Houtermann's model ages re-calculated from these isotope results by the author using the digital computer (see Table 37) give a mean model age of 270 m.y. (Moorbath's calculations give a mean of 280 m.y.), in good agreement with the age of the Dartmoor granite.

1. (4) GEOLOGICAL RELATIONS OF SAMPLES STUDIED.

In Appendix I are listed the geological data of the individual pitchblende samples studied in this work. Figure 1 shows the location of these samples

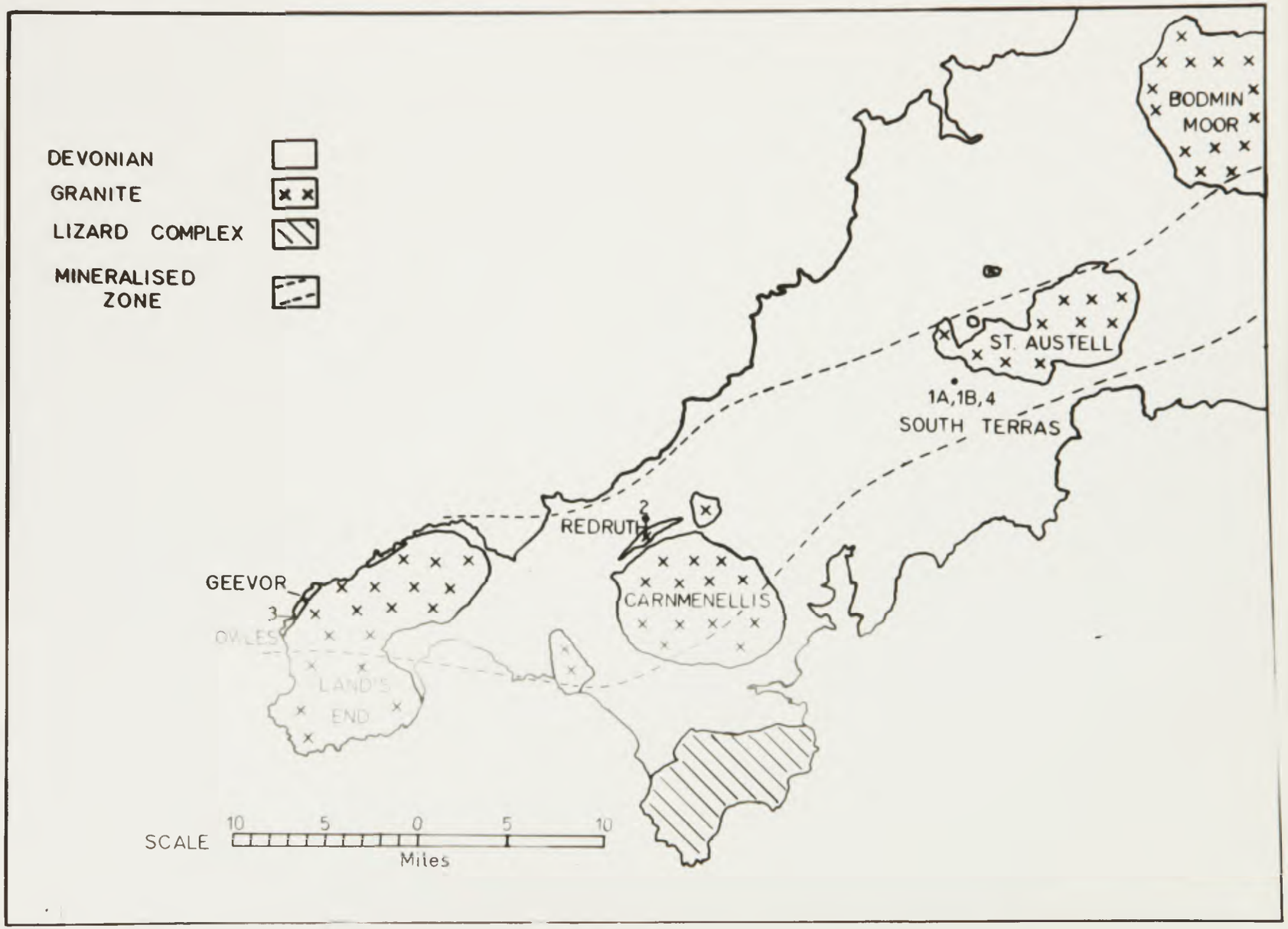


Figure 1: Map of Cornwall with Location of Pitchblende Specimens.

relative to the main granite bosses of Cornwall and to the Geevor uraninite.

Nos. 2 and 4 from the Redruth and South Terras Areas are not well localised, and so detailed local geological conclusions must not be based on their results. However, their origins are known sufficiently well for the general regional conclusions made here to be significant.

Nos. 1A and 1B definitely, and Nos. 2 and 4 probably, come from the later N-S "cross-courses". The samples from South Terras and Redruth come from mineralised areas closely associated with the St. Austell and Carn Brea granites respectively, for neither of which are absolute age measurements yet available. The age measurements of the Land's End granite to which the Owles sample is related are discussed in the previous Section.

There are some similarities between the occurrences of the Owles pitchblende and the Geevor uraninite. Both come from lodes trending N.W. through similar country rock. Both the Geevor and Owles mines produced tin, although it appears that the lode from which the Owles sample comes (Wheal Edward lode) was in a predominantly copper zone. (Dines, 1956, P.72; Davidson, 1956). The similarity ceases however, in a comparison of the specimens themselves. The Geevor uraninite is a concentrate from the tin ore; its occurrence was so sparse and fine-grained that its presence in a lode could generally be detected only with a rate-meter (Darnley, personal communication). However, the Owles pitchblende was a massive vein-stone.

The mineralisation in S. W. England has been reviewed thoroughly by Dines (1956), from which further details of these occurrences can be obtained. Davidson (1956) gives a very useful summary of the occurrence of uranium minerals in the area.

C H A P T E R 2

EXPERIMENTAL METHODS

2. (1) SAMPLE PREPARATION.

Specimens were broken with a hammer and selected pieces further reduced in a clean steel mortar to a suitable size (about 1-5 mm.). The cleanest and freshest pieces were selected after careful examination under a binocular microscope. The selected pieces were then ground to a fine powder in a motor-driven agate mortar, which was specially reserved for uranium minerals to avoid contamination. The mortar and pestle were cleaned very carefully between samples with hot water and "Zap", a mildly abrasive soap.

No further attempt was made to concentrate the samples with respect to pitchblende, for the hand picking process had removed most visible mineral impurities. However, with No. 3 from Owles it was not possible to avoid transferring to the powdered sample some of the contamination of the pitchblende by fine-grained inclusions of sulphides. (This sample was in fact supplied in powdered form, having already been prepared by Moorbath as described above.) In this case only it may have been worth attempting some physical method of separation of pitchblende - for example, the Frantz Magnetic Separator may have effected a partial separation of pitchblende from some of the coarser grained galena. The total contamination of this sample by other minerals was visually estimated to be ca. 1%. The polished section studies reported in Section 3. (6) showed this to be an underestimate.

2. (2) CHEMICAL ANALYSIS FOR URANIUM AND LEAD.

Samples were chemically analysed for uranium and lead, but not for thorium. Compared with uraninite, pitchblendes generally have low concentrations of thorium, (Dana, 1944, P.612, 614), which are far too small

to allow significant Pb^{208}/Th^{232} ratios and ages to be calculated.

This was confirmed for four of these specimens from the lead isotope abundances determined in the mass spectrometry. The Pb^{208} abundances were found to be identical to that of common (i.e. non-radiogenic) lead, and so could not have been enriched by the decay of Th^{232} in the pitchblendes. In the case of No. 3, a small enrichment of Pb^{208} was noted, indicating the presence of some Th^{232}, but this was insufficient to justify chemical analysis for thorium.

The choice of analytical method was governed by the relatively high uranium and lead content of the pitchblendes, which were likely to be 50-65% and 2-10% respectively. The first essential was the selection of the best available procedure for separation of uranium and lead from other elements in the pitchblendes. Provided a satisfactory separation was achieved, there were a number of possible finishing methods for determination of the two sought elements. This latter point is considered first. Highly sensitive instrumental methods were available for determining both elements, namely polarography and colorimetry for both uranium and lead, and fluorimetry for uranium. Polarography was chosen as the best general method for both elements and considerable work was done using a "Cambridge" Pen-recording Polarograph with these samples. With practice, the techniques developed, which are not described here in detail, gave fairly precise (i.e. reproducible) results for individual solutions, provided the solution temperature remained constant. However, polarographic currents vary by 1.5 to 2% per degree Centigrade change in solution temperature (Milner, 1957, P.104), and the insensitivity of the only available temperature control unit (a bi-metallic thermostat, which could at best keep the bath temperature constant to only

$\pm 2^{\circ}$C.) seriously affected the accuracy and precision of the results. The accuracy of the method was also impaired by the necessity for dilutions of the sample solutions to reduce concentrations to working levels for the polarograph (U:10^{-4} molar; Pb:10^{-5} molar). Instrumental methods generally require comparison with standard solutions, and, although good working curves (straight lines in fact) were obtained, errors are inherent in the comparison itself, and also in the preparation and measurement of the standard solutions.

Colorimetric and fluorimetric methods would have suffered from similar errors as the polarographic methods for specimens of these concentration levels, and were not attempted. In general, instrumental analysis was not considered to be sufficiently accurate or precise for the samples in hand.

Gravimetric finishes were found to have a high precision for both elements, and, as they were also believed to be the most accurate for these concentrations, were used in obtaining all the figures quoted.

Separation and Determination of Uranium.

A major advance in uranium analysis was made by Burstall and Wells (1951) in developing relatively simple and highly efficient methods of separation of uranium from other elements by the use of chromatography on cellulose. This work has been applied and tested extensively by E. H. Smith, also of the Chemical Research Laboratories, Teddington, Middlesex. Smith's (1955) handbook was used in applying these methods to the separation and determination of uranium in the pitchblende samples. The methods described in this handbook were very thoroughly tested by Smith and others, and, as this work was considered to be very reliable, the present author did not independently test them. As this handbook has not been published, the experimental details are now given in considerable detail with the author's minor variations and comments indicated.

(a) Solution of Pitchblende.

Smith suggests the use of nitric acid only for the solution of pitchblendes, but it was invariably found with the samples studied that a small insoluble residue remained. In order to ensure no error from this cause, complete solution was effected by the additional use of hydrofluoric acid as described below:-

(1) About 1 g. pitchblende was weighed accurately into a large Pt dish.

(2) The finely powdered mineral was moistened with de-ionised water (this water was used throughout), and 5 ml. conc. HNO_3 slowly added. (HNO_3 used throughout was special Pb-free Analar grade - Pb 0.005 ppm.). Effervescence usually occurred with evolution of NO_2, a watch glass covering the dish to prevent loss by spitting.

(3) The mixture was evaporated to small bulk on a water-bath, stirring frequently with a Pt spatula.

(4) The dish and contents were cooled and 5 ml. conc. HNO_3 added, followed by careful stirring. The solution was again evaporated to small bulk on the water-bath.

(5) Step (4) was repeated once more.

(6) 5 ml. conc. HNO_3 and then 5 ml. conc. HF (Pb-free) were added, and after stirring, the solution was evaporated to dryness, the last stage being done on a hot-plate.

(7) 5 ml. conc. HNO_3 was added and the solution evaporated to dryness after which the temperature was raised until the residue turned brown

(8) Step (7) was repeated twice more to ensure the removal of all HF and SiF_4.

(9) 3 ml. conc. HNO_3 and 10 ml. water were added and warmed with stirring, whereupon all the residue dissolved to give a clear solution. The solution was filtered warm through No. 41 paper (to remove dust impurity) into a 100 ml. standard flask. The dish was rinsed at least four times with warm water and the washings added to the filter. The flask was cooled for some hours before making up the volume.

(10) In one case a small residue did not dissolve in the last step. It was allowed to settle, the supernatant liquid decanted into the filter, and the residue dissolved by repeating steps (6) to (9) with appropriately reduced quantities of reagents.

(b) Separation of Uranium.

The method depends on the fact that uranyl nitrate dissolved in a nitric acid/ether mixture passes quantitatively through a column packed with cellulose, while most other ions are absorbed by the cellulose or move slowly compared with uranium. A complete separation of uranium can thus be achieved simply and rapidly, in comparison with classical text-book methods of separation which involve successive precipitations and extractions with chloroform or electrolysis.

A few ions inhibit or interfere with the chromatographic separation. These effects can be eliminated by the use of certain reagents, their action being described in notes to the experimental details.

(1) Preparation of the column.

Chromatographic columns were made according to Smith's description; viz. glass 18 in. long, 3-4 cm. diameter, opened into a funnel at the top and with a constriction and a fitting polyvinyl chloride tubing at the bottom with a screw clip. Control of flow of

solutions through such columns was found difficult, and the flexible tubing and clip were replaced by glass tubing and stop-cock. The fusion of a sintered glass disc into the bottom of the tube was another small improvement; this prevented the fine cellulose powder from coming through with the eluate in small amounts, which it tended to do with only a constriction or glass wool to hold it back.

(2) The column was thoroughly cleaned and washed with chromic acid and hot soapy water, followed by much rinsing with water and then acetone.

(3) It was filled with carbon tetrachloride, to remove grease and left for 1 hr. before draining.

(4) It was filled with "Repelcote" (a 2% solution of dimethylchlorosilane in $C Cl_4$, supplied by Hopkin & Williams) and left for 30 mins. before draining. After the solution had dried, no meniscus would form inside it with aqueous solutions. The stop-cock was left greaseless.

(5) The column was ⅔rds filled with the solvent of 1% HNO_3 in ether. Air bubbles were displaced by agitation with a long stirring rod flattened at one end. Cellulose powder (Whatman's Standard Grade for Chromatography) was added in small amounts to the column and agitated to remove air bubbles. The powder was first allowed to settle under its own weight, and then was packed down gently under the weight of the stirring rod. Successive amounts of powder were added until a column of about 8 cm. was obtained. After running out solvent until about 4 cm. remained above the top of the cellulose, the column was ready for use.

Use of Column.

(1) 10 ml. of sample solution (or appropriate volume required for suitable amount of U_3O_8 for weighing - preferably a minimum of 25 mg.) was accurately pipetted into a 100 ml. beaker.

(2) 1 ml. of 5 vol. H_2O_2 was added, and the solution heated on a steam bath until evolution of oxygen had visibly ceased. (This reduces ceric to cerous, the nitrate of the former being appreciably soluble in ether-nitric acid mixtures, whereas the nitrate of the latter is insoluble).

(3) 0.2 g. of $Fe(NO_3)_3.9H_2O$ was added with stirring and heating until all dissolved, followed by 0.2 g. of $Ca(NO_3)_2.4H_2O$. The heating was then continued until dryness was nearly reached. ($Fe(NO_3)_3$ is added mainly to complex with PO_4^{3-} ions, the presence of which strongly inhibits elution of uranium by complexing with it. $Fe(NO_3)_3$ also acts as a "salting out" agent. $Ca(NO_3)_2$ complexes with SO_4^{2-} ions which also inhibit elution of uranium. It is important to prevent formation of basic ferric nitrates by not evaporating solutions to dryness, for these compounds are rapidly eluted with the ether-nitric acid solvent).

(4) The beaker was placed under an infra-red lamp and heated for a few minutes. 7 ml. 25% HNO_3 was added and the solution heated under the lamp for a further 5 mins., after which it was thoroughly cooled under the tap.

(5) About 6 g. cellulose powder was stirred into the solution with a stout glass rod to give a crumbly mixture.

(6) The crumbly wad was transferred carefully to the top of the column, and once under the solvent was beaten up with the long flattened

stirring rod. It was allowed to settle as a continuation of the column with the help of the weight of the rod. It was important that no air bubbles remained trapped in the column as it was formed.

(7) Once the top of the column had clearly settled down, the stop-cock was opened and the solvent allowed to drain slowly into a Kjeldahl flask. (Smith claims that a rate of about 10 ml. solvent per minute steadily throughout the elution indicates that the column is correctly packed, but this rate was never attained in many determinations; however, steadiness in flow-rate was always reached, and this is probably a more important criterion).

(8) As it was seldom possible to transfer all of the wad from the beaker to the column in the first transfer, it was necessary to carefully wash out the beaker with solvent in 10 ml. portions, and in so doing to transfer the remaining portion of the cellulose from the beaker to the column. Washings were not added until the level of the solvent in the column had almost reached the top of the wad.

(9) Washing was continued until 150-200 ml. solvent had collected in the flask, when all the uranium in the original solution should have been eluted, all other ions remaining adsorbed on the cellulose. At this stage, as the solvent dripped into the flask, it was tested for the presence of uranium by shaking four drops of it with a solution of potassium ferrocyanide. The presence of uranium was shown by the development of a deep red colour. If the test was positive, more solvent was run through the column until a negative colour test was given.

(10) 50 ml. water was added to the eluate, followed by some pieces of Pt foil to prevent bumping.

(11) The flask was heated on a water-bath to evaporate all the ether present. An aqueous solution of nitric acid and uranyl nitrate, $UO_2(NO_3)_2$, remained.

(12) Water was evaporated by just boiling the solution over a semi-micro burner, until about 5 ml. solution remained.

(13) The warm solution was transferred into a previously ignited and weighed Pt crucible. The flask was washed out with successive small volumes of dilute HNO_3 and then water, each of which was heated and swirled in the flask before transfer.

(14) The solution in the crucible was heated on the water-bath until evaporation had proceeded almost to crystallisation point.

(15) One ashless tablet was broken up and added to the solution in the crucible to soak it up.

(16) The crucible was heated in an oven at 60°C. for 2-3 hrs. to dry the tablet.

(17) The crucible was then slowly heated in a furnace to 850°C., at which it was maintained for 5 hrs. (Smith claims that 30 mins. is sufficient but in this work many re-ignitions were found to be necessary in attaining constant weight unless there was a long first ignition).

(18) The crucible was cooled in a desiccator and rapidly weighed on the 5 place balance. (Rapid weighing was essential as the U_3O_8 was found to take up water at a disturbing rate if the weighing proceeded slowly).

(19) The crucible was re-ignited to constant weight ($\pm$0.05 mg.). The weight of the average ash produced from the "ashless" tablet (0.00029 g.) was subtracted before calculating U as U_3O_8.

Note on Polarographic Finish (Swales, 1946).

(1) 5 ml. each of conc. H_2SO_4 and conc. H Cl O_4 were added to the solution from Step (12), (P. 19), which was then evaporated to strong fumes of H_2SO_4 to remove HNO_3 and organic matter.

(2) The solution was cooled, a little water added and then 14 g. $NH_2OH.H$ Cl (to give conc. of 2 M in final solution). The solution was brought to the boil, cooled and 10 mg. gelatin added as a maximum suppressor.

(3) The resulting solution was filtered into a 100 ml. standard flask and the volume made up with water.

(4) A series of standard uranium solutions was made up with same concs. of H_2SO_4, NH_2OH. H Cl and gelatin.

(5) Sample and standard solutions were polarographed for U in succession.

(6) Blank runs done through the complete separation procedure gave no uranium detectable using the highest sensitivity on the polarograph. This provided a very useful check on reagents used in both gravimetric and polarographic determinations.

Separation and Determination of Lead.

Under conditions of carefully controlled pH, lead can be uniquely extracted into a chloroform solution of dithizone. The effect of interfering elements can be eliminated by preliminary treatment with suitable complexing agents. The method used is described by Sandell (1959, p. 569; for use in colorimetric determination of lead), and is not described in great detail here.

The most satisfactory weighing form of lead is undoubtedly the sulphate and the method described by Hillebrand et al. (1953, p.277) has been applied here.

Reagents.

Water .....Distilled and de-ionized used throughout

Chloroform ..... Analar grade

Dithizone solutions ..... 2 solutions were generally used, one fairly concentrated and the other comparatively dilute. The concentration of solution A was occasionally varied according to the concentration of lead in the sample, so that only a small number of extractions were necessary.

Soln. A 0.02%)
Soln. B 0.001%) made up in Analar chloroform

Ammonia solution ..... 0.880 soln., special Pb-free Analar grade, diluted according to need

Nitric acid ..... 1% prepared by diluting conc. Pb-free acid

Citric and tartaric acids ... 50% solns., prepared from Pb-free solid reagent

Potassium cyanide ..... 10% soln., prepared from Pb-free solid reagent

Hydroxylamine hydrochloride . 20% soln., prepared from Analar solid reagent (Pb less than 0.002%)

Sulphuric acid ..... conc., Pb-free

pH was determined throughout with a glass-electrode pH meter.

(1) 20 ml. pitchblende solution was accurately pipetted into a beaker, 5 ml. NH_2OH. H Cl solution added and brought to the boil. (This prevents interference by Fe^{3+} ions).

(2) 5 ml. each of citric and tartaric acids were added. (These prevent the precipitation of metal hydroxides).

(3) pH was adjusted to 9:5, using 1:1 NH_3 solution. (At this pH, lead

is not accompanied by other ions into the dithizone layer).

(4) 1 ml. KCN solution was added and the solution transferred to a separating funnel from which all grease had been removed from stop-cock and stopper. (Cyanide ion prevents all ions but Pb^{2+}, Bi^{2+}, Tl^{2+}, Sn^{2+} and possibly In^{2+} from complexing with dithizone).

(5) The lead was repeatedly extracted into 10 ml. volumes of dithizone Soln. A until no further colour change was observed (normally about five extractions). Complete extraction was tested by using 10 ml. dithizone Soln. B, and then the aqueous layer was washed with small volumes of chloroform.

(6) The lead was repeatedly extracted back from the combined dithizone and chloroform washings into 10 ml. volumes of HNO_3 solution; (generally only two or three extractions). The chloroform layer was washed with small volumes of water, washings being combined with the HNO_3 washings.

(7) The washings were evaporated to about 10 ml. and filtered with washings through a No. 41 paper into a 250 ml. beaker. The filtrate was evaporated to about 5 ml.

(8) 7 ml. sulphuric acid was added slowly to the solution with stirring. A fine white precipitate of $PbSO_4$ was formed.

(9) The solution was evaporated to fumes of H_2SO_4 on the hotplate. The complete removal of HNO_3 was ensured by repeating this twice, after successive additions of 3 ml. H_2SO_4.

(10) The solution was cooled and 150 ml. water carefully added with stirring the beaker was covered and stood for 24 hrs.

(11) $PbSO_4$ precipitate was removed on a previously ignited and weighed

semi-micro filter crucible, and washed with 3% H_2SO_4 saturated with $PbSO_4$, (this step is recommended by Craig and Vinel, 1939, reported in Hillebrand et al., 1953, p. 227, to avoid errors caused by the small solubility of $PbSO_4$ in water).

(12) The crucible was placed on a porcelain saucer, covered with a lid, heated to 110°C. in an oven for 2 hrs., and then ignited to constant weight (± 0.02 mg.) in a furnace at 550°C., the first ignition being for 3 hrs.

Note on Polarographic Finish (Scales, 1948).

(1) The combined extracted lead solution from Step (6), (p. 22), was filtered through a No. 41 paper into a 50 ml. standard flask.

(2) 2 g. NH_2OH. H Cl and 4.2 ml. (to make 1 M) conc. Pb-free H Cl and 2.5 mg. gelatin were added to the flask, dissolved with shaking and the volume made up to the mark.

(3) A series of standard lead solutions was made up with the same concn. of H Cl, NH_2OH. H Cl and gelatin.

(4) Sample and standard solutions were polarographed for Pb in succession.

(5) Blank runs done through the complete separation procedure gave no lead detectable using the highest polarograph sensitivity. This indicated that no lead contamination was likely from the reagents used.

2. (3) MASS SPECTROMETRY.

Preparation of Lead Sulphide Sample.

Lead was extracted from the pitchblende solution by the dithizone method described above for determination of total lead.

In step (7), (p. 22), the filtrate was collected in a centrifuge tube, then:

(1) pH was adjusted to 4.5 with dil. NH_3 solution and the solution heated nearly to boiling.

(2) H_2S, prepared by warming antimony sulphide (Sb_2S_3) with conc. Pb-free H Cl and passing through a spray trap and granulated fused $CaCl_2$, was passed into the hot solution until precipitation of PbS was complete.

(3) The precipitate was washed with water three times and transferred to a cleaned Pyrex tube and sealed with a polythene-covered cork.

Mass Spectrometry.

Some of the PbS sample was transferred to the two side filaments of a triple tungsten filament assembly. The mass spectrometry techniques were identical to those used for common leads, described in Section 6. (3), except that the greatly different isotopic constitution of these radiogenic leads required different sets of range factors for obtaining maximum peak heights for all isotopes.

The isotope data were calculated by digital computer as described in Chapter 7.

2. (4) X-RAY ANALYSIS.

All five pitchblende specimens were submitted to X-ray analysis by standard powder pattern measurements. A sample of uraninite, variety broggerite from Rade near Moss, Norway, (supplied by A. W. G. Kingsbury from the Oxford University Museum collection) and a galena from Manod Mine, Merioneth, Wales, were also photographed as reference samples. In addition, a powder photo. was taken of uraninite from Geevor, Cornwall, kindly supplied by A. G. Darnley, which was the subject of his age study (Darnley et al., 1960). The five pitchblende samples were photographed twice with separate sample rods made

for each measurement.

The X-rays were supplied by a Philips "Norelco" instrument and the camera used had a 11.46 cm. diameter. Finely powdered samples were mixed with gum tragacanth in making the rods for mounting in the camera. A copper target with a nickel filter was used. Exposures were 3 hrs. for all specimens using X-rays produced at 36 KV and 20 ma., and large collimators. Films were developed for four minutes.

Measurements of the diffraction lines on the developed films were made with a Hilger and Watts film measuring rule equipped with a Vernier reading to 0.05 mm.

2. (5) POLISHED SECTION AND AUTORADIOGRAPH STUDIES.

The polished sections were prepared from fragments of the original specimens of pitchblende, selected in the same way as the samples for crushing (although larger fragments were used here). No distinction could be drawn between Nos. 1A and 1B which were originally two separate selections of fragments from the same larger pieces, and so this polished section was called "No. 1: South Terras". The mounting and polishing of the specimens was skilfully done by Miss Dorothy Waring.

A. G. Darnley of the Atomic Energy Division of the Geological Survey of Great Britain, kindly offered to examine these sections. The author is very grateful to him for the considerable time which he spent on this work. Darnley examined all sections by taking autoradiographs and then by ore microscopy techniques.

C H A P T E R 3

CALCULATIONS and RESULTS

3. (1) THEORY

The general age equations and their derivation have been outlined by Kovarik (1931) and Keevil (1939). For the radioactive decay of a parent isotope to a daughter isotope, equations of the following form apply:

Number atoms daughter = Number atoms parent decayed

= Number (originally) - Number (now).

i.e. $N = N_o - N_p$

General radioactive decay relationship is: $N_p = N_o e^{-\lambda t}$

$$\therefore N_o - N_p = \frac{N_p}{e^{-\lambda t}} - N_p$$

$$N_d = N_p (e^{\lambda t} - 1)$$

$$\frac{N_d}{N_p} = e^{\lambda t} - 1$$

Thus in this work ages could be calculated from the equations:-

$$\frac{N_{206}}{N_{238}} = \exp(\lambda_{238} t) - 1$$

$$\frac{N_{207}}{N_{235}} = \exp(\lambda_{235} t) - 1$$

Also $$\frac{N_{207}}{N_{206}} = \frac{\exp(\lambda_{235} t) - 1}{k(\exp(\lambda_{238} t) - 1)}$$ where $k = \frac{U^{238}}{U^{235}}$ today

Greenhalgh and Jeffery (1959) published a series of tables for the solution of these equations; the intermediate ages have to be obtained by interpolation. More recently, the tables of Stieff et al. (1959) have become available, which have the advantages of using the most recent constants and also being calculated by digital computer to considerable accuracy. The small intervals of $\frac{1}{2}$ given avoid error in reading graphs and making interpolations. The inherent "calculation error" in each age, resulting from experimental errors in

the constants used, are quoted, thus enabling absolute errors (combination of experimental and "calculation" errors) to be estimated. These tables were used for all age calculations in this work. The constants used in preparing the tables are:-

U^{238} ..... $T_{\frac{1}{2}} = (4.51 \pm 0.01) \times 10^9$ yr.

$\lambda_{238} = 1.53_{69} \times 10^{-10}$ yr.

U^{235} ..... $T_{\frac{1}{2}} = (7.13 \pm 0.16) \times 10^8$ yr.

$\lambda_{235} = 9.72_{16} \times 10^{-10}$ yr.

U^{238}/U^{235} now : $k = 137.7 \pm 0.3_2$

3. (2) EXPERIMENTAL DATA.

(a) Chemical Data

The figures quoted in Tables 4 - 8 for weight per cent of uranium and lead are means of replicate (generally triplicate) analyses. The average atomic weight of the lead in each pitchblende was calculated from its isotope abundance data, and this was used in the calculation of the weight present of lead from the analytical data (e.g. No. 1A has average Atomic Weight of 206.91 as against 207.26 for the South Terras galena). The effect of this correction was generally small but could alter the lead figure by up to 0.5%.

The errors associated with the chemical data are estimations of the absolute error as there were insufficient numbers of analyses, for statistical treatment. These were based on the liberal estimation of the absolute accuracy of the methods from the many analyses of these elements made by the author.

The uranium analyses are considered accurate to 1%.

The lead analyses are considered accurate to 2%.

In cases where replicate analyses did not agree as closely as usual,

the error associated with the mean figure was increased by an appropriate amount.

(b) Isotope Data for Common Lead.

Moorbath's (1959 b) figures for the isotopic composition of seven galenas from S. W. England were used for the correction for common lead content in the pitchblendes studied. These are listed in Table 2. The numbering is that of Moorbath's thesis (1959 b) in which the location and geological details are given. The mean percentage abundance figures for the region and their errors were calculated by the author by weighting each figure according to its own error (Sect.7(12)). The error of each individual figure is twice the standard error of the mean, which is also the significance of the error of each mean regional figure.* This statistical procedure involves the necessary assumption that the different samples, grouped for the calculation of the mean, derive from a common source and that the variations between them represent a normal distribution.

(c) Isotope Data for Radiogenic Lead.

Nos. 2, 3 and 4 had their lead isotopic compositions determined once. As the age results for these samples were low, and clearly of no use in geological time-scale calibration, there was no need to repeat the determination to obtain a higher degree of accuracy. This does not invalidate the significance of the age results for these samples, for the greater errors

* However, each mean regional figure error has been somewhat increased from its calculated value (e.g. mean 204 = 1.375 ± 0.001$_2$% exactly, but is quoted as 1.375 ± 0.002% to give a more liberal estimate of the actual variations).

TABLE 2.

Isotopic Abundances of Lead from Galenas from S.W. England. (Moorbath 1959b)

No.	Locality	Percentage Isotope Abundances			
		204	206	207	208
M1.	Bere Alston, Devon	1.380±.004	25.01±.03	21.32±.02	52.29±.04
M2.	Wheal Rose, Porthleven, Cornwall	1.380±.006	25.02±.04	21.35±.04	52.25±.06
M3.	Vottle Shaft, Wheal Kitty, Cornwall	1.378±.003	25.08±.04	21.35±.03	52.20±.05
M4.	South Terras, St. Stephen -in-Brannel, Cornwall	1.375±.004	25.08±.03	21.34±.02	52.20±.03
M5.	Wheal Mary Anne Liskeard, Cornwall	1.374±.003	25.06±.03	21.34±.03	52.22±.04
M6.	Lambriggan nr. St. Agnes, Cornwall	1.372±.004	25.04±.04	21.29±.03	52.31±.04
M7.	Penberthy Croft, St. Hilary, Cornwall.	1.371±.004	25.02±.03	21.32±.02	52.29±.04
	Mean Abundances for Region	1.375±.002	25.04±.02	21.33±.01	52.25±.02

TABLE 3.

Isotopic Abundances of Lead

from Pitchblendes from Cornwall

No.	Locality	No. of Scans	Percentage Isotope Abundances			
			204	206	207	208
1A	South Terras		1.013±.003	43.54±.03	17.06±.03	38.58±.03
			1.012±.005	43.35±.07	17.03±.03	38.61±.06
			1.018±.004	43.37±.04	17.03±.02	38.59±.03
			1.010±.007	43.36±.06	17.05±.03	38.58±.06
			1.010±.004	43.40±.06	17.06±.03	38.53±.05
		142 (Total)	1.015±.005	43.41±.06	17.03±.02	38.54±.07
		Mean:	1.013±.002	43.36±.02	17.04±.01	38.58±.02
1B	South Terras		1.021±.003	43.07±.04	17.11±.02	38.80±.03
			1.013±.005	43.13±.06	17.07±.03	38.79±.06
			1.016±.003	42.99±.03	17.13±.02	38.86±.03
			1.013±.006	42.99±.06	17.11±.03	38.88±.07
			1.007±.005	43.07±.05	17.11±.04	38.81±.06
		143 (Total)	1.019±.006	43.10±.07	17.10±.03	38.78±.07
		Mean:	1.016±.002	43.04±.02	17.11±.01	38.82±.02
2.	Redruth Area	16	0.938±.004	47.23±.08	16.11±.04	35.72±.09
3.	Owles	19	1.167±.007	34.93±.11	18.89±.03	45.01±.09
4.	South Terras Area	24	1.174±.006	35.58±.06	18.80±.05	44.45±.06

associated with the mass spectrometry of these samples are reflected in the errors of the calculated ages.

For Nos. 1A and 1B, the U/Pb age results, calculated from the first isotopic determination of each, were very close and much greater than the other samples, indicating a possibly greater usefulness for the results. In order to reduce the contribution of mass spectrometer errors to the final errors in the ages of these samples, their isotopic compositions were more carefully determined. Three separate solutions of each sample were made, from each of which one lead sulphide sample was prepared. Duplicate mass spectrometer determinations were done on each lead sulphide sample, giving six determinations in all for each pitchblende sample. The duplicate determinationswere done two months apart to detect any variations in the mass spectrometer.

The lead isotope abundance figures are reproduced in Table 3. For each of Nos. 1A and 1B they are reproduced in the order - Solution 1: 1st Detn., 2nd Detn.; Solution 2: 1st Detn., 2nd Detn.; Solution 3: 1st Detn., 2nd Detn. Within the experimental error there is no detectable difference between the separate solutions of any one sample or between the 1st and 2nd determination on each solution. This indicates a high degree of reproducibility of both chemical and mass spectrometric techniques. This also provides confidence in the accuracy of the isotopic figures for those samples for which only one isotopic determination was done. The grand means and errors of the determinations on Nos. 1A and 1B were calculated by weighting each determination according to its own error (Sect.7(12)).

3. (3) SELECTION OF DATA FOR CALCULATIONS.

(a) Selection of Figures for Common Lead Correction.

The galena sample from South Terras (No. M4) was originally collected by

A. W. G. Kingsbury from the same lode as the pitchblende samples Nos. 1A and 1B. Moorbath's figures for the lead isotope abundances of this galena were used for the common lead correction for these two pitchblende samples. The errors associated with these South Terras figures were reduced to the values associated with the mean regional figures (before application to the calculation of the errors of the ages).

The mean regional figures and errors were used for the common lead correction in Samples 2 - 4. As there is a little doubt about the exact locality of No. 4, it was considered better to use the mean regional galena figures for its common lead correction, in preference to those of the South Terras galena.

Trial age calculations were performed with both South Terras and mean regional galena figures for common lead correction for Nos. 1A, 1B and 4. The difference between the two sets of ages was only 1 or 2 m.y. in 206/238 and 207/235 ages, because of the very small differences between the two sets of galena figures. So it was considered justifiable to use the South Terras galena figures for Nos. 1A and 1B, but the mean regional figures for No. 4.

(b) Selection of Isotope for Common Lead Correction.

The only non-radiogenic lead isotope is Pb^{204} and this is the one by which corrections for common lead content in U/Th minerals should be made. However, its absolute abundance is by far the lowest of all the four isotopes and thus, its percentage error is the highest. In addition, inter-laboratory comparisons have shown that the accuracy of Pb^{204} abundances is lower than for the other isotopes (see Chapter 8).

If a pitchblende has zero thorium content, then its Pb^{208} content is, like its Pb^{204} content, entirely due to common lead taken into its structure on

crystallisation. Under such conditions, the Pb^{208} isotope can also be used as the common factor between pitchblende and galena in correcting for common lead in the pitchblende. This has the advantages over the Pb^{204} correction of using larger, more accurate figures with lower percentage errors. Most pitchblendes fulfil the criterion of negligible thorium content, which is necessary before using Pb^{208} abundances for the correction in preference to Pb^{204} abundances.

In these studies, chemical analyses were not made for thorium as the isotopic analyses immediately showed that its amount was very low in all pitchblendes except No. 3. But there was an internal check on the justifiability of using the Pb^{208} correction:-

If the thorium content is negligible in a sample, the application of the Pb^{204} correction should give zero radiogenic Pb^{208} content. Conversely the Pb^{208} correction should give zero calculated Pb^{204} content (See Tables 4-8). If the first procedure works, then the second can be applied with confidence. This was found to be the case with Nos. 1A, 1B, 2 and 4 for which the discrepancy between the calculated Pb^{204} content and the measured value was within the experimental error. But with No. 3, the Pb^{204} correction had to be used owing to the presence of some radiogenic Pb^{208}.

3. (4) CALCULATION OF AGES AND THEIR ERRORS.

The calculations of the isotope ratios of radiogenic lead to uranium were carried out in the straightforward manner outlined in the introduction to the tables by Stieff et al. (1959). Before reading the age from these tables, the significance of each ratio was determined by first calculating its statistical error, and rounding-off the ratio to the same order as the error. The inclusion of more figures in the calculation than justified by the

experimental errors - as was done throughout their calculations by Darnley et al.(1960) - was thus avoided. The difference between age results calculated by rounding-off and not rounding-off figures in this way amounted up to 3 m.y. in trial calculations.

The final errors in Pb^{206}/U^{238}, Pb^{207}/U^{235} and Pb^{207}/Pb^{206} ratios were calculated using standard statistical formulae for the combination of errors. In this way, the error of every quantity used in calculating the final ratio contributed to the final error. Thus, errors in the following were taken into account:-

(a) Chemical analyses for Pb and U

(b) Mass spectrometry for Pb from Pitchblendes

(c) " " " " " Galenas

For the Pb^{206}/U^{238} ratio, the dominant experimental errors were those of the chemical analyses. For the Pb^{207}/U^{235} ratio, the mass spectrometric error made a large contribution (about $\frac{1}{2}$ to $\frac{2}{3}$ in most samples) to the final error. For the Pb^{207}/Pb^{206} ratio, the error was entirely due to the mass spectrometry.

The age corresponding to a given ratio was then read directly from the tables. The experimental error in the age was calculated by finding the ages corresponding to the maximum and minimum limits of the ratio, as defined by the error. The greater difference between these maximum and minimum ages and the mean age was taken as the error in the mean age.

These tables also give the "calculation errors" in ages due to errors in the physical constants used in computing the ages. The absolute error in an age was estimated by simple addition of the experimental error and the "calculation error". This gave a greater error (generally only slightly greater) than would have been obtained had they been summed according to the "square root of the sums of squares" rule. But it was considered a reasonable

procedure to give a more liberal estimate of the absolute error in the age.* This is the error quoted with the mean age in the ensuing tables.

The calculation of ages from the isotope ratios using Stieff's tables was compared with those using Greenhalgh and Jeffery's tables (1959). The latter used slightly different constants (e.g. $\lambda_{238} = 0.1541 \times 10^{-9}$ yr^{-1}). The resultant effect in this age range was negligible for 206/238 ages, but, for 207/235 and 207/206 ages, the tables of Greenhalgh and Jeffery gave slightly higher results. Some of these differences may be due to the method of computation and form of the tables.

On the following pages are Tables 4-8, which give the experimental data and the results of all important stages in the age calculations. The resulting ages are later summarised with the X-ray results in Table 10. Darnley's (1960) age results for the Geevor uraninite are also reproduced for convenience in Table 10.

* The mass spectrometric errors quoted are statistical estimates of precision and not of absolute accuracy (see Chapter 8). This procedure thus accounts to some extent for the absolute error of the mass spectrometry.

TABLE 4.

Summary of U/Pb Age Calculations.

Sample 1A : South Terras

Chemical Data: U = 59.9 ± 0.6%
Pb = 7.3 ± 0.15%

Mass Spectrometry Data:

Isotope	Sample Pb Abundances	Common Pb Abundances*	Normalising to Pb^{208} = 38.58	Radiogenic Pb
Pb^{204}	1.013±.002	1.375±.002	1.016	(-0.003)
Pb^{206}	43.36±.02	25.08±.02	18.54±.02	24.82±.03
Pb^{207}	17.04±.01	21.34±.01	15.77±.02	1.27±.02
Pb^{208}	38.58±.02	52.20±.02	38.58	-

* Using data of Moorbath for galenas from South Terras, with errors associated with average abundances for S.W. England.

Proportion of radiogenic Pb of total Pb = 26.1%

Isotope ratios	Resulting Ages with Absolute Errors.
$\frac{Pb^{206}}{U^{238}} = 0.0351 \pm .0008$	224 ± 6 m.y.
$\frac{Pb^{207}}{U^{235}} = 0.247 \pm .007$	227 ± 11 m.y.
$\frac{Pb^{207}}{Pb^{206}} = 0.0512 \pm .0008$	259 ± 100 m.y.

TABLE 5.

Summary of U/Pb Age Calculations

Sample 1B : South Terras

Chemical Data : U = 59.7 ± 0.6%
Pb = 7.5 ± 0.2%

Mass Spectrometry Data:

Isotope	Sample Pb Abundances	Common Pb Abundances*	Normalising to Pb^{208} = 38.82	Radiogenic Pb
Pb^{204}	1.016±.002	1.375±.002	1.023	(-0.007)
Pb^{206}	43.04±.02	25.08±.02	18.65±.02	24.39±.03
Pb^{207}	17.11±.01	21.34±.01	15.87±.02	1.24±.02
Pb^{208}	38.82±.02	52.20±.02	38.82	

* Using data of Moorbath for galena from South Terras, with errors associated with average abundances for S.W. England.

Proportion of radiogenic Pb of total Pb = 25.6%

Isotope ratios	Resulting Ages with Absolute Errors
$\frac{Pb^{206}}{U^{238}} = 0.0355 \pm .0010$	227 ± 7 m.y.
$\frac{Pb^{207}}{U^{235}} = 0.249 \pm .008$	229 ± 12 m.y.
$\frac{Pb^{207}}{Pb^{206}} = 0.0508 \pm .0008$	247 ± 100 m.y.

TABLE 6.

Summary of U/Pb Age Calculations

Sample 2 : Redruth Area

Chemical Data : U = 55.5 ± 0.6%
Pb = 3.06 ± 0.06%

Mass Spectrometry Data :

Isotope	Sample Pb Abundances	Common Pb Abundances*	Normalising to Pb^{208} = 35.72	Radiogenic Pb
Pb^{204}	0.938±.004	1.375±.002	0.940	(-0.002)
Pb^{206}	47.23±.08	25.04±.02	17.12±.04	30.11±.10
Pb^{207}	16.11±.04	21.33±.01	14.58±.04	1.53±.06
Pb^{208}	35.72±.09	52.25±.02	35.72	-

* Using data of Moorbath for average figures of S.W. England galenas.

Proportion of radiogenic Pb of total Pb = 31.6%

Isotope ratios	Resulting Ages with Absolute Errors
$\frac{Pb^{206}}{U^{238}}$ = 0.0192 ± .0004	124 ± 4 m.y.
$\frac{Pb^{207}}{U^{235}}$ = 0.135 ± .004	130 ± 7 m.y.
$\frac{Pb^{207}}{Pb^{206}}$ = 0.0508 ± .0020	241 ± 160 m.y.

TABLE 7.

Summary of U/Pb Age Calculations

Sample 3 : Owles

Chemical Data : U = 53.6 ± 0.8%
Pb = 3.04 ± 0.06%

Mass Spectrometry Data :

Isotope	Sample Pb Abundances	Common Pb Abundances*	Normalising to Pb^{204} = 1.167	Radiogenic Pb
Pb^{204}	1.167±.007	1.375±.002	1.167	-
Pb^{206}	34.93±.11	25.04±.03	21.25±.13	13.68±.17
Pb^{207}	18.89±.03	21.33±.01	18.10±.11	0.79±.11
Pb^{208}	45.01±.09	52.25±.02	44.34	(0.67)

* Using data of Moorbath for average abundances of S.W. England galenas.

Proportion of radiogenic Pb of total Pb = 14.5% (omitting Pb^{208} figure)

Isotope ratios	Resulting Ages with Absolute Errors
$\frac{Pb^{206}}{U^{238}}$ = 0.00898 ± .00025	58 ± 3 m.y.
$\frac{Pb^{207}}{U^{235}}$ = 0.071 ± .010	71 ± 12 m.y.
$\frac{Pb^{207}}{Pb^{206}}$ = 0.058 ± .008	542 ± 410 m.y.

TABLE 8.

Summary of U/Pb Age Calculations

Sample 4 : South Terras Area

Chemical Data : U = 45.6 ± 0.9%
Pb = 2.61 ± 0.08%

Mass Spectrometry Data :

Isotope	Sample Pb Abundances	Common Pb Abundances*	Normalising to Pb^{208} = 44.45	Radiogenic Pb
Pb^{204}	1.174±.006	1.375±.002	1.170	(0.004)
Pb^{206}	35.58±.06	25.04±.02	21.50±.04	14.28±.08
Pb^{207}	18.80±.05	21.35±.01	18.15±.03	0.65±.06
Pb^{208}	44.45±.06	52.25±.02	44.45	-

* Using data of Moorbath for average abundances of S.W. England galenas.

Proportion of radiogenic Pb of total Pb = 14.9%

Isotope ratios	Resulting Ages with Absolute Errors
$\frac{Pb^{206}}{U^{238}}$ = 0.0095 ± .0003	62 ± 3 m.y.
$\frac{Pb^{207}}{U^{235}}$ = 0.059 ± .006	59 ± 8 m.y.
$\frac{Pb^{207}}{Pb^{206}}$ = 0.0443	Negative

3. (5) DETERMINATION OF CELL SIZES FROM X-RAY POWDER PHOTOGRAPHS.

From the measurements of the position of the diffraction lines on a powder photograph, the angles of diffraction of the X-rays, 2θ, from the various planes in the crystal lattice were readily calculated. The distance in millimetres between corresponding pairs of lines in the diffraction (low angle, $2\theta < 90^\circ$) region equals 2θ in degrees in the camera used. In the back reflection (or high angle, $2\theta > 90^\circ$) region, the distance between corresponding pairs of lines equals $(360 - 4\theta)$ in degrees.

A correction was made for shrinkage of the film during processing for all films in which the mid-positions of the high angle lines could be determined with accuracy. In all these cases the correction was very small to negligible.

The Bragg equation $\lambda = 2d \sin \theta$ was solved for d in Angstroms, for the characteristic copper X-rays (resolution was never obtained between the $K\alpha_1$ and $K\alpha_2$ lines for pitchblende and uraninite specimens) and the measured and corrected values of 2θ for each pair of lines by use of the charts given by Parrish and Irwin (1953).

The lines were numbered according to the permitted values of $N(= h^2 + k^2 \times l^2)$ for a face-centred cubic lattice which uraninite, pitchblende and galena possess. The evaluation of the equation $a = d\sqrt{N}$ then gave a value for the cell size in Angstroms for each pair of lines.

All the uranium and lead samples showed absorption of X-rays by a general small apparent increase in a with increasing θ. This made the mean value of a, obtained by averaging all the separate values of a, lower than the correct value. This would be obtained for a hypothetical line with $2\theta = 180^\circ$, at the which the effect of absorption would be nil. Various methods have been proposed for extrapolation back to $2\theta = 180^\circ$ to find the most accurate value

of a corrected for absorption. The method adopted here was the most generally accepted one (originally proposed by Taylor and Sinclair, and Nelson and Riley, 1945), namely the plotting of a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ and extrapolating back to zero value of this function (which corresponds to $2\theta = 180^\circ$). Values of this function were obtained from tables given by Henry, Lipson and Wooster, (1960).

The line of best fit through the experimental points for each sample was found by carrying out a least squares analysis according to standard statistical methods, (e.g. Moroney, 1954). This gave the intercept on the a axis, which represents the value of the cell size corrected for absorption, and the standard error of this mean. The experimental error quoted is double this calculated standard error, which gives a 95% probability that the true value lies within these limits.

The detailed measurements of all photographs are not reproduced here. But Figure 3 shows the extrapolation curves for some of the photographs.

Figure 2 is a reproduction of the powder photographs obtained. The duplicate photographs also obtained for the five pitchblende samples were identical in quality (sharpness of lines, number of visible lines etc.) to the ones reproduced here. The reference photographs of bröggerite and galena are reproduced for comparison.

Qualitative examination of the original photographs shows the following (the reproduction has obscured some detail and heightened others, but is a fair representation of the originals):-

1. There is a marked difference between the relatively diffuse lines of all the pitchblende samples and the much sharper lines of the bröggerite and the Geevor uraninite sample.
2. In the pitchblende samples there is an increasing diffuseness on

Key to Figure 2

A: Bröggerite (Reference Sample)

B: Geevor Uraninite (Darnley)

C: South Terras Pitchblende (1A)

D: " " " (1B)

E: Redruth Area " (2)

F: Owles " (3)

G: South Terras Area " (4)

H: Galena (Reference Sample).

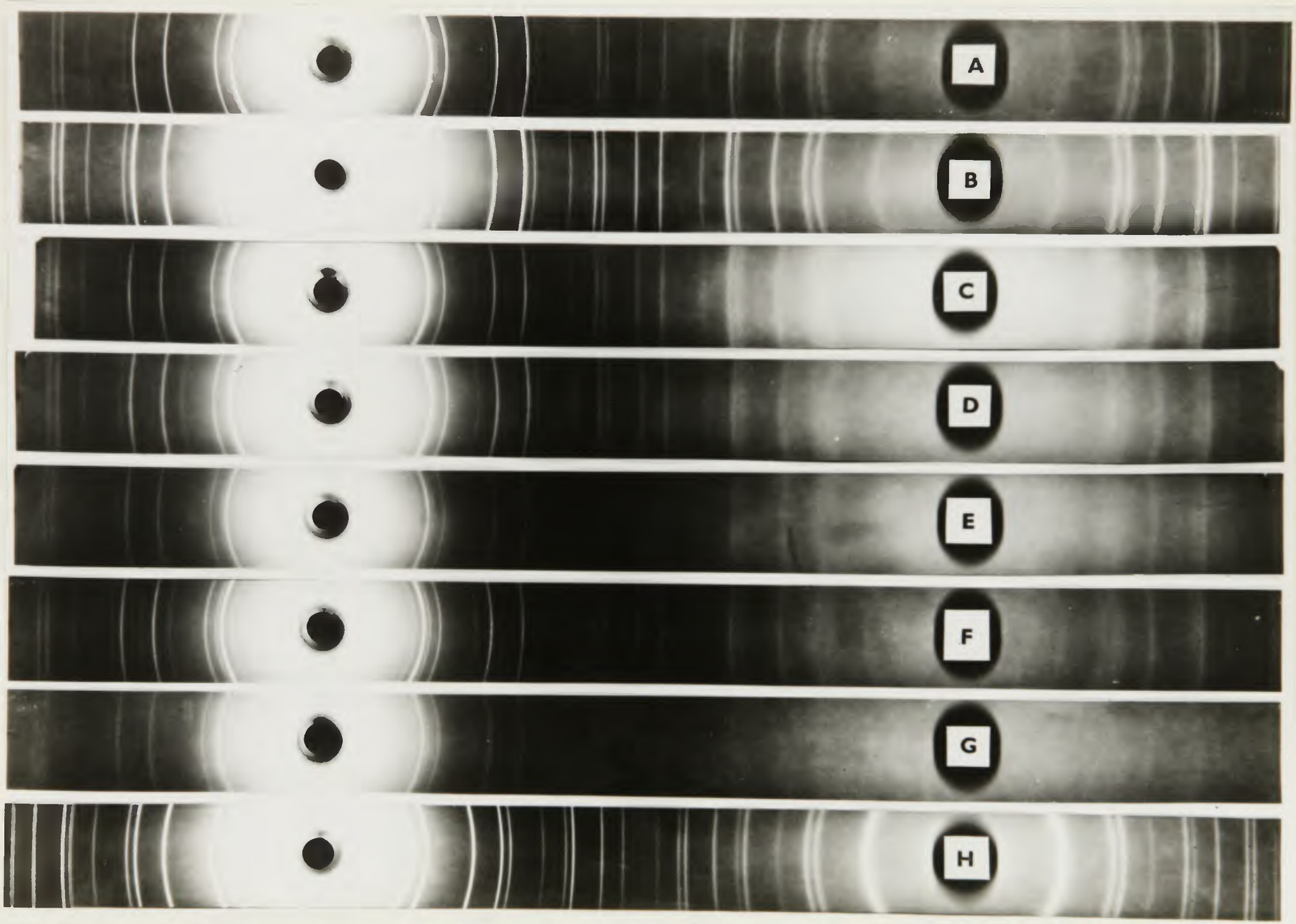


Figure 2: Reproduction of X-Ray Powder Pattern Photographs (key opposite).

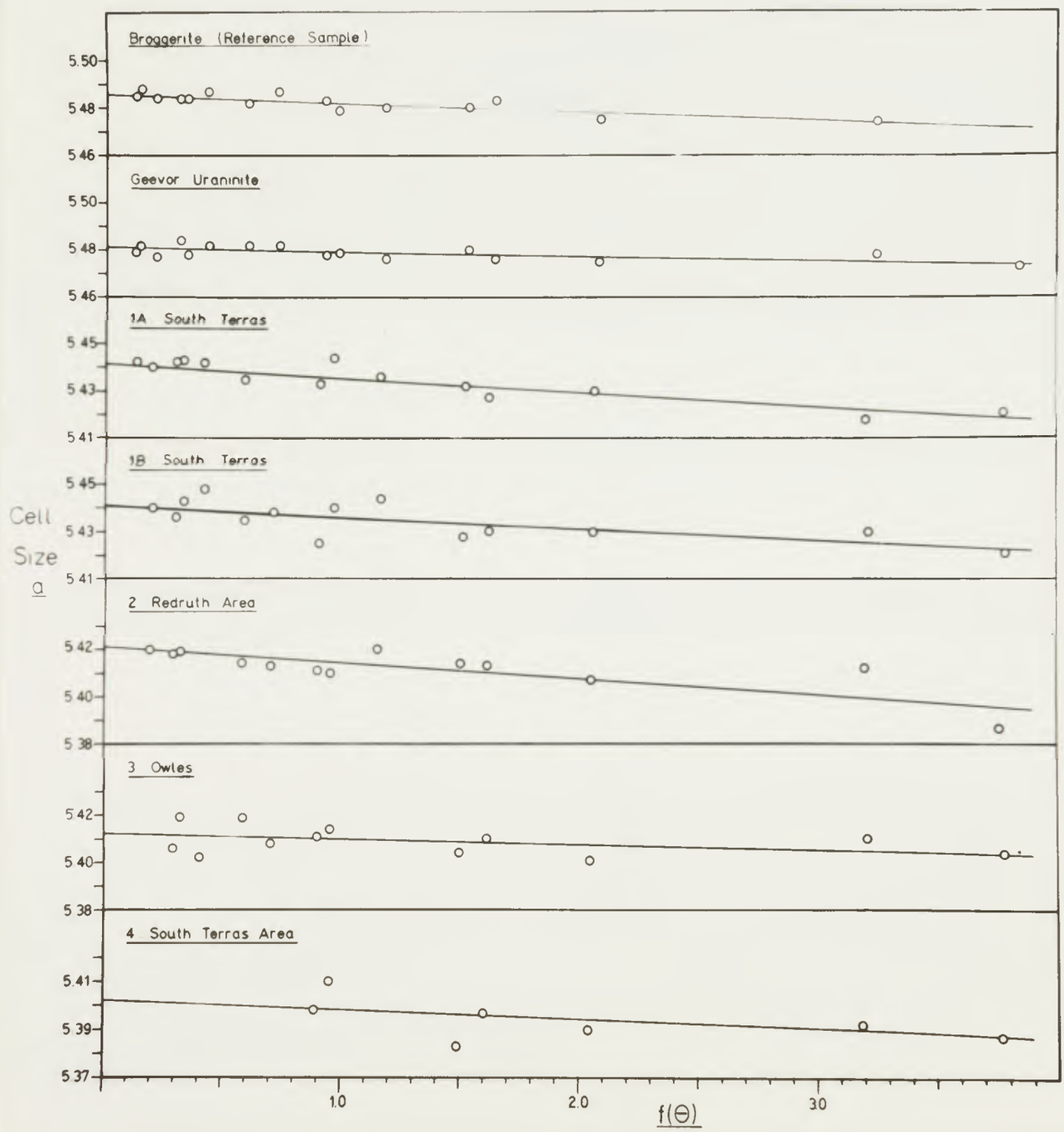


Figure 3: Extrapolation Graphs for Estimation of Cell Sizes of some Specimens.

TABLE 9.

Summary of Cell Size Determinations

No.	Mineral	Locality	Cell Sizes in A		
			Individual Determinations	Mean Figures	Mean Figures to nearest 0.01A (all with accuracy of ± 0.01A)
-	Broggerite	Rade, Norway (Reference Sample)	5.486±.004	5.486±.004	5.49
-	Uraninite	Geevor	5.481±.005	5.481±.005	5.48
1A	Pitchblende	South Terras	5.441±.006 5.448±.007	5.444±.005	5.44
1B	Pitchblende	South Terras	5.441±.010 5.449±.012	5.444±.008	5.44
2	Pitchblende	Redruth Area	5.431±.009 5.424±.008	5.423±.006	5.42
3	Pitchblende	Owles	5.412±.011 5.423±.006	5.420±.006	5.42
4	Pitchblende	South Terras	5.402±.014 5.412±.020	5.405±.011	5.41
-	Galena	Manod, Wales (Reference Sample)	5.942±.008	5.942±.008	5.94
-	Galena in Owles Pitchblende (Sample 3)		5.931±.006	5.931±.006	5.93

TABLE 10

Summary of U/Pb Age and Cell Size Results

No	Locality	Isotope used for common Pb correction.	% radiogenic Pb.	Age in millions of years $\frac{206}{238}$	$\frac{207}{235}$	$\frac{207}{206}$	$\frac{208}{232}$	Cell Size in A°
1A	South Terras	Pb^{208}	26.1%	224 ± 6	227 ±11	259 ±100	-	5.44
1B	South Terras	Pb^{208}	25.6%	227 ± 7	229 ±12	247 ±100	-	5.44
2	Redruth Area	Pb^{208}	30.6%	124 ± 4	130 ± 7	241 ±160	-	5.42
3	Owles	Pb^{204}	14.5%	58 ± 3	71 ±12	542 ±410	-	5.42
4	South Terras	Pb^{208}	14.9%	62 ± 3	59 ± 8	Negative	-	5.41
	Geevor Uraninite (Darnley et al., 1960)	Pb^{204}	99.9%	290 ± 7	291 ±15	302 ±85	308 ±85	5.48

moving down from Nos. 1A and 1B to No. 4. This results in back reflection lines being barely measurable in Nos. 2 and 3 and not present in No. 4.

3. No. 3 shows the presence of another compound with face-centred cubic structure. These extra lines match those shown in the galena photograph.

4. Some very weak extra lines are also shown by Nos. 2 and 4. They were too weak to measure in the original photographs but some could possibly be galena lines.

Table 9 gives the final results of all the cell sizes obtained by extrapolation. Mean results and their errors were calculated for each sample by weighting the individual means according to their associated errors (Sect. 7 (12)). The final column gives all the mean cell sizes with accuracy of ± 0.01A. These figures were the ones used in later calculations.

Table 10 summarises the age results for the Cornwall pitchblendes and their cell sizes. Darnley et al.'s (1960) age results for the Geevor uraninite are also included with the author's result for its cell size.

3. (6) RESULTS OF POLISHED SECTION AND AUTORADIOGRAPH STUDIES.

A. G. Darnley provided the following notes of his studies of the polished sections, which he has kindly given permission for reproduction here. His notes have only been altered to make the naming and numbering of the samples clearer. The specimens are described collectively and not individually, as the fragments in each polished section varied quite considerably in detail. Darnley's comments originally added to his observations are reproduced here for convenience, although discussion of the significance of the results is reserved to the next Chapter.

"1. Autoradiographs of all specimens except Owles (No. 3) show considerable variation in α-track density, which is principally attributable to varying proportions of pitchblende and a mineral of lower uranium content (identified as coffinite, see below). A few point-centres of intense radioactivity are present in the Redruth Area (No. 2) and South Terras (No. 1) specimens. These point centres are due to minute concentrations of radium, and experience has shown that their presence reflects radiometric disequilibrium. However they are not sufficiently numerous to suggest the disequilibrium is very marked - although this can only be an opinion. The percentage disequilibrium can of course be measured radiometrically, given sufficient material.

2. Coffinite has been identified by x-ray powder photographs in South Terras (No. 1) and Redruth Area (No. 2) specimens. Visual inspection confirms that it is also present in South Terras Area (No. 4), and to a minor extent in the Owles (No. 3) material. In the polished sections it can be distinguished from pitchblende by its lower reflectivity, the fact that it often contains numerous inclusions of sulphides, arsenides etc., and of course by its lower radioactivity. It can be distinguished from uranium 'secondaries' by the fact that it is opaque and isotropic, without (generally) internal reflections. For positive identification an x-ray photograph is essential in most circumstances. We have previously identified coffinite from all your localities in our own specimens. As usual, the coffinite tends to replace the smaller scattered pitchblende botryoids, forming a matrix enclosing both them and finely disseminated sulphides etc. It also marginally or zonally replaces larger areas of pitchblende. In some cases which can be seen in both Redruth Area (No. 2) and South Terras Area (No. 4) specimens pitchblende has been completely replaced, and only the relict

pattern of inclusions, characteristic of the original pitchblende enables this fact to be recognized. It should be noted that even where 'coffinite' has been very carefully selected, it is uncommon with Cornish material to obtain a powder photograph without the diffraction lines of oxidised uraninite being present.

I hesitate to give a figure for the coffinite:pitchblende ratio in your specimens, as individual fragments vary considerably and the replacement is on such a microscopic scale. The proportion in the Redruth area (No. 2) and South Terras Area (No. 4) specimens could be as high as 1 : 1, and in South Terras (No. 1) a little lower. In the Owles (No. 3) specimen the ratio is perhaps 1 : 10 or less.

3. Uranium 'secondary' minerals tentatively recognised by their yellow internal reflections are present to a very minor extent in South Terras (No. 1) and Redruth Area (No. 2) specimens. They are not obviously associated with microfractures, and they seem to form vugh fillings. I have noted this sort of occurrence in other specimens and I think it is quite possible that they are of low temperature hydrothermal rather than supergene origin. However, this point is difficult to prove, although I see no other signs of 'weathering'. All sulphides appear to be quite fresh.

4. Galena is, I think, most prominent in the Owles (No. 3) specimen, to a lesser extent in the South Terras (No. 1) and in Redruth Area (No. 2), and to a minor extent in the South Terras Area (No. 4) specimens. Superficial inspection suggests the Redruth Area (No. 2) specimen contains most galena, but the prominent white mineral is in fact tentatively identified as loellingite. Some finely disseminated galena within pitchblende can be found in all specimens, but it varies very much as does the amount of galena outside the botryoids.

5. Paragenesis. The relationships between the uranium minerals present fit into the general sequence deduced from our work in S. W. England:-

1. uraninite (Th bearing as at Geevor)
2. pitchblende
3. coffinite or 'ningyoite'
4. hypogene 'secondaries'
5. supergene 'secondaries'

↓ decreasing temperature; increasingly hydrous conditions.

The time interval between stages (1) and (4) is a matter for conjecture. It may or may not be geologically important.

Considering your age results, if all the uranium minerals were formed at more or less the same time, and recent lead loss is postulated as the explanation for the young ages obtained, then I am surprised that there were not some obvious mineralogical indications in the specimens concerned. If an appreciable proportion of the total lead had been recently leached from the Owles (No. 3) specimen, for example, I would expect to see some cavities! The alternative is to suppose that radiogenic lead in the pitchblende has been preferentially leached. I cannot help wondering whether or not there was hydrothermal alteration of the veins at, say, 70 m.y. ago, at which time varying proportions of the radiogenic lead then present were removed. The intensity of the supposed leaching could be reflected by the degree of oxidation of the pitchblende which you have established by your cell-size measurements. The proof of the matter would seem to rest in the isotopic composition of the galena associated with the pitchblende. If there has been significant re-crystallisation, as I suggest, then the galena may be expected to be anomalous."

C H A P T E R 4

GEOLOGICAL SIGNIFICANCE OF RESULTS

4. (1) Discussion of Age Results.

Figure 4 is a "concordia" plot of the type suggested by Wetherill (1956 a). If the experimental isotope ratios for a sample fall exactly on concordia, then the 206/238 and 207/235 ages calculated from these ratios will be identical. If the experimental point falls below concordia then the "majority" age pattern results (See Section 1. (1)). The "minority" age pattern results if the point falls above concordia. It should be noted that the curvature of concordia is very small in this low age range. The experimental isotope ratios determined in this work are plotted on Figure 4. The experimental errors of each isotope ratio pair are indicated by the ellipses drawn around them.

The following observations can be made on the individual age data summarized in Table 10 and graphically represented in Figure 4:-

Nos. 1A and 1B, South Terras : The 206/238 and 207/235 ages are very close together for each sample and lie within the errors. Both samples possess effectively the same degree of concordance as the Goevor uraninite. This can also be seen by the almost exact bisection of the error ellipses of all these samples by concordia. The differences between the 207/206 and 207/235 ages are much greater than the differences between the 207/235 and 206/238 ages, which results in the commonly observed "majority" age distribution. But these greater differences are to be expected whenever there is even a small difference between the 207/235 and 206/238 ages in this low age range. In addition, as the error of the 207/206 age is very much greater than for the other two ages, these 207/206 ages should not be considered significant.

No. 2. Redruth Area : The "majority" age pattern is observed. The 207/206 age is very much higher than the 207/235 and 206/238 ages, but the error is very

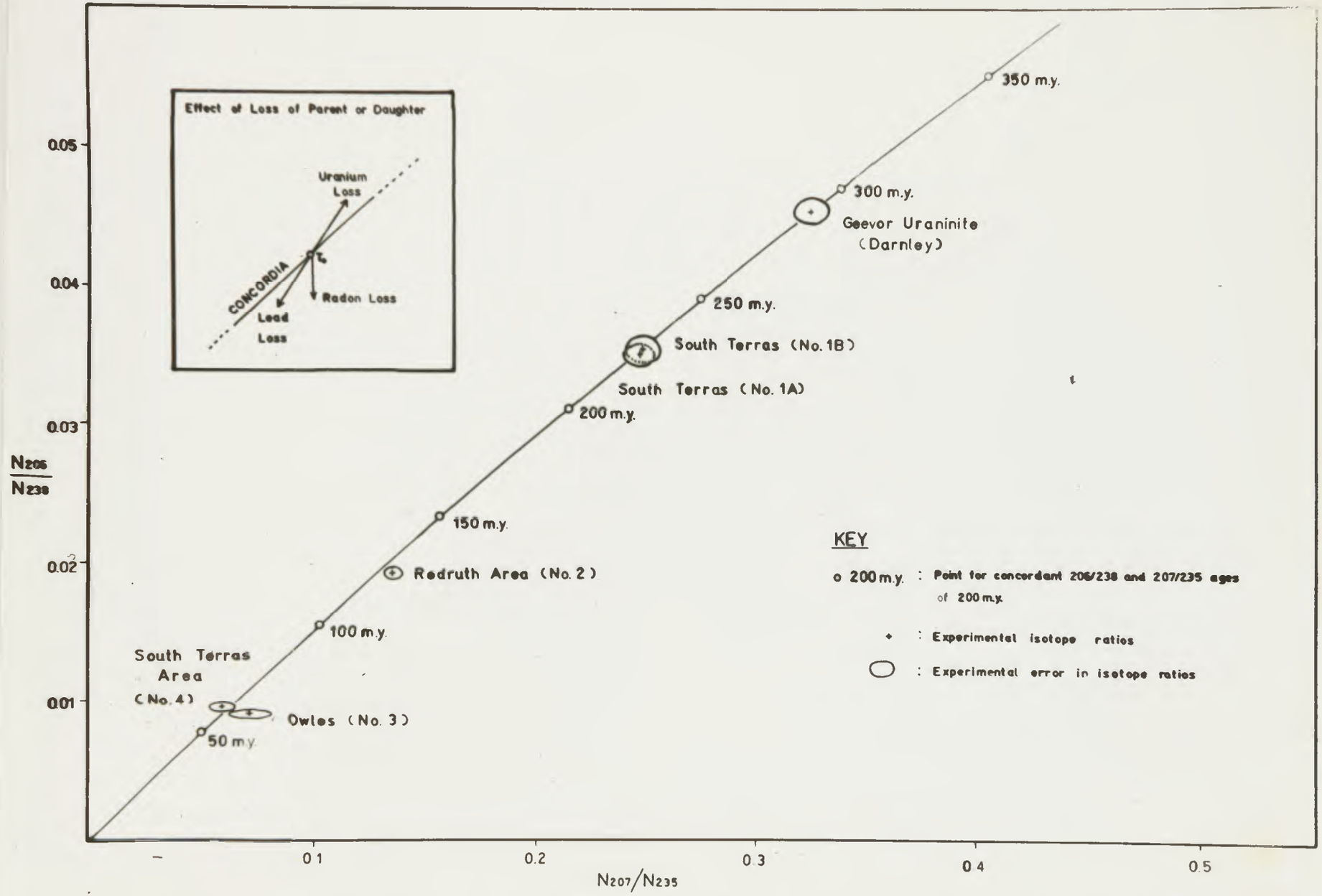


Figure 4: Concordia Diagram.

large. The exact agreement between this 207/206 age and that of No. 1B is probably just fortuitous. The 206/238 and 207/235 ages lie within each other's absolute errors, but the experimental error ellipse does not quite reach concordia.

No. 3. Owles : The common lead correction is very high. The "majority" age pattern is observed. The 207/206 age is so large and possesses such a high error that it has no meaning. The experimental point lies further from concordia than for any other sample, but a larger error in the 207/235 ratio brings the experimentil error ellipse as close to concordia as for No. 2.*

No. 4. South Terras Area : The common lead correction is very high. The "minority" age distribution is observed. The negative 207/206 age is meaningless. The 206/238 and 207/235 ages are close together and the experimental error ellipse intersects concordia.

The following observations can be made on the age data as a whole:-

1. In this low age range and with the large common lead corrections required, the 207/206 ages are of no significance and should be neglected.
2. There is a large common lead correction in all samples. But the contributions of all the errors involved in these corrections have been included in the final errors, and so the magnitude of the correction cannot account for the differences between the calculated ages. In particular, any suggestion that high common lead corrections are the indirect causes of low ages is refuted by No. 2, which has the smallest

* Nos. 2 and 3 have 206/238 and 207/235 ages agreeing within their absolute errors, but not within their experimental errors. Experimental errors are the only ones which can be represented on the concordia diagram, Fig. 4. However, absolute error is considered a better indication of uncertainty in ages than experimental error alone (See Footnote to P. 33). If absolute error could be represented on the concordia diagram, the error ellipse of Nos. 2 and 3 would intersect concordia.

common lead correction but the intermediate 206/238 age of 124 m.y. However, all samples have much higher common lead corrections than has the Geevor uraninite, for which this correction was negligible.

3. The degree of concordance between the 206/238 and 207/235 ages for all South Terras samples (Nos. 1A, 1B, 4) is sufficiently close for their experimental error ellipses to intersect concordia. As the errors in the 207/235 ages are considerably higher, and other evidence indicates the unlikelihood of radon loss, the 206/238 ages are considered the most reliable indications of the most recent crystallisations of these pitchblendes.

4. The agreement between the ages for Nos. 1A and 1B is very good for both pairs of 206/238 and 207/235 ages. These are essentially duplicate measurements on the same specimen and a mean 206/238 age of 225 ± 5 m.y. can be quoted with confidence.

5. The age difference between Nos. 1A and 1B on the one hand and No. 4 on the other is very large. However, it is possible that locality data for No. 4 is in error, and it may not come from the same lode as Nos. 1A and 1B

6. The errors in the 207/235 ratios for the two samples giving the youngest ages (Nos. 3 and 4) are large. The 206/238 ages for both these samples are close together, their mean being 60 ± 3 m.y.

7. Neither Nos. 2 nor 3 lies considerably below concordia.

8. The highest 206/238 age of all five samples (227 ± 7 m.y.) does not even closely approach the age of the Geevor uraninite or even the lowest absolute age measurement on S. W. England granites (See Table 1).

4. (2) <u>POSSIBLE INTERPRETATIONS OF AGE RESULTS.</u>

The following interpretations of the age results can be considered as

possibilities:-

1. The ages represent actual periods of primary mineralisation.

2. The ages are apparent only and do not represent actual periods of mineralisation. If so this may have been caused by:-

   (A) Loss of lead, which made the observed ages apparently low. This may have been caused by:-

      (a) Removal of the requisite amount by some process acting at a discrete period or periods. This may have occurred in:-

         (i) Recent times, or

         (ii) Intermediate times, later than the mineralisation

      (b) (a) may have been caused by:-

         (i) Simple weathering in situ, e.g. by circulating ground waters.

         (ii) Some other process; e.g. one involving the complete solution of the mineral and its re-crystallisation with less lead than before.

      (c) Removal of the requisite amount by some continuous process, such as solid diffusion during the whole period since mineralisation.

   (B) Preferential loss of radiogenic lead with respect to common lead. Radiogenic lead may be generated in microfissures within the pitch-blende, and so more readily ~~dissolved~~ separated from it by processes similar to those under (A) above.

   (C) Loss of radon by gaseous diffusion.

   (D) No. 4 may have suffered slight loss of uranium.

3. If the ages are apparent, then the primary mineralisation may have occurred:-

   (a) At a single period close to the age of the Geevor uraninite

(b) At some period (or periods) later than the Geevor mineralisation.

4. The isotopic composition of the lead used for common lead corrections may be grossly in error.

5. The samples may have all been mineralised at the same period, but in one or more later periods were "remobilised" or "rejuvenated" by hydrothermal processes involving the solution of the mineral and the complete or partial removal of lead from uranium on re-crystallisation. In this case the ages may represent the most recent re-crystallisations of these samples. Following remobilisation, the samples may have suffered loss of lead by one of the processes outlined under 2(A). (Remobilisation may be equivalent to 2(A)(b)(ii) above.)

The feasibility and probability of these interpretations are discussed in the following sections in the light of further calculations and experimental investigations.

4. (3) SIGNIFICANCE OF LEAD LOSS CALCULATIONS.

Before proceeding to discuss lead loss, it should first be briefly stated that the postulation of uranium loss for No. 4 is hardly necessary. The 206/238 and 207/235 ages are so close together that concordia actually intersects the experimental error ellipse. Thus, the observed "minority" age distribution cannot be considered significant enough for a uranium loss hypothesis to be necessary.

As observed in Section 4. (1), Nos. 2 and 3 are the only samples to have experimental error ellipses which are not intersected by concordia, but they lie very close to concordia. The exact concordance of the other samples can be accommodated by their experimental errors alone. See also footnote to P. 41.

Wetherill (1956 a) has outlined a graphical procedure to be used with

concordia diagrams for the estimation of the loss of daughter isotope. If t_o is the true age of mineralisation and t_1 is the time at which lead loss occurred, then the isotope ratios of samples which have lost varying proportions of lead will lie on a straight line connecting the points on concordia corresponding to ages t_o and t_1. The proportions of lead lost can be estimated from the position of the experimental point on the line relative to its length.

The simplest of the possibilities listed in Section 4. (2) which can be tested for these samples by this procedure is that which suggests that all the samples were originally mineralised at the 206/238 age of the Geevor uraninite (i.e. t_o = 290 m.y.), and that they have all suffered, to varying degrees, loss of lead in recent times (i.e. t_1 = 0 m.y.). With this hypothesis all experimental points should lie on a straight line connecting the origin with the 290 m.y. point on concordia. On trying this it is found that such a straight line does not intersect the error ellipse for No. 4, but does intersect the error ellipses of the other samples. It passes close to the experimental point for No. 2, but only just cuts the left of the ellipse for No. 3 and the right of the ellipses for Nos. 1A and 1B. It is thus only possible for this interpretation to be correct if extreme experimental errors be taken into account.

It is considered that the more detailed graphical and mathematical extensions of Wetherill's procedure as proposed by Stern et al. (1960) and Stieff and Stern (1961), are inapplicable to this problem because of the paucity of samples.

Simple calculations can be made to determine the actual degree of discordance which would result from lead loss of the magnitude necessary for it alone to account for an apparent decrease in the ages from an original 290 m.y. mineralisation. These calculations find their graphical representation in the

procedure described in the paragraph before last. The experimental 206/238 ratio of each sample is divided by the 206/238 ratio for an age of 290 m.y. to give the fraction of original radiogenic lead remaining. The 207/235 ratio for 290 m.y. is then multiplied by this fraction and the age calculated for the resulting figure. This calculated 207/235 age is compared with the experimental 206/238 and 207/235 ages (which are given in Table 10). The results are summarised below:-

Sample No.	Percentage Recent Lead Loss for Original Mineralisation at 290 M.Y.	Experimental 206/238 Age (M.Y.)	Experimental 207/235 Age (M.Y.)	Calculated 207/235 Age (M.Y.)
1A	23%	224	227	230
1B	22	227	229	233
2	58	124	130	133
3	81	57	71	63
4	79	62	59	67

In all cases except No. 3, the calculated 207/235 ages are greater than the experimental ones - i.e. the recent lead loss hypothesis results in a greater degree of discordance between the 206/238 and 207/235 ages than is observed experimentally. This degree of discordance could just be accounted for by the errors in Nos. 1A, 1B, 3 and 4 but not for No. 2. It is thus less likely that the hypothesis of recent lead loss accounts for the observations, but it cannot be conclusively rejected.

For No. 3 there is a smaller degree of discordance with the calculated 207/235 figure than with the experimental one, and for No. 4 the discordance is in the reverse direction. But the experimental 207/235 ages have low significance in this age range because the radiogenic Pb^{207} content is very small. Also both of these low ages have been calculated with very high common lead corrections and as a result they are not to be considered as reliable as the other ages. Thus it is considered that more detailed calculations on these

particular samples are unlikely to result in any definite conclusions.

For Nos. 1A, 1B and 4, as the degree of discordance in the experimental results is small and well within experimental errors, it is certainly not necessary to postulate lead loss to account for the observed results. One further observation to be made is the very high percentage lead loss required if the ages of the younger samples are to be accounted for by this process. This is further discussed in Section 4. (5).

For the same reasons that calculations based on lead loss in recent times are inconclusive, similar calculations for lead loss in intermediate times would be even less conclusive. This also applies to calculations based on continuous lead loss throughout the lifetimes of the minerals (e.g. Russell and Ahrens, 1957).

Preferential loss of radiogenic lead might be tested for by granulating the samples and subjecting them to acid wash experiments of the type undertaken by Tilton (1956) and Tilton and Nicolayson (1957). However, at the time of this work, techniques and a clean laboratory were not available which could handle the micro quantities of lead necessary for such experiments.

4. (4) SIGNIFICANCE OF X-RAY MEASUREMENTS.

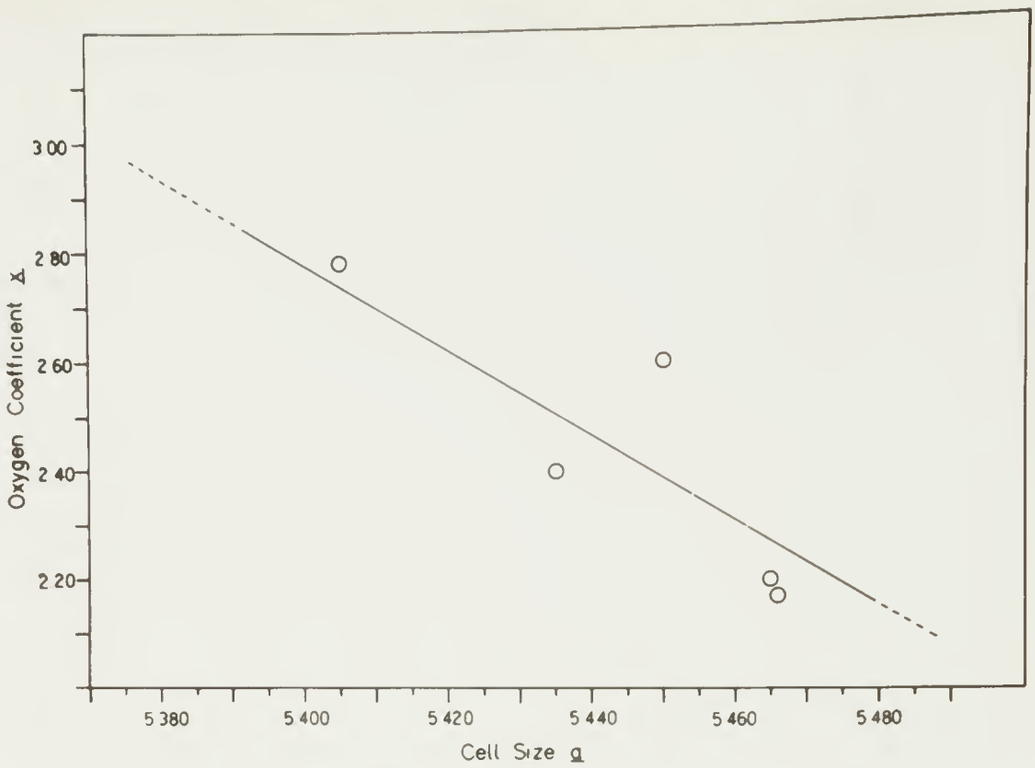
Variations in the cell sizes of uranium oxide minerals have been known from x-ray powder diffraction photo studies for some time. Goldschmidt and Thomassen (1923) found variations of 5.42 - 5.45A for the cell sizes of pitchblendes, which were somewhat smaller than those for uraninite samples. The variations were thought to be due to the presence of varying proportions of the different uranium oxides UO_2 and UO_3. Similar but larger variations in cell sizes (5.40 - 5.47 A) were observed in uraninite and pitchblende samples by Arnott (1950) and Rosenzweig et al. (1954).

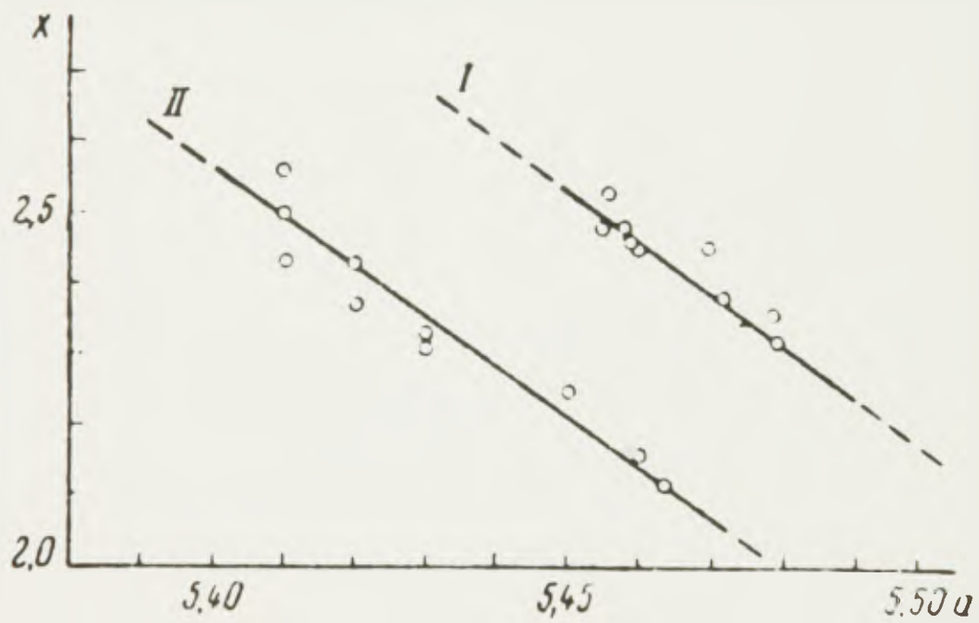
Conybeare and Campbell (1950) found cell sizes ranging from 5.39 - 5.45A

in nine pitchblendes from Goldfields, Saskatchewan. They took powder photos before and after heating their samples at 800°C. The powder patterns of some samples changed on heating - some with weak UO_2 patterns gave strong UO_2 patterns after heating, while some gave a combination of UO_2 and U_3O_8 patterns. It was claimed that this indicated the degree of oxidation of the pitchblende (no oxidation was considered to occur during heating). Also, the weakness of the original patterns was said to indicate that the samples were metamict.

Brooker and Muffield (1952) considered that the term "metamict" was inapplicable to pitchblendes - the loss of definition in a powder pattern of pitchblende was considered to be due to a reduction in grain size and the varying degrees of oxidation throughout a single sample. All sizes of pitchblendes from Lake Athabasca, Canada, ranged from 5.395 - 5.470A. The proportions of U^{4+} to U^{6+} in the samples were determined chemically by reaction with hydrofluoric acid which produces yellow soluble UF_6 and green insoluble UF_4 from U^{6+} and U^{4+} respectively. Decrease of cell size was found to accompany increasing degree of oxidation. The U^{6+} ion (ionic radius about 0.78A) is smaller than the U^{4+} ion (0.89A). On oxidation, U^{4+} changes to U^{6+} with entry of oxygen into the interstitial positions in the fluorite-type UO_2structure with a consequent shrinkage in cell size. Brooker and Muffield's results have been summarised graphically by the author in Figure 5; the best straight line drawn through the points was defined by a least squares statistical analysis.

Sidorenko (1958) found a similar relationship between cell sizes in uraninite and pitchblende and their degrees of oxidation, although no mention is made of the method of determining the latter. (Stonhill (1960) has reported a more satisfactory method for determining the oxidation states of





~~Fig. 3.~~ The x = f (a) relationship for uraninites (I) and pitchblende (II).

Figure 5: Graphs of Cell Size vs. Oxygen Coefficient.
Top: Data of Brooker and Nuffield (1952).
Bottom: Copied from Sidorenko (1958).

uranium by reaction with gaseous hydrogen fluoride - U^{4+} gives UF_4 and U^{6+} gives UO_2F_2. It is possible that other authors' oxidation state data are in some degree of absolute error, but it is unlikely that the qualitative trends shown by their methods are incorrect). Sidorenko found separate but similar linear relations for pitchblende and uraninite - lines I and II respectively in his graph reproduced in Figure 5.

Interesting alternative explanations of the cell size variations in uranium oxide minerals were put forward by Wasserstein in a series of papers (1951, 1954, 1955 a, b, c). He assumed that the shrinkage of the unit cell was due to the substitution of the radioactive parent U^{4+} and Th^{4+} ions in the lattice by their daughter Pb^{4+} ions. On the basis of measurements of samples which had been dated by the U/Pb method, a rate of shrinkage of 0.0035A per 100 m.y. was estimated. Wasserstein proposed this as a new method for age determination of pitchblendes. One sample to which he applied this is interesting to this study - he calculated a pitchblende from Cornwall to have an age of 400 m.y. Hoekstra and Katz (1955) and Hiemstra (1955) effectively refuted Wasserstein's hypothesis on several grounds. In particular, the radon ion, which is intermediate in the decay of both uranium and thorium to lead ions, is far too large to be accommodated in the lattice, and so lead is generated outside the lattice as isolated particles.

The hypothesis that increasing degree of oxidation causes cell size shrinkage is the only one to be backed by experimental evidence, and clearly is the most satisfactory explanation. It also appears that increasing loss of definition in a powder photo of pitchblende is due mainly to decreasing particle size.

Table 11 gives values for the oxygen coefficient of the pitchblendes studied as graphically interpolated from the data of Brooker and Nuffield

TABLE 11.

Oxidation States of Uranium in Cornwall Pitchblendes

Sample	Cell Size (in A)	Values of Oxygen Coefficient[1] Brooker and Nuffield (1958)	Sidorenko (1958) (Graph I)
1A: South Terras	5.44	2.45	2.30
1B: South Terras	5.44	2.45	2.30
2 : Redruth Area	5.42	2.65	2.45
3 : Owles	5.42	2.65	2.45
4 : South Terras Area	5.41	2.75	2.50
(Geevor Uraninite	5.48	-	2.30)[2]

[1] x is the oxygen coefficient of uranium oxide of the general formula UO_x.

[2] Sidorenko is only worker to give figures for uraninite as distinct from pitchblende. If this cell size for Geevor uraninite were applied to the data for pitchblendes of the Brooker and Nuffield, the oxygen coefficient would be almost exactly 2.

and Sidorenko (Line I) from Figure 5, using the cell sizes summarised in Table 10. It is apparent that these sets of data are not closely consistent. The most likely source of variation is in the chemical determination of the oxidation state. Nevertheless, both sets of data show the same direction and magnitude of variation in the oxygen coefficient. This is all that is important for this study, which is essentially comparative. The differing oxygen coefficients in the Cornwall pitchblendes are clearly significant. Although to the nearest 0.01A (which is a liberal estimate of the error), Nos. 2 and 3 have the same cell size, the 3rd decimal places (see Table 9) do indicate a slightly lower cell size for No. 3 than for No. 2. Thus the trend of increasing oxygen coefficients is probably continuous from Nos. 1 - 4, and not slightly discontinuous as indicated by the figures of Table 11. It is apparent from Tables 10 and 11 that decreasing ages are accompanied by increasing degrees of oxidation in these samples.

The qualitative observations of the photos also show that decreasing ages are accompanied by increasing diffuseness of the diffraction lines, probably caused by decreasing particle size.

The observed differing degrees of oxidation could represent variations in the original mineralising environment. In this case, if the observed ages actually represent the primary mineralisations, then the observed correlation between degree of oxidation and age would probably be fortuitous. However, it is possible that the differing degrees of oxidation have been imposed on the samples at some time since their original mineralisation. For example, the samples could have been subjected to varying degrees of alteration by solutions, which at the same time oxidised the uranium to similarly varying extents. The implications of these results are further discussed in Section 4. (7).

Brooker and Muffield studied pitchblendes from an area which has also been the subject of many U/Pb age determinations (Collins, 1952; Eckelmann and Kulp, 1956). The specimens for both Brooker and Muffield's and Eckelmann and Kulp's studies were provided by the same person, S. C. Robinson. But unfortunately, no significant correlations between the x-ray and age results can be made as only two of the same deposits were studied by both techniques, and there is no certainty that the same samples were used. As the work reported in this thesis is probably the only study involving both age and x-ray measurements on the same samples, no comparisons can be made with similar combined studies.

4. (5) SIGNIFICANCE OF POLISHED SECTION AND AUTO-RADIOGRAPH STUDIES.

The autoradiographs indicate a very low number of point-centres of intense radioactivity as are commonly generated by radium or radon. While not being conclusive evidence, this does make it unlikely that radon loss is a significant factor in these samples.

The detection of coffinite in these pitchblendes by Darnley is interesting, especially in view of the lack of observations from the author's x-ray powder photos of any mineral phase other than galena. Coffinite, a hydrous uranium silicate of the composition $U(SiO_4)_{1-x}(OH)_{4x}$, possesses a powder pattern quite distinct from that of pitchblende (Stieff et al., 1956). It is surprising that it was never observed in any of the x-ray photos of the powdered pitchblendes made here (Darnley identified coffinite by drilling a piece out from a polished section for x-ray analysis). It may be that the coffinite:pitchblende ratio is much lower in the selected grains used for age and x-ray analysis here than suggested by Darnley (the crushing and mixing of the powder would tend to average out small local concentrations of any

particular mineral). The presence of coffinite in the specimens, in significant quantities or not, does not invalidate the age determinations made on them.

The important feature about the detection of uranium "secondaries" in two of the samples is that Darnley does not consider them to be the products of weathering. The freshness of all sulphides and the absence of cavities and any other signs of alteration or weathering having affected the internal mass of the samples is the most important conclusion of these studies. The presence of finely disseminated galena in all samples is not unexpected. The Owles sample, in which the observation of galena was confirmed by the x-ray powder photo measurements, is thus not unique but merely the sample with the largest-sized galena inclusions.

It is likely that some of the common lead was contained in the observed inclusions of galena in the pitchblendes, although a significant proportion was probably also contained in non-crystalline lead. The extent of the total common lead contamination is shown by the Pb^{204} content, and was accurately corrected for in the calculations. But if it had been possible to separate the galena inclusions from the pitchblendes, then the common lead correction would have been reduced and the accuracy of the ages enhanced.

Darnley's comments and interpretations in his Para. 5 (Section 3. (6)), will be discussed more fully in Section 4. (7).

4. (6) REMOBILISATION HYPOTHESIS.

Davidson (1960) has reviewed some previous work on ore deposits in Western Europe for which there is geological evidence for local rejuvenation (or remobilisation) of uranium minerals, whose associations with Hercynian granites are clear. In particular, the well-known Jachymov, Bohemia,

pitchblende whose veins cut Tertiary dykes, and French and Portuguese occurrences of apparent Upper Mesozoic age are mentioned. Davidson does not consider it feasible that this rejuvenation has been caused by a lateral secretion process in which uranium was derived from rocks of the batholiths in, say, mid-Cretaceous times, because of the virtual absence of thorium from the pitchblende veins.

Davidson adduces U/Th/Pb age determinations on uranium minerals from European "Hercynian" mineralisations to support his hypothesis. It is unfortunate that many of the ages selected for inclusion in Davidson's table are of doubtful significance - e.g. descriptions of analytical method such as simply "isotopic" or even "full isotopic" give no indication of the reliability of each figure. The localisation of one specimen as "Central Europe" does not justify its inclusion, nor should 207/206 ages alone be treated with any reliability in this age range (see results of this study). One uraninite from Sierra de Albarrana, Spain, had "isotopic" ages of 250, 325, 290 m.y.; the isotopic ratio associated with each of these ages is not indicated, and the lack of concordance (whichever isotope ratios may the ages represent) provides no confidence in their significance. Few of the sources cited could be checked because of their rare nature.

The only ages quoted by Davidson which are likely to have any significance are those for Geevor (Darnley et al., 1960; results quoted in Table 10 of this thesis) and the last six in his table, which come from Wittichen, Black Forest; La Crougille, France; Urgeirica and Lenteiros (3 specimens), Portugal. Except for Lenteiros, there is no locality for which more than one determination is reported, and the ages for Lenteiros may well be within each other's experimental errors. Even with these ages there is no indication of which

age represents which isotopic ratio, and no errors are quoted. Without this information the reliability of these ages must remain in doubt.

It does appear that the ages quoted by Davidson are so few and of such doubtful significance that they are of little support to his general thesis that rejuvenation of Hercynian mineralisations is a widespread phenomenon. Nevertheless, his general thesis must be considered very seriously with relation to the mineralisation in Cornwall.

F. W. Dunning has drawn the author's attention to some little known work on the Saxony ore deposits, which provide definite evidence for hydrothermal regeneration. Baumann's (1958) conclusions from the geological evidence were supported by the absolute age determinations of Vinogradov et al. (1959) on five pitchblendes (one from Joachimov, four from Johanngeorgenstadt). The latter authors concluded that the ore deposits of Saxony were hydrothermally worked at least twice. This led to a regeneration of ores during the Cretaceous (before ca. 100 m.y.) and in Upper Tertiary time (before ca. 5 m.y.). The date of the original deposition is defined as 100 m.y. There are some important geochemical differences between the Saxony and Cornwall ore deposits (Dunning, personal communication), but there is a close similarity between the age data for the two regions.

The author had considered that some process involving the solution of an older pitchblende and its subsequent recrystallisation (i.e. remobilisation or rejuvenation) might explain the Cornwall results. It was considered that the lead isotope composition of galena co-existing with the pitchblendes was of vital importance to the question of possible remobilisation. If remobilisation had occurred at some time significantly later than the primary mineralisation of the pitchblende, and if this had occurred on a restricted local scale (i.e. no large-scale migration of solutions had occurred), then

it would be expected that galena co-existing with the recrystallised pitchblende would contain a measurable excess of radiogenic lead.

It would be important to apply this test only to a galena which had been in the same veins as the pitchblende concerned. Of the samples of this study, only Nos. 1A and 1B from South Terras and No. 3 from Owles are very accurately localised. A galena sample was obtained from the same lode as the South Terras pitchblendes by A. W. G. Kingsbury, and this galena was isotopically analysed by Moorbath. Kingsbury has never observed galena in situ or on dumps at the Owles mine. Dines (1956, p.72) does mention that argentiferous galena existed with the uranium ores in cross-veins of the Owles lodes. At the author's request, F. W. Dunning kindly searched for a galena sample from any of the Owles lodes in the Geological Survey collection, particularly Dines' own personal collection, with no success.

The Owles pitchblende contains visible minute crystals of galena finely disseminated throughout it (Appendix I). The separation of this galena (if possible) and its isotopic analysis would be an unsatisfactory substitute for the analysis of a separate but co-existing galena. With such small crystals of galena in intimate contact with uranium it would be likely that during or after crystallisation the galena might inherit some radiogenic lead, by, for example, solid diffusion. The presence (or not) of excess radiogenic component in such a galena would not answer the required questions.

The observation of an abnormally high radiogenic component in a galena co-existing with a pitchblende would be good evidence for the past occurrence of remobilisation. It would also be expected that isotopic mixing throughout a remobilised vein would be incomplete, so that the galenas with the abnormal radiogenic components would be variable in isotopic composition. The amount of added radiogenic isotopes would depend on the relative quantities of normal

and radiogenic lead being mixed during the remobilisation. Thus, the examination of a series of galenas from different parts of the occurrence could provide further evidence for this hypothesis. However, it is not necessarily correct that if a galena co-existing with a pitchblende is found to have normal isotopic composition compared with the region (i.e. without radiogenic component), then remobilisation has not occurred; for it is possible that one part of the vein has escaped remobilisation, or that mixing of radiogenic and normal isotopes has been so incomplete as to have left some galena unaltered. Nevertheless, the discovery of a normal galena co-existing with a pitchblende does reduce the probability of remobilisation having occurred.

Moorbath obtained isotope abundances for the South Terras galena which areas close as those of any of his other six S. W. England galenas to their mean abundances (See Table 2). This does reduce the probability of remobilisation of the South Terras pitchblende, although it would be more satisfactory if more galena samples had been available.

A problem is posed by No. 4, for if it does come from the same South Terras lode as Nos. 1A and 1B, then there is no doubt that remobilisation has occurred at least once in this lode. As more accurate location data cannot be obtained for No. 4, such a definite conclusion must be avoided.

The common lead isotope data of Moorbath for S. W. England do not furnish any evidence for or against remobilisation in theregion. The total amount of uranium minerals is minute compared to that of lead minerals in the area, and so it would only be on a very local scale that remobilisation would have caused significant addition of radiogenic lead to normal galena. It would be expected that conditions causing the remobilisation of pitchblende would also cause remobilisation of galena, but on its recrystallisation galena would

preserve its original isotopic composition unless it had been in contact with uranium minerals. Thus such a galena would possess a model age older than the age of its most recent recrystallisation. This might not be geologically detectable if this latest deposition had occurred in the same or similar veins in the same country rock as before remobilisation.

Finally, in this Section, the possibility is considered of the isotopic composition of the lead used for the common lead correction being grossly in error. Upper and lower limits to the model ages of galenas which could be used for the common lead correction are approximately 300 m.y. (from age of Geevor uraninite and Moorbath's mean figures for S. W. England galenas) and 50 m.y. (from youngest pitchblende of this study). The isotopic composition of galena varies only within narrow limits over this range. Trial calculations with different isotopic figures for common lead within these limits have shown that the magnitude of the resulting U/Pb ages is sensibly unchanged. In most cases it was found that the degree of discordance for each sample was increased somewhat by the use of common lead isotope figures with younger model ages than those of Moorbath's figures. For example, if the common lead isotope figures of Darnley et al. (1960) for galena from Geevor (which yield a model age of 230 m.y. with the constants used in this work, compared with a model age of 260 m.y. for Moorbath's South Terras galena) are used to calculate the U/Pb isotopic ages of No. 1A the following results are obtained:-

	Common Pb Figures Used				Ages (m.y.)		
	204	206	207	208	206/238	207/235	207/206
Moorbath:	1.375 (1.000	25.08 18.24	21.34 15.52	52.20 37.96)	224	227	259
Darnley et al.	1.000	18.32	15.55	38.10	223	232	313

Darnley's figures are less satisfactory for this purpose than Moorbath's on experimental grounds (fewer mass spectrometer scans, no experimental errors quoted) and also because they only represent one very minor lead occurrence. But they serve to illustrate the point adequately.

4. (7) CONCLUSIONS.

Most of the possible interpretations in Section 4. (2) of the age results have now been considered individually in detail. The important conclusions are now summarised:-

1. The 206/238 and 207/235 ages agree within their errors. Calculations of recent lead loss (prirary mineralisation at 290 m.y.) give a greater degree of discordance than experimentally observed in all but one sample, No. 3. Thus, lead loss is not a necessary hypothesis.
2. Polished section studies more definitely exclude the possibility of recent loss of lead on a large scale.
3. Autoradiographs show radon loss to be unlikely.
4. The ages obtained are relatively insensitive to changes ~~in~~ the common lead isotope figures used. Moorbath's figures give the most concordant ages.
5. X-ray studies indicate that the degree of oxidation of the pitchblendes significantly increases with decreasing age. From the polished section studies it is unlikely that this was caused by oxidising ground waters.
6. Isotope figures for galena co-existing with the pitchblendes are only available for the South Terras samples. This galena possesses no abnormal radiogenic component. It is possible that Nos. 1A and 1B represent λ_a primary mineralisation.
7. Moorbath's galena model ages for S. W. England support geological

evidence that the mineralisation throughout the area occurred in Hercynian times, and that younger U/Pb ages obtained for pitchblendes represent later alterations of these minerals rather than primary mineralisations (with the possible exclusion of Nos. 1A and 1B).

8. From the geological evidence of the close relation of all deposits to granite intrusions, it is highly unlikely that the younger ages represent primary mineralisations.

Many more samples are required to finally decide between the remaining possibilities. But from all the foregoing considerations, it does seem that the 206/238 ages probably do represent later events affecting the mineralisation in S. W. England. The following stratigraphical correlations can be made:-

Sample	206/238 Age (m.y.)	Stratigraphical Correlation (Time Scale of Kulp 1961)
Geevor (Darnley et al., 1961)	290 ± 7	Permian-Carboniferous (Hercynian)
Nos. 1A, 1B, South Terras	225 ± 5	Triassic Permian
No. 2, Redruth Area	124 ± 4	Lower Cretaceous
No. 3, Owles No. 4, South Terras Area	60 ± 3	Lower Tertiary (Eocene-Palaeocene).

It is noticeable that all except the 225 m.y. age correspond closely with major periods of orogeny and/or igneous activity in Europe. The 290 m.y age is a little older than the Hercynian granites of Cornwall but clearly is closely connected with them.

The 225 m.y. age, which is certainly the most accurate and reliable age obtained in this study, is some 55 m.y. younger than the igneous activity in S. W. England which concluded the Hercynian orogeny. This age is not connected with any known period of earth-movement in the area. But it is

noticeable that Darnley et al. (1960) obtained a 206/238 age of 230 ± 8 m.y. for a pitchblende from Tyndrum, Perthshire, and both Moorbath and the author (see Part II, this thesis) have measured many galena model ages of 220 - 230 m.y. in the British Isles. It is possible that this 225 m.y. age may represent a primary mineralisation which also affected other parts of the British Isles but was unconnected with significant earth movement and unaffected by later remobilisation.

The 124 m.y. age is placed just near the Albian-Aptian boundary on Kulp's time-scale. There is a period of folding strongly developed in the Upper Jurassic and earliest Cretaceous of North Germany called the Younger Cimmerian, for which there is also evidence on a smaller scale in England as far west as Wiltshire (Wells and Kirkaldy, 1959). This was followed by the westward-moving Albian-Cenomanian transgression. R. St. J. Lambert has pointed out to the author the possibility of a 1° tilt occurring during this transgression which could well produce an uplift of one mile in West Cornwall if it were continued linearly from Lyme Bay area. The 124 m.y. age could be connected with either or both of these earth-movements. (See also Vinogradov et al., 1959, for evidence of hydrothermal regeneration of Saxony pitchblendes in the Cretaceous).

The 60 m.y. ages are Tertiary which could well be connected with earth-movements preceding the main Alpine orogeny in the Miocene. A major break is observed in Britain between the Chalk and the Eocene. The latest Chalk beds, the Danian, and the lowest Eocene beds are absent from Britain, and the Cretaceous strata was uplifted, tilted and eroded before the first Eocene deposition.

The remobilisation of hydrothermal minerals would require the conditions of temperature and pressure which could be generated by major periods of earth-

movement. The correspondence of three of these ages with Post-Carboniferous earth-movements in S. W. England thus provides added support for the hypothesis of successive periods of remobilisation occurring on a local scale in the area.

There is, however, a further hypothesis which should be considered, namely that there has only been one period of remobilisation. This is essentially the suggestion also made by Darnley (Section 3. (6)), and may well prove to be the correct explanation. Such a single period would have occurred no earlier than the most recent age observed for the area, i.e. about 60 m.y. ago (Darnley suggests 70 m.y.). During remobilisation lead would have separated from uranium but in varying proportions. The 124 and 225 m.y. ages would thus be apparent ages caused by the partial loss of radiogenic lead (common lead would almost certainly have been lost as well), and the correspondence of the 124 m.y. age with a period of earth-movement, and of the 225 m.y. age with other dated mineralisations would be fortuitous.

This latter hypothesis provides an explanation of the increasing degree of oxidation observed with decreasing age - the solutions causing removal of lead in varying degrees from the pitchblende may have also caused oxidation of the uranium in corresponding proportions. With the first hypothesis, the differing degrees of oxidation could have been due to the remobilising fluids having increasing oxidising power relative to uranium in the successively later earth-movements, but this may be somewhat more fortuitous than the other explanation.

Finally, assuming that no other possible explanation of the results has been overlooked, it would appear that some degree of later remobilisation of minerals originally emplaced in Hercynian times has occurred in S. W. England. The most recent, and possibly only period of such remobilisation probably

occurred in Tertiary times about 60 m.y. ago. It is not possible on the present data to decide conclusively whether there have been other discrete periods of remobilisation between Hercynian and Tertiary times.

The study of further samples from the area by all the techniques used in this work is necessary to decide between these two possibilities. If other ages are obtained which also correspond with periods of earth-movement, then it would appear that remobilisation has been controlled by these movements. But if there has only been one major period of remobilisation and the observed ages have been caused by varying degrees of loss of radiogenic lead, then apparent ages would be obtained which were scattered randomly over the 280 - 60 m.y. range.

One further possibility, which does not contradict either of the two remobilisation hypotheses, is that Nos. 1A and 1B indicate that there may have been a primary mineralisation at about 225 m.y. ago in Cornwall, as well as one in Hercynian times.

4. (8) TWO RECENT U/Pb AGES FROM S. W. ENGLAND (Postscript).

A. G. Darnley has kindly supplied the author with details of his latest U/Pb age results for S. W. England since the preceding four Chapters were typed. These results are reproduced, with a comment by Darnley, in Table 12. The following comments are inserted here as a postscript because of the importance of every new age result from S. W. England to the interpretation of the author's results.

1. The errors in the ages cannot be estimated because no errors are quoted for the chemical and isotopic analyses. These errors will probably become available later.
2. The chemical weight percent figures for U and Pb are quoted to optimistically high accuracies. On the other hand, the isotope abundances apparently were determined to only three significant figures.
3. No common lead minerals were analysed isotopically from the same occurrences as the uranium minerals. Moorbath's isotope data for S. W. England galenas were used to calculate the quoted ages, Pb^{208} evidently being used for the common lead corrections.
4. Trial calculations show that there is a discrepancy, in the case of the Kingswood Mine specimen a very large one, between the non-radiogenic Pb^{204} and Pb^{208} abundances in both samples. If Pb^{204} is used for the common lead correction this discrepancy is even more striking. The most likely cause of this is a large abnormal radiogenic component in the common lead contained in both samples, as also suggested by Darnley in Note 2 to Table 12. This would cause all the calculated ages to be too high. The $\frac{206}{238}$ age quoted for the Kingswood Mine sample could be too high by 100 m.y. and for the Wheal Bray sample by 30 m.y.
5. The excess radiogenic component in the common lead incorporated in these

Table 12.

Recent U/Pb ages from S.W. England[1]

Kingswood Mine

Buckfastleigh, Devon.
(margin Dartmoor Granite)

Material collected in situ from lode.

Pitchblende-coffinite concentrate

38.59% U_3O_8; 0.0033% ThO_2; 1.60% Pb

204 : 1.06% 206 : 67.4% 207 : 10.9% 208 : 20.7% [2]

Common Pb = 39.6% total

Provisional results : $\frac{206}{238}$ = 209 m.y.

$\frac{207}{235}$ = 181 m.y.

$\frac{207}{206}$ - ve

Wheal Bray

nr. Altarnun, Cornwall
(margin Bodmin Moor Granite)

Material obtained from drill hole core.

21.26% U_3O_8; 0.0023% ThO_2; 0.876% Pb

204 : 0.82% 206 : 58.8% 207 : 15.1% 208 : 27.3%

Common Pb = 52.25% total

Provisional results: $\frac{206}{238}$ = 166 m.y.

$\frac{207}{235}$ = 145 m.y.

$\frac{207}{206}$ - ve

[1] Reproduced by permission of A.G. Darnley and the Atomic Energy Division of the Geological Survey of Great Britain.

[2] Note that the common lead correction, if based on Moorbath's S.W. England value (or any approximation to this), does not reduce both the 204 and 208 values to zero, as it should. This suggests either an error in mass spectrometry or an abnormal radiogenic component in the common Pb present.

uranium minerals could have originated from remobilisation of older uranium minerals. During this process, the radiogenic lead from the old mineral would have been incorporated as common lead in the new mineral (cf. the author's samples 2, 3, 4 for which, if remobilisation occurred, only common lead of normal (Hercynian) isotopic composition was incorporated in the uranium minerals on recrystallisation).

6. Moorbath's common lead figures are clearly not applicable to the calculation of ages for these samples. If common lead minerals cannot be obtained from these occurrences, the analysis of several other uranium mineral samples from the same occurrences might show the extent of the radiogenic component in the common lead, and thus allow approximate ages to be estimated.

7. Replicate analyses are required for these samples, particularly to check these most unusual isotope figures.

8. In the meantime, the ages and percentage common lead contents quoted do not have even an approximate significance, and unfortunately cannot be used to resolve any of the problems posed by the author's results. Nevertheless, these results do illustrate the complexity of the mineralisation in S. W. England which was first evident from the author's results. The Atomic Energy Division of the Geological Survey of Great Britain are having more uranium samples analysed by other laboratories, and it is to be hoped that their results will solve these problems.

PART II

LEAD ISOTOPE STUDIES OF GALENAS FROM IRELAND AND FRANCE

PART II

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CHAPTER 5

INTRODUCTION

5. (1) HISTORICAL OUTLINE.

During his pioneering studies of lead isotopes with his newly developed mass spectrograph, Nier (1938; - et al, 1941) investigated both radiogenic leads from uranium and thorium minerals (see Section 1.(1)) and common leads from various sources. The common lead minerals were found to -

(a) be uranium- and thorium-free,

(b) have apparently constant atomic weights for lead,

(c) have marked variations in lead isotope composition.

In most cases Nier observed a regular change in lead isotopic composition with the apparent geological age of the mineral deposit: the younger the mineral, the greater was the proportion of the radiogenic isotopes Pb^{206}, Pb^{207} and Pb^{208}, relative to the non-radiogenic isotope Pb^{204}. These changes could not have occurred after the mineral crystallised in view of the absence of uranium and thorium.

Nier suggested that the different proportions of the isotopes observed were the result of the progressive decay of uranium and thorium to lead in the source, from which lead was extracted and concentrated during the mineralisation process. The proportions, relative to Pb^{204}, of Pb^{206}, Pb^{207} and Pb^{208} in this source would increase with time at a rate determined by the half-lives of their radioactive parent isotopes (U^{238}, U^{235} and Th^{232} respectively). On mineralisation the isotopic composition of the lead in the mineral would be "frozen", and would indicate the lead isotopic composition of

the source at the time of mineralisation. This qualitative explanation has formed the basis of all later quantitative theories of common lead isotope variations.

The 1939-45 war interrupted extensions to Nier's work, and it was not until about 10 years ago that any new common lead isotope measurements were made. Meanwhile theories had been advanced for the observed variations in lead isotopes, primarily with a view to estimating the age of the earth. Thus Gerling (1942), Holmes (1946, 1947a, 1947b, 1949), and Houtermans (1946, 1947, 1953) advanced essentially similar theories, and used Nier's data for their estimations. The refinement of these estimates by later measurements of the lead isotope composition of meteorites and modern ocean sediments, mainly by Patterson and associates (1953, 1955, 1956), is discussed in Chapter 9.

The above theories and those of Alpher and Herman (1951), Damon (1954), Marshall (1957) and Russell and associates (1954, 1955, 1956, 1960a, 1960b) have been applied mainly to the problem of estimating the actual age of lead mineralisations from their isotopic compositions. Over the past 10 years rapidly accumulating numbers of common lead isotope analyses have emerged from several laboratories (notably Bern, Bonn, California, Columbia, Leningrad, Moscow, Oak Ridge, Oxford, Tokyo, Toronto and Washington). Russell and Farquhar (1960b) have compiled a useful series of tables with most of the available lead isotope data. Cannon et al. (1961) estimate that ca. 2,000 such analyses have already been reported.

At the present time more workers are applying the Holmes-Houtermans model to their lead isotope data than any other theories (notably those of Russell and associates). The relative merits of these models are

discussed in Chapter 9. The Holmes-Houtermans model, which is used throughout this thesis, permits the calculation of a "model age" for the mineralisation of each common lead mineral whose isotopic composition has been determined. The geochemical ratios U^{238}/Pb^{204} and Th^{232}/U^{238} for the source material of the lead mineral can also be calculated. Lead model ages do not possess the accuracy of absolute ages measured by the U/Pb, K/Ar and Rb/Sr methods, but are of comparable usefulness when sufficient numbers of lead mineral samples are studied from any one region. The most immediately useful application of lead isotope data is for the identification of genetic similarities and differences between lead-bearing mineral deposits on the basis of characteristic model ages and geochemical ratios.

Despite the regular behaviour of lead isotopes in the majority of common lead samples ("normal" leads), there is a significant number of results ("anomalous" leads) which do not follow the predictions of any one model. No single model advanced so far has fully accounted for the isotopic compositions of both normal and anomalous leads. Many more isotopic analyses and theoretical investigations are still required before the behaviour of lead isotopes over geological time can be fully understood.

5. (2) AIMS OF THIS STUDY.

Once reliable, accurate and precise mass spectrometers were developed for reasonably rapid work, they were applied to making wide-ranging surveys of the lead isotope composition of some of the major lead deposits of the world. This work delimited the maximum variations of common lead isotopes on a world-wide basis, and thus revealed the major problems for theoretical explanation and many interesting regions for more intensive study. However, some of this work suffered from low accuracy in the mass spectrometry.

Other workers, while providing excellent isotope data, omitted much of the geological information which is essential to the interpretation of such results.

In 1958, Moorbath started a detailed reconnaissance study of lead mineralisation in the British Isles. This work had the following characteristics:-

(a) Sampling over a relatively small area (100 galena specimens analysed from the British Isles), and not limited to major deposits.

(b) The geology of the general area is probably better known than any comparable area elsewhere.

(c) The geological settings of the mineral deposits sampled were carefully studied, thus allowing detailed geological considerations to be made on the basis of the isotope data.

(d) The mass spectrometer used yielded results whose precision was comparable with the best obtained elsewhere.

Some of the results have been published in a preliminary communication (Moorbath, 1959a). All the results are reported and discussed in full in his thesis (Moorbath, 1959b). The dependence by the author on the principles and results of Moorbath's work is evident from the frequent reference which is made to his thesis throughout the present work.

Moorbath isotopically analysed 17 galenas from Ireland. The results were of sufficient interest to suggest that a more detailed reconnaissance study of the lead deposits of Ireland might prove fruitful. In the course of the author's work 63 new galena samples from Ireland were studied. Moorbath's unpublished isotope and geological data on his 17 Irish galenas have been reproduced in this thesis, so that a complete coverage of all the Irish galenas to have been isotopically analysed could be presented.

A suite of 11 galena specimens from the Armorican massif, Bretagne and Normandie, France, was also isotopically analysed. This region was of particular interest because it was originally considered that these specimens might present an analogous set to the 7 galenas from S. W. England, which Moorbath found to form a well-defined group. No other isotope analyses had been reported on galenas from France prior to the author's studies. Recently, Durand (1960) has published lead isotope data for 13 French galenas. The significance of these, relative to the author's results, is discussed in Chapter 11.

Throughout the author's work, subsidiary aims of improving the precision of the mass spectrometer results, and of examining the statistical significance of these results have been borne in mind.

CHAPTER 6

MASS SPECTROMETRIC TECHNIQUES

The basic features of the Metropolitan-Vickers Type MS5 solid-source mass spectrometer used in this work have been described in sufficient detail by Moorbath (1959b, Section 2.2) and this is not repeated here.

6.(1) PREPARATION OF SAMPLES.

Clean galena grains were separated from the specimen. Most specimens were sufficiently coarse-grained to allow hand-picking, but in the case of some fine-grained specimens the method of separation described in Appendix III was necessary to obtain a sufficient concentrate of galena. The galena was ground fine and dissolved in warm 1:1 nitric acid (all reagents were Pb-free, and water used was de-ionised). After filtration to remove the very fine colloidal suspension of sulphur which frequently formed, the pH was adjusted to 4.5 with ammonia solution. PbS was precipitated as described for radiogenic samples in Section 2.(3).

The presence of other sulphide minerals (e.g. pyrite, chalcopyrite and sphalerite, often in excess) with the galena sometimes led to difficulties in the separation of pure PbS samples due to contaminating ions in the solutions. The purification of PbS precipitates was sometimes desired after poor emission was obtained on the mass spectrometer. In these cases one or both of the following methods were used to obtain purer PbS.

PbS was dissolved as described above for galena, and lead extracted by:-

(a) Dithizone process - as described for radiogenic samples in Section 2.(2).

(b) Sulphate process - $PbSO_4$ was precipitated by treatment with dilute Pb-free sulphuric acid. This precipitate was dissolved in ammonium acetate solution, filtered and PbS precipitated as before.

The aim of these processes was to remove contaminating elements, but it cannot be claimed that excellent separations were always obtained. For example, the most commonly detected contaminant in PbS samples was thallium, the two isotopes of which (mass numbers 205 and 203) were almost invariably observed to some extent in the mass spectrum of lead. Some PbS samples prepared direct from the galena without purification were found to give relatively enormous thallium peaks on mass analysis. After "purification" by one or both of the above methods, thallium was found to follow lead persistently and was never entirely removed from such samples. Mass spectrometry observations gave no idea of the absolute quantities of thallium present, but it appears from neutron activation analyses (Appendix IV) that it is present only in the low p.p.m. range. Thus very low amounts of thallium can give very high emissions. If thallium is present in the chemically prepared PbS, it is likely that trace amounts of other elements such as bismuth, arsenic and antimony may also follow lead through the purification processes. Small bismuth peaks at mass number 209 were detected in only two samples. Long et al. (1960) also consider that the presence of trace elements in lead sulphide may hinder surface ionisation of the lead in the mass spectrometer.

Next to purity, the reproducibility of the physical form of the PbS precipitate was important. For any one galena sample a series of tests showed that the factors affecting the form of the precipitate were concentration, pH, temperature and rate of bubbling of H_2S. Although the form was not very sensitive to changes in these factors, they were standardised for all samples. A galena solution concentration of 5% or less and a slow steady rate of bubbling of H_2S were found to be the most suitable. Similarly a pH of 4.5 and a temperature just under boiling helped to give a satisfactory sample form.

Identical conditions did not always produce similar precipitates with

different samples. Precipitates which gave relatively large thallium peaks were generally in coarser aggregates than those without thallium; and the former were sometimes dark brown rather than black. It is likely that such differences were caused by a whole assemblage of trace elements in the sample rather than by thallium alone. A finer and blacker precipitate was generally obtained after submitting a coarse and brownish one to purification. Poor ion emission in the mass spectrometer could often be correlated with observed abnormalities in the thallium content and/or sample form.

Ion exchange techniques have recently been developed by Catanzaro and Gast (1960) for separation of trace amounts of lead, and by Long et al. (1960) for purification of lead from galenas. With the present methods of preparation there were a number of failures in mass spectrometric analysis of poor samples. The application of the relatively simple ion exchange techniques to the purification of macro amounts of lead from all galenas would greatly increase the certainty of obtaining satisfactory emission in the mass spectrometer.

6. (2) ALTERNATIVE SAMPLE FORM.

The possibility of contamination in chemical extraction and purification procedures is ever-present in the preparation of samples for mass spectrometry. In this study, 0.5 g of galena was generally taken for processing, and significant contamination of this relatively large amount from the carefully cleaned apparatus and the special Pb-free ($Pb < 0.005$ p.p.m.) reagents used was very unlikely.

Nevertheless, it was considered worth while to try eliminating chemical procedures altogether. Galena was carefully separated from all gangue minerals by the methods described in Appendix III. Some of the fine-ground sample was placed under de-ionized water in a tube and was mounted as a slurry

direct on to the tungsten triple filament, in the same way as chemically prepared lead sulphide. The galena grains did not stick on the filament as firmly as precipitated lead sulphide unless they were ground very fine beforehand.*

Although treated identically in the mass spectrometer, a galena sample invariably gave better emission than that of a precipitated sample prepared from it. Working emission was reached at a centre filament current about 0.5 amp. lower (working range usually 3.8 - 4.3 amp.), and the emission remained higher and steadier than with precipitated samples. Generally about 1 mg. of galena was necessary to produce an even layer on both side filaments, which was up to five times more than the normal amount of precipitated lead sulphide used (see Section 6.(3)a). This did not cause the continual decrease of emission which was the characteristic behaviour of a filament overloaded with precipitated sample. The method was tested with several samples, and no poor emission was ever obtained. It would seem that a more satisfactory sample form for use in this mass spectrometer has been found for galena samples. It is also recommended as the better method for future work, in view of the elimination of chemical procedures. Chemical procedures would still have to be used with very fine-grained galena samples, such as those from Kilmacoo, Ireland (Nos. 56 and 57 of this thesis).

This sample form is closely comparable to that used at Bonn (Ehrenburg et al., 1955) where galena samples were vapourised directly from a crucible

* Lay (1960; personal communication) has recently used the same sample form for isotopic analyses of galenas with a similar mass spectrometer and identical tungsten triple filament sources to those used in this work. Lay mounted the fine-ground galena on the filament as a slurry with a dilute aqueous solution of borax. On gentle heating, the crystallised borax bound the galena grains tightly on the filament.

before ionisation in the source region. Tungsten filaments have the advantage of requiring less sample than the Bonn technique, which uses at least several milligrams of lead per run, although this factor is only important when little pure galena is available.

The use of this sample form was not tested until the author's mass spectrometry work using precipitated lead sulphide samples was about two-thirds completed. It was decided to complete this study using precipitated samples throughout. However, in two cases the results quoted in this thesis are of determinations using fine-ground galena, viz.

(a) No. 40 - all the precipitated sample had been used in trying to obtain satisfactory emission, and only a small amount of galena remained.

(b) No. 76 - supplied as powdered galena.

The times taken to prepare chemical precipitates and galena concentrates by the method of Appendix III were comparable. Mineral concentration was relatively faster when purification procedures had to be applied in the chemical method.

6. (3) OPERATION OF INSTRUMENT.

Since Moorbath (1959b) has outlined the techniques of operating the mass spectrometer, only modifications of these techniques are discussed here.

(a) Amount of Sample.

By loading the filament to capacity with 1-2 mg. PbS (Moorbath, 1959b, p.15), it was found that ion emission was relatively high in intensity, but generally decreased so rapidly that measurements could not be made. After prolonged heating at running currents, the emission of such large samples would frequently steady out, presumably due to a decrease in the amount of PbS present

This characteristic effect could be avoided by "painting" on to the side

filaments only a very fine even layer of PbS. Weights of sample added to the filament varied, but several weighings showed that the normal amount was ca. 200 - 400 μg. With two samples, less than 100 μg. PbS was loaded on the filament, and yet excellent emission was still obtained. Nevertheless it is considered that the lower limit of sample weight for the tungsten triple filament source is ca. 50 - 100 μg. Single filament techniques are the most likely to give successful results when less than 50 μg. PbS is available.

(b) Pre-Treatment of Sample.

Moorbath (1959b, p. 25) advocated a period of several hours of "outgassing" a lead sample before carrying out measurements, in order to give an ultimately steadier emission. Tests showed that the lack of such a period seldom affected the emission characteristics of a sample. Samples were heated overnight at ca. 3 amp. before bringing up to running currents, and the resulting emission compared with that obtained by bringing the same sample up to the same running current in five minutes without preliminary heating. The only difference observed was that the latter method sometimes gave slightly better emission. The wide variations observed in the emission characteristics for individual samples were not affected by any preliminary treatment at ca. 3 amp.

Whatever its preliminary treatment, the most important factor in obtaining optimum emission for a given sample was its treatment above 3 amp., this being termed the "warming-up period" for convenience. The operating principle in this period was that emission had to be allowed to steady out at each current before increasing the current to obtain higher emission.

Samples containing thallium gave peaks at mass numbers 205 and 203, whose heights were in the ratio of ca. 7:3 respectively and were readily recognised. Tests on such samples showed that a long period of "burning off" thallium at low currents was profitable in only a few cases. For most samples containing

thallium the behaviour of the thallium peaks was ignored, the rate of increase of filament current being governed by the behaviour of the lead peaks. The higher the current was raised, the faster the thallium burned off. It was always found that thallium emission had decreased to reasonable levels by the time the lead emission had reached working levels.

(c) Scanning.

The mass spectrometer was equipped with an automatic range-changing system which never operated satisfactorily. Manual range-changing was used throughout.

25 - 30 complete scans were generally taken with each sample, which was about five more than generally taken by Moorbath. This increase partly compensated for the greater scatter of results of individual scans caused by the ageing of the first electron multiplier (see (f) below, and Section 8.(1)). A complete run took about two hrs. once scanning was started. Warming-up periods normally took $\frac{1}{2}$ to $\frac{3}{4}$ hr.

The rate of "production" of determinations was increased by eliminating any prolonged preliminary heating. Normally, four samples could be run in a 14 hr. working day, with an effective average of three samples per day due to difficult runs and machine faults.

(d) Effect of Instrument Controls.

Various systematic tests were carried out to determine any effects which alteration of certain instrument controls might have on the results obtained.

(i) Zero : Test runs showed that raising the electrical zero for the Pb^{204} peak had no effect on the measured abundance of that isotope, as once suspected. A Base Speed setting of 40 for the motor-drive of the magnet current scan potentiometer was found to be the most suitable for drawing a good zero between peaks.

(ii) Peak Speed ; The peaks obtained in this work always showed some degree of asymmetry. The optimum setting for the Peak Speed of the motor-drive was determined by the shape of the peaks produced (higher settings gave sharper peaks) A setting of 16-20 was generally used. Test runs on the same sample using a Peak Speed of 20 (giving rather pointed peaks in this instance) and a Peak Speed of 12 (giving wide, round-topped peaks) gave results which agreed closely. The results obtained appeared to be remarkably insensitive to peak shapes.

(iii) Range Factors ; The groups of amplifier sensitivities, or range factors, normally used for the common lead work are given in Table 13. During any one run 2 - 4 groups of range factors were used. At an early stage in this work it was suspected that there were small errors in the range factors, whose exact integral values listed in Table 13 were used in the calculations. Checking of the resistor chain in the sensitivity manual by the manufacturers eliminated the possibility of error there. Nevertheless, every run was thoroughly checked for evidence of any systematic differences between range factors.

No differences were found until a series of tests at the end of the first electron multiplier's life. Three complete determinations, each of ca. 25 scans, were done on a sample, which gave remarkably steady emission, using only one set of range factors per determination. The results were:-

Range Factors Group	Percentage Isotope Abundances			
	204	206	207	208
-1	1.327 ± .006	25.02 ± .03	21.22 ± .03	52.43 ± .04
-2	1.385 ± .009	25.01 ± .06	21.05 ± .07	52.55 ± .09
-4	1.379 ± .005	25.12 ± .06	21.22 ± .05	52.28 ± .06

Other less thorough comparisons indicated that Group -3 also gave different results from Group -4. In general it appeared that the lower the relative height of a particular isotope peak in a certain group of range factors, the lower was its calculated isotope abundance.

During the extensive overhaul and testing of the mass spectrometer, following the rebuilding of the electron multiplier, I. E. Long calibrated the range factors and the recorder. Very small differences were found in the range factors from the integral values, but these were well within the experimental errors of any run and did not change the observed values. The differences in calculated abundances were found to be largely due to non-linearity of response of the recorder (see (e) below). But the application of corrections for this effect did not bring these results entirely into agreement, and so many runs made at this time had to be rejected (see Section 8.(1)). No differences between range factors were found when the new electron multiplier was used together with application of the recorder non-linearity correction.

(e) Non-Linearity of Recorder Response.

Long's calibration of the recorder showed that small recorder deflections were lower than their correct values. The calibration yielded a series of positive correction factors which increased with decreasing recorder deflections (Table 15). This effect was almost certainly caused by a worn slide wire in the recorder balancing circuit. The correction was only applied to results obtained after this calibration (see Section 7.(5)).

(f) Electron Multiplier.

The high tension applied at first to the electron multiplier of this mass spectrometer was 2.0 KV., and it was increased later to 2.3 KV. (Moorbath 1959b Section 2.4). During the first half of the author's work, a high tension of

2.5 KV. was used, but in August, 1960, it became evident that the multiplier was "ageing" rapidly. Repeat determinations of samples which earlier had given good emission with filament currents of 4.5-4.8 amp. were now giving poor emission, high currents of 4.8-5.5 amp. being necessary to obtain scans. Electronic noise was increased, peaks were pointed and asymmetric, experimental errors were increased, and agreement with previous determinations was poor.

The electron multiplier was then rebuilt with recoated Be-Cu dynodes. With a high tension of 1.2 KV., this new multiplier proved most satisfactory. Electronic noise was a little greater, but the experimental errors obtained were lower than those of any previous runs. All other previous disturbing features were eliminated. The gain of the multiplier at this high tension has been measured to be ca. 12,000.

Corrections were made throughout this work for electron multiplier efficiency, which increases with decreasing ion mass, according to the square root of the mass numbers of the isotopes being compared. Giletti and Moorbath's demonstration of the validity of this correction for this instrument (Moorbath, 1959b, p. 21) has been repeated recently by Hamilton and Long with similar results. The application of this correction is discussed in Chapter 7

C H A P T E R 7

THE CALCULATION OF LEAD MASS SPECTROMETRY DATA AND MODEL PARAMETERS BY DIGITAL COMPUTER

7. (1) RAW DATA OF A MASS SPECTROMETER MEASUREMENT OF LEAD ISOTOPES.

The purpose of this Chapter is to describe the methods developed and applied in this work to the calculation of lead isotope compositions from raw mass spectrometry data, and the calculation of model parameters from the isotope data. It is necessary to outline first the raw data of a mass spectrometer measurement of lead isotopes.

The relative abundances of the four lead isotopes were recorded on the chart of the mass spectrometer as peaks, the heights of which were proportional to the isotope abundances. Each scan consisted of a sweep across the lead mass spectrum, starting just above mass number 208 and finishing just below 204 and then sweeping back in the reverse sense. This produced eight peaks with one pair of peaks for each isotope. Maximum peak heights were obtained by use of a sensitivity switch. Measurements of peak heights were made visually to the nearest 0.5 mm. with an accurate scale. In order to compare the measured peak heights on the same scale, they were multiplied by the range factors used. This is illustrated in the following table:-

Lead Isotope	Peak Height	Range Factor	Total Peak Height
208	114 mm.	200	22800 units
207	92.5	100	9250
206	109	100	10900
204	148	4	592
204	145	4	582
206	103	100	10300
207	87	100	8700
208	106.5	200	21300

Range factors were used in a limited number of groups. Each group was

Table 13.

Programme Code Numbers for Mass Spectrometer Range Factors Groups

Programme Code No.	Mass Spectrometer Range Factors Groups				Mass Spectrometer Sensitivity Numbers
	208	207	206	204	
-1	200	100	100	10	0, 1, 1, 4
-2	200	100	100	4	0, 1, 1, 5
-3	100	40	40	4	1, 2, 2, 5
-4	100	40	40	2	1, 2, 2, 6
-5	40	20	20	2	2, 3, 3, 6
-6	40	20	20	1	2, 3, 3, 7
-7	40	10	10	1	2, 4, 4, 7
-8	20	10	10	1	3, 4, 4, 7
-9	200	100	200	10	0, 1, 0, 4
-10	200	100	200	4	0, 1, 0, 5
-11	100	40	100	4	1, 2, 1, 5
-12	100	40	100	2	1, 2, 1, 6
-13	100	40	20	2	1, 2, 3, 6
-14	100	20	40	2	1, 3, 2, 6
-15	40	20	40	2	2, 3, 2, 6
-16	40	20	40	1	2, 3, 2, 7
-17	40	10	20	1	2, 4, 3, 7

used for a number of scans, until the decrease of emission with time, or an increase of filament current, necessitated a different group to maximise the peak heights on the recorder (see Table 13).

The complete raw data of a mass spectrometer run thus consisted of:-

(a) Peak Heights
(b) Range factors for each scan
(c) Total number of scans

7. (2) RESULTS REQUIRED FROM RAW DATA OF EACH RUN.

(A) The following three series of results were required from all lead isotope measurements:-

1. Isotope abundances, expressed as percentages of the whole:-

(a) Percentage Pb^{204} (abbreviated hereafter to % 204)
(b) " Pb^{206} (" " " % 206)
(c) " Pb^{207} (" " " % 207)
(d) " Pb^{208} (" " " % 208)

2. Ratios of isotope abundances relative to Pb^{204}:-

(a) Pb^{206}/Pb^{204} (abbreviated hereafter to $\frac{206}{204}$)
(b) Pb^{207}/Pb^{204} (" " " $\frac{207}{204}$)
(c) Pb^{208}/Pb^{204} (" " " $\frac{208}{204}$)

3. Ratios of isotope abundances relative to Pb^{206}, expressed as percentages:-

(a) $Pb^{204}/Pb^{206} \times 100$ (abbreviated hereafter to $\frac{204}{206} \times 100$)
(b) $Pb^{207}/Pb^{206} \times 100$ (" " " $\frac{207}{206} \times 100$)
(c) $Pb^{208}/Pb^{206} \times 100$ (" " " $\frac{208}{206} \times 100$)

(B) The following additional results were required from measurements of common lead minerals:-

4. Model age in m.y. (P) (Holmes-Houtermans theory).

5. Geochemical ratios:-

(a) U^{238}/Pb^{204} (V_p)

(b) Th^{232}/U^{238} (K_p) (see Section 9.(2))

These values are expressed as the means of the results for the 20 - 30 individual scans comprising the run. The statistical accuracy of each mean is expressed as twice the standard error of the mean. This gives a 95% probability that the true values lie within the limits defined by their errors (Moroney, 1954). These errors can be calculated for Results 1 - 3 using standard statistical formulae. The calculation of the error in the model age is discussed later. Up to the present no errors have been quoted in the literature for the geochemical ratios.

7. (3) COMPUTER CALCULATION - INTRODUCTION.

The computer used in this work was the Ferranti "Mercury" Computer of the Oxford University Computing Laboratory.

A programme consists of a breakdown of all the required calculations into a series of simple operations which the computer can perform at high speed. The programmes presented here are largely written in the Manchester Mercury Autocode System.

Programmes and data are fed to the computer by means of punched tape. The computer performs the required calculations and punches out the desired results on another tape, which is printed out in readable form by a teleprinter. As many series of data as time allows can be supplied in succession to the computer without re-inserting the programme.

7. (4) COMPUTER CALCULATION OF LEAD MASS SPECTROMETRY DATA - (A) Presentation of Raw Data.

A programme can be planned to take the data in almost any suitable form,

NOTE

TABLES 14, 16, 17, 18, 19, 23, 24
25, 26, 27, 28, 29, 30

- all the computer programmes, data and results referred to in this Chapter, are bound at the end of this thesis, following p.213, so as not to interrupt the text of this Chapter.

within a limit of 64 characters per line. Table 14 is an annotated teleprinter "print-out" of a typical set of raw mass spectrometer data ready for calculation. The form of the data is so arranged that it can be punched out on the teleprinter directly from a mass spectrometer chart with its measured peak heights. It is important that the data be punched out in exactly the form as shown, otherwise it will not be accepted by the computer.

In Table 13 are listed the groups of range factors used during the author's 250 lead mass spectrometer measurements. Each group is given a programme code number, and these are all stored in the programme itself. Other groups with new code numbers can be added to the programme if necessary. The negative sign is the signal for the computer to refer to this store and bring the group of range factors indicated into use. This group remains in use until it is cancelled by the appearance of another negative sign in the data. Thus it is necessary to punch in a range factor code number only where a change of range occurs in the measurement.

7. (5) COMPUTER CALCULATION OF LEAD MASS SPECTROMETRY DATA -
(B) Correction for Non-linearity in Recorder of Mass Spectrometer.

In Table 15 are listed the data obtained by L. E. Long from his calibration of the response of the recorder of the mass spectrometer (See Section 6.(3)(e)). In order to estimate the appropriate correction factors for intermediate peak heights, Long's data were plotted graphically and a smooth curve drawn through the experimental points - Figure 6. The interpolations read off this curve at 10 mm. intervals in peak heights are reproduced in the second half of Table 15.

The computer programme designed to carry out this correction is presented as a print-out in Table 16. An example of the results produced by this programme from the data of Table 14 is printed-out in Table 17. The essential features

TABLE 15

Correction for Recorder Non-Linearity

DATA

Observed fraction of full-scale deflection.	Peak Height (in.)	Peak Height (mm.)	Correction Factor.
0.1	1	25	1.024
0.2	2	50	1.016
0.3	3	75	1.012
0.4	4	100	1.008
0.5	5	125	1.006
0.6	6	150	1.003
0.7	7	175	1.002
0.8	8	200	1.001
0.9	9	225	1.000

INTERPOLATIONS FROM GRAPH (Figure 6)

Peak Height Ranges (mm)	Mean Correction Factor	Peak Height Ranges (mm)	Mean Correction Factor
0 - 10	1.033	90 - 100	1.009
10 - 20	1.028	110 - 120	1.007
20 - 30	1.024	120 - 130	1.006
30 - 40	1.020	130 - 140	1.005
40 - 50	1.017	140 - 150	1.004
50 - 60	1.015	150 - 160	1.003
60 - 70	1.013	160 - 180	1.002
70 - 80	1.012	180 - 210	1.001
80 - 90	1.010	210 - 250	1.000

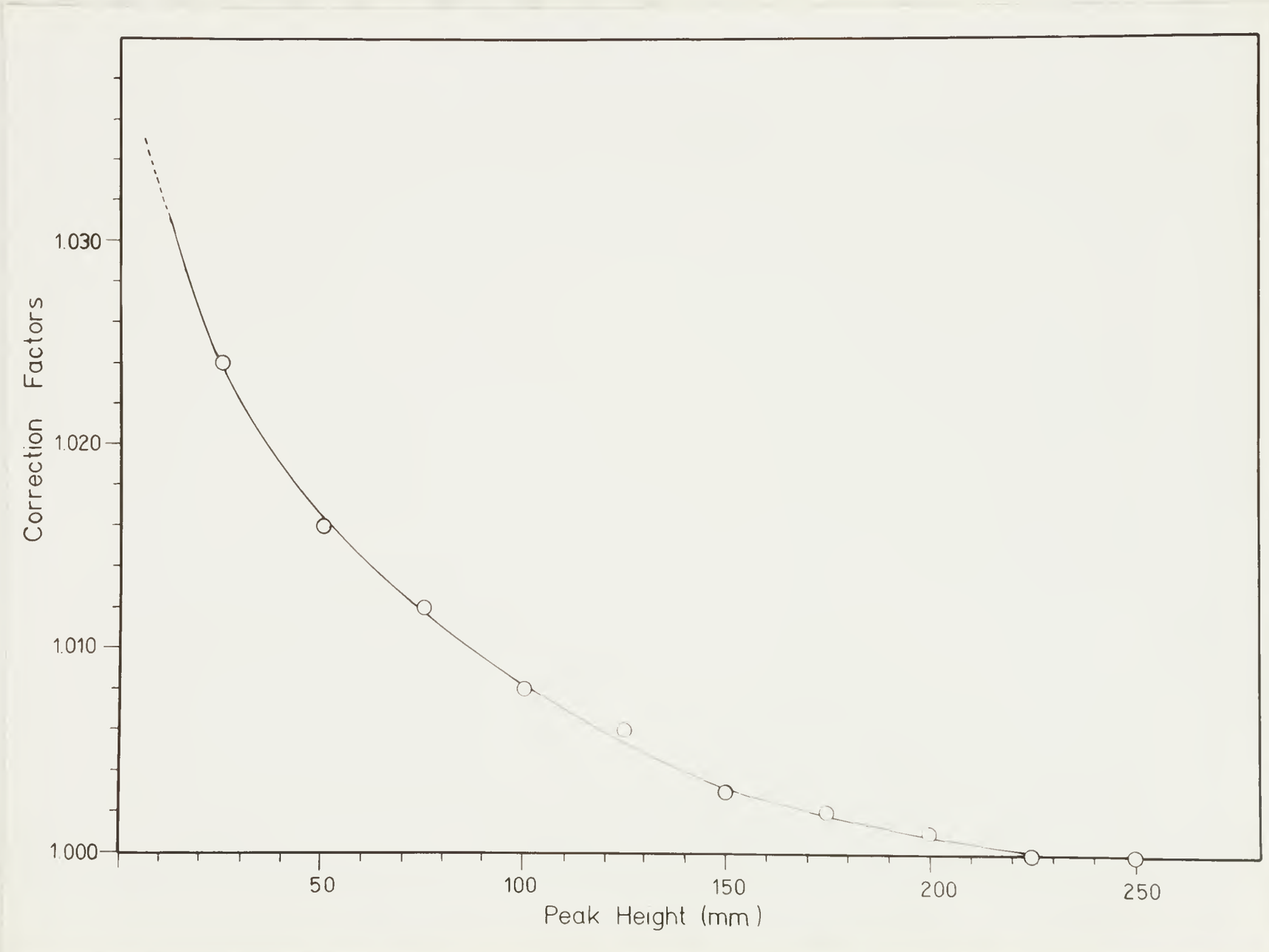


Figure 6: Correction for Recorder Non-Linearity.

of the programme are:-

(a) Copying of title from original data and addition to it of "NEW PK HTS" to distinguish corrected from uncorrected data.

(b) Recognition and direct copying of negative numbers (range factor code numbers).

(c) Reading of numbers from the data (i.e. peak heights) and finding their correct intervals by trial-and-error. The number is then multiplied by the appropriate correction factor and the result printed-out as the corrected peak height.

(d) Tabulation of results in same format as original data, so that the mass spectrometer calculation programmes (see following Sections) would accept both original data (for which they were designed) and corrected data. The output tape of the recorder correction programme is fed directly to the computer as data for the mass spectrometer programme.

This recorder correction programme was applied to all of the author's runs which were done after the calibration of the recorder.

Computation Time - ca. 40 sec. (for run of 25 scans).

7. (6) COMPUTER CALCULATION OF LEAD MASS SPECTROMETRY DATA - (C) Description of Method of Calculation.

Table 18 is an annotated print-out of Programme B, which was used for calculating all the common lead mass spectrometer runs of this study. Table 19 is a print-out of the results produced by Programme B from the corrected data of Table 17 (the results are produced in exactly the same form for corrected and uncorrected data). The calculation is outlined in the annotations to Tables 17 - 19.

The main feature of this programme is that the model parameters are calculated for each scan of the run. The mean values and errors of the model parameters are calculated from the values for the individual scans. This gives an accurate estimation of the experimental errors in the model parameters.

The formulae used in the calculations are given below.

(2) The Holmes-Houtermans equation in general form is :

$$\frac{x_i - x_o}{y_i - y_o} = B \cdot \frac{\exp(CE) - \exp(0.001\,CP)}{\exp(DE) - \exp(0.001\,DP)}$$

(see Section 9. (2). The symbols used here were chosen with reference to the variables used in the computer programmes - see Key to Table 18 - and are sometimes different from those used in Chapter 9.)

Substitution of the values given in Table 35 in the equation gives :

$$\frac{x_i - 9.50}{137.8(y_i - 10.36)} = \frac{2.0006 - \exp(0.0001541\,P_i)}{79.3604 - \exp(0.000972\,P_i)}$$

The equation cannot be made explicit in P_i and has to be solved by trial-and-error. L.H.S. is evaluated from the experimental values of x_i and y_i calculated for the particular scan :

$$\frac{x_i - 9.50}{137.8(y_i - 10.36)} = L_i$$

The value of R.H.S. is calculated for values of P_i increasing from -500 m.y. in increments of 10 m.y. (maximum value + 2500 m.y.) :

$$\frac{2.0006 - \exp(0.0001541\,P_i)}{79.3604 - \exp(0.000972\,P_i)} = R_i$$

For each P_i value, R_i is evaluated and $(L_i - R_i)$ is formed, the sign of this function being checked. The value of P_i which causes L_i to be most nearly equal to R_i is found by noting when the difference function changes sign. This solves the equation for P_i to the nearest 10 m.y..

Note : A different method of solving the equation was tried with repeated failure. It was attempted to match L_i and R_i within certain limits, but this reacted to certain unpredictable special values by giving the nonsense solution of P_i = 2500 m.y.. The method given above was always most satisfactory; checks of its results always agreed with those obtained by graphical means within $\pm$10 m.y., this variation always being due to graphical error.

(2) The geochemical ratios are evaluated for each scan by direct substitution of the calculated values of x_i, z_i and P_i in the following formulae (quoted with substitutions made of the physical constants) :

$$\frac{U^{238}}{Pb^{204}} = V_i = \frac{x_i - 9.50}{2.0006 - \exp(0.0001541\ P_i)}$$

$$\frac{Th^{232}}{U^{238}} = K_i = \frac{z_i - 29.40}{x_i - 9.50} \times \frac{2.0006 - \exp(0.0001541\ P_i)}{1.2516 - \exp(0.0000499\ P_i)}$$

(3) The formula used for calculation of twice the standard errors of the means is :

e.g. for $\int 208$:

$$\frac{2 \times \sqrt{\Sigma \sigma_{a_i}^2}}{r} = S_a$$

where $\sigma_{a_i} = (a_{ic} - \bar{a})$
(ignoring rejected scans).

7. (7) COMPUTER CALCULATION OF LEAD MASS SPECTROMETER DATA - (D) Summary of Different Programmes.

Six different programmes were developed for calculation of lead mass spectrometry data, all applying the basic method of calculation described in the preceding Section. The other programmes are essentially similar to Programme 3 (Table 18), and so are not reproduced here. All the programmes accept data in the same form, but are used for the different requirements outlined in the following table :

Prog.	Title	Results Printed Out	Use	Approx. Computation Time
Series I	(A - C)	Results 1-5 of Section 7.(3)	For common lead samples for which P, V, K required	-
A	"Full Printing"	Every step of calculation	To allow manual checking of calculation during development of these programmes.	4½ min.
B	"Reduced Printing"	See Table 19	Routine calculation of mass spectrometer data	2½ min.
C	"Means Only"	Title, no. scans, temporary means, rejected scans, means and errors only.	1. Rapid calculation of mean results only. 2. Checking effect of changes in data 3. Recalculation of P, V, K substituting different physical constants	1 min.
Series II	(D - F)	Results 1-3 of Section 7.(3) (Chapter 2 omitted from Progs. A - C).	e.g. For Radiogenic leads	-
D	"Arithmetic Full Printing"	As for Prog. A omitting P, V, K throughout	As for Prog. A	2½ min.
E	"Arithmetic Reduced Printing"	The counterpart of Programme B		1½ min.
F	"Arithmetic Means Only"	The counterpart of Programme C		½ min.

Two small variations of Programme B have also been used to cater for common lead samples whose model ages are either very negative or very high. This involved the following changes in Chapter 2 of Programme B (See Table 19).

which altered the ranges over which trial values of P_1 were substituted in R.H.S. of the Holmes-Houtermans equation:-

Programme B_1 (Negative P) : line 19 changed to: -1000 + 10J

Programme B_2 (Large P) : " " " " : 1000 + 10J

7. (C) SUGGESTED IMPROVEMENTS TO THE BASIC LEAD MASS SPECTROMETRY CALCULATION PROGRAMMES.

With the experience in using these programmes, the following improvements can be suggested:-

(A) Improvements to the Method of Calculation.

(i) Instead of an increment of 10 m.y. with no rounding-off in the calculation of P for each scan, it might be better to use an increment of 5 m.y. with rounding-off to the nearest 10 m.y.

This would have the disadvantage of doubling the number of trial calculations required to reach the solution of the equation, and so would increase the computation time.

(ii) With the present check step there is a possibility of P_c being 10 m.y. higher than $\overline{P}$ (the difference cannot be more than 10 m.y.) The check step should either be omitted or should use an increment of 5 m.y. in trial values of P.

(iii) The criterion for rejection of scans is a subjective one, although found remarkably successful in practice. Statistical criteria, dependent upon the scatter of results within each individual run, would be more objective, and would be ideally suited to application by the computer.

(iv) The ratio $\frac{204}{206} \times 100$ could also be calculated.

(B) Increasing the Flexibility of the Programmes.

(i) Programmes A - C could be made more flexible by introducing instructions into Chapter 2 to cater for:-

(a) Calculation of model ages of any value by having alternative ranges for trial values of P.

(b) Generalisation of physical constants used in the calculation of P, V, E, so that any desired values could be substituted in the equations, as in Programme 30 (Section 7.(11)).

(ii) One master programme could be devised from each of Programmes A - C and Programmes D - F (and possibly one programme could cover all of Programmes A - F, although this might be cumbrously long). Different groups of printed results could be requested by the use of coded instructions in each set of data.

(iii) There are other methods for measuring lead isotope peaks in which only four peak heights per scan are measured. This could be accommodated in these programmes by means of a few extra alternative instructions in Chapter 1 and a coded "switch" operated by a preliminary instruction in the data.

(iv) The correction for recorder non-linearity could be included in a master programme.

7. (9) COMPARISON OF MANUAL AND COMPUTER CALCULATIONS OF LEAD MASS SPECTROMETRY DATA.

The main steps in Moorbath's manual method of calculation, which is not described in his thesis, are outlined below, with discussion where it differs from the computer method.

Step (1): The individual isotope abundances were calculated for each scan.

Step (2): Temporary means of all these abundances were calculated.

Step (3): Individual abundances were examined for abnormal deviations from their temporary means. No strict criteria were used for rejection, but the deviations considered abnormal were comparable to those causing rejection in the computer method. Only those isotope figures which were considered doubtful were rejected - in the computer method the whole scan was rejected if only one of its isotope abundances were rejected.

Step (4): After rejections, the final mean abundances were calculated.

Step (5): The errors of the mean abundances were calculated by the same formula as used in the computer method. (Section 7.(6), Step (11)).

Step (6): The mean abundances were corrected for mass discrimination in the electron multiplier. The method employed an unnecessary step of dividing by % 204 before applying the correction factors and then multiplying by % 204 again. Rounding off the figures during these operations has been shown to make frequent small errors in the final corrected ratios, which led to differences of 10 - 20 m.y. in the model ages calculated from them. This source of error is avoided in the computer calculation.

Step (7): The errors of the uncorrected final mean abundances were associated with the corrected abundances.

Step (8): The isotope ratios were calculated from the corrected final mean abundances.

Step (9): The errors of the isotope ratios were estimated from the errors of the abundances by a rapid approximate procedure, which always gave an error up to 50% larger than if the appropriate statistical formula had been used (see Section 7.(11)). In the computer method, the mean ratios and their errors were calculated from the individual ratios for each scan.

Step (10): The model age and its error were calculated graphically from isochron charts. The construction of these charts is described in Chapter 9. Figure 7 is a reproduction of part of an isochron chart. Model ages were estimated to the nearest 10 m.y. from this chart by interpolating between the 100 m.y. isochrons. On this small scale an error of $\pm$10 m.y. could very easily be made in interpolations. This could have been minimised by construction of charts on a larger scale, but never avoided entirely.

The only numerical method of solving the Holmes-Houtermans equation exactly is that of successive iteration. The manual labour required to carry this out would be prohibitive, but the problem is ideally suited to computational techniques, by which solutions can be rapidly found to any accuracy desired.

Another less satisfactory feature of Moorbath's method is that the error in the model age, estimated by the method outlined in Figure 7 and its caption, does not have any particular statistical significance. The errors quoted in the model ages by Moorbath certainly signify the relative magnitudes of the errors in the ratios from which the model ages were calculated, but they do not necessarily have the same statistical significance as the errors in the

Key to Figure 7

The figures in brackets are the model ages (in m.y.), estimated by interpolation for particular points on the chart. The point P represents the mean isotope ratios, x(206/204) and y(207/204), for the sample. The points of maximum individual variation of the ratios x and y, as defined by their associated errors, are plotted as points, A, B, C, D. The mid-points of AB, CD are located as points E, F. The greatest difference between the mean model age (point P) and the model ages of points E, F is taken as the error in the mean.

Thus in this example: $x = 18.07 \pm 0.11$

$y = 15.50 \pm .09$

Mean model age (P) = 370 m.y.

Extreme model ages (E, F) = 460, 270 m.y.

$\therefore$ Error in mean = $\pm$ 100 m.y.

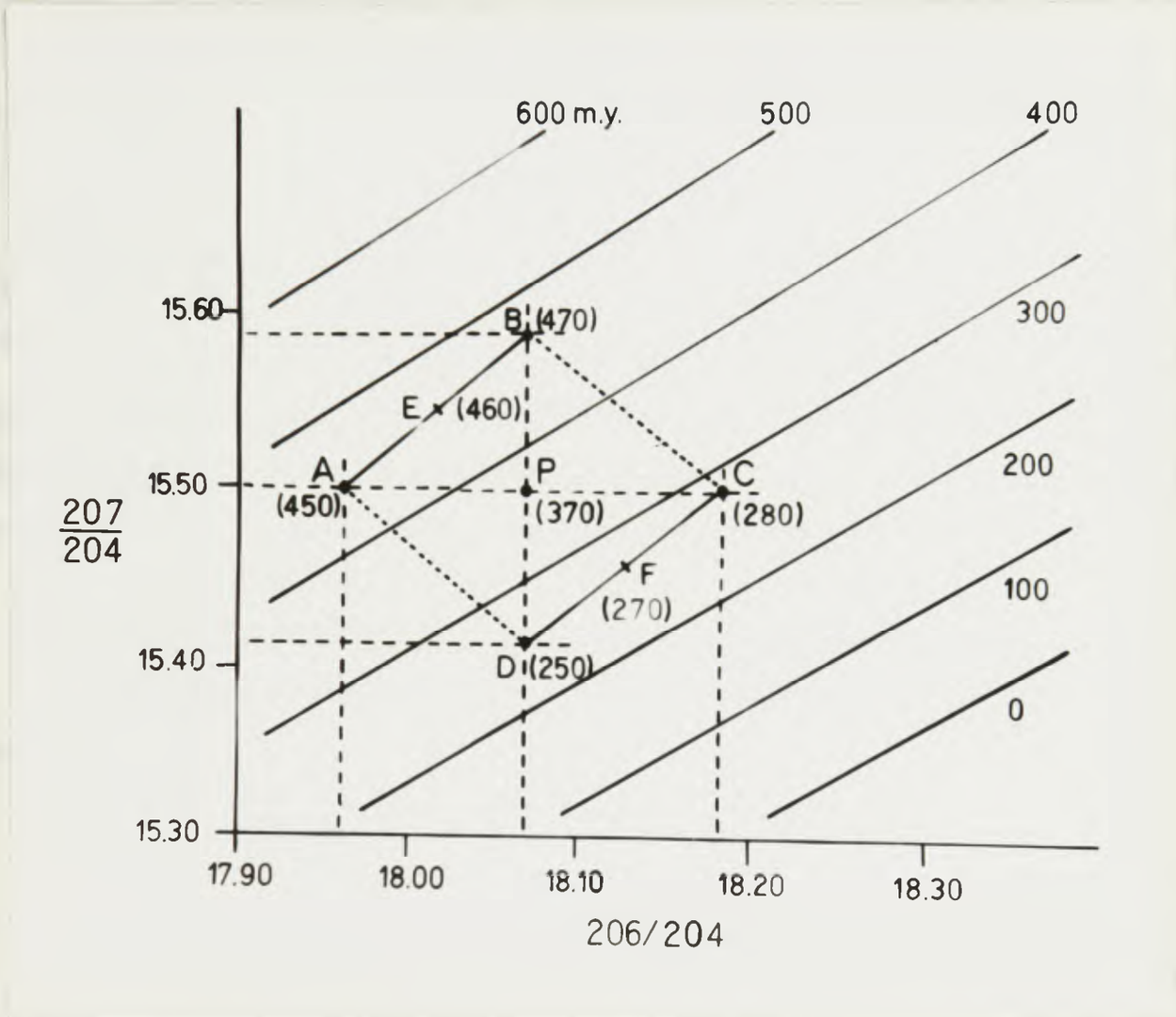


Figure 7: Graphical Estimation of Model Age and its Error using Isochron Diagrams.

(Englargement of portion of Figure 8. Scale of this reproduction is same as that of original charts used by Moorbath and the author).

ratios. There are other methods for graphical estimation of errors in model ages. Thus Lay (1960) describes a method which is found to yield errors in the model ages about half those estimated by Moorbath's method from the same data - see Section 11. (4).

The author's method of calculating model ages and their experimental errors is described in Section 7.(7). The deviations of individual model age results from their mean might seem very large at first sight (see, for example, the individual P values for the scans in Table 19). Yet the calculated error of ± 30 m.y. in the mean of 310 m.y. accurately represents the statistical uncertainty in the mean calculated from the 26 scans in this example.

Step 11: The evaluation of the geochemical ratios V and K, although laborious, were quite accurate. The experimental errors in V and K were estimated in the computer method, but this could not be done in the manual method.

To sum up, the computer method of calculation has the following advantages:-

1. More accurate calculation of model age
2. More valid calculation of error in model age
3. Calculation of error in geochemical ratios, impossible beforehand.

The following additional advantages of the computer method are of less importance, but still of great value:-

4. Very greatly increased productivity of calculations. (Once programmes were developed, only real time involved was 5 min. per run to punch data. Manual method took ca. 3 hr. for complete calculation).
5. Very great reduction of fatigue (Calculation of run of 25 scans by manual method involved 775 separate simple calculations, 2 longer calculations, 8 summations of 25 numbers, and the writing of 714 numbers).
6. Impossibility of human error in calculation.
7. Incidental advantages of:
   (a) Storage of raw data in small tapes and on compact tables, which can be readily recalculated.
   (b) Production of results in standard printed form.

7. (10) COMPUTER CALCULATION OF LEAD MODEL AGE TABLES.

Digital computers are not widely available for accurate calculations of model ages. Nor is it convenient to visit a computing laboratory for only a few calculations. More important, amongst those lead isotope geochemists who use the Holmes-Houtermans theory, there has been a notable lack of uniformity in methods and constants used in calculating model ages. This has not infrequently resulted in some confusion about geological conclusions. To overcome these difficulties a series of tables have been computed for the calculation of lead model ages. Copies of these tables, with introductory notes have been circulated privately, and are included inside the back cover of this thesis as Tables 20 - 22. The tables are self-explanatory and only the programmes used for their calculation are discussed here.

Programme 1G (Table 23) calculated Tables 21 and 22.

Programme 1I (Table 24) calculated Table 20.

The essential difference between these programmes is the increment in the ratio F. They are both reproduced here because they are each useful for a particular purpose:-

(a) Programme 1G - increment of 0.001 in F.
- used for calculation of longer tables when there is a need for accuracy in avoiding interpolations.

(b) Programme 1I - increment of 0.01 in F.
- used for rapid calculation of series of shorter tables with different physical constants.

The method of calculation used in these programmes is similar to that used in Chapter 2 of Programmes A - C (see Section 7. (6), Step (5)). Programmes A - C use machine language instructions for the model age calculation, whereas Programmes 1G and 1I use Autocode. The essential features of Programmes 1G and 1I are:-

(a) They are specifically designed to use any values for the physical

constants. These four constants comprise the data.

(b) The R.H.S. of the equation (see introduction to Tables 20 - 22) is evaluated for values of the model age increasing in increments of 0.5 m.y. The solution is found when an increase in the trial value of 0.5 m.y. first makes R.H.S. greater than the given value of F (L.H.S.). The value of the model age is rounded off to the nearest 1 m.y. before printing-out. This device avoids any positive bias in the final result - the solution is exact to the nearest 1 m.y.

(c) The results are produced in the tabulated form of Tables 20 - 22, which, except for the headings, are actual print-outs of the results tapes of these programmes.

Tables 21, 22 were checked by Programme 2D (Table 25), the results of which are not reproduced here because of their bulk (6500 separate values of F for each set of constants). This programme evaluates R.H.S. of the Holmes-Houtermans equation to five decimal places for any given values of the physical constants and for values of the model age increasing in increments of 1 m.y. The tables produced are less convenient to use than Tables 20 - 22, but were used to check all the values in the latter tables. Selected values produced by Programme 2D were checked manually and the perfect agreement found provided confidence in the values of Tables 20 - 22.

Computation Times:-

Programme 1G : ca. 30 min. (calculation of 1500 model ages)

Programme 1I : ca. 5 min. (calculation of 150 model ages)

Programme 2D : ca. 30 min. (evaluation of 6500 expressions)

7. (11) COMPUTER CALCULATION OF LEAD MODEL PARAMETERS FROM LEAD ISOTOPE RATIOS AND ABUNDANCES.

The manual calculation of a large number of lead model parameters is a long and tedious task. Two programmes were devised to carry out such calculations rapidly - one using lead isotope ratios as data (Programme 3C), and the other using lead isotope abundances (Programme 3D).

The operation of Programme 3C (Table 26) is explained by the annotations

to it and to the example series of data (Table 27) and results (Table 28). The errors of the isotope ratios are included in the data and reproduced in the results for completeness, although they are not used in any calculations. The method of calculating the model age differs from that used in the model age table programmes only in that an estimated lower limit to the model age is included in the data to save computer time. The model age is rounded off to the nearest 10 m.y. before substitution in the equations for calculation of the geochemical ratios.

Computation Time:- ca. 12 min. for 100 complete sets of data.

The annotations to Programme 3D (Table 29) and example sets of data (Table 27) and results (Table 30) for it explain its operation. The six isotope ratios are calculated from the isotope abundances, and the errors in the ratios calculated from the errors in the abundances by the statistical formula:-

$$E_r = \frac{\sqrt{a^2 E_b^2 + b^2 E_a^2}}{b^2}$$

where $r = \frac{a}{b}$, E_r = error in r
E_a = error in a
E_b = error in b

The statistical significance of the error in the ratio is the same as that of the abundances from which it is calculated. The calculations of model parameters in Chapter 2 are identical to those in Chapter 1 of Programme 3C.

Computation Time:- ca. 20 min. for 100 complete sets of data.

Both Programmes 3C and 3D calculate model ages to the nearest 1 m.y. Quotation to this accuracy allows rounding off to any desired accuracy without

incurring errors. In this work, model ages are quoted to the nearest 10 m.y.

Both these programmes have been designed to take any values for the physical constants, which are punched at the head of each data tape. This provision has allowed extensive use of these programmes in recalculating large series of model parameters from other isotope data using the same physical constants throughout. Thus Programme 3D has been used to check Moorbath's calculations of model parameters from his data.

For the author's data, the grand mean isotope abundances and their errors were first calculated from the replicate runs on each sample (see next Section). These mean abundances and errors were then applied as data to Programme 3D. The resulting isotope ratios and their errors, and the mean model parameters are the ones quoted throughout this thesis.

7. (12) COMPUTER CALCULATION OF MEANS AND ERRORS OF REPLICATE DETERMINATIONS.

Each of the author's runs was calculated individually by one of Programmes A - F. Provided that the replicate results for each sample agreed within their errors, the isotope abundances, ratios and model parameters of each run were averaged by weighting each figure according to its error by the following formulae:-

$$w_i = \frac{1}{\sigma_i^2}$$

$$\bar{x} = \frac{\Sigma w_i x_i}{\Sigma w_i}$$

$$\text{Error of } \bar{x} = \sqrt{\frac{1}{\Sigma w_i}}$$

where x_i = individual mean
σ_i = error of x_i
$\bar{x}$ = grand mean

This gave a series of grand mean values for each sample of the abundances, ratios and model parameters, each with associated errors. Occasionally these results were not exactly internally consistent - e.g. the

isotope ratios may have been 0.01 different from those calculated from the grand mean isotope abundances. In order to avoid these small inconsistencies the grand mean isotope abundances and their errors were applied to Programme 3D (see preceding Section). The resulting ratios and their errors were taken as the final mean results; the errors in the ratios calculated this way were always identical or very close to those calculated by the above formulae from the errors of the individual runs.

The values of the model parameters calculated by Programme 3D from the grand mean isotope abundances were also taken as the final mean results. Sometimes there was a difference of 10 m.y. between the model age value calculated as the weighted mean of individual values and that calculated by Programme 3D. In these cases the mean error calculated from the individual errors was increased by 10 m.y. - e.g. mean model age calculated from individual runs for sample No. 8 = 390 ± 40 m.y.; model age calculated by Programme 3D from grand mean isotope abundances = 380 m.y.; the latter value was taken as the final mean model age, but with an error of ± 50 m.y. i.e. Model Age = 380 ± 50 m.y.

The calculations of grand mean values and errors from results of individual runs were carried out using the computer. The programmes, based on the above formulae, are not reproduced here because they are very simple, and served solely to save labour.

7. (13) COMPARISON OF MODEL PARAMETERS CALCULATED MANUALLY BY MOORBATH AND BY USING COMPUTER METHODS.

Moorbath's 107 results have been recalculated from his isotope abundances using Programme 3D, so that they can be strictly compared with the author's results. Throughout all the computer calculations exactly the same values of the physical constants were used as by Moorbath. The recalculated results are

not tabulated here, but a summary of the differences between Moorbath's and the computer calculations is presented below:-

P values:	2	computer values	are	30 m.y.	smaller	than	Moorbath's	values
	4	"	"	20 m.y.	"	"	"	"
	37	"	"	10 m.y.	"	"	"	"
	6	"	"	10 m.y.	greater	"	"	"
V_p values:	4	computer values	are	> 0.04	smaller	than	Moorbath's	values (1 x 0.06, 3 x 0.05)
	3	"	"	0.04	"	"	"	"
	23	"	"	0.03	"	"	"	"
	22	"	"	0.02	"	"	"	"
	45	"	"	0.01	"	"	"	"
	2	"	"	0.01	greater	"	"	"
R_p values:	5	computer values	are	> 0.01	greater	than	Moorbath's	values (2 x 0.10, 1 x 0.05, 2 x 0.02)
	37	"	"	0.01	"	"	"	"
	5	"	"	0.01	smaller	"	"	"
	4	"	"	> 0.01	"	"	"	" (1 x 0.16, 1 x 0.11, 1 x 0.03, 1 x 0.02)

Owing to the difficulty of interpolation on the scale of isochron charts used by Moorbath, occasional errors of $\pm$ 10 m.y. compared with the exact computer solutions were to be expected. But whereas 43 computer values are smaller, only six computer values are larger than Moorbath's values. There can be no doubt that the computer solutions are correct. It is thus difficult to avoid the conclusion that Moorbath's calculations of P values are slightly in error, possessing a positive bias. Perhaps this is due to a small but definite inaccuracy in the construction of Moorbath's isochron charts. The larger differences of 20 and 30 m.y. are more difficult to explain on these grounds, and are presumably due to inaccurate reading of the isochron charts.

It might be claimed that these differences are not important as they are less than the average errors of $\pm$ 70 m.y. quoted by Moorbath in his model ages. But these are experimental errors which do not cover inaccuracies in calculating the mean values. The general effect on Moorbath's geological conclusions of substituting the computer values of the model ages for Moorbath's

values is not great. The effect on the overall distribution of model ages and Moorbath's definition of periods of mineralisation from them is discussed in Chapter 12. The effect on conclusions about individual samples is greatest for the six samples with differences of 20 and 30 m.y. in their model ages. The mean model ages calculated by Moorbath for several regions have to be reduced by 10 m.y. notably for the Cornwall-Devon region (see also Section 9.(6)).

Most of the differences in the V_p values are quite small and are caused by the general reduction in the P values used in their calculation. However, the general trend is to reduce the mean V_p value for Moorbath's samples. Similar considerations also apply to the K_p values, but here the trend is for a small increase in their mean. In addition, there are four K_p values which evidently have been incorrectly calculated by Moorbath (the four computer values which differ from Moorbath's values by 0.10 or more).

It is beyond the scope of the present work to enter into detailed discussions of the effect of these differences in Moorbath's results, except in so far as they affect the immediate problems of this thesis.

C H A P T E R 8

RESULTS

8. (1) PRECISION OF THE MASS SPECTROMETRY.

In any method of instrumental analysis, rigorous checks must be applied to determine the precision of the instrument (i.e. the reproducibility of separate determinations on the same samples) and the absolute accuracy of the results obtained (i.e. how near they approach to the true result).

Moorbath (1959 b) has reported that he carried out duplicate measurements on the mass spectrometer of over half his samples, and that in all but a very few cases, the results of duplicate runs agreed within the experimental errors. However, in this work, the frequency of agreement between duplicate runs was much lower than reported by Moorbath. Without doubt, the major cause of this was the electron multiplier. The ageing of the multiplier and its eventual rebuilding has been discussed in Section 6.(3). The author's mass spectrometry can be very clearly divided into three periods on the following basis:-

Period A - Runs 1 - 144; May, 1959, to April, 1960; old multiplier; precision reasonably good, but not as good as claimed by Moorbath for work prior to this Period.

Period B - Runs 145 - 190; August to November, 1960; old multiplier; precision fair for runs done only in this Period, but very poor when compared with runs done in other Periods; large experimental errors; other direct evidence for ageing of multiplier.

Period C - Runs 191 - 253, January to April, 1961; new multiplier; recorder calibration applied; very high precision for all runs done in this Period and generally good agreement with runs done in Period A; much lower experimental errors than previously obtained for lead on this instrument.

The differences obtained between Period B and Periods A and C were subtle, and it was not until a large number of runs had been made that it was clear

TABLE 31.

Some Results of Individual Lead Isotope Determinations.

No.	Sample	Period	Run No.	No. Scans	Percentage Isotope Abundances 204	206	207	208	
13	Abbeytown D	C	195	28	1.388±.003	25.03±.03	21.51±.02	52.07±.03	*
		C	219	27	1.386±.004	25.04±.04	21.50±.03	52.07±.03	*
19	Coolsartra	A	24	24	1.373±.006	24.86±.06	21.39±.04	52.38±.07	
		A	79	25	1.372±.008	24.92±.04	21.32±.02	52.39±.05	
		B	149	27	1.394±.008	24.92±.04	21.25±.05	52.44±.07	
		C	193	27	1.387±.004	24.87±.03	21.41±.02	52.33±.04	*
		C	231	21	1.385±.004	24.90±.03	21.39±.02	52.32±.03	*
24	Tynagh	A	35	21	1.391±.007	24.94±.06	21.41±.02	52.25±.07	*
		A	85	24	1.388±.007	24.97±.04	21.34±.02	52.30±.05	*
		B	148	28	1.394±.007	24.97±.06	21.37±.05	52.27±.06	*
29	Kilbreckan	A	41	26	1.384±.005	25.03±.04	21.35±.03	52.24±.06	*
		A	84	24	1.358±.009	25.04±.04	21.33±.03	52.27±.05	
		B	150	24	1.393±.008	24.91±.08	21.26±.06	52.43±.09	
		C	211	23	1.383±.002	24.99±.04	21.38±.04	52.25±.05	*
35	Knocksanroe B	A	101	27	1.372±.005	25.04±.04	21.30±.03	52.29±.05	*
		A	123	27	1.372±.008	25.04±.05	21.27±.04	52.31±.04	*
66	Poullsouen	A	132	26	1.375±.010	24.98±.04	21.21±.04	52.43±.07	
		A	141	25	1.367±.006	25.06±.05	21.30±.02	52.28±.05	
		B	166	27	1.387±.010	25.03±.05	21.26±.03	52.32±.06	
		C	226	25	1.372±.003	24.98±.02	21.35±.02	52.30±.03	*
		C	243	23	1.371±.003	24.97±.04	21.33±.02	52.33±.04	*

* indicates the runs whose results agreed closely and were selected for calculation of final means.

that they were real and significant. Nearly all the runs from Period B were discarded.

This discussion is best illustrated by some notes on the few examples reproduced in Table 31. These have been selected with a view only to this discussion and do not represent a fair sample of all the results. Only percentage isotope figures are reproduced for comparison here, but the isotope ratios were also considered when comparing runs in practice.

Close agreement within Period A is shown by Nos. 24, 35.
Poor " " " " " " " " 19, 29, 66.
Close " between " A and C is shown by No. 29.
" " " " B and other Periods is shown by No. 24 (very rare).
Poor " " " " " " " " Nos. 19, 29, 66 (very common).
Close " within Period C is shown by Nos. 13, 19, 66.

Even in the 63 runs in Period C, two runs failed to agree with other runs on the same samples in the same period. This is a very much lower frequency of rejected runs than in Period A, but nevertheless it demonstrates the necessity for having at least two separate runs on every sample. Without the confirmation of a duplicate run, there could be no certainty that the results of a single run were correct (cf. Moorbath's single runs on his 17 Irish galenas - Table 34). In Tables 33 and 34, the figure in the "No. Runs" column gives the number of runs actually used in the calculation of the final means quoted in the table (the number of rejected runs has been omitted). The author is confident that all the figures quoted in Table 33 are as precise as could be obtained with this instrument, with two exceptions noted in Section 8. (3). The following table shows the distribution of rejected runs:-

No. of Runs on each Sample	Total No. Samples	No. Samples for which following No. of Runs were Rejected			
		3 Runs Rejected	2 Runs Rejected	1 Run Rejected	0 Runs Rejected
5	5	4	1	-	-
4	19	-	14	3	2
3	13	-	-	6	7
2	39	-	-	-	39
1	1	-	-	-	1
Totals:	77	4	15	9	49

Some runs had to be rejected for ½rd of the samples.

The degree of precision of the instrument in Period C was within 0.2% for isotopes 206, 207, 208 and 0.4% for 204. These estimates also cover the degree of precision in all the figures quoted, but this ignores the rejection of some runs, and so does not accurately represent overall experimental precision in the earlier Periods A and B, for which the degree of precision seemed to vary, and so is difficult to estimate.

8. (2) ACCURACY OF THE MASS SPECTROMETRY.

The degree of precision is not necessarily related to the accuracy of a particular measurement. Accuracy is much more difficult to estimate for mass spectrometry of some elements, for which the preparation of very accurate independent standards often presents problems. No such standard for lead isotopes is yet available.

Inter-laboratory comparisons are of great importance in estimating the accuracy of any technique or instrument. Moorbath (1959 b) has reported the results of a series of lead isotopic analyses carried out with other laboratories, notably Toronto, Lamont, Harwell and Bonn. In general the

agreement was very close between laboratories which used solid-source techniques (Oxford, Harwell, Lonn). But systematic differences, outside the range of experimental error, were observed when results of solid-source and gas-source techniques (Toronto, Lamont) were compared. The largest differences were observed in the 204 isotope abundance which was invariably lower for gas-source techniques.

One of the major difficulties in comparing the mass spectrometry results of different laboratories has been doubt about the exact equivalence of the samples used for comparison. The National Bureau of Standards, Washington D.C. (N.B.S.) has established a stock of reference samples for mass spectrometric analysis, and has acted as a clearing house for data obtained on them. This service is clearly a far more satisfactory means of establishing the relative accuracy of a particular instrument or technique, than the private circulation of samples between some laboratories. Through F. L. Mohler and V. H. Dibeler of N.B.S., portions were obtained of the only two N.B.S. lead reference samples suitable for the Oxford instrument. The results of the author's analyses are reproduced in Table 32, together with the results of all other measurements made on the same samples (N.B.S. Technical Note 51, May, 1960, (Mohler, 1960)). No further results are available at the time of writing (V. H. Dibeler, personal communication). It is to be hoped that these samples will be more widely studied to allow more detailed comparisons, for the data available are too few for definite conclusions to be drawn from them yet. However, these results are important and are discussed below.

At the top of Table 32 are reproduced the results of a comparison within this laboratory between Moorbath and the author. The measurements were carried out about three years apart and with different electron multipliers, but the isotope abundances are in close agreement, notably that of the 204 isotope.

The experimental errors of the author's results are considerably lower than Moorbath's due to the much larger number of scans taken and probably also to the new electron multiplier. It should be noted here that the mean model age obtained for this sample by Moorbath (260 ± 70 m.y.) is a little higher than that by the author (230 ± 30 m.y.) but they agree within experimental errors. The isotopic differences are experimentally insignificant, and so these results serve to show the sensitivity of calculated model ages to the isotope results.

The analyses of the two N.B.S. reference samples are the most thorough investigations yet reported of them. The three separate determinations of each sample were carried out over three months during Period C (see previous Section) and the close agreement between the separate results provides an estimate of the precision of the instrument during this Period. The error associated with the 204 abundance for Sample 200a is larger than normally obtained during this Period, due probably to the increased scatter of individual scans caused by an unusually rapid decrease of emission.

In comparing the author's results with others, the significance of the errors quoted is of considerable importance. The definition of the experimental uncertainty of the results quoted in N.B.S. Technical Note 51 as "mean deviations" is vague at best. If all the errors quoted actually do represent "mean deviations" as suggested in the Note, then all the analyses reported would be much more precise than those of the author, since in normal statistical nomenclature the "mean deviation" is greater than twice the "standard error" when they are both calculated from the same values. This is most unlikely on experimental grounds, and Dibeler (personal communication) considers this aspect of the Note unsatisfactory. It does seem highly desirable that a standard method of statistical treatment should be adopted for isotope results.

TABLE 32.

Reference Samples in Comparison with Results of Other Workers

No.	Sample	Analyst	NR ou .n s	NS oc .a n s	Percentage Isotope Abundances 204	206	207	208
75	Lambriggan Cornwall (Galena)	R.F.C. Pockley[1]	2	52	1.372 ±.002	25.08 ±.02	21.30 ±.02	52.24 ±.04
		S. Moorbath[2]	2	29	1.372 ±.004	25.04 ±.04	21.29 ±.03	52.31 ±.04
76	N.B.S. Sample 200 (Galena)	R.F.C. Pockley[3]	3	71	1.544 ±.002	22.51 ±.03	22.65 ±.02	53.30 ±.03
		T.J. Chow[4]	?	36	1.541 ±.002	22.48 ±.01	22.62 ±.01	53.36 ±.02
77	N.B.S. Sample 200a (PbI_2)	R.F.C. Pockley[5]	3	69	1.556 ±.005	22.54 ±.02	22.66 ±.02	53.23 ±.02
		G.L. Bate[6]	?	11	1.53 ±.006	22.60 ±.04	22.56 ±.02	53.31 ±.03
		W.D. Harman[7]	?	12	1.54 ±.01	22.49 ±.03	22.68 ±.03	53.29 ±.05
		L.R. Stieff[8]	?	?	1.539 ±.003	22.53 ±.04	22.63 ±.02	53.29 ±.06

Notes on experimental methods are given on following page.

Table 32. continued.

Notes on Experimental Methods.

1, 2 : All determinations done using same precipitated PbS sample prepared by Moorbath. Moorbath's determinations done in March and July, 1958; Pockley's determinations done in January and March, 1961. Same mass spectrometer used except for new electron multiplier used for Pockley's determinations.

1, 2, 3 : Errors quoted represent twice the standard error of the mean.

3 : Sample form was fine-powdered galena, as supplied by National Bureau of Standards, mounted direct on filaments without further purification.

4, 6, 7, 8 : Results and experimental details reported in F.L. Mohler : National Bureau of Standards Technical Note No.51 (May, 1960). Errors generally represent "mean deviation".

4 : Multiple filament surface ionization source; velocity correction applied.

5 : PbS precipitated from hot solution of PbI_2. Mass spectrometry as for 1, 2, 3.

6 : Lead tetramethyl prepared from PbI_2.

7 : PbI^+ spectrum measured

8 : Mean of 3 sets of analyses, 2 on Pb^+ ions and 1 on PbI^+ ions.

Comparison of the author's results for N.B.S. Sample 200 with those of T. J. Chow shows a very close agreement except for a small difference between the 208 abundances. Chow's techniques appear to have been similar to those of the author, but, although not actually stated, it is likely that Chow used a sample form for mass analysis which had been chemically prepared from the actual galena reference sample. The author's techniques had the advantage of volatilising the galena direct in the mass spectrometer without chemical treatment. It is likely that Chow's errors would have been larger if they had been estimated in the same way as the author's, and the two sets of 208 abundances would then be within each other's errors. This close agreement is similar to that found by Moorbath with other laboratories using solid-source techniques.

The agreement between the author's results and those of the other three analysts for N.B.S. Sample 200a is not so close. This sample was provided as lead iodide mainly for use in instruments using the lead iodide volatilisation techniques originally developed by Nier, which were used by Harman and Stieff in obtaining their figures. The results of these two analysts do agree within the errors quoted, although the lack of further information about their techniques is not satisfactory. The data of Nate give the 207 abundance as smaller than the 206 abundance, which is the reverse of all other data on this sample and on the Ivigtut galena from which this lead iodide was prepared (Moorbath, 1959 b). In addition Nate used the lead tetramethyl technique and obtained a 204 abundance significantly lower than the author's figure; this is another illustration of the systematic difference which Moorbath and others observed between figures obtained using lead tetramethyl and solid-source techniques.

On the basis of these comparisons, no definite conclusions can yet be reached about the absolute accuracy of the data reported in this thesis. It

is to be hoped that more workers will analyse these reference samples, so that they might eventually approach the status of standards. In the meantime, these results provide further confidence that solid-source techniques are the most precise and accurate for lead isotope analyses.

6. (3) EXPERIMENTAL ISOTOPE RESULTS.

In the following Table 33 are listed all the common lead isotope results obtained in this study and also the model parameters calculated from them. These results represent the final means of replicate determinations calculated as described in Chapter 7. The number of runs of each sample used in calculating these final means and the total number of scans in these runs are quoted for comparative purposes. Moorbath's isotope data for 17 Irish galenas are reproduced in Table 34, so that all the available isotope data for Irish galenas are assembled here for later discussion. In order that they may be strictly comparable with the author's results, Moorbath's isotope ratios and their errors and the model parameters have been checked using the same computer programme as for the author's results (see Chapter 7). The errors in the model ages are those estimated graphically by Moorbath. No errors were quoted by Moorbath for V_p and μ_p.

The isotope data in Tables 33 and 34 are listed in the same way as in the comprehensive compilation of lead isotope data by Russell and Farquhar (1960 b). For each sample, the normal percentage isotope abundances are given on the top line. The middle line gives the isotope ratios relative to the 204 abundance, and the bottom line gives the isotope ratios (multiplied by 100) relative to the 206 abundance. The error quoted with each figure is twice the standard error of the mean.

The results of Nos. 12 and 37 should be noted as not being so precise as

the others. The 204 abundances of the two runs on No. 12 did not agree within experimental error, but no sample remained for a third run. The figure quoted here represents the weighted mean calculated in the usual way, but a more liberal estimate of the error is quoted than that calculated. For No. 37 only one somewhat unsatisfactory run could be made. The relative importance of these results is not so great since other samples were measured from the same localities.

TABLE 33.

Results of Isotopic Analysis and Model Parameters.

No.	Locality	NR ou ·n s	NS oc ·a n e	204	206	207	208	Model Age (m.y.)	Vp	Kp
IRELAND										
	Donegal									
				1.390 ±.004	25.21 ±.03	21.40 ±.03	52.00 ±.04			
1.	Keeldrum	2	54	1.000	18.14 ±.06	15.40 ±.05	37.41 ±.11	180 ±60	8.88 ±.12	3.67 ±.06
				5.514 ±.017	100	84.89 ±.16	206.3 ±.3			
				1.392 ±.006	25.08 ±.03	21.42 ±.02	52.11 ±.03			
2.	Faymore	3	77	1.000	18.02 ±.08	15.39 ±.07	37.44 ±.16	260 ±60	8.88 ±.11	3.75 ±.04
				5.550 ±.025	100	85.41 ±.15	207.8 ±.3			
				1.396 ±.006	24.86 ±.03	21.28 ±.04	52.47 ±.05			
3.	Glentogher	2	49	1.000	17.82 ±.07	15.25 ±.06	37.61 ±.14	230 ±60	8.63 ±.13	3.92 ±.05
				5.611 ±.021	100	85.60 ±.19	211.1 ±.3			
				1.383 ±.004	24.97 ±.03	21.39 ±.03	52.27 ±.04			
4.	Ardaturr	2	49	1.000	18.05 ±.06	15.47 ±.05	37.79 ±.11	340 ±50	9.05 ±.12	3.92 ±.06
				5.539 ±.017	100	85.66 ±.16	209.3 ±.3			
				1.370 ±.004	25.28 ±.03	21.09 ±.03	52.27 ±.04			
5.	Knockybrin	2	55	1.000	18.45 ±.06	15.39 ±.05	38.15 ±.12	-80 ±50	(8.84 (±.12	3.83) ±.04)
				5.419 ±.017	100	83.43 ±.15	206.8 ±.3			
				1.384 ±.003	25.13 ±.02	21.36 ±.02	52.13 ±.04			
6.	Glennboghil	2	50	1.000	18.16 ±.04	15.43 ±.04	37.67 ±.09	200 ±40	8.93 ±.07	3.79 ±.05
				5.507 ±.013	100	85.00 ±.10	207.4 ±.2			

Table 33. cont'd.

No.	Locality	NR ou .ns	NS oc a ns	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Sligo-Leitrim									
				1.385 ±.003	25.06 ±.03	21.36 ±.02	52.20 ±.03			
7.	Rosses Upper	2	51	1.000	18.09 ±.04	15.42 ±.04	37.69 ±.08	250 ±30	8.94 ±.06	3.84 ±.04
				5.527 ±.014	100	85.24 ±.13	208.3 ±.3			
				1.393 ±.004	24.89 ±.03	21.44 ±.02	52.27 ±.03			
8.	Twigspark	2	49	1.000	17.87 ±.06	15.39 ±.05	37.52 ±.11	380 ±50	8.90 ±.11	3.88 ±.04
				5.597 ±.017	100	86.14 ±.13	210.0 ±.3			
				1.384 ±.005	25.09 ±.04	21.38 ±.02	52.13 ±.05			
9.	Lugawarry	2	48	1.000	18.13 ±.07	15.45 ±.06	37.67 ±.14	260 ±40	8.99 ±.12	3.81 ±.05
				5.516 ±.022	100	85.21 ±.16	207.8 ± .4			

Table 33 cont'd.

No.	Locality	NR ou. no.	NS oc. no.	204	206	207	208	Model Age (m.y.)	Vp	Kp
Sligo-Leitrim (cont.)										
				1.388 ±.003	25.05 ±.04	21.48 ±.02	52.09 ±.04			
10.	Abbeytown 2 A		54	1.000	18.05 ±.05	15.48 ±.04	37.53 ±.09	360 ±60	9.06 ±.09	3.80 ±.04
				5.541 ±.015	100	85.75 ±.16	207.9 ±.4			
				1.385 ±.003	25.05 ±.03	21.45 ±.02	52.16 ±.03			
11.	Abbeytown 2 B		44	1.000	18.10 ±.04	15.51 ±.04	37.72 ±.08	360 ±60	9.11 ±.06	3.86 ±.04
				5.525 ±.014	100	85.70 ±.13	208.4 ±.3			
				1.386 ±.009	25.01 ±.05	21.42 ±.03	52.18 ±.04			
12.	Abbeytown 2 C		51	1.000	18.04 ±.12	15.45 ±.10	37.65 ±.25	320 ±90	8.99 ±.17	3.85 ±.11
				5.542 ±.038	100	85.65 ±.21	208.6 ±.5			
				1.387 ±.002	25.03 ±.02	21.51 ±.02	52.07 ±.03			
13.	Abbeytown 2 D		55	1.000	18.05 ±.03	15.51 ±.03	37.54 ±.06	390 ±40	9.11 ±.06	3.81 ±.03
				5.541 ±.009	100	85.94 ±.11	208.0 ±.2			
				1.388 ±.002	25.04 ±.02	21.49 ±.02	52.08 ±.03			
14.	Abbeytown 2 E		49	1.000	18.04 ±.03	15.48 ±.03	37.52 ±.06	370 ±30	9.07 ±.06	3.80 ±.03
				5.543 ±.009	100	85.82 ±.11	208.0 ±.2			
				1.392 ±.002	25.09 ±.02	21.50 ±.02	52.08 ±.03			
15.	Abbeytown 2 F		51	1.000	18.02 ±.03	15.45 ±.03	37.37 ±.06	330 ±30	8.98 ±.07	3.75 ±.03
				5.548 ±.009	100	85.69 ±.10	207.3 ±.2			
				1.389 ±.002	25.04 ±.02	21.50 ±.02	52.07 ±.02			
16.	Abbeytown 2 G		51	1.000	18.03 ±.03	15.48 ±.03	37.49 ±.06	370 ±30	9.06 ±.07	3.79 ±.04
				5.547 ±.009	100	85.86 ±.11	207.9 ±.2			

Table 33. cont'd.

No.	Locality	NR ouns	NS ocans	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Monaghan									
				1.389 ±.005	24.86 ±.03	21.31 ±.02	52.45 ±.03			
17.	Derry-leedigan	2	49	1.000	17.90 ±.07	15.34 ±.06	37.76 ±.14	290 ±50	8.80 ±.12	3.96 ±.05
				5.587 ±.021	100	85.72 ±.13	211.0 ±.3			
				1.374 ±.005	24.98 ±.02	21.30 ±.02	52.36 ±.03			
18.	Lisdrum-gormley	2	49	1.000	18.18 ±.07	15.50 ±.06	38.11 ±.14	280 ±60	9.07 ±.14	4.00 ±.07
				5.500 ±.020	100	85.27 ±.11	209.6 ±.2			
				1.386 ±.003	24.89 ±.02	21.40 ±.02	52.32 ±.02			
19.	Coolartra	2	48	1.000	17.96 ±.04	15.44 ±.04	37.75 ±.08	370 ±40	8.98 ±.08	3.94 ±.05
				5.569 ±.013	100	85.98 ±.11	210.2 ±.2			

Table 33. cont'd.

No.	Locality	NR ons.	Ns ocans	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Mayo and N. Galway.									
				1.382 ±.005	25.06 ±.03	21.34 ±.03	52.21 ±.03			
20.	Tullyduff	4	100	1.000	18.13 ±.07	15.44 ±.06	37.78 ±.14	250 ±40	8.98 ±.09	3.86 ±.04
				5.515 ±.021	100	85.16 ±.16	208.3 ±.3			
				1.378 ±.005	24.95 ±.04	21.31 ±.02	52.36 ±.03			
21.	Ballykine Lower	3	79	1.000	18.11 ±.07	15.46 ±.06	38.00 ±.14	280 ±50	9.00 ±.13	3.98 ±.06
				5.523 ±.022	100	85.41 ±.16	209.9 ±.4			
				1.379 ±.006	25.02 ±.03	21.35 ±.02	52.27 ±.03			
22.	Grallagh	3	75	1.000	18.14 ±.08	15.48 ±.07	37.90 ±.17	290 ±60	9.05 ±.15	3.92 ±.07
				5.512 ±.025	100	85.33 ±.13	208.9 ±.3			
				1.387 ±.003	25.00 ±.02	21.45 ±.02	52.18 ±.03			
23.	St. MacDara's Island.	2	54	1.000	18.02 ±.04	15.47 ±.04	37.62 ±.08	370 ±50	9.05 ±.08	3.86 ±.04
				5.548 ±.013	100	85.80 ±.11	208.7 ±.2			

Table 33. cont'd.

No.	Locality	No. Runs	No. Accepted Runs	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Clare and S. Galway									
				1.391 ±.004	24.96 ±.03	21.38 ±.02	52.28 ±.03			
24.	Tynagh	3	73	1.000	17.94 ±.06	15.37 ±.05	37.58 ±.11	300 ±50	8.85 ±.09	3.86 ±.05
				5.573 ±.017	100	85.66 ±.13	209.5 ±.3			
				1.378 ±.003	25.06 ±.02	21.35 ±.02	52.23 ±.03			
25.	Ailwee	3	78	1.000	18.19 ±.04	15.49 ±.04	37.90 ±.09	360 ±40	9.05 ±.09	3.89 ±.04
				5.499 ±.015	100	85.20 ±.10	208.4 ±.2			
				1.382 ±.005	25.01 ±.03	21.34 ±.02	52.28 ±.03			
26.	Knocka-phreaghaun	2	49	1.000	18.10 ±.07	15.44 ±.06	37.83 ±.14	270 ±50	8.98 ±.13	3.90 ±.07
				5.526 ±.021	100	85.33 ±.13	209.0 ±.3			
				1.383 ±.002	25.02 ±.02	21.33 ±.02	52.25 ±.03			
27.	Milltown A	2	44	1.000	18.09 ±.03	15.42 ±.03	37.78 ±.06	250 ±40	8.94 ±.07	3.88 ±.04
				5.528 ±.009	100	85.25 ±.11	208.8 ±.2			
				1.383 ±.003	25.00 ±.03	21.39 ±.02	52.24 ±.04			
28.	Milltown B	2	49	1.000	18.08 ±.04	15.47 ±.04	37.77 ±.09	320 ±40	9.03 ±.08	3.89 ±.06
				5.532 ±.014	100	85.56 ±.13	209.0 ±.3			
				1.383 ±.002	25.01 ±.03	21.36 ±.02	52.25 ±.04			
29.	Kilbreckan	2	49	1.000	18.08 ±.03	15.44 ±.03	37.78 ±.06	280 ±30	8.97 ±.07	3.89 ±.04
				5.530 ±.010	100	85.41 ±.13	208.9 ±.3			
				1.378 ±.003	24.98 ±.04	21.38 ±.02	52.26 ±.04			
30.	Ballyhickey	2	53	1.000	18.13 ±.05	15.52 ±.04	37.92 ±.09	340 ±30	9.11 ±.11	3.94 ±.06
				5.516 ±.015	100	85.59 ±.16	209.2 ±.4			

Table 33. cont'd.

No.	Locality	NR ous. ns	NS occ. ans	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Silvermines									
				1.378 ±.008	24.99 ±.03	21.37 ±.02	52.28 ±.04			
31.	Shallee	2	48	1.000	18.13 ±.05	15.51 ±.04	37.94 ±.09	330 ±40	9.10 ±.07	3.95 ±.04
				5.514 ±.014	100	85.51 ±.15	209.2 ±.3			
				1.379 ±.006	25.10 ±.03	21.32 ±.02	52.22 ±.05			
32.	Gorteen-adiha	2	54	1.000	18.20 ±.08	15.46 ±.07	37.87 ±.17	210 ±50	8.99 ±.13	3.86 ±.07
				5.494 ±.025	100	84.94 ±.15	208.0 ±.3			
				1.380 ±.004	25.09 ±.04	21.32 ±.02	52.22 ±.04			
33.	Ballynoe	2	52	1.000	18.18 ±.06	15.45 ±.05	37.84 ±.11	210 ±40	8.97 ±.11	3.86 ±.05
				5.500 ±.018	100	84.97 ±.16	208.1 ±.4			
				1.381 ±.002	25.06 ±.03	21.38 ±.02	52.19 ±.04			
34.	Knockanroe A	2	45	1.000	18.15 ±.03	15.48 ±.03	37.79 ±.06	280 ±30	9.04 ±.05	3.86 ±.03
				5.511 ±.010	100	85.32 ±.13	208.3 ±.3			
				1.372 ±.004	25.04 ±.03	21.29 ±.02	52.30 ±.03			
35.	Knockanroe B	2	54	1.000	18.25 ±.06	15.52 ±.05	38.12 ±.11	260 ±50	9.12 ±.14	3.97 ±.05
				5.479 ±.017	100	85.02 ±.13	208.9 ±.3			

Table 33. cont'd.

No.	Locality	NR occ. ns	NS occ. ns	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Silvermines (cont'd)									
				1.380 ±.005	25.04 ±.02	21.38 ±.02	52.20 ±.03			
36.	Gortahan-roe A	2	51	1.000	18.14 ±.04	15.49 ±.04	37.83 ±.09	300 ±30	9.06 ±.08	3.89 ±.04
				5.511 ±.013	100	85.38 ±.11	208.5 ±.2			
				1.382 ±.011	24.25 ±.07	21.27 ±.04	52.41 ±.10			
37.	Gortahan-roe B	1	18	1.000	18.37 ±.16	15.65 ±.13	38.57 ±.32	320 ±80	(9.34 ±.29	4.13 ±.11)
				5.445 ±.047	100	85.22 ±.29	210.0 ±.7			
				1.383 ±.002	25.04 ±.02	21.41 ±.02	52.19 ±.03			
38.	Gortahan-roe C	2	53	1.000	18.11 ±.03	15.48 ±.03	37.74 ±.06	310 ±30	9.05 ±.06	3.86 ±.04
				5.525 ±.009	100	85.50 ±.11	208.4 ±.2			
				1.380 ±.002	25.00 ±.02	21.40 ±.02	52.22 ±.02			
39.	Garrane	2	52	1.000	18.12 ±.03	15.51 ±.03	37.84 ±.06	330 ±40	9.09 ±.06	3.91 ±.03
				5.520 ±.009	100	85.60 ±.11	208.9 ±.2			
	N. of Silvermines									
				1.378 ±.002	25.01 ±.02	21.39 ±.02	52.23 ±.03			
40.	Killeen	2	47	1.000	18.15 ±.03	15.52 ±.03	37.90 ±.06	330 ±30	9.12 ±.08	3.92 ±.03
				5.510 ±.009	100	85.53 ±.11	208.8 ±.2			
				1.373 ±.004	25.08 ±.04	21.36 ±.02	52.25 ±.04			
41.	Oulahills	2	50	1.000	18.22 ±.06	15.56 ±.05	38.06 ±.11	320 ±60	9.18 ±.09	3.96 ±.08
				5.488 ±.018	100	85.37 ±.16	208.8 ±.4			

Table 13. cont'd.

No.	Locality	No. Grains	No. Grains	204	205	207	208	Model Age (m.y.)	Vp	Rp
	S. Derry and S.W. Cork.									
				1.882 ±.004	24.97 ±.03	21.31 ±.02	59.55 ±.04			
42.	Bere Island	2	56	1.000	18.07 ±.06	15.42 ±.06	37.87 ±.11	360 ±60	8.98 ±.12	3.98 ±.06
				5.535 ±.017	100	85.34 ±.13	209.6 ±.3			
				1.379 ±.003	24.96 ±.03	21.39 ±.03	52.97 ±.08			
43.	Tuckroma	3	78	1.000	18.10 ±.09	15.51 ±.07	37.90 ±.17	360 ±40	9.11 ±.11	3.95 ±.09
				5.525 ±.026	100	85.70 ±.21	209.4 ±.5			
				1.376 ±.008	25.00 ±.03	21.32 ±.03	52.29 ±.04			
44.	Chena-garry	3	71	1.000	18.17 ±.07	15.49 ±.06	38.00 ±.14	360 ±40	9.05 ±.12	3.98 ±.07
				5.506 ±.021	100	85.28 ±.13	209.2 ±.3			
				1.380 ±.003	24.97 ±.02	21.29 ±.03	52.27 ±.03			
45.	Glomtoo	4	101	1.000	18.09 ±.04	15.50 ±.04	37.88 ±.08	340 ±30	9.07 ±.07	3.94 ±.04
				5.527 ±.013	100	85.66 ±.14	209.3 ±.2			
				1.364 ±.005	25.05 ±.03	21.28 ±.02	52.29 ±.04			
46.	Osbarnore	2	52	1.000	18.37 ±.07	15.60 ±.06	38.34 ±.14	370 ±40	9.26 ±.13	4.01 ±.08
				5.446 ±.021	100	84.96 ±.13	208.7 ±.3			
				1.374 ±.008	24.96 ±.03	21.26 ±.03	52.41 ±.06			
47.	Kilfreen-age	2	53	1.000	18.17 ±.07	15.47 ±.06	38.14 ±.14	350 ±60	9.02 ±.13	4.01 ±.09
				5.505 ±.021	100	85.13 ±.16	210.0 ±.3			
				1.386 ±.003	24.96 ±.03	21.40 ±.02	52.37 ±.03			
48.	Duneen	2	51	1.000	18.01 ±.04	15.45 ±.04	37.74 ±.08	340 ±40	8.99 ±.07	3.91 ±.04
				5.553 ±.014	100	85.81 ±.15	209.6 ±.3			

Table 33. cont'd.

No.	Locality	NR ou. ns	MS oc. ans	204	206	207	208	Model Age (m.y.)	Vp	Kp
	S.E. Ireland									
				1.371 ±.004	25.04 ±.03	21.34 ±.02	52.26 ±.04			
49.	Templey vrick	2	47	1.000	18.26 ±.06	15.57 ±.05	38.12 ±.11	310 ±50	9.20 ±.12	3.97 ±.07
				5.475 ±.017	100	85.22 ±.13	208.7 ±.3			
				1.354 ±.003	25.34 ±.02	21.10 ±.02	52.21 ±.03			
50.	Tankards-town A	2	47	1.000	18.71 ±.04	15.58 ±.04	38.56 ±.09	-20 ±30	(9.18 ±.10	3.91 ±.05)
				5.343 ±.013	100	83.27 ±.10	206.0 ±.2			
				1.369 ±.006	25.05 ±.05	21.27 ±.02	52.32 ±.05			
51.	Tankards-town B	2	44	1.000	18.30 ±.09	15.54 ±.07	38.22 ±.17	250 ±60	9.15 ±.12	3.99 ±.06
				5.465 ±.026	100	84.91 ±.19	208.9 ±.5			
				1.375 ±.004	25.04 ±.02	21.33 ±.02	52.26 ±.03			
52.	B arrys-town	3	81	1.000	18.21 ±.05	15.51 ±.05	38.01 ±.11	270 ±50	9.09 ±.10	3.93 ±.07
				5.491 ±.017	100	85.18 ±.10	208.7 ±.2			
				1.377 ±.002	24.91 ±.02	21.38 ±.02	52.33 ±.03			
53.	Browns-ford	2	49	1.000	18.09 ±.04	15.53 ±.04	38.00 ±.09	390 ±40	9.15 ±.07	4.01 ±.04
				5.528 ±.013	100	85.85 ±.11	210.1 ±.2			
				1.387 ±.003	24.74 ±.02	21.52 ±.02	52.34 ±.03			
54.	Cairn	2	50	1.000	17.84 ±.04	15.52 ±.04	37.74 ±.08	560 ±30	9.16 ±.08	4.05 ±.04
				5.606 ±.013	100	86.98 ±.11	211.6 ±.2			

Table 33. cont'd.

No.	Locality	NR ouns	NS ocans	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Wicklow									
				1.363 ±.005	25.09 ±.02	21.24 ±.02	52.31 ±.03			
55.	Ballin-temple	2	47	1.000	18.41 ±.07	15.58 ±.06	38.38 ±.14	210 ±40	9.21 ±.15	4.00 ±.07
				5.432 ±.020	100	84.66 ±.10	208.5 ±.2			
				1.374 ±.004	24.90 ±.02	21.43 ±.02	52.30 ±.03			
56.	Kilmacoo A	2	52	1.000	18.12 ±.05	15.60 ±.05	38.06 ±.11	450 ±40	9.28 ±.09	4.03 ±.05
				5.518 ±.017	100	86.06 ±.11	210.0 ±.2			
				1.386 ±.004	24.90 ±.03	21.44 ±.02	52.27 ±.03			
57.	Kilmacoo B	2	47	1.000	17.97 ±.06	15.47 ±.05	37.71 ±.11	400 ±50	9.04 ±.09	3.93 ±.05
				5.566 ±.017	100	86.10 ±.13	209.9 ±.3			
				1.362 ±.005	25.08 ±.03	21.24 ±.02	52.32 ±.04			
58.	Brockagh	2	42	1.000	18.41 ±.07	15.59 ±.06	38.41 ±.14	220 ±50	9.22 ±.13	4.02 ±.06
				5.431 ±.021	100	84.69 ±.13	208.6 ±.3			

Table 33. cont'd.

No.	Locality	NR ous	MS ocs	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Dublin									
				1.375 ±.004	25.04 ±.03	21.35 ±.03	52.25 ±.04			
59.	B ally-corus	2	48	1.000	18.21 ±.06	15.53 ±.05	38.00 ±.11	300 ±30	9.14 ±.08	3.94 ±.04
				5.491 ±.017	100	85.26 ±.16	208.7 ±.3			
				1.369 ±.005	25.09 ±.04	21.20 ±.02	52.35 ±.04			
60.	Corbally	2	53	1.000	18.33 ±.07	15.49 ±.06	38.24 ±.14	150 ±60	9.04 ±.15	3.96 ±.09
				5.456 ±.022	100	84.50 ±.16	208.6 ±.4			
				1.363 ±.003	25.10 ±.03	21.23 ±.02	52.31 ±.03			
61.	Clontarf	2	48	1.000	18.42 ±.05	15.58 ±.04	38.38 ±.09	200 ±50	9.20 ±.08	4.00 ±.05
				5.430 ±.014	100	84.58 ±.13	208.4 ±.3			
	Northern Ireland.									
				1.367 ±.002	25.42 ±.02	21.15 ±.02	52.07 ±.03			
62.	Slieve Binian A	2	51	1.000	18.60 ±.03	15.47 ±.03	38.09 ±.06	-80 ±40	(8.98 (±.07	3.74) ±.04)
				5.378 ±.009	100	83.20 ±.10	204.8 ±.2			
				1.364 ±.003	25.40 ±.03	21.16 ±.02	52.08 ±.04			
63.	Slieve Binian B	2	35	1.000	18.62 ±.05	15.51 ±.04	38.18 ±.09	-40 ±30	(9.06 (±.06	3.78) ±.03)
				5.370 ±.013	100	83.31 ±.13	205.0 ±.3			

Table 33. cont'd.

No.	Locality	MR ou. ns	MS oc. ans	204	206	207	208	Model Age (m.y.)	Vp	Kp
FRANCE										
				1.373 ±.002	25.06 ±.02	21.37 ±.02	52.21 ±.02			
64.	Pierre-ville	2	49	1.000	18.25 ±.03	15.56 ±.05	38.03 ±.06	300 ±40	9.18 ±.07	3.98 ±.04
				5.479 ±.009	100	85.28 ±.10	208.3 ±.2			
				1.370 ±.006	25.06 ±.03	21.28 ±.02	52.30 ±.04			
65.	Huelgoat	2	56	1.000	18.29 ±.08	15.53 ±.07	38.18 ±.17	230 ±40	9.11 ±.14	3.97 ±.06
				5.467 ±.025	100	84.92 ±.13	208.7 ±.3			
				1.372 ±.002	24.98 ±.02	21.34 ±.02	52.31 ±.02			
66.	Poullaouen	2	48	1.000	18.21 ±.03	15.55 ±.03	38.13 ±.06	320 ±40	9.17 ±.07	4.00 ±.04
				5.492 ±.009	100	85.43 ±.11	209.4 ±.2			
				1.372 ±.005	25.09 ±.03	21.32 ±.03	52.23 ±.04			
67.	Tréguson	2	52	1.000	18.29 ±.07	15.54 ±.06	38.07 ±.14	250 ±50	9.14 ±.14	3.92 ±.06
				5.468 ±.021	100	84.97 ±.16	208.2 ±.3			
				1.369 ±.005	25.03 ±.03	21.29 ±.02	52.33 ±.05			
68.	Le Hinglé	2	48	1.000	18.28 ±.07	15.55 ±.06	38.22 ±.14	270 ±50	9.16 ±.12	4.00 ±.06
				5.469 ±.021	100	85.06 ±.13	209.1 ±.3			

Table 33. cont'd.

No.	Locality	NR ou. ns	NS oc. ans	204	206	207	208	Model Age (m.y.)	Vp	Kp
FRANCE (cont.)										
				1.374 ±.006	24.88 ±.03	21.32 ±.03	52.42 ±.04			
69.	La Touche 2 A	55		1.000	18.11 ±.08	15.52 ±.07	38.15 ±.17	360 ±60	9.12 ±.16	4.06 ±.08
				5.523 ±.025	100	85.69 ±.16	210.7 ±.5			
				1.377 ±.004	24.92 ±.03	21.38 ±.02	52.34 ±.04			
70.	La Touche 2 B	46		1.000	18.10 ±.06	15.53 ±.05	38.01 ±.11	380 ±40	9.15 ±.08	4.00 ±.05
				5.526 ±.017	100	85.79 ±.15	210.0 ±.5			
				1.368 ±.005	25.06 ±.02	21.26 ±.02	52.30 ±.05			
71.	Pont-Péan 2	51		1.000	18.32 ±.07	15.54 ±.06	38.23 ±.14	220 ±50	9.15 ±.12	3.98 ±.06
				5.459 ±.020	100	84.84 ±.10	208.7 ±.2			
				1.380 ±.005	24.91 ±.03	21.46 ±.02	52.25 ±.04			
72.	La Chapelle St. Melaine 2 A	53		1.000	18.05 ±.07	15.55 ±.06	37.86 ±.14	440 ±50	9.19 ±.12	3.97 ±.07
				5.540 ±.021	100	86.15 ±.13	209.8 ±.3			
				1.389 ±.002	24.85 ±.02	21.53 ±.02	52.23 ±.03			
73.	La Chapelle St. Melaine 2 B	50		1.000	17.89 ±.03	15.50 ±.03	37.60 ±.06	500 ±30	9.11 ±.07	3.93 ±.04
				5.590 ±.009	100	86.64 ±.11	210.2 ±.2			
				1.376 ±.007	25.05 ±.05	21.32 ±.02	52.27 ±.05			
74.	St. Pierre Montlimart 2	57		1.000	18.20 ±.10	15.49 ±.08	37.99 ±.20	260 ±60	9.07 ±.18	3.93 ±.08
				5.493 ±.030	100	85.11 ±..19	208.7 ±.5			

Table 33 cont'd.

No.	Locality	NR ons.	NS ocans	204	206	207	208	Model Age (m.y.)	Vp	Kp
REFERENCE SAMPLES										
				1.372 ±.002	25.08 ±.02	21.30 ±.02	52.24 ±.04			
75.	Lambriggan, Cornwall	2	52	1.000	18.28 ±.03	15.52 ±.03	38.08 ±.06	230 ±30	9.10 ±.06	3.93 ±.03
				5.470 ±.009	100	84.93 ±.10	208.3 ±.2			
				1.544 ±.002	22.51 ±.03	22.65 ±.02	53.30 ±.03			
76.	N.B.S. Sample 200 (Galena)	3	71	1.000	14.58 ±.03	14.67 ±.02	34.52 ±.05	2140 ±30	8.33 ±.07	4.34 ±.06
				6.859 ±.013	100	100.62 ±.16	236.8 ±.3			
				1.556 ±.005	22.54 ±.02	22.66 ±.02	53.23 ±.02			
77.	N.B.S. Sample 200a (PbI_2)	3	69	1.000	14.49 ±.05	14.56 ±.05	34.21 ±.11	2110 ±40	8.10 ±.11	4.14 ±.06
				6.903 ±.023	100	100.53 ±.13	236.2 ±.2			

TABLE 34.

Moorbath Results of Isotopic Analyses

and Model Parameters for Irish Galenas.

No.	Locality	NR ou ·ns	NS oc ·an s	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Northern Ireland									
				1.384 ±.004	25.01 ±.02	21.35 ±.03	52.85 ±.03			
M 84	Castleward, Down	1	26	1.000	18.07 ±.07	15.43 ±.06	37.75 ±.13	280 ±60	8.96	3.88
				5.534 ±.017	100	85.4 ±.2	208.9 ±.3			
				1.379 ±.004	24.82 ±.04	21.38 ±.03	52.42 ±.05			
M 85	Conlig, Down	1	22	1.000	18.00 ±.08	15.50 ±.07	38.01 ±.14	420 ±70	9.10	4.06
				5.556 ±.018	100	86.1 ±.3	211.2 ±.5			
				1.376 ±.004	24.97 ±.04	21.36 ±.03	52.29 ±.05			
M 86	Creggan,	1	22	1.000	18.15 ±.08	15.52 ±.07	38.00 ±.15	330 ±70	9.12	3.97
				5.511 ±.018	100	85.5 ±.3	209.4 ±.5			

Table 34. cont'd.

No.	Locality	Mineral	Rock	204	206	207	208	Model Age (m.y.)	Vp	Kp
	S.E. Ireland			1.568 ±.006	25.02 ±.05	21.29 ±.03	52.53 ±.06			
M 87	Glendalough, Wicklow	1	19	1.000	18.29 ±.11	15.56 ±.09	38.25 ±.21	280 ±90	9.19	4.01
				5.468 ±.026	100	85.1 ±.5	209.2 ±.7			
				1.370 ±.004	25.07 ±.03	21.28 ±.03	52.28 ±.04			
M 88	Glenmalure, Wicklow	1	20	1.000	18.30 ±.07	15.53 ±.07	38.16 ±.14	230 ±70	9.12	3.96
				5.465 ±.017	100	84.9 ±.2	208.5 ±.5			
				1.371 ±.006	25.01 ±.06	21.29 ±.03	52.33 ±.06			
M 89	Barristown, Wexford	1	21	1.000	18.24 ±.13	15.53 ±.09	38.17 ±.20	280 ±80	9.14	4.00
				5.482 ±.027	100	85.1 ±.4	209.2 ±.7			
				1.380 ±.004	24.87 ±.04	21.43 ±.02	52.33 ±.05			
M 90	Avoca, Wicklow No.271	1	29	1.000	18.02 ±.08	15.53 ±.06	37.92 ±.15	440 ±70	9.16	4.01
				5.549 ±.018	100	86.2 ±.2	210.4 ±.5			
				1.377 ±.005	24.84 ±.04	21.41 ±.03	52.38 ±.06			
M 91	Avoca, No.DP21	1	23	1.000	18.04 ±.09	15.55 ±.08	38.04 ±.18	450 ±70	9.19	4.06
				5.543 ±.022	100	86.2 ±.3	210.9 ±.6			
				1.373 ±.004	24.88 ±.04	21.41 ±.03	52.35 ±.06			
M 92	Avoca, No.3C	1	19	1.000	18.12 ±.08	15.59 ±.07	38.13 ±.15	440 ±70	9.26	4.06
				5.518 ±.018	100	86.1 ±.2	210.4 ±.6			
				1.383 ±.006	24.88 ±.03	21.42 ±.04	52.32 ±.05			
M 93	Avoca, No.AEA	1	19	1.000	17.99 ±.10	15.49 ±.09	37.83 ±.20	410 ±70	9.08	3.98
				5.559 ±.025	100	86.1 ±.3	210.3 ±.4			

Table 34. cont'd.

No.	Locality	NR ou. ns	NS oc. ns	204	206	207	208	Model Age (m.y.)	Vp	Kp
	Western Ireland									
				1.369 ±.008	25.01 ±.03	21.35 ±.03	52.27 ±.06			
M 94	Abbeytown, Sligo	1	24	1.000	18.27 ±.13	15.60 ±.11	38.18 ±.25	330 ±90	9.25	4.00
				5.474 ±.033	100	85.4 ±.2	209.0 ±.5			
				1.391 ±.004	24.88 ±.04	21.35 ±.02	52.38 ±.05			
M 95	Sheeffry, Mayo	1	25	1.000	17.89 ±.08	15.35 ±.06	37.66 ±.14	310 ±70	8.82	3.92
				5.591 ±.018	100	85.8 ±.2	210.5 ±.6			
				1.411 ±.004	24.41 ±.04	21.79 ±.03	52.39 ±.05			
M 96	Clements, Galway	1	27	1.000	17.30 ±.08	15.44 ±.07	37.13 ±.14	860 ±70	9.08	4.05
				5.780 ±.019	100	89.3 ±.2	214.6 ±.6			
				1.409 ±.006	24.62 ±.04	21.62 ±.04	52.35 ±.05			
M 97	Glengowla, Galway	1	26	1.000	17.47 ±.11	15.34 ±.09	37.15 ±.20	620 ±80	8.85	3.93
				5.723 ±.026	100	87.8 ±.3	212.6 ±.6			
				1.412 ±.005	24.66 ±.05	21.74 ±.04	52.19 ±.07			
M 98	Cloosh, Galway	1	22	1.000	17.46 ±.09	15.40 ±.09	36.96 ±.18	700 ±80	8.98	3.85
				5.726 ±.023	100	88.2 ±.4	211.6 ±.8			
				1.417 ±.005	24.73 ±.06	21.68 ±.02	52.17 ±.06			
M 99	O'Flaherty's Shaft, Galway	1	27	1.000	17.45 ±.11	15.30 ±.07	36.82 ±.17	580 ±80	8.76	3.76
				5.730 ±.025	100	87.7 ±.3	211.0 ±.7			
				1.393 ±.006	24.95 ±.04	21.41 ±.03	52.26 ±.06			
M 100	Lough Corrib, Galway	1	24	1.000	17.91 ±.11	15.37 ±.09	37.52 ±.20	320 ±80	8.85	3.85
				5.583 ±.026	100	85.8 ±.3	209.5 ±.5			

CHAPTER 9

MODELS FOR THE INTERPRETATION OF LEAD ISOTOPE DATA

9. (1) INTRODUCTION.

It has been stated in preceding Chapters that the Holmes-Houtermans model for the interpretation of lead isotope compositions was used throughout the present study. Calculations of model ages and geochemical ratios based on this theory have already been made and quoted. Before proceeding to detailed discussions of the geological significance of the individual results, the Holmes-Houtermans theory is outlined briefly below, and also compared with the models of Russell and associates.

It is not proposed to enter into detailed geological arguments regarding the validity of the major assumptions of these theories. In this respect, Moorbath (1959 b) has advanced a detailed support of the Holmes-Houtermans model from the geological evidence. Russell and Farquhar's (1960 b) monograph on the subject reviews all the relevant models, but naturally is biassed in favour of the Russell models.

The author's investigations into the effects of the use of different constants in the calculation of Holmes-Houtermans model ages are also included in this Chapter.

9. (2) HOLMES-HOUTERMANS MODEL.

The main assumptions leading to the mathematical formulation of the theory by Holmes (1946, 1947 a, 1949) and Houtermans (1946, 1947, 1953) are:-

1. For a comparatively short period after its formation, the earth was fluid and homogeneous, resulting in a uniform distribution of uranium, thorium and lead.

2. Also at this time, all the lead in the earth had the same isotopic

composition. This is termed "primeval" lead.

3. Within a short time the differentiation of the crust led to the development of inhomogeneities, exhibited by small differences in the U/Pb and Th/U ratios between different regions.

4. The only process altering terrestrial lead isotope ratios and U/Pb and Th/U ratios has been the radioactive decay of uranium and thorium to lead. The amount of Pb^{204} in the earth has remained unaltered.

5. Lead minerals contain negligible amounts of uranium and thorium. Thus on mineralisation lead was separated from a U/Th/Pb environment and the lead isotopic composition has remained unchanged ever since.

6. The lead isotopic composition of iron meteorites is assumed to be equivalent to that of primeval lead. (These meteorites contain negligible amounts of uranium and thorium; the isotopic compositions of many elements have been found to be identical in meteoritic and terrestrial material).

The derivation of the Holmes-Houtermans equation from these assumptions is given in full by Geiss (1954) and Russell and Farquhar (1960 b), and is only summarised here.

Symbols Used in this Chapter (different from those of Chapter 7).

Lead Isotope Ratios	206/204	207/204	208/204
Primeval (i.e. at $t = t_o$)	x_o	y_o	z_o
Observed (i.e. at time t)	x	y	z
Modern (i.e. at $t = o$)	x_p	y_p	z_p

Decay Constants (in $yr.^{-1}$)

λ_1 : U^{238}

λ_2 : U^{235}

λ_3 : Th^{232}

Modern Isotope Ratio $k = U^{238}/U^{235}$

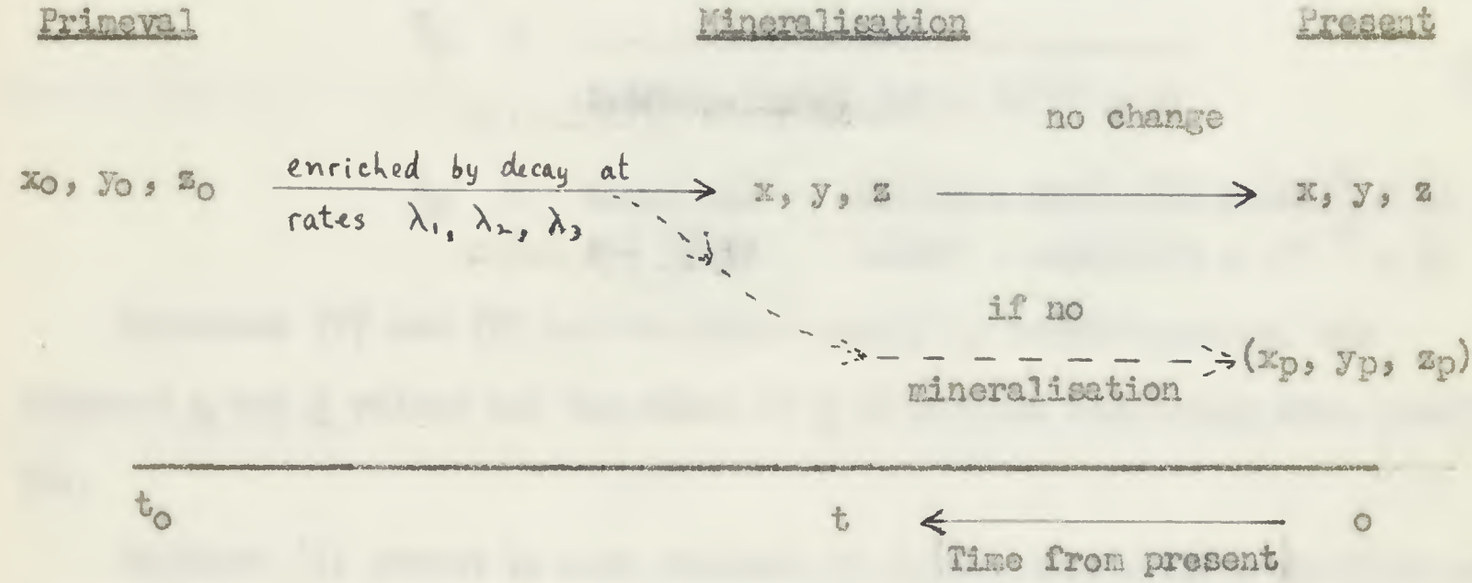
t_o = Age of the Earth in yr. (i.e. time since formation of local inhomogeneities in U-Pb distribution).

t = Time of Formation, or "Model Age" of mineral in yr. (i.e. time since separation of lead from uranium and thorium).

V_p = U^{238}/Pb^{204} in source of lead minerals extrapolated to present time.

K_p = Th^{232}/U^{238} " " " " " " " " "

The following diagram illustrates the meaning of the lead isotope ratio symbols:-



At time t:

$$x = x_o + V_p (e^{\lambda_1 t_o} - e^{\lambda_1 t}) \quad (1)$$

$$y = y_o + \frac{V_p}{k} (e^{\lambda_2 t_o} - e^{\lambda_2 t}) \quad (2)$$

Thus,

$$\frac{y - y_o}{x - x_o} = \frac{1}{k} \frac{(e^{\lambda_2 t_o} - e^{\lambda_2 t})}{(e^{\lambda_1 t_o} - e^{\lambda_1 t})} \quad (3)$$

The values of the parameters V_p and K_p calculated with respect to the present time, are given by the following equations:-

$$V_p = \frac{x - x_o}{e^{\lambda_1 t_o} - e^{\lambda_1 t}} \quad (4)$$

$$K_p = \frac{z - z_o}{x - x_o} \frac{e^{\lambda_1 t_o} - e^{\lambda_1 t}}{e^{\lambda_3 t_o} - e^{\lambda_3 t}} \quad (5)$$

The values of the constants used by Moorbath and the author for solving

equations (3), (4), (5) are listed in Table 35. The selection of these constants is discussed in detail in Section 9.(6). Substitution of these values in the equations gives:-

$$\frac{y - 10.36}{x - 9.50} = \frac{1}{137.8} \cdot \frac{\exp(0.1541 \times 4.50) - \exp(1.541 \times 10^{-10} \times t)}{\exp(0.972 \times 4.50) - \exp(9.72 \times 10^{-10} \times t)}$$

$$\frac{y - 10.36}{x - 9.50} = \frac{1}{137.8} \cdot \frac{2.0006 - \exp(1.541 \times 10^{-10} \times t)}{79.3604 - \exp(9.72 \times 10^{-10} \times t)} \qquad (6)$$

$$V_p = \frac{x - 9.50}{2.0006 - \exp(1.541 \times 10^{-10} \times t)} \qquad (7)$$

$$K_p = \frac{z - 29.49}{x - 9.50} \cdot \frac{2.0006 - \exp(1.541 \times 10^{-10} \times t)}{1.2517 - \exp(0.499 \times 10^{-9} \times t)} \qquad (8)$$

Equations (7) and (8) are evaluated simply by substitution of the observed x and z values and the value of t calculated previously from equation (6).

Equation (6) cannot be made explicit in t, the only unknown quantity once the experimental values of x and y have been substituted. Prior to the development of computer methods for the exact numerical solution of this equation, it was most conveniently solved by a graphical method. The graphical expression of the equation is still essential to an understanding of the theory.

A chart is constructed for this purpose by giving convenient values to y (between 10.36 and 15.73; primeval and modern values respectively) and t (at suitable intervals, say 100 m.y., between 0 and 4,500 m.y.) and the corresponding values of x are calculated from equation (6). This yields a series of straight lines radiating out from a point corresponding to the primeval (≡ meteoritic) lead isotope ratios - see Figure 8. These lines are called "isochrons" because leads whose isotopic ratios lie on a single isochron all have the same model age. The position on an isochron of the isotope

Table 35

Values of Parameters and Constants used for Calculation of Model Parameters

Primeval Isotope Ratios:	Pb^{206}/Pb^{204}	$(x_o) = 9.50$	(1)
	Pb^{207}/Pb^{204}	$(y_o) = 10.36$	(1)
	Pb^{208}/Pb^{204}	$(z_o) = 29.49$	(1)
Modern Isotope Ratios:	Pb^{206}/Pb^{204}	$(x_p) = 18.93$	(2)
	Pb^{207}/Pb^{204}	$(y_p) = 15.73$	(2)
	Pb^{208}/Pb^{204}	$(z_p) = 38.80$	(2)
	U^{238}/U^{235}	$(k) = 137.8$	(3)
Decay Constants:	U^{238}	$(\lambda_1) = 1.541 \times 10^{-10} yr.^{-1}$	(4)
	U^{235}	$(\lambda_2) = 9.72 \times 10^{-10} yr.^{-1}$	(5)
	Th^{232}	$(\lambda_3) = 0.499 \times 10^{-10} yr.^{-1}$	(6)
Age of the Earth		$(t_o) = 4.50 \times 10^9$ yr.	(7)

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References

(1) Patterson (1955, 1956).

(2) Patterson et al. (1953)

(3) Inghram (1946).

(4) Kienberger (1949).

(5) Fleming et al. (1952)

(6) Kovarik and Adams (1938)

(7) Moorbath (1959b); This thesis, Section 9.6.

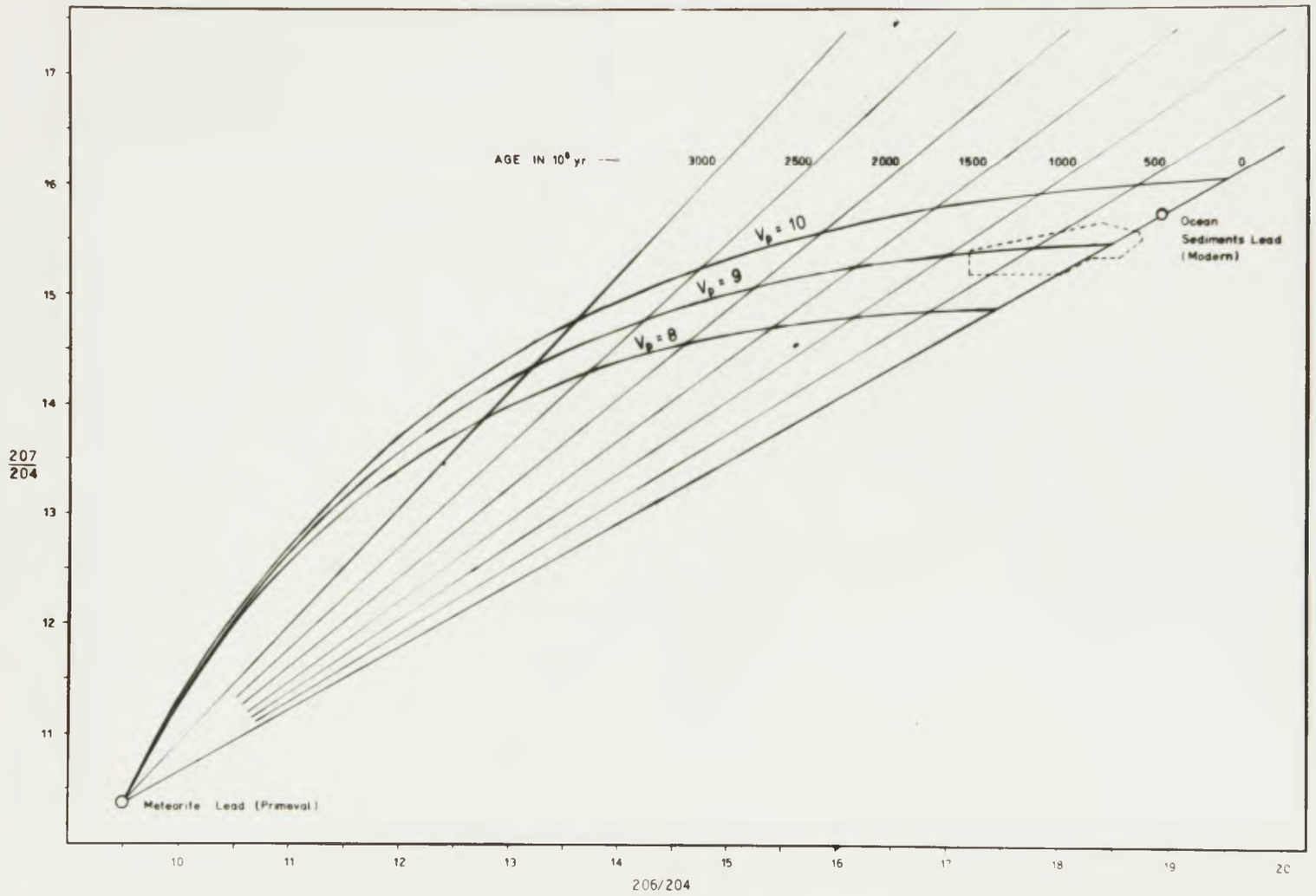


Figure 8: Isochron Diagram (showing some Growth Curves).
Dotted lines enclose all Irish and French galenas (see Figure 16).

ratios of a lead mineral is determined by the regional U^{238}/Pb^{204} ratio ($= V_p$) in the source material from which the lead was extracted. A few "growth curves" are plotted on Figure 8 to illustrate this - the isotopic composition of lead in a source with a particular V_p ratio will evolve or "grow" along that particular theoretical curve. The zero isochron passes through the points representing lead isotope ratios of iron meteorites and modern ocean sediments. The model age of a lead mineral can be found by determining the position of its (x, y) point relative to the isochrons.

Because the calculation of t, Vp, Kp from the isotope ratios of a sample depends on the validity of the initial set of assumptions of the Holmes-Houtermans theory, they are always referred to as the "model" parameters of the sample. Apart from considerations of errors in the experimental ratios and constants used, the accuracy of the calculated model parameters for a sample is dependent on how close the lead of that sample obeyed the Holmes-Houtermans model. Samples which have not obeyed the model (which appear to be only a small minority of British and Irish galenas) are classified as "anomalous", and are discussed in Section 9.(5).

9. (3) MODELS OF RUSSELL AND ASSOCIATES.

(a) Russell-Farquhar-Cumming Model (Russell and Farquhar, 1960 b)

Alpher and Herman (1951) assumed that ore lead was derived from a homogeneous source material produced by geological processes which extensively mixed the crustal rocks of the earth. Thus simple equations based on constant U-Th-Pb ratios could be proposed:-

$$x = x_p - V_p\,(e^{\lambda_1 t} - 1) \qquad (9)$$

$$y = y_p - \frac{V_p}{137.8}\,(e^{\lambda_2 t} - 1) \qquad (10)$$

$$z = z_p - W_p (e^{\lambda_3 t} - 1) \qquad (11)$$

$$(W_p = \frac{Th^{232}}{Pb^{204}} = V_p \cdot \kappa_p)$$

Since these equations do not allow for regional variations in U-Th-Pb ratios, they are fundamentally different from the Holmes-Houtermans equation. Russell, Farquhar and associates have always favoured theories postulating mantle origins for ore leads. The mantle of the earth is supposed to possess a uniform U-Th-Pb distribution, and so if the mantle is the source of lead ores, equations (9) to (11) would apply. Cumming (in Wilson et al., 1956) proposed values for V_p, W_p, x_p and z_p, application of which to equations (9) and (11) allowed the calculation of two independent ages (t_{206} and t_{208}) for a lead sample from the experimental values of x and z. The calculated ages are more sensitive to experimental errors in the isotope abundances, particularly to errors in Pb^{204}, than those calculated from the Holmes-Houtermans equation. The uncertainties in the ages due to all factors were too high for ages of less than 1000 m.y. to be of much geological use.

(b) Russell-Stanton-Farquhar Model (Russell and Farquhar, 1960 a, b)

This model is based on the hypotheses of Stanton regarding the genesis of certain types of lead ore deposit (e.g. Stanton and Russell, 1959). These "conformable" deposits are considered to have been formed from lead of volcanic origin (assumed to be derived from the mantle) which replaced iron in iron sulphide lenses precipitated in off-shore reef facies associated with seaboard volcanism. The major assumptions of this model are quoted from Russell and Farquhar (1960 a).

1. "All terrestrial lead develops isotope ratios by the accumulation of radiogenic lead in the mantle which is uniform in U, Th, Pb.

2. Conformable leads as considered (and selected) by Stanton provide samples

of mantle lead.

3. All other lead ores, and particularly vein leads may have resulted from the migration of lead through crustal rocks of variable radioactivity and variable Th/U ratios, and therefore have had the opportunity of becoming anomalous leads by picking up radiogenic lead developed in surface rocks.

4. The observed scatter of the abundance of all ore leads about a single growth curve is solely the result of the inclusion of a large number of anomalous leads that have not been recognized as such."

Using Patterson's values for meteoritic leads, a growth curve was constructed for lead in the earth's mantle. The isotopic composition of eight lead deposits meeting Stanton's criteria for the conformable type, were found to fit this growth curve well. Equations were derived for the dating of conformable deposits which allow calculation of ages from the ratios Pb^{206}/Pb^{207} (t_{6-7}) and Pb^{206}/Pb^{204} (t_{6-4}).

It should be noticed that Russell and Farquhar dismiss other types of lead ores (to which belong the majority, if not all, of British, Irish and French deposits studied by Moorbath and the author) as potentially anomalous, or at least suspicious. Although they do suggest a procedure for estimating wide upper and lower limits to the ages of non-conformable deposits, in effect they deny the possibility of reasonably accurate dating for any but conformable deposits.

Russell, Farquhar and Stanton's hypothesis of a mantle source for lead ores may apply to this category of eight conformable deposits. But their dismissal of other lead ores as anomalous does seem unwise in view of the hundreds of such leads which have been successfully dated by the Holmes-Houtermans model.

9. (4) COMPARISON OF RESULTS FROM HOLMES-HOUTERMANS AND RUSSELL MODELS.

For the purposes of this comparison, ten of the author's galenas from Ireland and four from France were selected to represent the whole range of isotopic compositions found in these regions. Model ages were calculated for these samples using the three models discussed in the previous two Sections. The computed tables of Russell and Farquhar (1960 b) for the calculation of all their types of model ages were applied to the author's isotopic data. The physical constants used by Russell and Farquhar in computing their tables are slightly different from those used in this thesis. The author's Holmes-Houtermans model ages were recalculated using Russell and Farquhar's constants so that the comparison would be valid. (This was done using model age Table 22; note that the value of $t_o = 4.50 \times 10^9$ yr. was used in calculation of Holmes-Houtermans model ages with both sets of physical constants). The results are reproduced in Table 36.

The change of physical constants to those used for calculation of the Russell ages has caused a reduction of 30 m.y. in all the Holmes-Houtermans model ages. The model age differences between specimens are preserved with these new values, but a systematic re-evaluation of their stratigraphical correlations would be required if they were to be used for geological considerations.

Table 36 shows clearly that very few of the Russell model ages are meaningful in geological terms for those specimens. The Russell-Farquhar-Cumming model ages are systematically higher than the corresponding Holmes-Houtermans model ages, and many of the former model ages are older than the host-rocks in which the specimens occurred. Those specimens with t_{206} ages which do not contradict the geological data have t_{206} ages in complete

Table 36.

Model Ages Calculated from some Irish and French Lead Isotope Data using Holmes-Houtermans and Russell Methods.

No.	Locality	Model Ages (in m.y.)					
		Holmes-Houtermans. Constants:*		Russell, Farquhar & Cumming *		Russell, Stanton & Farquhar *	
		B	E	t_{206}	t_{208}	t_{6-7}	t_{8-4}
IRELAND							
5	Knockybrin	-80	-110	203	461	-188	357
62	Slieve Binian A	-80	-110	117	490	~ -222	394
60	Corbally	150	120	271	418	1	314
61	Clontarf	200	170	219	351	178	245
50	Tankardstown A	-20	-50	53	269	-198	140
51	Tankardstown B	250	220	289	427	71	321
9	Lugawarry	260	230	384	695	128	651
10	Abbeytown A	360	330	429	747	206	729
56	Kilmacoo A	450	420	390	504	253	417
57	Kilmacoo B	400	370	473	671	260	627
FRANCE							
71	Pont Péan	220	190	277	423	70	318
68	Le Hinglé	270	240	300	427	94	321
69	La Touche A	360	330	396	461	196	357
72	La Chapelle St. Melaine A	440	410	429	600	268	533

* Note - See Table 37 for groups of constants used in these calculations. All Russell ages calculated using constants group E. Constants group B were those used for calculating model parameters in this thesis.

disagreement with both the t_{206} age and the geology. Also this theory does not resolve the problems of specimen Nos. 5, 50, 62, 63, which are negatively anomalous on the Holmes-Houtermans model.

The Russell-Stanton-Farquhar model should strictly be considered only for those deposits which are of the conformable type defined by Stanton. Nevertheless the ages from this model have been calculated for all the specimens here to show the extreme variability found. The only one which might be similar to the conformable type is the replacement-type deposit of Avoca (Kilmacoo),* and possibly also that of Abbeytown. Even with these specimens there is no agreement between the t_{6-7} and t_{3-4} ages. It is clear why Russell and associates suspect all vein leads to be anomalous when their models yield such geologically meaningless results.

Moorbath (1959 b) also compared the model ages of some British galenas on the Holmes-Houtermans and Russell-Farquhar-Cunning models and found similar results. It can only be concluded from this that, whereas Russell's models might apply to the limited type of conformable lead ore deposit, they cannot be used to obtain meaningful model ages for the majority of young leads.

9. (5) ANOMALOUS LEADS.

On any model for the interpretation of lead isotope compositions, the term "anomalous leads" is reserved for those which do not obey the assumptions of the model - this is generally shown when the calculated model age disagrees with the geological evidence for the age of the deposit outside the limits of experimental error, or when wide regional variations are shown in the isotope compositions.

* Russell and associates do consider Avoca to be a typically conformable deposit, but have not reported any measurements of their own on it yet. (Moorbath, personal communication).

It has been stated previously that Russell and associates consider all non-conformable lead deposits to be potentially anomalous. This classification is not considered to apply to the great majority of British, Irish and French galenas studied by Moorbath and the author, and so in all following discussions in this thesis the term "anomalous" is used only for those leads which do not give meaningful ages on the Holmes-Houtermans model. Moorbath (1959 b) has dealt at some length with the geological theories explaining anomalous leads and the following discussion is largely an abbreviation of his treatment.

Anomalous leads fall into two major classes -

(a) Anomalously old leads - model ages significantly older than the rocks in which they occur, and thus older than the true age of mineralisation.

(b) Anomalously young leads - model ages significantly younger than their minimum ages defined from geological evidence. These leads often give negative model ages.

(a) Anomalously Old Leads.

The two type-deposits, in which anomalously old leads were first recognised are the Blaiberg, Austria, and Ivigtut, Greenland mineral deposits. Such "B-type leads" are generally considered to have resulted from one of the following processes:-

1. Remobilisation of the lead of an older mineralisation and its migration to a younger geological environment (Eberhart et al., 1955; Holmes and Cahen, 1955; Cahen et al., 1958). Provided that the remobilising solutions contained no other lead of different isotopic composition, and that during migration they did not pass through lead-bearing formations, the isotopic composition of the new deposit will reflect the age of the original mineralisation of the lead (i.e. of its original separation from uranium and thorium). The possibility of a mixture of leads of different isotopic composition resulting from such migration must also be considered.

2. Inhomogeneous hydrothermal extraction of lead from a mass of rock. If the more easily leached radiogenic lead is removed from a mass of rock it will leave the rock mass deficient in radiogenic lead. The isotopic composition of this remaining lead will be apparently older, while that of the extracted lead will be apparently younger than the average isotopic composition over the whole rock mass prior to inhomogeneous extraction. Subsequent homogeneous extraction of the remaining lead and its deposition would lead to a B-type lead.

Moorbath considers the Ivigtut lead, whose model age of 2150 m.y. is 900 m.y. greater than a Rb/Sr age on biotite from the same pegmatite, has "originated by large-scale remobilisation or refusion of the ancient basement rocks which are presumed to have had an overall low U/Pb ratio and a deficiency in radiogenic lead" (1959 b, p.175). The Bleiberg lead and other B-type European and N. African deposits are considered by Cahen et al. (1958) to have been rejuvenated from older mineralisations. The low silver content of these deposits compared with deposits yielding normal model ages appears to be diagnostic of remobilised lead.

Moorbath has identified several B-type leads in the British Isles from the North-West Highlands, Scotland, and the Oughterard area, Co. Galway, Eire. Both these series of small deposits appear to have resulted from local remobilisation of older lead, probably during Caledonian times. No comparable series of leads has been found by the author in Ireland; no more were found in the Oughterard area. The possibility of two or three isolated Irish leads being B-type is discussed in the text of the next Chapter, but definite identification of them is hampered either by a lack of geological evidence for the age of the host-rocks or by the model ages being only slightly greater than the geological age.

(b) Anomalously Young Leads.

The type-deposit of these "J-type leads" (Joplin-type) is the Mississippi Valley, U.S.A., group of deposits (Kulp et al., 1956). This type of anomalous deposit is generally characterised by:-

1. Excess of radiogenic Pb^{206}, Pb^{207}, Pb^{208} over that expected from the geological age of the deposit, often resulting in a negative model age.

2. Variability of isotopic composition over whole area, or even within one small deposit.

It is generally considered that these isotopic compositions have resulted from one of three main processes:-

(i) Inhomogeneous hydrothermal extraction of lead from underlying basement rocks, in which the radiogenic lead isotopes were preferentially removed (Nate and Kulp, 1955). The acid-washing experiments of Tilton (1956) and the demonstration by Brown et al. (1953) that radiogenic lead is preferentially concentrated in inter-granular surfaces of granite support the possibility of this and the next process.

(ii) Lateral secretion of lead from enclosing sediments (Doyle, 1959). This is somewhat analogous to (i) above in its effects on isotopic composition.

(iii) Removal of radiogenic lead from nearby earlier uranium-thorium minerals by lead-bearing mineralising fluids. This can be inferred directly in the Lake Athabasca deposit, Saskatchewan, Canada (Eckelmann and Kulp, 1956) and in the Witwatersrand deposit, South Africa (Horne and Davidson, 1955).

In all the above processes, incomplete mixing of the lead-bearing fluids would result in the variability in isotopic composition observed.

The author has found J-type anomalies in four galenas from three deposits in Ireland (Specimen Nos. 5, 50, 62, 63), which are the first such leads to be discovered in the British Isles. The anomalous nature of these leads is quite clear when their isotope compositions are compared with those of the other normal leads from Ireland (see Figure 16), but in no case is the radiogenic component very large. The Knockybrin galena (No. 5) and Slieve Binian galenas (Nos. 62, 63) are from very small isolated deposits from which further sampling is prevented by lack of exposures. The Tankardstown A galena (No. 50) comes from the Donnahon mining area, Co. Wicklow, in which galena is a very rare constituent; but this is the only one of the three deposits worth searching for a further number of samples from which its unusual isotopic history might be deduced. The Slieve Binian galenas are the only ones for which there is any direct evidence of radiogenic addition to the lead-bearing fluids from the surrounding rocks. These deposits are discussed in more detail in the next Chapter.

9. (6) CHOICE OF CONSTANTS FOR CALCULATION OF MODEL PARAMETERS.

It was essential that the model parameter results of the author's work be strictly comparable with those of Moorbath. Hence exactly the same constants were used by the author in calculating model parameters as by Moorbath (1959 b), and these are listed in Table 35. The validity of the choice of these constants is re-examined in this Section with special reference to the effect of using different constants on the calculated model age. Reference should be made throughout to Table 37, which shows the results of the use of different series of constants on the model ages calculated from Moorbath's seven Cornwall-Devon galenas. Series B is the group of constants used by Moorbath and the author.

TABLE 27.

Effect on Model Ages of Use of Different Constants

No.	Location	Isotope Ratios $\frac{206}{204}$	Isotope Ratios $\frac{207}{204}$	Series –	A	B	C	D	E	F	G	H	I	J
					Model Ages in m.y.									
				k =	137.8	137.8	137.8	137.8	137.8	137.8	137.8	137.8	137.7	137.7
				$\lambda 238 \times 10^9$ =	0.1541	0.1541	0.1541	0.1537	0.1537	0.1537	0.1537	0.1541	0.1541	0.1537
				$\lambda 235 \times 10^9$ =	0.972	0.972	0.972	0.9722	0.9722	0.9722	0.972	0.9722	0.972	0.9722
				$\lambda 232 \times 10^9$ =	0.0499	0.0499	0.0499	0.0499	0.0499	0.0499	0.0499	0.0499	0.0499	0.0499
				t_o (in 10^9 yr.)=	4.51	4.50	4.49	4.51	4.50	4.49	4.50	4.50	4.50	4.50
M1	Bere Alston	18.12	15.45		210	260	300	180	230	270	230	250	250	220
M2	Wheal Rose	18.13	15.47		230	280	320	200	250	290	250	270	270	240
M3	Vottle Shaft	18.20	15.49		210	260	300	180	230	270	230	250	250	220
M4	South Terras	18.24	15.52		210	260	300	180	230	270	230	250	250	220
M5	Wheal Mary Anne	18.24	15.53		230	280	320	200	250	290	250	270	270	240
M6	Lambriggan	18.25	15.52		210	260	300	180	230	270	230	250	250	220
M7	Penberthy Croft	18.25	15.55		250	290	330	220	260	300	260	280	290	260
				Mean:	220	270	310	190	240	280	240	260	260	230

(a) Age of the Earth (t_o)

The values of the model age are particularly sensitive to changes in t_o. Thus it can be seen from Series A, B, C in Table 37 that an increase in t_o from 4.50 to 4.51 x 10^9 yr. results in an average decrease in the model age of 50 m.y., and a decrease in t_o from 4.50 to 4.49 x 10^9 yr. results in an average increase in the model age of 40 m.y.*

Moorbath justified his choice of t_o = 4.50 x 10^9 yr. largely on the grounds that the mean model age of his seven Cornwall-Devon galenas calculated with this t_o value was 280 m.y., which was in good agreement with the U/Pb age of 290 ± 7 m.y. for a uraninite from Geevor, Cornwall (Darnley et al., 1960). Moorbath and the author had also calibrated the zero isochron of the Holmes-Houtermans equation by substitution in this equation of the isotope ratios for modern oceanic lead (quoted in Table 35). This method of calculating t_o is explained in the introductions to Tables 20 - 22. With the physical constants used, this also led to a value of 4.50 x 10^9 yr. for t_o to the nearest 0.01 x 10^9 yr. This was exactly the same value as that chosen somewhat arbitrarily to match model ages with geological and absolute age data. This is now re-examined in the light of more recent work under several points:-

1. Recalculation of Moorbath's model ages for Nos. M1 - 7 yield a mean of 270 m.y., 10 m.y. lower than Moorbath's calculation (see Section 7.(13)), and 20 m.y. lower than the age of Geevor uraninite.

2. K/Ar and Rb/Sr age measurements on the Dartmoor granite yield a mean of

* Note - Moorbath (1959 b, p.54) states that "an increase (in t_o) from 4.50 x 10^9 yr. to 4.51 x 10^9 yr. would change the Cornwall-Devon model age from 280 ± 30 m.y. to about 310 ± 30 m.y.; and, similarly, in the opposite direction for a decrease in t_o." This is mistaken, as the effect of change in t_o on the model age is in the opposite direction.

277 ± 9 m.y. (Long, 1961), which is 13 m.y. lower than the age of the Geevor uraninite. Clearly the mineralisation is cogenetic with the granitic intrusions in S. W. England, and so there is a possibility that the Geevor age is incorrectly high by ca. 10 m.y., and that 260 m.y. should be the age for correlation of Cornwall-Devon mean model ages.

3. U/Pb age measurements reported in Part I of this thesis indicate that hydrothermal mineralisation in S. W. England was more complex than indicated by the first U/Pb age. Some remobilisation may have occurred in later times.

4. A remeasurement by the author of one of Moorbath's galenas (No. M6) gave isotope data in reasonable agreement with Moorbath's but resulted in a model age of 230 ± 30 m.y. (No. 75 of this thesis; see Tables 32, 33). The recalculated model age for No. M6 from Moorbath's data was 260 ± 70 m.y. While these two model ages agreed within their errors, the author's model age falls within Moorbath's period of mineralisation at 220 ± 30 m.y. rather than his period at 280 ± 30 m.y.

5. Patterson's (1956) values for primeval lead isotope ratios (the average of the values for the Honbury and Canon Diablo meteorites) have not been superseded. Also his calculation of the age of meteorites as being 4.55×10^9 yr. is still considered the most reliable. Patterson equated this value with the time since the earth attained its present mass. Since t_o strictly represents the time since commencement of local inhomogeneities in terrestrial U/Pb distribution, it could well be somewhat later than 4.55×10^9 yr.

6. The values for oceanic lead of Patterson et al. (1953) used in calibrating the zero isochron have been superseded by later measurements of many more samples by Chow and Patterson (1959). The means for their 34 samples are 206/204 = 18.92 and 207/204 = 15.60, but considerable isotopic variation was observed according to the locality of the sample. If these more recent mean values of oceanic lead are taken as representing modern lead, then re-calibration of the zero isochron leads to a value of t_o = 4.52×10^9 yr. (using the physical constants of both groups B and E in Table 37). Use of this value for t_o in the calculation of model ages would lead to an overall reduction of ca. 80 - 100 m.y. from the values quoted in this thesis. In general, the resulting model ages would be

rather unlikely from geological considerations. Moreover, if the variation in oceanic leads is considered, a variation in the model age of up to ± 200 m.y. could be expected. It appears that many more measurements of oceanic lead are required before an accurate average modern lead isotopic composition can be quoted. Thus this method of confirming the choice of t_o is of little value at the moment.

7. There is no group of Irish and French galenas comparable to Moorbath's Cornwall-Devon galenas, which can be correlated with independently determined ages.

While later work thus shows the need for further detailed work on this problem, Moorbath's initial choice of $t_o = 4.50 \times 10^9$ yr. is retained here for the purpose of strict intra-laboratory comparison. This practice has also been followed by the Bern geochronology group who still use the now superseded constants and parameters of Geiss (1954), e.g. $\lambda_{235} = 9.80 \times 10^{-10}$ yr.$^{-1}$, $t_o = 4.456$ m.y., k = 139 (F. G. Houtermans, personal communication). Nevertheless, the possibility of recalculating all the Oxford model ages, when more accurately calibrated values for t_o become available must be constantly borne in mind.

(b) Physical Constants.

Whereas the sensitivity of model ages to changes in t_o has been widely recognised, it has not been generally appreciated that very small variations in the physical constants also have a large effect on model ages. Table 37 clearly illustrates this by giving model ages calculated for the seven Cornwall-Devon galenas using ten different combinations of constants and t_o values (Programme 30 of Section 7.(11) was used for these calculations). The groups of constants are chosen so that the effect of variation of each value alone can be seen.*

* Most of the values presented in this table are not true model ages, because t_o should be calibrated for each set of constants used.

Stieff et al. (1959) have summarised some of the different values used for the physical constants in U-Th-Pb age calculations. Moorbath and the author's physical constants are used in Series A - C in Table 37; Russell and Farquhar's (1960 b) in Series D - F (each with different values of t_0). Senftle et al.'s (1957) value for k is used in Series I, J. Series G, H represent other possible combinations. It is clear from Table 37 that:-

1. The 1% change in λ_{238} from 0.1541 to 0.1537 x 10^{-9} yr.$^{-1}$ results in a reduction of ca. 30 m.y. in the calculated model age. (cf. Series D and G).

2. The use of the 4th significant figure in λ_{235} instead of three figures (as by Moorbath and the author) can occasionally alter the model age by 10 m.y. (The exact difference is smaller but is magnified on rounding off to the nearest 10 m.y.) (cf. Series B and H, E and G.)

3. The change in k from 137.8 to 137.7 causes a general reduction in model age by 10 m.y. (cf. Series B and I, E and J.)

On the basis of these and similar results, the effect of experimental errors in the values of the physical constants on the model ages is estimated to be of the order of ± 100 m.y. in this age range. These are not included in the errors quoted for model ages in this thesis, which only represent errors in the isotopic analyses. But both sources of error must be taken into account in assessing the absolute errors of lead model ages, and the validity of making stratigraphical correlations from them.

The value of λ_{238} = 0.1537 x 10^{-9} yr.$^{-1}$ appears to be the most generally accepted one at the present. The possibility of recalculating all of Moorbath's and the author's model ages using this value must be seriously considered in the near future. The resulting reduction in model ages could be balanced by a decrease in the value of t_0 to bring the S. W. England model ages to the mean value of 280 m.y. But even with this calibration of t_0 for

one value of the model ages, the change in the value of λ_{238} will alter other model age values to different extents (see Series E, S, F). At the present stage it is not possible to use an entirely consistent set of constants. Nevertheless, it is considered important to use the most accurate values for the physical constants in the calculations of model ages.

CHAPTER 10

DISCUSSION OF LEAD ISOTOPE RESULTS FROM IRELAND

10. (1) INTRODUCTION.

This chapter and the next are concerned with discussion of the individual isotope results from Ireland and France. The results from each country are dealt with collectively in Chapter 12, which should be consulted for the discussion of the general principles governing the consideration of individual results.

The discussion of the individual results follows the order of the specimen numbers which are based on geographical distribution. For convenience, the specimens have been grouped regionally according to their localities. These groupings do not necessarily have geological significance. Moorbath's specimens are prefixed by "M" and their numbering is the same as in his thesis (1959b). Map references, geological and mineralogical details and some literature references for the specimens are given in Appendix II.

Figure 9 is an outline geological map of Ireland (based on the Geological Survey). Some of the major faults near lead mineralisations studied in this thesis are marked on the map. The author's specimen localities are accurately located from 6 in. map references.

As the discussion has particular reference to variations in model parameters, these are tabulated throughout the text. The isotope data from which these parameters were calculated are given in Table 33. The model parameters for Moorbath's galenas quoted in the text were calculated by digital computer from his isotope data so that they would be strictly comparable with the author's results (see Chapter 7). The differences from Moorbath's original calculations are negligibly small except where indicated in the text.

Figures 9, 10, 11.



Figure 9: Geological Map of Ireland with Specimen Localities



Figure 10: Distribution of Model Ages in Ireland.
(On the same scale as Figure 9).



Figure 11: Distribution of Geochemical Ratios in Ireland. (For each specimen there is a number pair of which V_p is the upper member and K_p the lower. On the same scale as Figure 9.)

The correlations made between model ages and the geological time scale in Chapters 10 and 11 are considered to be accurate to within ±50 m.y. (see Section 12.(6)).

Figure 10 summarises the model age results for the author's Irish specimens and shows their geographical distribution. Figure 11 shows their geochemical ratios. The regional groups used for discussion in the text are marked on Figures 10 and 11.

10. (2) DONEGAL.

No.	Locality	Model Age (m.y.)	Vp	Kp
1	Keeldrum	180 ± 60	8.88 ± 0.12	3.67 ± 0.06
2	Faymore	260 ± 60	8.88 ± 0.11	3.75 ± 0.04
3	Glentogher	230 ± 60	8.63 ± 0.13	3.92 ± 0.05
4	Ardaturr	340 ± 50	9.03 ± 0.12	3.92 ± 0.06
5	Knockybrin	-80 ± 50	(8.84 ± 0.12)	(3.83 ± 0.04)
6	Glenaboghil	200 ± 40	8.93 ± 0.07	3.79 ± 0.05

Mineralisation in Donegal is scattered sparsely throughout the metamorphic rocks - schists, quartzites, crystalline limestones - which dominate the county. These presumed Eocambrian-Cambrian rocks possess a NW-SE trend and are correlated with the Dalradian of Scotland. There are no major mineral deposits in the region. Eight small similar occurrences, including Nos. 4 and 6, are scattered along the major fault marked in Figure 9 near the S. E. margin of the Donegal granite, (see Note to Nos. 4 and 6 in Appendix II). Nos. 1, 2, 4 and 6 all occur close to the margins of the Donegal granite, but there is no geological evidence to connect these mineralisations with the intrusion of the granite. No absolute age determinations are yet available for the Donegal granite or the neighbouring metamorphics. However, from geological similarities with other dated granites and metamorphics of Scotland and Ireland, it is likely that the main Donegal granite is

Caledonian, i.e. ca. 390-400 m.y. old (Lambert and Mills, 1961), and that the latest metamorphism of the country rocks (Dalradian) occurred about 470 m.y. ago (Giletti, Lambert and Moorbath, 1961).

The isotope data and model ages vary more widely for this region than for any other in Ireland; positive model ages range from 180 to 340 m.y. with no evident grouping.

The Knockybrin specimen (No. 5) was the first galena with a negative model age to be found in the British Isles. At some stage during its mineralisation, the Knockybrin galena became slightly enriched in radiogenic lead, probably picked up from the country rock. The results of isotopic analyses of more specimens from this occurrence might have explained this anomalous model age, but only one sample could be obtained, since there are unfortunately now no exposures at this locality.

The geochemical ratios have been calculated for No. 5 using its negative model age. Although the significance of these ratios is therefore doubtful, it is interesting to note that they are not noticeably different from the ratios for the other Donegal samples. A large difference is noted between the V_p values for No. 3 and the other samples. No. 3 may have come from a source slightly deficient in uranium compared with the other samples, for which the mean value of V_p is 8.91. There is a wider regional variation in K_p than is normally found. The largest (Nos. 3 and 4) and smallest (No. 1) K_p values lie well outside their errors.

Ratemeter studies over much of Donegal have so far failed to reveal any local concentrations of radioactivity (M. V. O'Brien, personal communication). Nevertheless, as one galena from the region possesses a definitely abnormal radiogenic component, the possibility must be considered of all the samples in the region being anomalously young. One possible explanation is that

the leads consist of mixtures of ordinary lead and a single radiogenic lead, (i.e. one of a particular isotopic composition) in different proportions. If this were true, linear plots would have been observed between the experimental isotope ratios 207/204 and 206/204, and between 208/204 and 206/204 for these specimens. But randomly scattered points were obtained in both plots, thus refuting this explanation.

It is therefore more probable that only No. 5 is anomalously young, and that the other model ages represent actual periods of primary mineralisation. The observation that Nos. 4 and 6, which are in geologically similar settings in relation to a single fracture zone have widely different model ages lying outside each other's errors was thus unexpected. The solution of the complex pattern of isotope results in Donegal is dependent on the analysis of many more samples from the region and from different parts of each deposit. The foregoing conclusions should thus be considered as somewhat tentative.

10. (3) SLIGO-LEITRIM.

No.	Locality	Model Age (m.y.)	Vp	Kp
7	Rosses Upper	250 ± 30	8.94 ± 0.06	3.84 ± 0.04
8	Twigspark	380 ± 50	8.90 ± 0.11	3.88 ± 0.04
9	Lugawarry	260 ± 40	8.99 ± 0.12	3.81 ± 0.05
10	Abbeytown A	360 ± 60	9.06 ± 0.09	3.80 ± 0.04
11	" B	360 ± 60	9.11 ± 0.06	3.86 ± 0.04
12	" C	320 ± 90	8.99 ± 0.17	3.85 ± 0.11
13	" D	390 ± 40	9.11 ± 0.06	3.81 ± 0.03
14	" E	370 ± 30	9.07 ± 0.06	3.80 ± 0.03
15	" F	330 ± 30	8.98 ± 0.07	3.73 ± 0.03
16	" G	370 ± 30	9.06 ± 0.07	3.79 ± 0.04
M 94	Abbeytown	330 ± 90	9.25	4.00

All the specimens studied from this area come from occurrences in Carboniferous limestone, which is the most common host-rock for lead-zinc deposits throughout Ireland. No. 7 is from irregular veinlets typical of these

occurrences. Nos. 8 - 16 and M 94 are from bodies of irregular and partial replacement of bedded, gently dipping and gently folded limestones by blende, galena, some pyrite and rare chalcopyrite, Dolomite is associated but it is not proved whether the dolomitisation occurred before or during sulphide mineralisation. The sulphide replacements have a tendency to follow some bedding planes (notably at the top of a sandy limestone), weak folds and impersistent fractures (M. V. OBrien, personal communication).

The Abbeytown deposit has been thoroughly sampled from different areas and stratigraphic horizons (See Appendix II). This has yielded the most detailed isotopic study so far of a single lead occurrence in the British Isles. The arithmetic mean of the model ages of Nos. 10 - 16 of 360 m.y. lies within the errors of the model ages of the individual specimens. In Section 8.(3) it was pointed out that the measurement of No. 12 was less precise than the others. No. 12 does give the lowest model age (320 m.y.) for the Abbeytown specimens, but the experimental uncertainty is represented fairly by the large error associated with it. The results for No. 12 are considered valid because of the existence of the similarly low, but much more precise, model age for No. 15 of 330 m.y. There is no geological evidence to indicate more than one period of mineralisation at Abbeytown. This is now confirmed beyond doubt by the isotopic evidence.

The geochemical ratios for Nos. 10 - 16 all lie within their errors giving arithmetic means of $V_p = 9.05$ and $K_p = 3.81$. The degree of variation in the model parameters observed in the Abbeytown specimens indicates the variations from the true means which might be expected in a single specimen from a similar deposit.

Moorbath's measurement of a galena from Abbeytown (No. M 84) yielded a model age of 330 m.y. in agreement with the author's results (Moorbath's own

calculation gave a model age for No. M 84 of 340 m.y.). Specimen No. M 84 is not stratigraphically localised like Nos. 10 - 16, but could not be from a source differing geologically from the latter group in any radical way. But the values of both V_p and K_p for No. M 84 are considerably higher than the author's results. Unless Moorbath's single mass spectrometer run on his sample was in error, this difference remains unexplained.

The marked geological similarities between the Twigspark, Lugawarry and Abbeytown deposits are described in Appendix II. Yet there is a significant difference between the model ages of the Lugawarry galena and the Twigspark and Abbeytown galenas. M. V. OBrien has supplied the following communication regarding this problem:-

"Lugawarry, Abbeytown and Twigspark all lie 1 m. or less N.W. of a major SW-NE fault which brings down beds of Carboniferous limestone against Moinian schists, the latter being on the S.E. side of the fault.

Lugawarry lies about 1 m. S.W. of Abbeytown. Although much less well known from surface exposure or diamond drilling, the mineralisation at Lugawarry appears to be quite similar to that of Abbeytown.

Twigspark lies approximately 17 m. N.E. of Abbeytown. Between the two, the above-mentioned fault has some fairly small offsets, but there seems no real doubt that it is the same fault or at least a very closely related series of fractures in the same fault system. There is some evidence that the fault was active at different periods. For instance near Twigspark a pre-Carboniferous serpentine which was intruded along the fault is itself much broken by further movement. In addition to its general structural similarity with Abbeytown, the Twigspark mineralisation shows mineralogical similarities."

The model age of 380 m.y. for Twigspark is close to the mean of 360 m.y. for the Abbeytown specimens, indicating a common age for these mineralisations.

The model ages of the Rosses Upper and Lugawarry galenas also agree closely, their mean of 260 m.y. being a typical Permo-Carboniferous (≡ Hercynian) value. The existence nearby (see Figure 9) at Rosses Upper of a galena of similar age to the Lugawarry galena confirms that there is a significant difference between the ages of mineralisation of the Lugawarry and the Abbeytown deposits.

Stratigraphical correlations based on the time-scale of Kulp (1961) place the mineralisations at both Abbeytown (360 m.y.) and Twigspark (380 m.y.) in the Devonian. Both these ages are older than that of the Carboniferous limestone in which the samples occur, and for which a maximum age of ca. 350 m.y. may be assumed. However, the differences are small and may be accounted for by experimental error. Thus it is not considered necessary to suggest that the Abbeytown and Twigspark deposits are remobilised older leads.

Several authors (e.g. Charlesworth, 1953, pp. 10, 49) have correlated the fault which passes by the Twigspark, Abbeytown and Lugawarry deposits with the Highland Boundary Fault of Scotland. McKerrow (1959; personal communication) has cast doubt on such a correlation. The isotope data do suggest that mineralisation connected with this fault has occurred in at least two periods. But, since lead model ages cannot be used to accurately date tectonic episodes, the isotope data do not bear on this problem.

10. (4) MONAGHAN.

No.	Locality	Model Age (m.y.)	V_p	K_p
17	Derryleedigan	290 ± 50	8.80 ± 0.12	3.96 ± 0.05
18	Lisdrumgormley	280 ± 60	9.07 ± 0.14	4.00 ± 0.07
19	Coolartra	370 ± 40	8.96 ± 0.08	3.94 ± 0.05

The mineralisation in Monaghan occurs generally as small, sparse breccia- and fault-fillings in N-S fractures in Lower Palaeozoic (presumed Silurian) siltstone, e.g. Nos. 18, 19. No. 17 is from a similar occurrence some 15 m.

from the other two specimens, but in Carboniferous limestone, not far above the unconformity on the Lower Palaeozoic.

Nos. 17 and 18 have very similar model ages, which are values typical of Hercynian (Permo-Carboniferous) mineralisations. No. 19 has a significantly older model age than its geologically similar neighbour No. 18. The existence of more than one period of mineralisation for this region was not expected from the geological evidence. The isotopic and geological study of more specimens from these occurrences might yield even more interesting results.

The values of K_p for all three specimens lie within their errors. The V_p value for No. 17 indicates that its source was slightly deficient in uranium compared with that of the other two galenas.

The isotope data suggest two periods of mineralisation in the Silurian of Monaghan. The first occurred in about Middle to Upper Devonian times; it was probably later than the strong Caledonian folding which affected the country rock, but could have been contemporary with the intrusion of the Newry granite 15 m. to the East. The later period of mineralisation occurred in Permo-Carboniferous times; there is no evident connection of this with any contemporary granitic intrusions or any folding in the region (although some weak Hercynian folding did occur).

10. (5) MAYO AND N. GALWAY.

No.	Locality	Model Age (m.y.)	V_p	K_p
20	Tullyduff	250 ± 40	8.98 ± 0.09	3.86 ± 0.04
21	Ballykine Lower	280 ± 50	9.00 ± 0.13	3.98 ± 0.06
22	Grallagh	290 ± 60	9.05 ± 0.15	3.92 ± 0.07
23	St. MacDara's Is.	370 ± 50	9.05 ± 0.08	3.86 ± 0.04
M 95	Sheefry	310 ± 70	8.82	3.92
M100	Lough Corrib	320 ± 80	8.86	3.85

The author's four specimens plus No. M 100 from this region can be

divided into two groups according to the country rock. Nos. 20, 21 and M 100 occur as small veins in Carboniferous limestone. Nos. 22 and 23 occur as small veins cutting granites. No. M 95 is the sole specimen from an occurrence in Lower Palaeozoic sediments.

The geology of the region is of considerable interest because of the presence of the Galway and associated granites and the Connemara schists. Absolute age determinations (Rb/Sr) have been carried out on the main Galway granite by Giletti, Moorbath and Lambert (1961) giving an age of 365 ± 10 m.y.. Giletti, Lambert and Moorbath (1961) determined that the most recent metamorphism of the Connemara schists occurred ca. 475 m.y. ago.

The granite of St. MacDara's Is. is petrologically similar to and is probably cogenetic with the main Galway granite (M. V. OBrien, personal communication). The model age of 370 m.y. for the galena from St. MacDara's Is. is in very close agreement with the age of the main Galway granite. There are several similar occurrences of galena veins with fluorite, and occasionally with chalcopyrite and sphalerite as well, along the S. margin of the main granite. The isotope evidence indicates that these mineralisations probably occurred only shortly after the consolidation of the granite. More measurements from similar occurrences would be desirable to confirm this conclusion.

There is a lack of positive evidence regarding the relative ages of the Omey and main Galway granites. In his gravity survey of the area, Murphy (1952) made measurements between these two granites but considered them too few to make conclusive interpretations. However, there are indications that the Omey and main Galway granites have comparable thicknesses. At Maam Cross a sharp gravity anomaly was observed, which was interpreted as being the N.W. limit of the main Galway granite. Intermediate readings do not indicate a connection at depth between the Omey and main Galway granites. However, from

field studies, E. J. Cobbing (personal communication) considers that these two granites are probably cogenetic.

The model age of the Grallagh galena, from a rare quartz-galena vein in the margin of the Omey granite, indicates a Permo-Carboniferous age of mineralisation, which is younger than the ages of the Galway granite and the St. MacDara's Is. galena. The Grallagh vein could be mineralogically distinct from the fluorite-bearing group typified by the St. MacDara's Is. galena. (M. V. OBrien, personal communication; see also Section 10.(7)). The model age difference is therefore considered significant.

Nos. 20 and 21 from the Carboniferous limestone have ages which differ by 30 m.y. but lie well within each other's errors. Grouping these with No. 22 yields a mean model age of 270 m.y., which indicates that Specimen Nos. 20 - 22 were probably all mineralised in Permo-Carboniferous times.

Moorbath's specimens, Nos. M 95 and M 100 come from about 15 m. N.W. and 10 m. S.S.W. of No. 21 respectively. Their model ages of 310 and 320 m.y. are intermediate between those of Nos. 20 - 22 and No. 23. They each have a large experimental error and could thus be fitted into agreement with either a 270 m.y. or 370 m.y. model age. Replicate mass spectrometer determinations might indicate whether they are contemporaneous with either of these groups, or whether their mean model age of 320 m.y. represents a distinct intermediate time of mineralisation.

The V_p and K_p values for the author's specimens agree within their errors, except for the K_p value of No. 21 which is slightly higher than the others. The V_p values of Nos. M 95 and M 100 are slightly lower than of Nos. 20 - 23, but since the errors of Moorbath's values are probably twice that of the author's, the differences are not significant.

10. (6) OUGHTERARD AREA (Moorbath, 1959b).

No.	Locality	Model Age (m.y.)	V_p	K_p
M 96	Clements	860 ± 70	9.08	4.05
M 97	Glengowla	620 ± 80	8.85	3.93
M 98	Cloosh	700 ± 80	8.98	3.85
M 99	O'Flaherty's Shaft	580 ± 80	8.76	3.76

These four galenas have been grouped separately here because their model ages are very much greater than for any other nearby galenas. Moorbath's original consideration of these results was hampered by lack of available information on the age of the country rocks. Recently Giletti, Lambert and Moorbath (1961) have shown the most recent metamorphism of the Connemara schists, in which Nos. M 96 - 98 occur, to be 475 m.y. No. M 99 occurs in the Oughterard granite, which may be older than the main Galway granite.*

Moorbath's (1959b) tentative conclusion that these galenas are anomalously old is thus confirmed. His explanation (p.119) that "they represent remobilised older material from the metamorphic basement during intrusion and consolidation of the Oughterard granite" still appears the most likely.

* W. S. McKerrow (personal communication) considers that the Oughterard granite is pre-Silurian, which would make it at least 60 m.y. older than the Galway granite (364 m.y. old). Moorbath had tentatively considered these two granites to have been cogenetic.

10. (7) CLARE AND S. GALWAY.

No.	Locality	Model Age (m.y.)	V_p	K_p
24	Tynagh	300 ± 50	8.85 ± 0.09	3.86 ± 0.05
25	Ailwee	260 ± 40	9.05 ± 0.09	3.89 ± 0.04
26	Knockaphreaghaun	270 ± 50	8.98 ± 0.13	3.90 ± 0.07
27	Milltown A	250 ± 40	8.94 ± 0.07	3.88 ± 0.04
28	" B	320 ± 40	9.03 ± 0.08	3.89 ± 0.06
29	Kilbreckan	280 ± 30	8.97 ± 0.07	3.89 ± 0.04
30	Ballyhickey	340 ± 30	9.11 ± 0.11	3.94 ± 0.08

All seven galenas were collected from occurrences in Carboniferous limestone, which here lies conformably on Devonian sandstone. The lead ores of Clare were usually argentiferous (Cole, 1922).

The two most northerly specimens in this region, Nos. 24 and 25, have reasonably close model ages. Their mean model age of 280 m.y. indicates a Permo-Carboniferous age for these mineralisations. The V_p value for No. 24 is considerably lower than for Nos. 25 - 30. This value is similar to those of Nos. M 95 and M 100 (see Section 10. (5)). In fact the close similarity of all model parameters between Nos. 24, M 95 and M 100 may indicate a common age and/or source for these mineralisations distinct from other nearby mineralisations. However, these tentative correlations do not justify drawing any distinction between the model ages of Nos. 24 and 25.

The mineralisations at Ailwee (No. 25) and nearby are different from those near Ennis (Nos. 26 - 30). The former are fissure fillings with associated fluorite and a little calcite. There are fluorite-galena veins in the S margin of the Galway granite. The latter are often replacement deposits with massive calcite and frequent arsenical minerals, but no fluorite.

The gravity survey of Murphy (1952) indicated that the Galway granite dips gently away to S from N shore of Galway Bay and underlies the Carboniferous limestone of N. Clare for about 10 m. It was thus estimated that the Ailwee mineralisation is ca. 1000 ft. above the unconformable junction over the granite. The mineralogical similarities between the mineralisations at Ailwee and in the S margin of the granite might suggest a common source and period of mineralisation. But the model ages of galenas from these two areas, Ailwee (No. 25) and St. MacDara's Island (No. 23), do not support this. McKie and Burke (1955) in their study of the islands of S. Connemara, although not conclusive in this respect, considered they may have observed the actual

S margin of the granite. More gravity measurements are thus desirable to decide definitely whether Ailwee is underlain by granite at no great depth.

In the group of specimens from E of Ennis (Nos. 26 - 30), the largest difference in the model ages is observed between No. 27 (250 m.y.) and No. 30 (340 m.y.). This would be considered significant if there were not also three other model ages from this region between these values. If one's consideration of lead model ages is governed by the idea of discrete periods of mineralisation, then these specimens may be grouped into Nos. 26, 27 and 29 (mean model age - 270 m.y.) and Nos. 28 and 30 (mean model age - 330 m.y.). However, there is considerable overlap between these groups when errors are applied.

The difference of 70 m.y. between the model ages of the two specimens from Milltown is unexpected as there is no geological evidence for more than one period of mineralisation there (Note, however, that both samples were from dump material). These two specimens may represent an extreme case of model age differences from the same deposit (the greatest variation in model age over the Abbeytown mine was also 70 m.y. - see Section 10. (3)), and so these differences would be apparent only.

Nos. 26 - 30 present a borderline case for the definition of different periods of mineralisation. Some mineralisation certainly occurred in Permo-Carboniferous times. This may have been preceded by some earlier mineralisation in about Middle to Lower Carboniferous times, but this remains a tentative hypothesis dependent on the study of more specimens. If there was only one period of mineralisation, a mean model age of 290 m.y. could be quoted for Nos. 26 - 30.

Some data are available on silver contents in galenas from these localities (Cole, 1922; el Shazly et al., 1956 ("Ballylickey" ≡ Ballyhickey); Morris and Killick, 1959; this thesis, Appendix IV). The Ballyhicky galena appears to

have a distinctly lower silver content than the other galenas. The Ballyhickey galena also has the highest model age. These two facts might serve to distinguish it from its otherwise similar neighbours.

10. (8) SILVERMINES.

No.	Locality	Model Age (m.y.)	V_p	K_p
31	Shallee	330 ± 40	9.10 ± 0.07	3.95 ± 0.04
32	Gorteenadiha	210 ± 50	8.99 ± 0.13	3.86 ± 0.07
33	Ballynoe	210 ± 40	8.97 ± 0.11	3.86 ± 0.05
34	Knockanroe A	280 ± 30	9.04 ± 0.05	3.86 ± 0.03
35	" B	260 ± 50	9.12 ± 0.14	3.97 ± 0.05
36	Gortshanroe A	300 ± 30	9.06 ± 0.08	3.89 ± 0.04
37	" B	320 ± 80	(9.34 ± 0.29)	(4.13 ± 0.11)
38	" C	310 ± 30	9.05 ± 0.06	3.86 ± 0.04
39	Garrane	330 ± 40	9.09 ± 0.06	3.91 ± 0.03

Irregular mineralisation occurs at Silvermines along two miles of an E-W normal fault in Carboniferous limestone and Devonian and Silurian sediments. This has recently been described in detail by Rhoden (1958-9) and succinctly by OBrien (1959). The exact locations of the samples studied here can be obtained from the detailed maps of Rhoden.

The specimens were carefully selected to represent each of the three main types of mineralisation found in the Silvermines area. Some specimens had to be obtained from dump material but in only one case (the block yielding Nos. 37 and 38) was there slight doubt about their origin. The characteristic types of mineralisation are represented as follows:-

(a) Fracturing zone (breccia-filling) type in Devonian and Silurian sediments - Nos. 31, 36 - 39

(b) Replacement type in Carboniferous dolomite - Nos. 34, 35

(c) Main fault type - Nos. 32, 33

It is interesting that the specimens can be classified into the same three groups according to their model ages. The replicate specimens from the same mines give closely agreeing model ages. The following table gives the

stratigraphical correlations of the mean model ages according to Kulp's (1961) time-scale:-

Mineral Type	Specimen Nos.	Model Ages (m. y.)	Mean Model Age (m.y.)	Stratigraphical Correlation
(a) Fracturing Zone type	31	330		
	36	300		
	37	320		
	38	310		
	39	330	320	Carboniferous
(b) Replacement type	34	280	270	Permian-Carbonif-erous (≡ Hercynian)
	35	260		
(c) Main fault type	32	210		
	33	210	210	Triassic

It is realised that the model age differences between No. 34 and Nos. 36 and 38 are within their errors, and so the distinction in model ages between types (a) and (b) may not be real. Nevertheless, the mean model ages of types (a) and (c) lie outside their errors, and thus there is no doubt that at least two - — · —— — — separate periods of mineralisation have affected the Silvermines area. On the grounds that the mean model age of type (b) can be correlated with many other similar model ages in Ireland, it is further suggested that a third intermediate period of mineralisation may have occurred in the area.

Rhoden (1958-9) found no positive evidence for the age of the mineralisation but suggested that it was of Triassic to early Jurassic age. The isotopic evidence shows a greater complexity than was previously understood. The fault pattern is complicated, but Rhoden considers that it was all formed in Hercynian times. If this is correct, the model ages indicate that mineralisation would have occurred before, during and after faulting. This is not inconsistent with the mineral types observed, for the breccia-filling type (a) could well have been originally mineralised before major faulting

caused the fracturing. However, the possibility of more than one period of faulting may now be entertained, because the mineralisation is so evidently connected with the faults.

The V_p and K_p values for No. 37 have large errors because of the nature of the measurement (see Section 8.(3)) and should be ignored. (The model age of this sample has been included in the above considerations because of its close agreement with the model ages of Nos. 36 and 38 from the same mine.) Without the values for No. 37, the mean V_p value for Silvermines is 9.05 and the mean K_p value is 3.89, with close agreement between individual values.

10. (9) S. OF SILVERMINES.

No.	Locality	Model Age (m. y.)	V_p	K_p
40	Killeen	330 ± 30	9.12 ± 0.08	3.92 ± 0.03
41	Oolahills	320 ± 60	9.18 ± 0.09	3.96 ± 0.08

OBrien (1959; personal communication) considers that the Killeen deposit in the Silurian could be the exposed root of the Silvermines type mineralisation. The Oolahills deposit, with Carboniferous limestone on either side of the fault, is at the same structural level as Silvermines or higher. Barytes is common to the Killeen, Oolahills and Silvermines deposits.

The agreement in model ages between these two galenas and their similarity to the model ages of the fracturing zone type galenas of Silvermines supports OBrien's argument. The mean values for V_p of 9.15 and K_p of 3.94 for Nos. 40 and 41 are not significantly higher than those for Silvermines.

10. (10) S. KERRY AND S. W. CORK.

No.	Locality	Model Age (m.y.)	V_p	K_p
42	Ross Is.	260 ± 60	8.93 ± 0.12	3.93 ± 0.06
43	Muckross	360 ± 40	9.11 ± 0.11	3.95 ± 0.09
44	Shanagarry	280 ± 40	9.06 ± 0.12	3.95 ± 0.07
45	Cloontoo	340 ± 30	9.07 ± 0.07	3.94 ± 0.04
46	Cahermore	270 ± 40	9.26 ± 0.12	4.01 ± 0.09
47	Killaveenoge	250 ± 60	9.02 ± 0.13	4.01 ± 0.09
48	Duneen	340 ± 40	8.99 ± 0.07	3.91 ± 0.04

These specimens can be conveniently grouped further on a county basis, which also corresponds with the country rock in which they occur. Nos. 42 - 45 are in Co. Kerry and occur in cleaved, folded and recrystallised Carboniferous limestone and are relatively minor occurrences. There are close similarities between these specimens. They occur in two pairs, Nos. 42 and 43, and Nos. 44 and 45, the geological setting of the members of each pair being similar. There is also a similar mineralogy for the members of each pair (except that No. 43 has some arsenical ore). These mineralisations all appear to be closely related to the Hercynian earth-movements which affected the area. Thus Nos. 42 and 43 are just N. of a large fault by which Devonian sandstone is steeply overthrust against Carboniferous limestone. Nos. 44 and 45 are from the tightly folded rocks (overthrust to some degree) of the Kenmare Syncline, a feature post-dating the Carboniferous limestone.

The second member of each pair has a model age higher than the first member. The difference between the model ages of No. 42 (260 m.y.) and No. 43 (360 m.y.) is definitely significant. The difference between the model ages of No. 44 (280 m.y.) and No. 45 (340 m.y.) is not so great and could just be accounted for by their errors. Grouping Nos. 42 and 44 gives a mean model age of 270 m.y. and Nos. 43 and 45 gives 350 m.y. The difference between these is significant. It thus appears that mineralisation occurred in the Carboniferous limestone of Kerry in the Devonian-Carboniferous (ca. 350 m.y.) and also in

Permo-Carboniferous (ca. 270 m.y.) times.

However, there is strong structural evidence at Muckross (No. 43), and to a lesser extent at Cloontoo (No. 45), that the mineralisations are post-tectonic (e.g. no crushing evident) and are contemporary with their neighbouring veins. The folding can be assumed to have occurred between 300 and 280 m.y. ago, and so the 350 m.y. group of model ages is older than the folding. Thus, while the model age of 350 m.y. probably represents the original period of mineralisation of Nos. 43 and 45, it appears that they may have been subsequently remobilised and redeposited, presumably in Permo-Carboniferous times and contemporaneously with their neighbouring veins. More detailed sampling of these groups of veins would indicate whether there had been any significant mixing of the remobilised, older lead and primary, younger lead. Trace element investigations might also serve to distinguish between remobilised and primary lead.

The remaining three specimens in this region come from the Upper Devonian or basal Carboniferous sediments of Co. Cork, and occur in coastal exposures. The Cahermore deposit (No. 46) is two m. S of, but mineralogically dissimilar from the quartz-chalcopyrite (with minor tetrahedrite, pyrite and siderite) lodes at Allihies. The latter are clearly post-Devonian and have been described by OBrien (1959). The similarities with mineralisation in S. W. England has led to the acceptance of a Hercynian age for the W. Cork mineralisation (P. F. P. Matthews, personal communication). The model ages for Nos. 46 and 47 have a mean of 260 m.y., which strongly supports this suggestion.

The V_p value for No. 46 of 9.26 is one of the highest for any Irish galena and is significantly different from the other samples of the region. In the absence of further samples this can only be explained as an unusual local

variation in the U/Pb ratio of the crustal source of this galena.

The Duneen galena (No. 48) has the unexpectedly high model age of 340 m.y. The mineralogy of the deposit is similar to that at Killaveenoge (No. 47). The vein is strike-wise but appears to be later than the cleavage of the Upper Devonian country rock. The model age of No. 48 is consistent with a Carboniferous age for the mineralisation. Because of the similarity of the model ages of No. 48 and Nos. 43 and 45, remobilisation may have occurred at Duneen; but in the absence of more definite geological evidence and further specimens, this cannot be confidently asserted.

10. (11) S. E. IRELAND.

No.	Locality	Model Age (m.y.)	V_p	K_p
49	Templeyvrick	310 ± 50	9.20 ± 0.12	3.97 ± 0.07
50	Tankardstown A	-20 ± 30	(9.18 ± 0.10)	(3.91 ± 0.05)
51	" B	250 ± 60	9.15 ± 0.12	3.99 ± 0.06
52	Barrystown	270 ± 50	9.09 ± 0.10	3.93 ± 0.07
53	Brownsford	390 ± 40	9.15 ± 0.07	4.01 ± 0.04
54	Cain	560 ± 30	9.16 ± 0.08	4.03 ± 0.04
M 89	Barrystown	280 ± 80	9.14	4.00

The Bonmahon copper mining district of Co. Waterford is represented here by three specimens, Nos. 49 - 51. Galena is very rare in the two principal quartz-chalcopyrite Stage and Tankardstown lodes. No. 50 is one of these rare occurrences from the breccia zone associated with the Tankardstown lode. No. 49 is from a lode which has most of the characteristics of the two principal lodes, but which lies near the W. margin of the district. No. 51 comes from the townland of Tankardstown but not from the Tankardstown lode; it is from a quartz-calcite-chalcopyrite-galena vein, 100 yds. E. of No. 50, a type which is generally of peripheral occurrence in the Bonmahon district.

There is unusually strong evidence for an upper age of the principal

copper lodes; The steeply-dipping Stage lode is cut by the Upper O.R.S. conglomerates, which indicates a pre-Upper O.R.S. age of mineralisation. A minimum lead model age of ca. 370 m.y. would be required for confirmation of this. The similar direction and mineralogy of the principal lodes make more than one period of mineralisation for them unlikely. The minor, marginal calcite-bearing veins are not found in the Upper O.R.S. nearby, but there is no positive structural evidence for their age.

It is immediately apparent that none of the model ages of Nos. 49 - 50 can be correlated with a pre-Upper O.R.S. age. But since one of the specimens from the district has an anomalous model age, the possibility of the other two specimens also having anomalous ages must be considered.

No. 50 has a negative model age, similar to, but less negative than, the Knockybrin galena No. 5. The model age of No. 50 is only just negative; the application of maximum positive error could just allow correlation with a Tertiary age. Nevertheless, its anomalous nature is emphasised by the great differences between its model age and those of No. 49 (from the same vein-type) and No. 51 (from very close by), and by its position on the isochron chart relative to other Irish galenas (see Figure 16). The most likely explanation for this anomaly is that, on passage through the country rocks, the lead-bearing mineralising fluids came into contact with a small local concentration of uranium. Provided this uranium had itself been in situ for some time, it would contain sufficient radiogenic lead for mixing with the common lead in the fluids to produce the observed isotopic composition. Field evidence on this point is negative, for ratemeter studies made on some of the veins have shown no evidence of any radioactive minerals (M. V. OBrien, personal communication).

Geochemical ratios are quoted for No. 50, although, as was pointed out for No. 5, the significance of these is doubtful, having been calculated using the

negative (and so incorrect) model age. Accordingly it is interesting to note that the V_p and K_p ratios for Nos. 49 - 51 agree closely within their errors.

No. 51 has a model age of 250 m.y. which is apparently normal, and could be correlated with a Permian mineralisation. As pointed out above, there is no structural evidence to preclude an age for the calcite-bearing veins, such as No. 51, different from that of the principal lodes.

On the other hand the model age of 310 m.y. for No. 49 seems incompatible with the geological evidence for an age greater than ca. 370 m.y. The mixture of common lead with a smaller proportion of radiogenic lead than with No. 50 would lead to an anomalously young, but positive model age. A similar history may pertain to No. 51, but this is not so necessary. All the same, the presence of one anomalously young galena in this small region makes the reliability of all other model ages from nearby somewhat suspect. The scarcity of galena in these lodes makes more thorough sampling difficult, but it clearly is necessary for the lead isotope history of this district to be elucidated.

The E-W lode in Lower Palaeozoic rocks at Barrystown, was sampled both by the author (No. 53) and Moorbath (No. M 89). The isotope data for these two specimens agree closely, yielding almost identical model ages (270 and 280 m.y. respectively). Moorbath's conclusion of a Hercynian age for this mineralisation is thus confirmed. The values of V_p and K_p for the two specimens also agree within the errors. (Moorbath's calculation of K_p value of 4.16 for No. M 89 was incorrect).

The remaining two specimens of this regional group and those of the following Wicklow and Dublin groups must be considered in connection with the dominating Leinster granite massif which lies close to all these occurrences. No. 53 is from a vein in the granite near its margin. The Caledonian age of this granite has been confirmed by absolute age measurements. Kulp et al. (1960) obtained a mean age of 386±6 m.y. from 4 K/Ar measurements. Lambert and

Mills (1961) obtained a mean age of 405±12 m.y. from 4 Rb/Sr measurements on the same samples. Lambert and Mills consider a mean age of 395 m.y. to be close to the true age of this and the other Caledonian intrusives measured (Shap adamellite, Westmorland; Creetown granite, Kirkudbrightshire).

The model age of 390 m.y. for the Brownsford galena (No. 53) is in very close agreement with the age of intrusion of the granite. It thus appears that the time between the consolidation of the margin of the granite and this mineralisation was small. OBrien (Appendix II, Note to No. 53) has pointed out the geological similarity between this occurrence and the Glendalough, Co. Wicklow (Nos. 58, M 87, M 88) and the Ballycorus, Co. Dublin (No. 59) veins. (See also Sections 10.(12), 10.(13)). The isotopic evidence does not support a common age for these deposits. (Glendalough galenas give model ages of 220, 280 and 230 m.y.; Ballycorus galena has model age of 300 m.y.).

Caim (No. 54) lies in Lower Palaeozoic silty mudstones. The gently dipping E. flank of the granite massif probably underlies Caim at depth; Caim is ten miles from the exposed margin of the granite. OBrien (1959) states that this occurrence "lies mid-way between Avoca and Bonmahon but does not share the major characters of either."

The model age of 560 m.y. for No. 54 is 60 m.y. older than the base of the Ordovician (500 m.y.) on Kulp's (1961) time scale. If the country rock is Ordovician as stated in the Note to No. 54 (Appendix II), then this galena is apparently older than its host rocks. This would mean that this galena was originally mineralised at some earlier time, but was later remobilised, preserving the isotopic composition characteristic of its time of original mineralisation. Alternatively, it may be lead which has been remobilised from the metamorphic basement rather than from a concentrated lead deposit.

However, the geology of this area is not well known. W. S. McKerrow

(personal communication) has pointed out that there is a distinct lack of Graptolites throughout the wide area around Cairn, which is marked Ordovician on the Geological Survey Map of Ireland. The correlation of the large area of sediment around Cairn with the Ordovician was based on lithology. In this region no quartzites are found which are typical of the proved Cambrian sediments elsewhere in Ireland (M. V. OBrien, personal communication). Nevertheless, the country rock at Cairn might possibly be Cambrian. The stratigraphical correlation of the model age of 560 m.y. is about Middle Cambrian (the age of the base of the Cambrian is still somewhat in doubt). With this doubt about the age of the country rock, it is considered unjustifiable at the moment to postulate that No. 54 is an anomalously old, remobilised galena.

Attention may be drawn here to the notable general increase in values of V_p for galenas from the regional groups of S. E. Ireland, Wicklow and Dublin compared with those from elsewhere in Ireland. This can readily be seen from the values marked on Figure 11. A similar but smaller increase in the values of K_p is also evident, but this is not so significant. These V_p and K_p values are similar to those found by Moorbath (1959 b) for galenas from Wales.

10. (12) WICKLOW.

No.	Locality	Model Age (m.y.)	V_p	K_p
55	Ballintemple	210 ± 40	9.21 ± 0.15	4.00 ± 0.07
56	Kilmacoo A	450 ± 40	9.28 ± 0.09	4.03 ± 0.05
57	" B	400 ± 50	9.04 ± 0.09	3.93 ± 0.05
58	Brockagh	220 ± 50	9.22 ± 0.13	4.02 ± 0.06
M 87	Glendalough	280 ± 90	9.19	4.01
M 88	Glenmalure	230 ± 70	9.12	3.96
M 90	Avoca 271	440 ± 70	9.16	4.01
M 91	" 21	450 ± 70	9.19	4.06
M 92	" 30	440 ± 70	9.26	4.06
M 93	" B8A	410 ± 80	9.08	3.98

Although the Ballintemple occurrence (No. 55) is only 1 m. from the Avoca

mineral belt, it differs from the replacement type lode of the latter in being a quartz-carbonate fissure vein. Its model age of 210 m.y. is half that of the mean model age of the Avoca and Kilmacoo galenas. The Ballintemple galena was, without doubt, mineralised much later than the Avoca ore-body, probably in Triassic times.

Moorbath (1959 b, pp. 113 - 115) has outlined the geology of the mineralisation in the Avoca belt. His specimens were selected from the two main facies of mineralisation - the "South Lode" facies (Nos. M 90, M 91) and the "Pond Lode" facies (Nos. M 92, M 93).

"The Pond Lode facies occurs in shales and phyllites in which the schistose fabric is undeformed and still well-preserved, although the rock matrix has often been intensely disseminated with very finely-divided sulphide, suggestive of colloidal deposition. The South Lode facies is a somewhat younger mineralisation and much more diffuse than the Pond Lode, being formed of a larger number of narrow parallel zones, ribs and veins with varying mineral content, while the rock between them is barren. It has an altogether coarser-grained aspect. There are other important differences between these two facies." (Moorbath, 1959 b, pp. 114, 115). The model ages of Nos. M 90-93 agree closely with a mean value of 440 m.y., there being no distinction between the samples from the two facies. (Moorbath's calculation of the model age of No. M 93 (420 m.y.) was 10 m.y. too high).

The author's two Kilmacoo specimens (Nos. 56, 57) are from the N.E. end of the Avoca mineral belt. No. 56 is a very fine-grained mixture of sulphides from the Pond Lode facies. No. 57 is a similar specimen, but not as fine-grained as No. 56. The model ages of 450 and 400 m.y. are not significantly different as they agree within their errors. In addition they agree remarkably well with Nos. M 90 - 93, giving a mean model age of 430 m.y. for these six Avoca specimens.

These new measurements confirm Moorbath's classification of the Avoca mineralisation as Caledonian in age. This is in agreement with OBrien's (1959) similar conclusions from the geological evidence.

There is a large difference between the V_p values of Nos. 56 and 57 which is outside their errors. It is noticeable that No. M 93 also has the lowest model age and much the lowest V_p value of Nos. M 90 - 93. While no distinction can be significantly drawn between the model ages it does appear that there may have been two crustal sources for the lead with slightly different U/Pb ratios.

Nos. 58 and M 87 come from the same series of overlapping narrow N-S and NE-SW veins in the E. margin of the Leinster granite at Glendalough (OBrien, 1959). No. M 88 comes from a very similar deposit at Glenmalure 2 m. S.W. of the other samples. Recalculation of the model age of No. M 88 gives 230 m.y. (Moorbath - 240 m.y.). This difference is small when compared with the error of 70 m.y., but is important because, using a model age of 240 m.y. for No. M 88, Moorbath grouped it with No. M 87 (280 m.y.) to give a mean model age of 260 m.y. Now No. 58 is available for consideration, and its model age (220 m.y.) is in closer agreement with the recalculated model age for No. M 88 (230 m.y.) than with the value for No. M 87 (280 m.y.). The occurrence nearby at Ballintemple (No. 55) and Clontarf (No. 61) of model ages of 210 and 200 m.y. respectively, increases the probability of a significant period of post-Hercynian mineralisation having occurred in the region. No. M 87 may represent a Hercynian mineralisation, but its error of ±90 m.y. is very large and a repeat isotopic determination would be desirable. It is the author's opinion that a post-Hercynian - probably Triassic - age is more likely than a Hercynian age for the mineralisation at Glendalough-Glenmalure. Nevertheless, the new measurement of No. 58 confirms Moorbath's refutation of Tremlett's (1960) suggestion of a near-Caledonian age for these deposits.

The values of V_p and K_p for Nos. 58, M 87 and M 88 agree within their errors. The mean values of 9.18 for V_p and 3.99 for K_p are typical of this region, being higher than those found in W. and N. Ireland.

10. (13) DUBLIN.

No.	Locality	Model Age (m.y.)	V_p	K_p
59	Ballycorus	300 ± 30	9.14 ± 0.08	3.94 ± 0.04
60	Corbally	150 ± 60	9.04 ± 0.15	3.96 ± 0.09
61	Clontarf	200 ± 50	9.20 ± 0.08	4.00 ± 0.05

The Ballycorus occurrence (No. 59) is similar to the Glendalough-Glenmalure series of veins. These veins all have the same mineral assemblage and occupy linear fractures in the E. margin of the Leinster granite. The model age for No. 59 indicates a Hercynian mineralisation. A consideration of the errors shows no overlap between the model ages of No. 59 and Nos. 55, 58 and 61, indicating a distinct period of mineralisation for No. 59 (cf. No. M 87 whose large model age error allows no distinction between its age and those of Nos. 55, 58 and 61).

The Corbally vein (No. 61) cuts diorite which is older than the main Leinster granite. This galena has the youngest positive model age (150 m.y.) so far measured in Ireland. Despite a relatively large error in the model age, there is no doubt that this represents a post-Hercynian mineralisation, a Jurassic age being indicated. The V_p value for No. 60 of 9.04 is markedly lower than for most galenas in the regions of Dublin, Wicklow and S. E. Ireland. This also distinguishes the mineralisation of No. 60 from those of Nos. 55, 58, 61 and M 88, whose model ages lie in the 200-230 m.y. range.

The Clontarf galena (No. 61) also has a low model age (200 m.y.). Its V_p value agrees with those of Nos. 55, 58 and M 88, which have similar model ages, and is higher than that of No. 60. This distinguishes the model age of

this isolated mineralisation at Clontarf from that at Corbally (No. 60). It appears that the Clontarf mineralisation probably occurred in Triassic times and was contemporaneous with the mineralisation at Ballintemple (No. 55), Brockagh (No. 58) and Glenmalure (No. M 88).

10. (14) NORTHERN IRELAND.

No.	Locality	Model Age (m.y.)	V_p	K_p
62	Slieve Binian A	-80 ± 40	8.98 ± 0.07	3.74 ± 0.04
63	" " B	-40 ± 30	9.06 ± 0.06	3.78 ± 0.03
M 84	Castleward	280 ± 60	8.96	3.88
M 85	Conlig	420 ± 70	9.10	4.06
M 86	Creggan	330 ± 70	9.12	3.97

Except for one isolated specimen from the Lake District (Ruthwaite Lodge, No. M 31), Moorbath did not find any galena from the British Isles whose model age could be correlated with Tertiary times. The hydrothermal veins in the Mourne Mountains granite were thus of special interest because of the proved Tertiary age of this granite. These veins, which are few and small, have been observed in the Slieve Binian Tunnel driven through the granite and described by J. A. Robbie (1955). One of these veins contained a small amount of galena. The only existing specimen of this Tertiary galena was provided by Robbie for isotopic analysis.

Only one other galena has been reported with a stratigraphically proved Tertiary age in the British Isles. Fowler (1959) observed galena in the joints of the Scrabo dolerite sill (a Tertiary intrusion) from cores of a bore-hole about 2 m. WSW of Newtownards, Co. Down. A specimen of this galena was sought with no success.

The field evidence for a Tertiary age for the Mourne Mountains Granite is indirect. The granite is intruded into greywacke, hardened shales or slates and grits of Silurian age (Richey, 1928). The granite cuts a set of dykes which are

regarded as being part of the Tertiary dyke swarm. The granite is cut by another set of dykes. It is inferred that the granite is of Interbasaltic age, corresponding with the outpouring of rhyolite which occurred during the Interbasaltic period in Co. Antrim (e.g. at Tardree). The stratigraphical correlation of the Interbasaltic period remains doubtful. Plant remains in the laterite between the Lower and Upper Basalts are poorly preserved and could indicate an Eocene, Oligocene or possibly later age (Charlesworth, 1953). Thus a maximum age of 60 m.y. (corresponding to the base of the Eocene) may be placed on the intrusion of the Mourne Mountains granite. No absolute age determinations are yet available for this granite.

There are no significant differences in the isotope data and model parameters between the two galena samples from Slieve Binian (Nos. 62, 63). The two galena samples were selected from opposite ends of the 6 in. hand specimen to detect any gross isotopic variations within the hand specimen. A mean model age of -60 m.y. may be quoted for the galena from this hand specimen. This is clearly a negative anomaly which cannot be accounted for by experimental error.

This is the third galena to be found in Ireland with a negative model age. Unlike Nos. 5 and 50, however, positive evidence for addition of radiogenic lead isotopes does exist for the Slieve Binian galena. The Mourne Mountains granite is relatively strongly radioactive, being comparable in strength with some of the Cornish granites (J. A. Robbie, personal communication). This is caused by the presence of uranium- and thorium-containing heavy minerals, notably zircon, in the granite (Taylor, 1935).

On passing through the granite, the hydrothermal fluids may have leached some of the radiogenic lead, largely Pb^{206}, from the radioactive mineral grains, thus producing the observed anomalous isotopic composition. The time interval

between intrusions of the granite and the veining of it by hydrothermal minerals is not known. If this interval were short, then the uranium may not have decayed long enough to produce sufficient radiogenic lead for mixing with common lead in the proportions observed. However, this problem might not arise, since the total amount of lead in the hydrothermal veins is clearly very small and only a minute total addition of radiogenic lead to a normal common lead of Tertiary model age would be required to produce the observed isotopic composition. It is the author's opinion that this explanation is more likely on the present evidence, than that the lead was remobilised from the country rock and picked up some radiogenic lead from the surrounding Lower Palaeozoic rocks.

A feature of J-type galenas is their variability of isotopic composition even within small deposits (e.g. Mississippi Valley group of deposits; Kulp et al., 1956). This might be expected in the Slieve Binian veins if more galena specimens could be obtained for isotopic analysis. A minimum age for the mineralisation might be indicated from such results. An absolute age measurement of the granite would provide a maximum age for the mineralisation.

The three isotopic measurements of Northern Irish galenas by Moorbath (Nos. M 84 - 86) indicate three probable times of mineralisation in Cos. Down and Armagh. - Caledonian (No. M 85), Carboniferous (No. M 86; Moorbath's calculation of model age for this sample gave 340 m.y.) and Hercynian (No. M 84) times. The model ages obtained do not support the suggestions of Lamplugh (1904) and Fowler (1959) of a Tertiary age for the Conlig-Newtownards lode (No. M 85).

CHAPTER 11

DISCUSSION OF LEAD ISOTOPE RESULTS FROM FRANCE

11. (1) INTRODUCTION.

The general geology of Bretagne and the West of the Cotentin Peninsula, Normandie, is reasonably well known, the Armorican massif dominating the region. The marked Hercynian folding which affected the region is evident from the grain of the country (see Figure 12). The major folds run largely WNW-ESE, while in the North the folding tends to be arc-shaped.

There are numerous granite intrusions, which are generally aligned along the major folds, and most of which are considered to be Hercynian in age. There are close petrological similarities between some of the granites and those of S. W. England. It has been generally supposed that the hydrothermal mineralisation in the region was controlled by the orogeny and granitic intrusions in Hercynian times. But afew geologists have considered that some mineralisations may have also occurred earlier than Hercynian times. This is illustrated by the following extract (translated from the French) from a personal communication from Y. Milon.

"I have thought that the major part of our sulphide mineralisation (i.e. in Bretagne) was late Hercynian, that is without doubt, mostly Permian, such as the very numerous dykes of dolerite which cut all the Palaeozoic up to and including the Pennsylvanian.

We do not have any evidence in Bretagne of an actual Caledonian orogenic phase. Meanwhile, in the Upper Ordovician, there are important changes in facies and a development of volcanism in certain regions which could represent, in my view, an echo, albeit a little feeble, of a Caledonian or Taconic orogeny." (See also Milon, 1935, in which these views were first published).

Figure 12 is a copy of a geological map of Bretagne, supplied by Y. Milon,

Figures 12, 13, 14.



Figure 12: Geological Map of Bretagne and Normandie, France with Specimen Localities. (Scale - ca. 1 : 4,000,000).



Figure 13: Distribution of Model Ages in France.

(On the same scale as Figure 12).



Figure 14: Distribution of Geochemical Ratios in France. (For each specimen there is a number pair of which V_p is the upper member and K_p the lower.) On the same scale as Figure 12.

with the localities and numbers of the author's galena specimens marked on it. Figures 13 and 14 show the distribution of model ages and geochemical ratios for these galenas.

All the available geological information on the specimens is given in Appendix II and the text of this Chapter.* The numbering of the specimens is purely geographical. The following discussion is arbitrarily divided into two convenient parts.

The only other lead isotopic measurements so far reported for Bretagne are those of Durand (1960) and Lay (1960). Since it is considered that these measurements have little bearing on the present work, a detailed discussion of them is reserved until the end of the Chapter.

11. (2) SAMPLE NOS. 64 - 68.

No.	Location	Model Age (m.y.)	V_D	K_D
64	Pierreville	300 ± 40	9.18 ± 0.07	3.93 ± 0.04
65	Huelgoat	230 ± 40	9.11 ± 0.14	3.97 ± 0.06
66	Poullaouen	320 ± 40	9.17 ± 0.07	4.00 ± 0.04
67	Trémuson	250 ± 50	9.14 ± 0.14	3.92 ± 0.06
68	Le Hinglé	270 ± 50	9.16 ± 0.14	4.00 ± 0.06

The Pierreville galena (No. 64) is the only one of this study to come from Normandie. Its geological setting is not certain, but it probably occurs in Devonian sediments. The model age of 300 m.y. indicates a Hercynian age for the mineralisation.

The geological setting of the Huelgoat galena (No. 65) suggests a close connection between the mineralisation and the Huelgoat granite massif which lies immediately to the West. This granite is the only one so far for the whole of Bretagne whose absolute age has been determined (although Deutsch and Chauris

* The notes given for the French galenas in Appendix II are fuller than those for the Irish galenas, because there is little published information available on these French mineral deposits. In order to avoid lengthy repetition, only a few of these details are repeated in the text of this Chapter.

(1958) have examined some granites from Normandie by the approximate age method of pleochroic halos). Deutsch and Chauris (1960) obtained the following ages for the two facies of the Huelgoat granite:-

Facies	K/Ar Age Quoted	Rb/Sr Age Quoted[1]	Recalculation of Rb/Sr Age[2]
Huelgoat	290 m.y.	310 m.y.	291 m.y.
La Feuillée	290	317	298

[1] Using $t_{\frac{1}{2}} = 5.0 \times 10^{10}$ yr. (S. Deutsch, personal communication)
[2] Using $t_{\frac{1}{2}} = 4.7 \times 10^{10}$ yr.

Mean Age Quoted (K/Ar and Rb/Sr) = 300 m.y.
Mean Age using recalculated Rb/Sr Ages = 290 m.y.

The agreement between the quoted K/Ar and Rb/Sr ages is not close. If the more commonly accepted half-life for the Rb/Sr decay of 4.7×10^{10} yr. is used, these ages agree more satisfactorily with the K/Ar ages. The recalculated mean age of 290 m.y., agrees well with the accepted Hercynian age for the Dartmoor granite, Cornwall, of 285 m.y. (Lambert and Nills, 1961; Long, 1961, prefers a mean age of 277 m.y.). An age of 290 m.y. for the Huelgoat granite places it stratigraphically near the Permian-Carboniferous boundary, and not in the Middle Carboniferous as claimed by Deutsch and Chauris from their mean age value.

The model age of the Huelgoat galena (No. 65) of 230 m.y. is ca. 60 m.y. lower than the age of the granite with which it is supposedly connected. The geological setting of the Poullaouen galena (No. 66) is apparently similar to that of No. 65. There is a difference of 90 m.y. between the model ages for No. 66 (320 m.y.) and No. 65 (230 m.y.), which is outside the ranges of their errors. The model age of the Poullaouen galena is close enough to the 290 m.y. age of the Huelgoat granite for errors to account for the difference. But for

the Huelgoat galena, the difference between the granite age and galena model age is just outside the limit of error. The simplest explanation is that the Poullaouen galena was deposited in Hercynian times, roughly contemporaneously with the Huelgoat granite, and that the Huelgoat galena was formed from a later mineralisation (possibly in Upper Permian times). The strikes of the Huelgoat and Poullaouen veins are identical, so it is possible that the later mineralisation followed the course of earlier (Hercynian) fractures or veins.

The geological setting of galena No. 67 from Trémuson indicates a Hercynian mineralisation. The model age of 250 m.y. for this galena may support this suggestion. But this value is also close to the 230 m.y. model age for No. 65 for which a Permian age has been suggested. The model age could also reflect a time of mineralisation intermediate between Hercynian times and that of No. 65. It is not possible to decide which of these suggestions is correct until more galenas are isotopically analysed from each area.

The model age of the Le Hinglé galena (No. 68) of 270 m.y. is probably a Hercynian value. The geological information, although limited, does not contradict this conclusion.

11. (3) SAMPLE Nos. 69 - 74.

No.	Locality	Model Age (m.y.)	V_p	K_p
69	La Touche A	360 ± 60	9.12 ± 0.15	4.06 ± 0.08
70	" " B	380 ± 40	9.15 ± 0.08	4.00 ± 0.05
71	Pont Péan	220 ± 50	9.13 ± 0.12	3.98 ± 0.06
72	La Chapelle St. Melaine A	440 ± 50	9.19 ± 0.12	3.97 ± 0.07
73	" " B	500 ± 30	9.11 ± 0.07	3.93 ± 0.04
74	St. Pierre Montlimart	260 ± 60	9.07 ± 0.18	3.93 ± 0.08

Y. Milon (Appendix II, Note to No. 69) states that the La Touche deposit is connected with the granite massif of Fougères, for which a Precambrian age is suggested. When the model age of 360 m.y. was obtained for No. 69, another

sample (No. 70) was specially obtained from the same occurrence. The isotope data for the two samples agree well, giving a mean model age of 370 m.y. for the mineralisation. Thus this mineralisation is distinctly pre-Hercynian and also post-Cambrian. The mean model age can be correlated with a Middle to Upper Devonian age for the mineralisation. This is in agreement with several model ages obtained for galenas in the British Isles which are connected with a Caledonian intrusion (Moorbath, 1959b; this thesis). It would thus not be surprising if the Fougères granite was also of Caledonian age (assuming that the field evidence connecting the granite and mineralisation is sound).

The field evidence for the age of the Pont-Péan galena (No. 71) indicates a post-Hercynian, probably Permian, mineralisation. This geological conclusion is strongly supported by the model age of 220 m.y., which is correlated with the Lower Triassic. The existence of this post-Hercynian mineralisation makes it more probable that mineralisation also occurred in other parts of the Armorican massif in similar times (see discussion on Huelgoat galena, No. 65, in Section II.(2)).

The first galena from La Chapelle St. Melaine (No. 72) analysed gave the relatively high model age of 440 m.y. Another specimen, specially obtained from this locality (No. 73), also gave a high model age (500 m.y.). Although the agreement between the two model ages is not close, it is not considered justifiable to distinguish between them. The mean model age of 470 m.y. lies just within the errors of both results. This places the mineralisation in the Middle Ordovician, which is also the stratigraphic age of the slaty rocks in which the veins were emplaced. The mineralisation is definitely older than that at La Touche. If correlations with British mineralisations are justifiable for only two French specimens, the La Chapelle St. Melaine galenas may have been mineralised contemporaneously with galenas at Harlech-Plynlimon, Wales, in Aberdeenshire and at Avoca, Co. Wicklow (Moorbath, 1959b; this thesis).

The last specimen is from St. Pierre Montlimart (No. 74) and has a typical Hercynian model age, which is supported by the field evidence. The somewhat lower V_p value for this galena compared with other French galenas is not considered significant since it also possesses the largest experimental error.

The constancy in the values of V_p and K_p over all these samples is noted here. This is discussed in Section 12.(5)/.

In conclusion it is pointed out that there is overall agreement between these French results and those for the British Isles, due to similarity in geological settings, but more work is required to substantiate the French results.

11. (4) OTHER ISOTOPIC ANALYSES OF FRENCH GALENAS.

The only other isotopic data yet available on French galenas are reproduced in Table 38, which is taken directly from Durand (1960). This work, as reported, suffers from the following disadvantages:-

(a) No information is given about the exact locations and geological environments of the galena samples.

(b) Figures are not quoted for the Pb^{208} isotope.

(c) The statistical significance of the errors associated with the isotope ratios and model ages is not clear.

(d) The errors in the isotope ratios (whatever their significance) are much larger than those obtained with the Oxford instrument. (Durand used a Metropolitan-Vickers Type MS2 mass spectrometer with solid-source attachment, which is very similar to the Type MS5 instrument used here). The errors in the model ages are much larger than those quoted in this thesis; so much so in several cases as to make geological conclusions unjustifiable.

(e) The physical constants used in the calculation of the Holmes-Houtermans model ages are not quoted. This is a serious omission in view of the sensitivity of calculated ages to small changes in these constants.

(f) No mention is made of analyses of any inter-laboratory reference samples which makes it impossible to assess the accuracy of the analyses.

Table 38

Lead Isotopic and Model Age Results for French Galenas (Durand, 1960)

No.	Locality	206/204	207/204	206/207	Model Age (m.y.)
SG1	Ambernac (Charente)	18.49 ± .22	15.48 ± .27	1.195 ±.010	-60 ± 100 *
SG2	Confolens (Charente)	18.30 ± .30	15.63 ± .25	1.17 ±.01	260 ± 100
SG3	Sentein (Ariège)	18.14 ± .22	15.79 ± .22	1.15 ±.01	565 ± 100
SG4	Guern (Morbihan)	18.36 ± .25	15.58 ± .20	1.18 ±.01	170 ± 90
SG5	Melle (Deux-Sèvres)	18.37 ± .30	15.50 ± .23	1.18 ±.01	50 ± 90
SG6	Plelauff (Côtes-du-Nord)	18.40 ± .35	15.68 ± .31	1.175 ±.008	250 ± 80
SG7	Trémuson (Côtes-du-Nord)	18.08 ± .32	15.39 ± .28	1.17 ±.01	140 ± 100
SG8	Surtainville, La Gadaillerie (Manche)	18.34 ± .34	15.64 ± .22	1.17 ±.01	250 ± 80
SG9	Carnoet, Villeneuve (Côtes-du-Nord)	-	-	-	(100 ± 100 (400 ± 100
SG10	Ville Alhen (Morbihan)	18.15 ± .30	15.35 ± .26	1.17 ±.008	250 ± 70
SG11	Huelgoat (Finistère)	18.26 ± .14	15.59 ± .14	1.171 ±.005	250 ± 110
SG12	Pontpéan (Ile-et-Vilaine)	18.47 ± .30	15.60 ± .26	1.185 ±.01	100 ± 100
SG13	Poullaouen (Finistère)	18.34 ± .27	15.67 ± .26	1.17 ±.01	300 ± 70

* Durand quotes this model age as 60 m.y., but this is a misprint and should be negative (Lay, 1960).

(g) No mention is made of the time-scale used in making the stratigraphical correlations for the model ages quoted.

(h) Isotope data are not given for No. SG9, and so the two separate model ages quoted for this occurrence must remain suspect.

(i) The geological conclusions are summarised too briefly to be of much value.

(j) Y. Milon (personal communication) considers several of the model ages obtained by Durand to be most improbable from the geological evidence for the age of the deposits. (Nos. SG4, 7, 9(both), 12, 13).

Several of the queries posed by Durand's paper have been cleared by personal communications from C. Lay, of the Université Libre de Bruxelles. Durand's isotopic data are also reported in Lay's thesis (1960), but with no geological elaboration. These points are dealt with under the same headings as above.

(b) The Pb^{208} isotope peaks were not measured in the mass spectra obtained.

(c), (d) The statistical errors quoted represent the standard deviations of measurements of ca. 34 separate mass spectra taken for each sample in a single run. Before calculation of the mean values and the errors, the individual measurements were examined for abnormal deviations by a graphical method. On the average, 1 in 5 measurements were rejected - a much larger frequency of rejection than in the present work, when 1 in 12 were normally rejected.

A graphical method, based on the error in the 206/207 ratio, was used for estimating the error in the model age from the statistical errors in the isotope ratios. If the graphical method of Moorbath (see Chapter 7), which gives errors in the model ages comparable to the author's computer method, is used on Durand and Lay's isotope data, it is found that the errors obtained are at least double those quoted by Durand and Lay.

The errors in the isotope data of this thesis are double the standard errors of the means. On the basis of the number of measurements made in the respective analyses, the author's errors are half the standard deviations which would have been calculated on his runs by the method of Durand and Lay. Even on doubling the author's errors for comparison, the errors in the isotope ratios of Durand and Lay are generally three times greater than the author's. These considerations indicate the relative significance of

Table 39

French Localities Sampled by both Pockley and Durand (1960)

Sample Locality	Pockley Number	Durand Number
Surtainville La Godaillerie		SG 8*) ?
Pierreville	64*	)
Huelgoat	65	SG11
Poullaouen	66	SG13
Trémuson	67	SG 7
Pont Péan	71	SG12

Table 40

Comparison of Model Ages of Samples Measured by Pockley and Durand

Durand Number	Model Age (m.y.)		
	Durand's Isotope Results		Bockley's Isotope Results
	Calculated by Durand	Calculated by Pockley using same constants as for Pockley's Isotope Results	Calculated by Pockley
SG 7	140	210	250
SG 8	250	330	300*
SG11	250	330	230
SG12	100	190	220
SG13	300	380	320

* Note - No.64 may not come from the same occurrence as No.SG 8.

measurements made by the author and Durand and Lay on samples from the same occurrences.

(g) The time-scale of Holmes (1960) was used for stratigraphical correlations.

(a), (e), (f), (h), (i), (j) - No further information obtained.

Table 39 lists localities sampled by both the author and Durand. Table 40 summarises calculations of model ages for these localities using the two sets of isotope ratios. The model ages in the 2nd and 3rd columns of this table are the ones to be compared, since they have all been calculated by digital computer using the same constants. The model ages for Durand's samples calculated in this way are 70 - 90 m.y. higher than his own calculations. This difference is almost certainly due to the different constants used by Durand. With the constants used in this thesis, the model age of No. SG1 is 10 m.y. There is thus no need to classify this sample as negatively anomalous.

In three out of the five cases, the difference between the author's model ages and those of Durand is reduced by this recalculation. With the large errors involved in Durand's work, his results are not incompatible with the author's, although agreement is never close. In view of the foregoing considerations, Durand's results are not significant enough to have been considered in detail with the author's results in the preceding Sections.

CHAPTER 12

DISTRIBUTION OF LEAD MODEL PARAMETERS IN THE BRITISH ISLES AND FRANCE

12. (1) MOORBATH'S DEFINITION OF PERIODS OF MINERALISATION IN THE BRITISH ISLES.

Before proceeding to a discussion of the author's results, a re-assessment is made of Moorbath's definition of periods of mineralisation in the British Isles (Moorbath 1959b, Chapter 10).

Moorbath grouped his model ages into periods on the basis of the isotope data and geological evidence. When the model age of a galena was midway between two periods, its classification into one or the other was decided on the geological data. In a few cases, it could not be decided to which period a given sample belonged. Moorbath's six periods of mineralisation are shown in Figure 15(a), which is a histogram constructed from his calculations of the model ages, including all results up to 600 m.y., except a definitely anomalous model age of 580 m.y. (No. M 99).

Moorbath calculated the means and errors for the model ages grouped into a period by weighting each mean value according to the individual values comprising it (see formulae in Section 7.(12)). This statistical procedure is only strictly applicable when the values being combined can reasonably be assumed to form replicate measurements of the same quantities, with a normal distribution applying to the variation of the individual values; e.g. this applies to the isotope abundances of the scans of a mass spectrometer run. Moorbath thus implied that the differences observed in the values for the model ages within each group represent random variations about a single true mean value. The author considers that this assumption is valid only for groups of closely similar isotope data and for model ages of replicate samples from the same deposit. In the manner they have been calculated, the meaning of Moorbath's periods is that there have been certain discrete times at which mineralisation

has occurred, represented by the mean model ages of the periods, and their errors represent experimental variations from the true mean values.*

For example, the definition of the Hercynian period of 280 ± 20 m.y. means that Hercynian mineralisation occurred at some discrete time between 260 and 300 m.y., most probably at 280 m.y.; but statistically this does not mean that Hercynian mineralisation may have occurred at several times between 260 and 300 m.y. This distinction is discussed further in Section 12.(6) with the additional evidence of the author's results. It is more valid to calculate and use the plain arithmetic means of such groups of model ages, than to use weighting procedures or to quote statistical errors for the means. Nevertheless, weighted and arithmetic means calculated from the same data seldom differ appreciably.

The effect of error in the individual model ages has been minimised by Moorbath's procedure. The average individual model age error of Moorbath's 107 samples is ±70 m.y., yet two of his periods are defined with errors of ±20 m.y. and three periods with errors of ±30 m.y. Even so, his periods present an almost continuous spread of values from 100 to 470 m.y., with overlap between the periods - 280 ± 20 m.y., 320 ± 20 m.y. and 360 ± 30 m.y. (See Figure 15(a)).

The mean model ages of Moorbath's periods do correspond to the more frequent model age values in Figure 15(a). In order to assess the significance of these values a scan was made across the histogram, observing the total number of the values which lay within ±70 m.y. of each particular model age; these frequencies, with a smooth curve drawn through them, are reproduced in Figure 15(b).

* Moorbath (personal communication) does not now consider that all the mineralisations within a given 'period' were contemporaneous. This confirms the author's opinion that it is misleading to quote mean model ages of 'period' and errors of the means calculated by weighting procedures.

Figures 15(a), (b), (c).

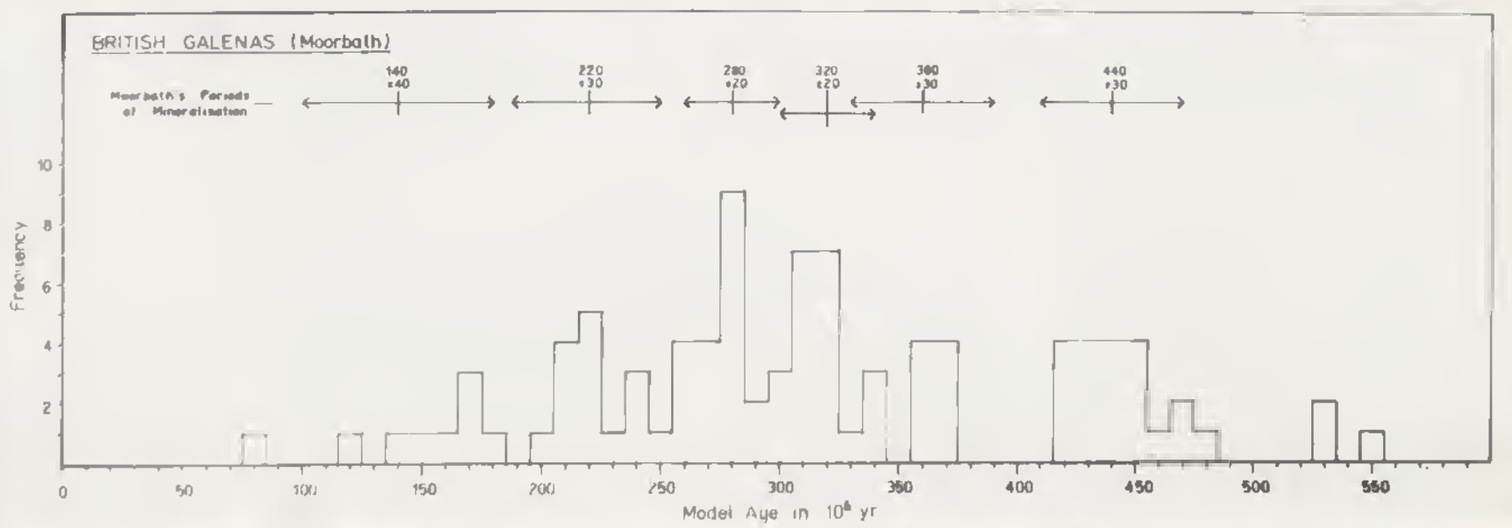


Figure 15(a): Histogram of Model Ages of British Galenas (Moorbath).

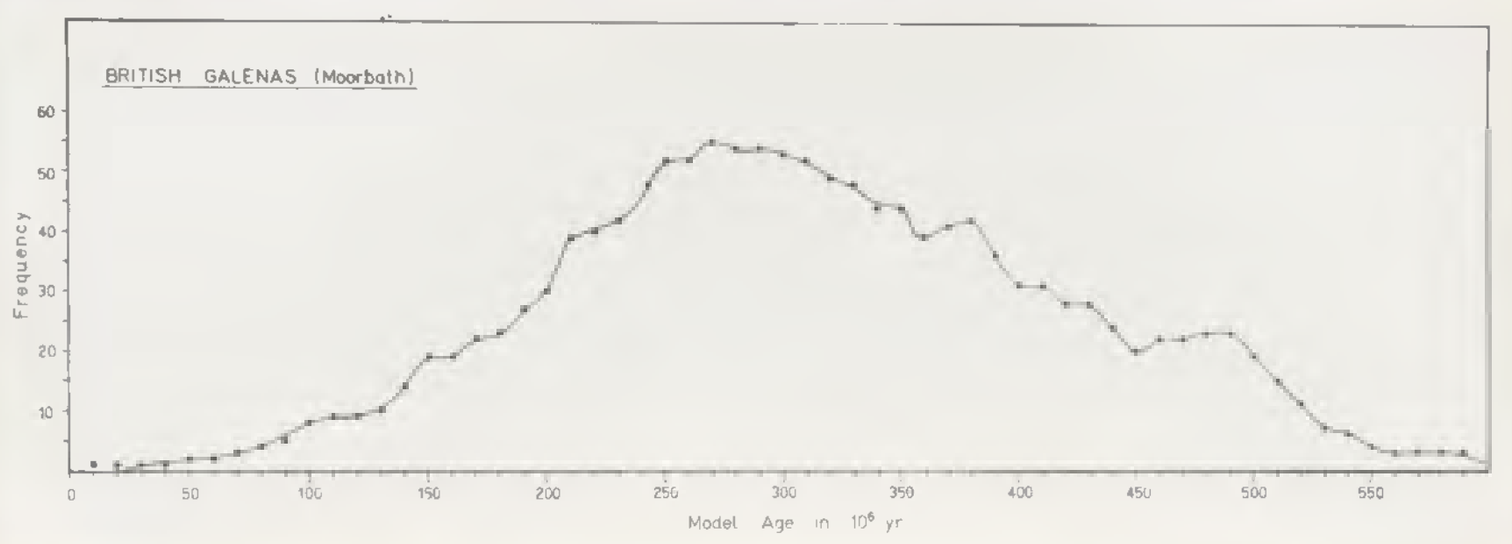


Figure 15(b): Scan over Figure 15(a).

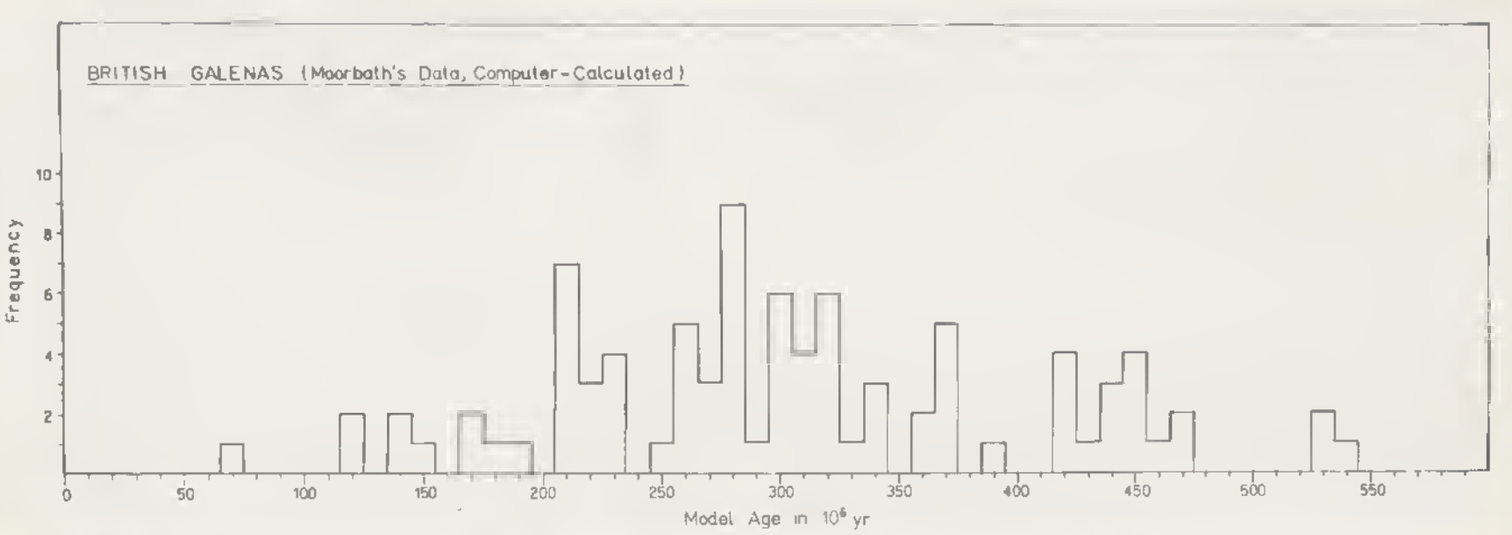


Figure 15(c): Histogram of Model Ages of British Galenas (Moorbath, Computer-Calculated).

Significant groupings of model ages would be shown by maxima on this diagram. Maxima are observed in Figure 15(b) at 270 m.y., 370 m.y. and 490 m.y.*, but not at 140 m.y., 220 m.y. and 320 m.y. which are the mean model ages for Moorbath's other three periods. Moorbath has clearly considered the individual model age values to be more accurate than is indicated by their experimental errors.

Figure 15(c) is a histogram of the model age results recalculated using the computer (see Section 7.(13)). The overall reduction in model ages gives a slightly different pattern from Figure 15(a), but the broad distribution remains unchanged.

Figure 15(b) gives only a semi-quantitative estimation of the significance of grouped model ages (see Section 12(3)). The lack of significant groupings does not invalidate the individual results around 140 and 220 m.y. since there is strong supporting geological evidence that the mineralisation of several British galenas occurred about these times.

12. (2) DISTRIBUTION OF MODEL AGES IN IRELAND.

Consideration is given first to Figure 16 which is an enlargement of that portion of the isochron diagram (Figure 8) which includes the isotope ratio points for all the Irish and French galenas measured by Moorbath and the author. The majority of Irish galenas cluster together fairly closely, indicating a general similarity in their sources. The two groups of anomalous leads are evident on this diagram by their isolation from the other leads. Moorbath's four anomalously old leads from the Oughterard area (Nos. M 96 - 99) all have low 206/204 ratios. The author's four leads with negative model ages (Nos. 5, 50, 62, 63) are clearly separated from the majority of leads; this supports

* The last value would be decreased to ca. 460 m.y. by the exclusion from the histogram of the three model ages greater than 500 m.y., which may possibly be anomalously old (Moorbath excluded these three model ages in defining his periods of mineralisation).

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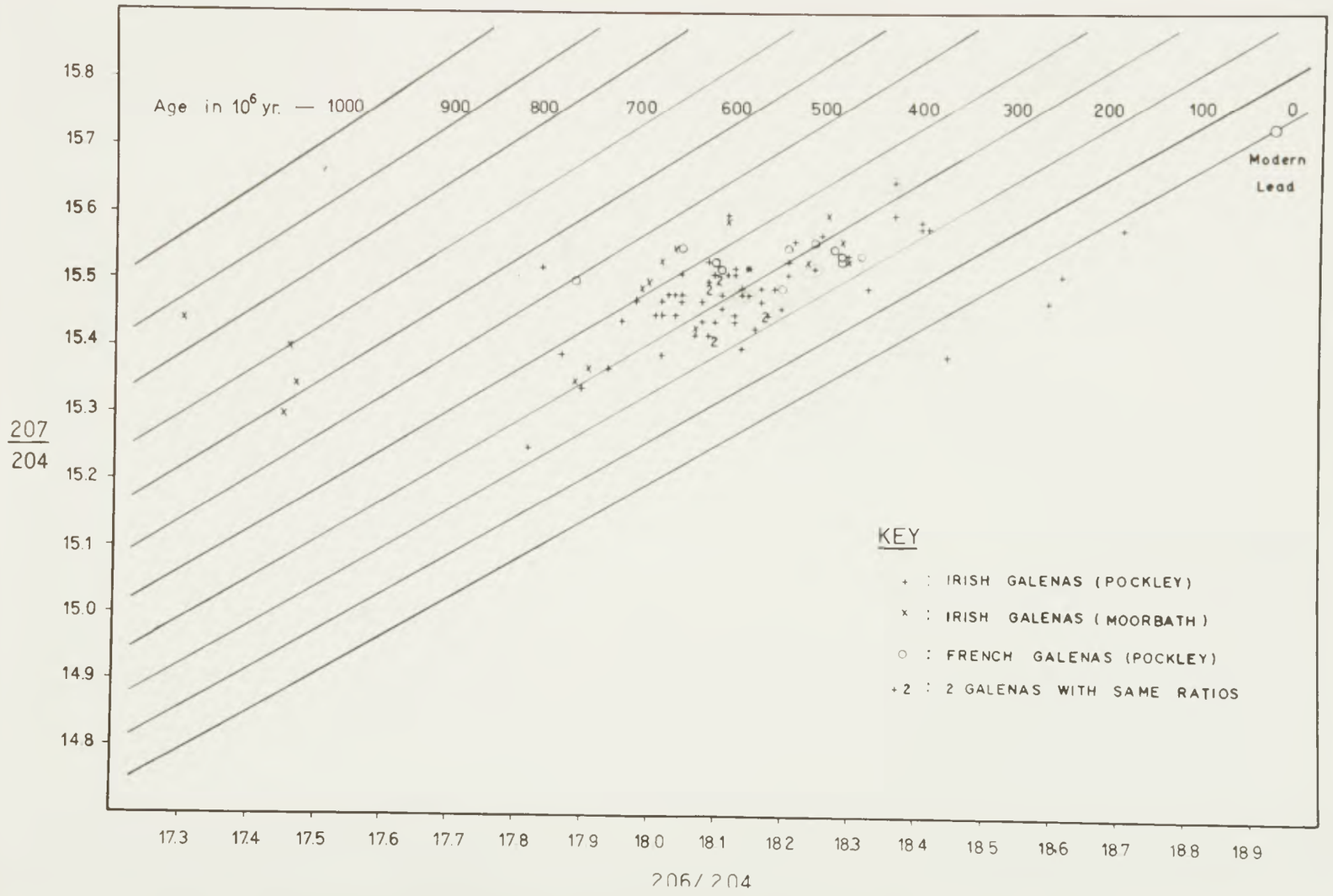


Figure 16: Isochron Diagram for Irish and French Galenas. (Enlargement of portion of Figure 8).

Figures 17(a), (b), (c).

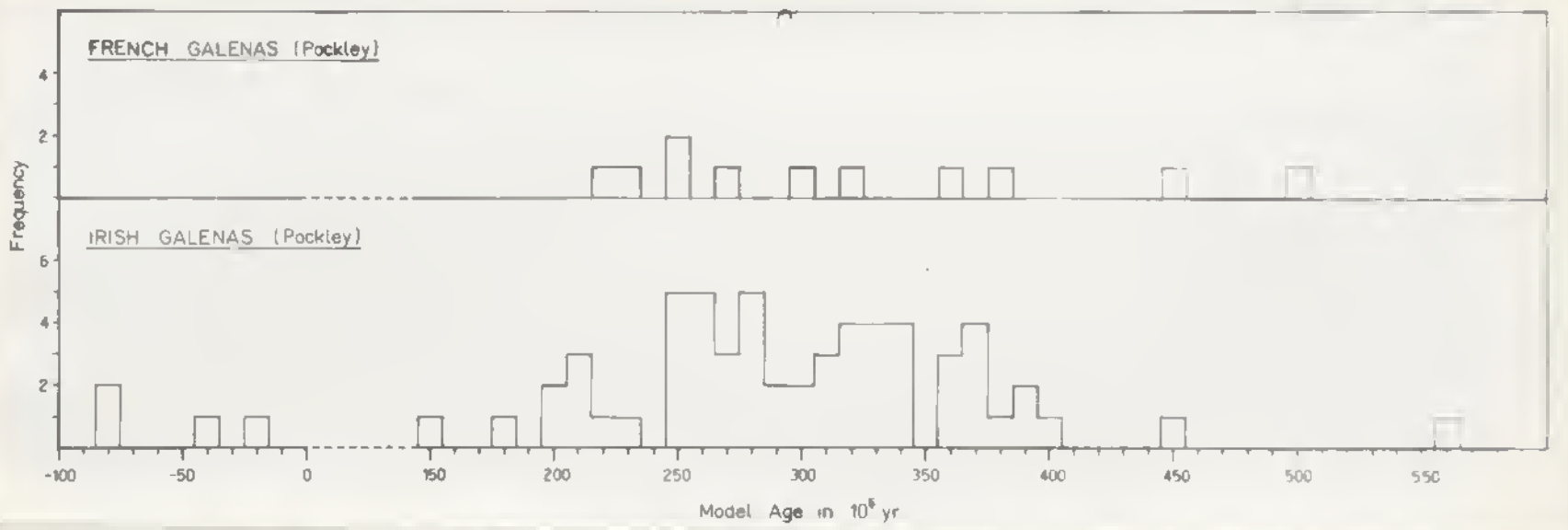


Figure 17(a): Histogram of Model Ages of Irish and French Galenas (Pockley).

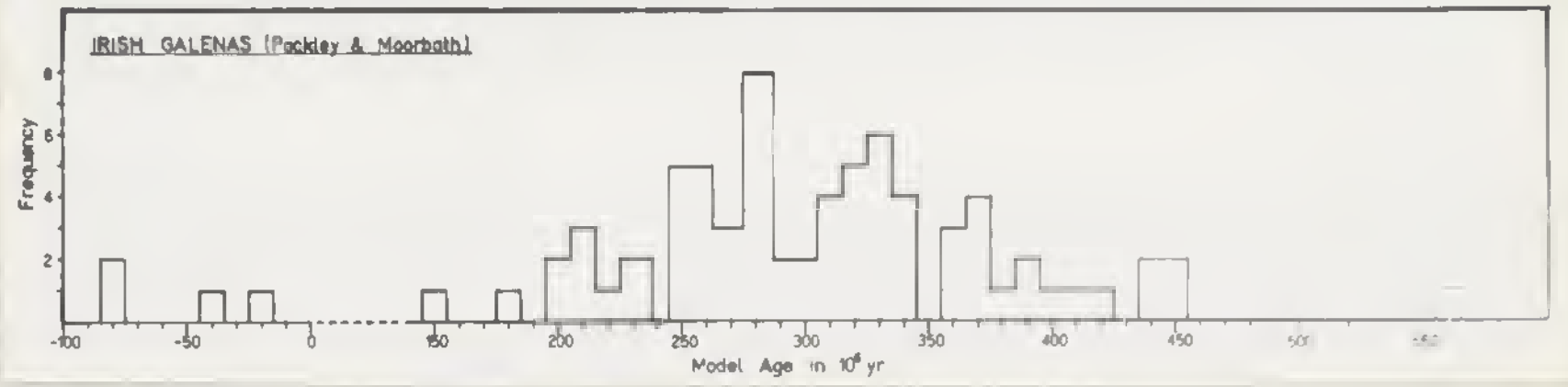


Figure 17(b): Histogram of Model Ages of Irish Galenas (Pockley and Moorbath).

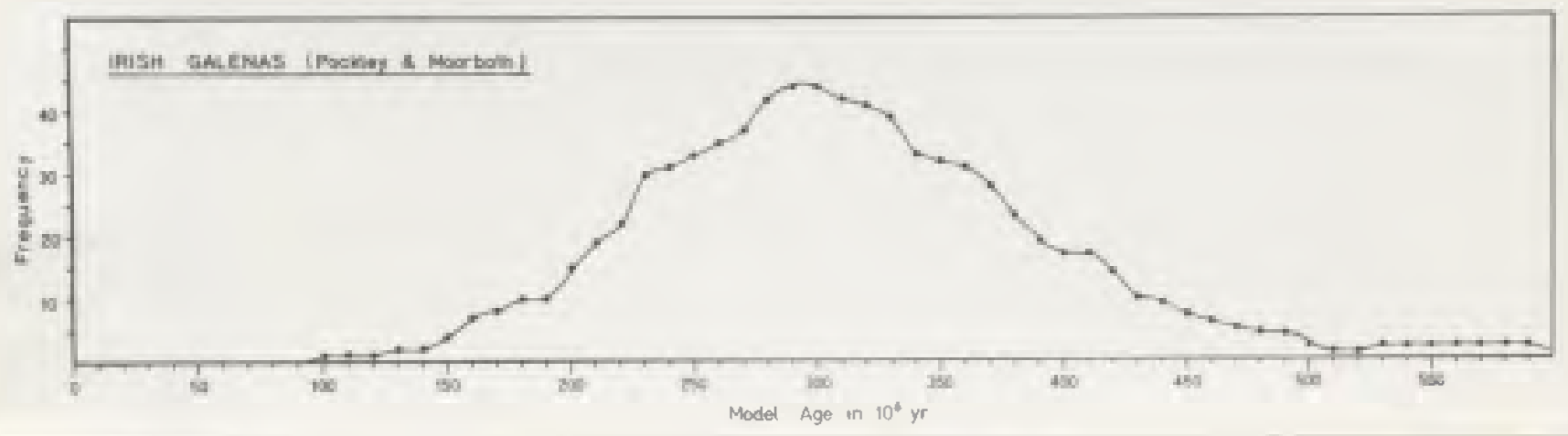


Figure 17(c): Scan over Figure 17(b).

their identification as anomalously young leads. If the isotope ratios had been plotted on trilinear co-ordinates, as suggested recently by Cannon et al. (1961), similar groupings of points would be noticed.

Figure 17(a) includes histograms of all the author's Irish and French model ages. Figure 17(b) is a histogram combining Moorbath's and the author's Irish model ages. The Irish model ages show an almost continuous distribution from 180 to 450 m.y. A maximum at 290 - 300 m.y. is evident in Figure 17(c) which is a scan of Figure 17(b) made with a scanning width of ±40 m.y., the average error in the author's model ages. The other most frequent model ages in Figure 17(b) are not distinct enough to give maxima, but have caused changes in the gradient of the curve in Figure 17(c).

12. (3) DISTRIBUTION OF MODEL AGES THROUGHOUT THE BRITISH ISLES.

The histograms presented in this Chapter must be used advisedly since they do not represent entirely satisfactory statistical distributions for two reasons:

(a) The individual values are spread over wide ranges.

(b) The galenas studied do not represent a controlled statistical sample of the mineralisations of the British Isles. Thus the more available galenas have been preferred in collecting for analysis, and the histograms are biassed in favour of their model ages. For example, seven galenas from the single deposit at Abbeytown, Co. Sligo, with model ages between 320 and 390 m.y., are all included in Figures 17(a) and 17(b).

Similar considerations apply to Figures 15(b) and 17(c), which represent only semi-quantitative examinations of the histograms. The careful selection of a great many more galenas for isotopic study could lead to a truly statistical treatment, but this is premature at the present stage. Nevertheless the model ages as a whole must be examined by such methods as are used here in order to avoid distinguishing too finely between close results.

Figure 18 is a histogram which was constructed from computer-calculated model age values for all 163 galenas from the British Isles measured in Oxford,

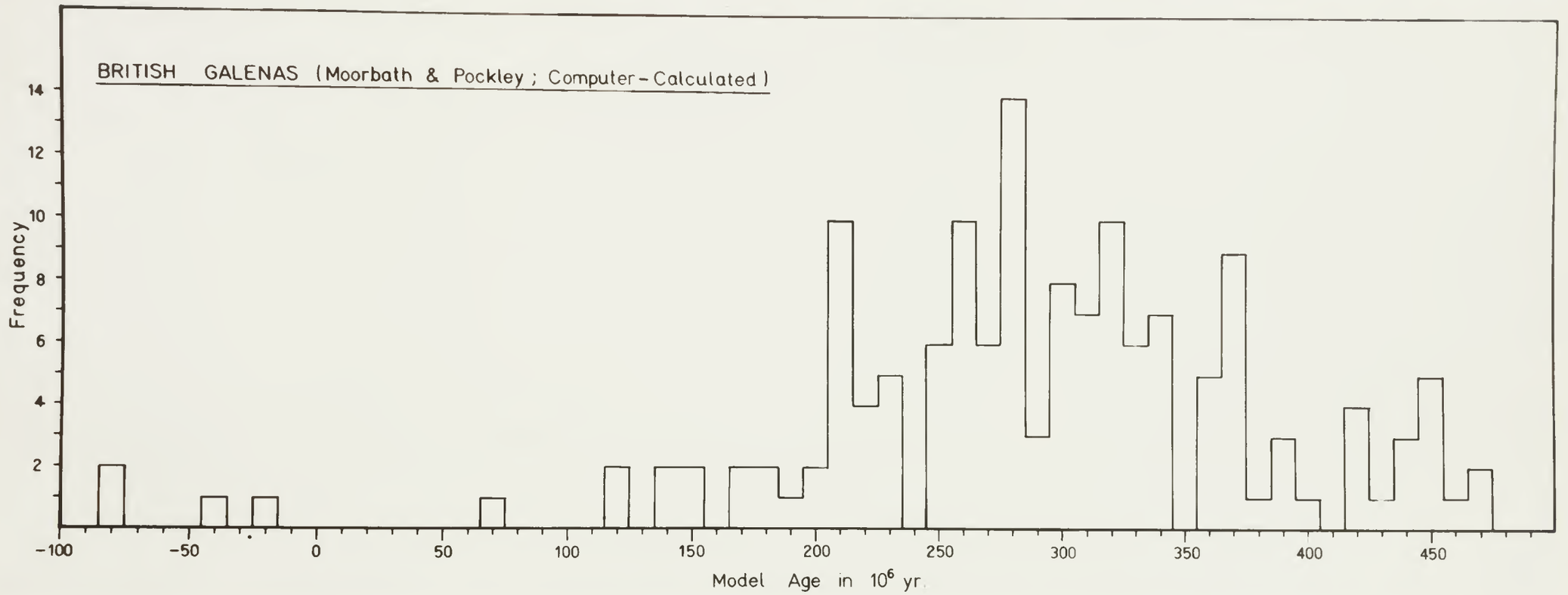


Figure 18: Histogram of Model Ages of British Galenas (Moorbath and Pockley).

(model ages > 500 m.y. omitted). The overall distribution is more complex than that of Moorbath's original values (Figure 15(c)). The fortuitous nature of the discontinuities at 240 and 350 m.y. is shown by the fact that several individual runs gave these values for the model age but they were all slightly modified on averaging with replicate runs. Thus a more or less continuous distribution of model ages is shown from 120 to 470 m.y.; certain values appear more frequently and the great majority of galenas have model ages between 210 and 370 m.y. inclusive. An interpretation of these results is made in Section 12.(6)).

12. (4) DISTRIBUTION OF MODEL AGES IN BRETAGNE AND NORMANDIE, FRANCE.

Figure 17(a) includes a histogram of the model ages of the author's eleven galenas from this region. It is justifiable to distinguish large differences between the ages of mineralisation of individual galenas, and speculations may be made on correlations with possible periods of mineralisation in the British Isles. But it is premature to define, even qualitatively, groups of model ages from these few data. Nevertheless, it can be concluded that mineralisation has occurred in this region at different times during the approximate period 500 to 210 m.y. ago.

The distribution of the isotope ratios for the French galenas is shown in Figure 16. It is noticeable that the 207/204 values vary little. The growth curve for their mean V_p value of 9.14 would pass very close to all the isotope ratio points on this diagram.

12. (5) DISTRIBUTION OF GEOCHEMICAL RATIOS IN THE BRITISH ISLES AND FRANCE.

Figures 19 and 20 are histograms of the values of the geochemical ratios for Moorbath's and the author's galenas. All the values used in constructing these histograms were computer-calculated.

The British galenas (excluding Irish samples) exhibit a distribution of V_p

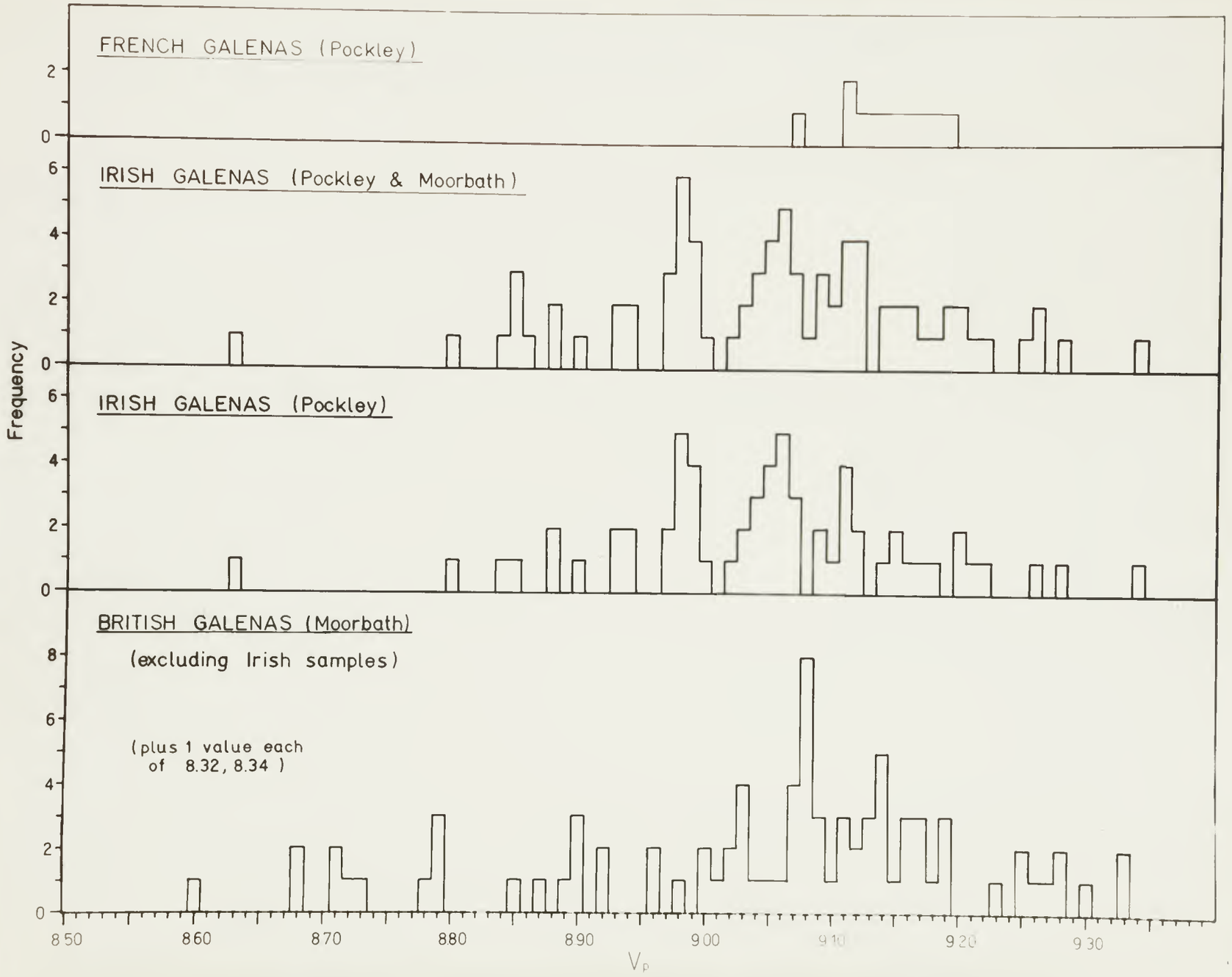


Figure 19: Histogram of V_p Values.

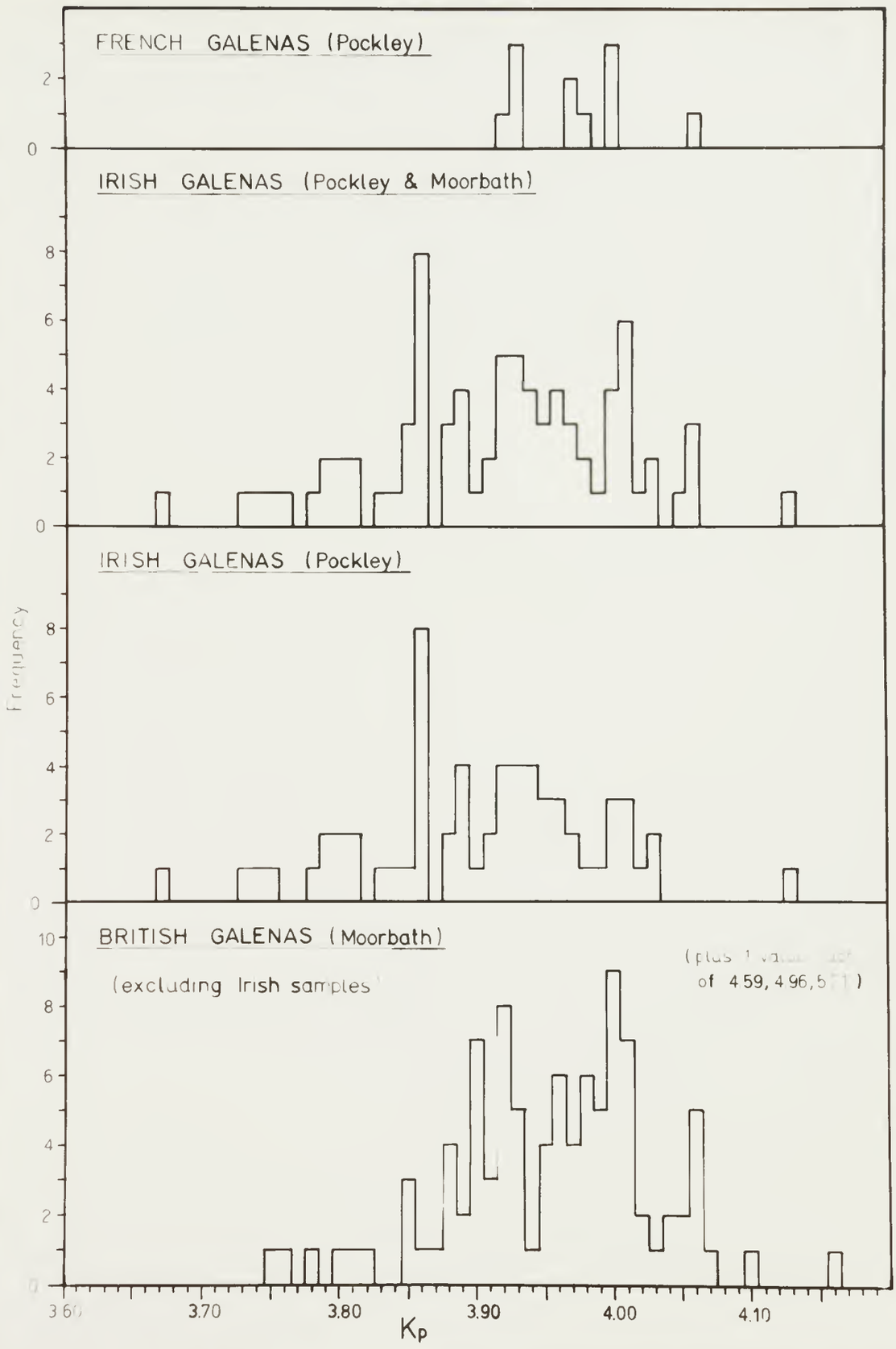


Figure 20: Histogram of K_p Values.

values between 8.60 and 9.33, with the most frequent values between 9.00 and 9.19. The Irish galenas exhibit a similar overall distribution, with a slight bias towards lower values. Some geographical grouping of V_p values has been noted for Britain by Moorbath (1959b, p.144) and for Ireland by the author (Section 10.(11)).

The distribution of K_p values for British and Irish galenas follows that of V_p values, except that the total range of values is smaller. There appears to be a particularly favoured value of 3.96 for K_p of Irish galenas. The extreme values of V_p and K_p, which are outside the histogram ranges for the British galenas, are associated with anomalously old leads. The larger variations in V_p and K_p values are shown to be experimentally significant by comparing them with the average errors for the author's results of ±0.10 for V_p and ±0.05 for K_p.*

The range of model ages used in calculating V_p and K_p values is almost as great for the French as for the Irish galenas (see Figure 17(a)). But for the French galenas, the values for V_p, in particular, and for K_p form close groups, the variations within which can be almost entirely accounted for by experimental error. The contrast between these French results and those for Irish and British galenas is clear from Figures 19 and 20. The constancy of the French V_p and K_p values over the wide geographical area is also striking (see Figure 14).

The uniformity of their V_p and K_p values does not imply a mantle source for the French galenas - see Table 36 for demonstration of the inapplicability of Russell's mantle-origin theories to the French galenas. The uniformity of crustal U-Th-Pb ratios in this region probably indicates that the basement

* The errors in Moorbath's values for V_p and K_p are probably about double those quoted here for the author's results.

complex had originally undergone very large-scale homogenisation processes.

12. (6) SIGNIFICANCE OF INDIVIDUAL AND GROUPED MODEL AGES.

The fundamental questions to be answered from the isotope data now available for galenas from the British Isles and France are:-

(a) What is an experimentally significant difference between individual model ages?

(b) Can these model ages be validly grouped together, and if so, what is an experimentally significant difference between the means of these groups?

(c) How accurate are correlations made between model ages and the geological time-scale?

(d) Do the model age data for these regions indicate that mineralisation occurred:
   (1) more or less continuously over the geological period considered, or
   (2) more or less continuously, but with increased activity during certain relatively long periods, or
   (3) at certain discrete times, of relatively short duration?
   If hypotheses (2) or (3) are correct, what are the geological ages of these periods or times?

These questions are considered under the same headings:

Question (a): This depends entirely on the accuracy and precision of the experimental data. Small differences can be identified only when all the measurements have been made on the same mass spectrometer using standard techniques. The errors of individual results must be considered in each case, but the following table indicates the general magnitude of significant differences for the results considered in this thesis (errors estimated by the same method as near as possible):

Analyst	Average error of Individual Model Age	Significant difference between Individual Model Ages
Durand (1960)	ca. ±100 - 120 m.y.	ca. 200-240 m.y.
Moorbath (1960b)	± 70 m.y.	ca. 140 m.y.
Pockley	± 40 m.y.	ca. 80 m.y.

Question (b): The conclusions regarding question (b) for Moorbath's data (Section 12.(1)) are not altered by the new data for Irish and French galenas. The general validity of grouping model ages depends entirely on the actual distributions observed. For example, in the combined data of Moorbath and the author for British galenas (Figure 18), there is a large number of individual values intermediate between the mean model ages of Moorbath's 'periods' of mineralisation (440, 360, 320, 280, 220, 140 m.y.). In view of the average errors of Moorbath's and the author's model ages (see above), it is probably not justifiable to define groups of model ages with intervals of less than 80 m.y. Thus Moorbath's 320 m.y. 'period' cannot really be distinguished from his 280 m.y. or 360 m.y. 'periods'. On this basis, only four significantly different 'periods' could be defined between 120 and 440 m.y. These 'periods' could have mean ages of, e.g. 140, 270, 360, 440 m.y., but there could be an alternative series with mean ages of 140, 220, 320, 440 m.y. Either series of defined 'periods' omits many model ages as intermediate values, which is inevitable if 'periods' of mineralisation must be defined from these data. A more flexible and satisfactory approach might be to dispense entirely with attempts to define such 'periods' over the whole of the British Isles, and to concentrate more on distinguishing differences between individual deposits.

Question (c): If the time-scale is assumed to be without error, then the accuracy of correlations of model ages with it is dependent on:-

(i) The accuracy of the correlation of the mean model ages of Moorbath's seven Cornwall-Devon galenas with absolute age data for the region.

(ii) The experimental error.*

* The error due to uncertainties in constants and parameters (ca. ±100 m.y.; see Section 9.(12)), does not enter into these considerations. The use of different constants would be compensated for by arbitrarily choosing the value of t_o so that the best possible correlations of model ages with the time-scale were obtained.

Question (d): Hypothesis (1) is most unlikely in view of the model age and geological data. Neither hypothesis (2) nor hypothesis (3) is contradicted by the geological data for the ages of the galenas studied. Hypothesis (3) is only supported by the distribution of model ages in Figure 18 if it is assumed that all the variations of model ages from a few discrete values are due to experimental error. The observed distribution supports hypothesis (2), and it is this one which is favoured by the author dependent on further data. Moorbath's arguments proceeded from the assumption of hypothesis (3), and this cannot be excluded conclusively on the evidence available so far. The addition of the author's Irish data to the considerations render Moorbath's original definition of 'periods' of mineralisation somewhat less distinct.

It seems preferable at the present stage to use a more general conceptual framework, i.e. of more frequent mineralisation occurring during certain times without accurately defined mean ages and errors, than to use a more specific framework, i.e. of 'periods' of mineralisation defined by statistical means and errors.

12. (7) CONCLUSIONS.

GENERAL.

1. The Holmes-Houtermans model provides the most satisfactory interpretations of the lead isotope data for galenas from the British Isles and France.

2. Holmes-Houtermans model ages are very sensitive to changes in the constants and parameters used in their calculation. The value of 4.50×10^9 yr., used for the age of the earth in these calculations, was chosen so that the calculated model ages for galenas from Cornwall and Devon would agree with absolute age measurements in the region.

3. Time-scale correlations of the author's model ages are considered to be accurate to within ±50 m.y.

4. Differences of 80 m.y. between model ages are considered experimentally significant for the author's results.

(B) FRENCH GALENAS.

1. Lead Mineralisation occurred in Bretagne and Normandie probably in Ordovician, Devonian, Permo-Carboniferous, and possibly also Permo-Triassic times, i.e. from ca. 500 to 220 m.y. ago. There are insufficient data to define the relative extents of mineralisations at different times. Eleven galenas were isotopically analysed.

2. No anomalous leads have been identified in the region.

3. The geochemical ratios V_p and K_p are very similar for all samples, despite the wide range in model ages. A uniform crustal source, homogeneous in U-Th-Pb ratios, is postulated for the lead minerals of the region.

(C) IRISH GALENAS.

1. The major lead mineralisation in Ireland occurred from ca. 450 to 200 m.y. ago (i.e. from Ordovician to Triassic times).

2. Four anomalously young and four anomalously old leads have been definitely identified in Ireland. Excepting a small number of doubtful cases, the remaining 72 Irish galenas measured appear to follow the Holmes-Houtermans model.

3. The distribution of model ages is basically similar to that for galenas from England, Scotland and Wales.

4. The geochemical ratios, V_p and K_p, vary within similar limits to other British galenas. There is some geographical zoning of these ratios.

(D) BRITISH ISLES GALENAS (including Irish galenas).

1. The great majority of these galenas obey the Holmes-Houtermans model and have geologically reasonable model ages.

2. The major lead mineralisation in the British Isles has occurred from ca. 470 to 120 m.y. ago (i.e. from Ordovician to Cretaceous times).

3. Model ages are distributed almost continuously over this period, but the greater frequency of certain values indicates that more frequent mineralisation occurred during certain times.

4. The most frequent mineralisation in the British Isles has occurred probably in the following times: Ordovician (450 - 420 m.y.), Devonian-Carboniferous (360 - 350 m.y.), Middle Carboniferous (330 - 300 m.y.), Carboniferous-Permian (280 - 250 m.y.) and Permian-Triassic (230 - 210 m.y.). Some minor mineralisation probably also occurred in Jurassic-Cretaceous times (180 - 120 m.y.). The model ages (in brackets) are not definitive and some mineralisation may have also occurred between all of these times. It is not possible to distinguish positively between successive groups of these model ages unless they are at least 80 m.y. apart. Thus groups of model ages with means of 440, 360, 280, 140 m.y. can be positively distinguished, as also can groups of model ages with means of 440, 320, 220, 140 m.y. Most model ages can be correlated with periods of tectonic or igneous activity in the British Isles, but these are not

necessarily of short duration.

5. Significant variations in the ratios, V_p and K_p are found throughout the British Isles, indicating small but definite inhomogeneities in the U-Th-Pb ratios in the crustal sources of the galenas.

APPENDICES

A P P E N D I X I

PITCHBLENDE SPECIMENS - LOCATION, GEOLOGY & MINERALOGY.

Nos. 1A & 1B. South Terras. St. Stephen-in-Brannel, Cornwall, 1 mile S. W. of St. Stephen. 1 in. geol. 347; 6 in. Cornwall (2nd ed. 1908) 50 S.W. 2 similar specimens selected from the same hand specimen, collected and supplied by A. W. G. Kingsbury. The specimens consisted of massive pitchblende* with small amounts of erythrite and skutterudite. The pitchblende was fresh, with only a small amount of surface staining. The specimen came from a N-S cross-course vein in the South Shaft of the mine. Small amounts of chalcopyrite, pyrite, mispickel, galena and traces of Ni, Co, Bi and Cr have been reported from this vein, but only Ni and Co were observed in these specimens.

The country rock is Lower Devonian "killas" and greenstone dykes. The uranium-bearing lode intersects an earlier E-W lode of magnetic iron ore and a tin lode coursing E of N. South Terras Mine was the most important uranium producer in Cornwall. It flanks the S. edge of the St. Austell granite. (Dines, 1956, p. 540-543).

No. 2. Redruth Area, Cornwall. Supplied by F. W. Dunning from the Geological Survey and Museum Collection.

* The terms "pitchblende" and "uraninite" are sometimes used loosely. The more common usage is employed here, such as is defined in Berman (1957), of "uraninite" for crystalline and pegmatitic specimens, and of "pitchblende" for massive and visibly amorphous specimens, generally occurring in vein and sedimentary deposits. The samples studied here are all from vein deposits and none are visibly crystalline and so are described as pitchblendes. Pitchblende is also described as a massive variety of crystalline uraninite (Dana, 1944, p.612). However, the distinction is important, as pitchblendes are more likely to suffer leaching and radon loss than uraninites (Giletti and Kulp, 1955).

The specimen consisted of massive pitchblende with a little chalcopyrite, chalybite and quartz and traces of lollingite and a cobalt arsenide.

This is the least satisfactory specimen from the point of view of information about its locality and the nature of its occurrence, for the label on the specimen bottle simply stated "Near Redruth, Cornwall". The observed mineral assemblage is typical of the cross-course lodes in the Redruth area (Dines, 1956; Kingsbury, personal communication), but although this evidence supports its general area, it is insufficient to localise it further.

This specimen and No. 4 were collected in the 19th century, and the Geological Survey and Museum do not possess any further documentation about them. But unlike No. 4, this specimen could have come from any of a large number of known uranium occurrences in the Redruth Area (Collins, 1876, and Hill and MacAlister, 1906, each list some dozen occurrences). A likely origin of the specimen is the East Poole and Agar Mine which Dines (1956, p. 39-42, 326-333) lists as the only mine in the area to have produced uranium. This is also favoured by Dunning (personal communication) who suggests the East Pool - Barncoose - Carn Brea - Tincroft group of mines W. of Redruth.

However, despite the unsatisfactory nature of the locality data, it is certain that the specimen actually came from the highly mineralised Redruth area, which borders the N. edge of the Carnmenellis granite. If the specimen does come from the more localised area suggested (i.e. East Pool etc.) the country rock consists of thermally metamorphosed Devonian killas and greenstone which overlie the N. flank of the Carn Brea granite ridge, and the granite itself. Uranium minerals typically occur in this area in small quantities in the later stage cross-courses in the upper parts of the workings, and occasionally in the main E-W veins, some of which were probably traversed by

the mineral fluids associated with the cross-courses (Kingsbury, personal communication).

No. 3, Owles, St. Just, Cornwall. Collected and supplied by A. W. G. Kingsbury.

The specimen was collected loose from just inside the adit of the cliff section of the Wheal Owles Mine in Wheal Edward Town, this section being also known as Wheal Edward Cliff Lode.

1 in. geol. 351, 358; 6 in. Cornwall (2nd ed. 1908) 67 S.W.

The specimen consisted of fresh massive pitchblende, mainly clean but with a little surface alteration and some iron staining. Some finely disseminated specks of galena, chalcopyrite and other sulphides (Bi?) occur with the pitchblende.

The lode sampled trends N. W. through the narrow coastal strip of highly metamorphosed killas and greenstone bordering the Land's End granite. The lode traverses the killas-granite contact almost at right angles. The uranium ores were separated from the lode walls by earthy limonite, and the presence of some of this on one side of the specimen suggests that it may have come from the edge of the lode (Dines, 1956, p. 71; Kingsbury, personal communication).

No. 4, South Terras Area, Cornwall. Supplied by F. W. Dunning from the Geological Survey and Museum collection.

The specimen consisted of massive pitchblende with chalcopyrite and some quartz, and contained more alteration products (not identified) than Nos. 1A and 1B, but these were on the surface only.

The locality and general notes on the occurrence are presumed to be the same as for Nos. 1A and 1B. The label on the specimen bottle actually stated

"Pitchblende, Grampound Mine, South Terras", but this probably means that it comes from the South Terras Mine itself. "The specimen has presumably been described as coming from the Grampound district (in which South Terras lies) and someone has come to the wrong conclusion and written "Grampound Mine"", (Dunning, personal communication). However, as there is some doubt about its exact locality, it has been called here "South Terras Area".

APPENDIX II

GALENA SPECIMENS - LOCATION, GEOLOGY AND MINERALOGY

Numbering of specimens and their grouping into regions was done on a purely geographic basis. The regional groups do not necessarily have geological significance.

Suppliers of specimens and accompanying information, to whom grateful acknowledgement is given here, were:

Nos. 1 - 61 (except No. 28): The Geological Survey of Ireland through the Director, Mr. Murrogh V. OBrien.

No. 28 : Dr. D. F. C. Morris of the Brunel College of Technology: originally from Mr. P. G. Embrey of the British Museum (Natural History) who collected the specimen and provided the information.

Nos. 62, 63: Mr. J. A. Robbie, the Director of the Geological Survey in Northern Ireland.

Nos. 64 - 74: Prof. Y. Milon of the Institut de Géologie, University of Rennes; and Dr. R. St. J. Lambert of this Department, who first obtained most of these specimens from Prof. Milon and supplied much of the information.

No. 75 : Dr. S. Moorbath, originally collected by Mr. A. W. G. Kingsbury of this Department.

Nos. 76, 77: The National Bureau of Standards, U. S. Department of Commerce, Washington, D.C.

Literature References can be found in Appendix V. For the Irish specimens, frequent reference is made to the publications given in Appendix V under "Cole, G. A. J.; 1922" and "OBrien, M. V.; 1959" - These are abbreviated in the following text to "Cole" and "OBrien" respectively.

Specimen Information: Map references for Irish galenas are given first to the numbers of the relevant Ordnance Survery of Ireland 1 - inch maps, and then to the 6 - inch maps (grouped on a county basis), which are divided into four sectors, NE, SE, SW, NW for the final reference.

Any other numbers given after the location data are the suppliers' own collection numbers.

The information on the deposits was compiled from the suppliers' notes and published material. References to a deposit are quoted at the end.

Under the heading "Sample", the form of the galena in the specimen used in these studies is recorded.

Under the heading "Assn." (abbreviation for "Association") are listed the minerals observed in association with the galena in the deposit, together with any other important minerals observed in the actual specimen studied. The following abbreviations are used :-

alt prod	: alteration product	dol	: dolomite	sed	: sediment
amt	: amount	Fe ox	: iron oxide	ser	: sericite
angl	: anglesite	fl	: fluorite	sid	: siderite
arspy	: arsenopyrite	gal	: galena	Sil	: Silurian
ba	: barytes	goe	: goethite	sph	: sphalerite
cc	: calcite	gr	: grained	sst	: sandstone
Carb	: Carboniferous	lr	: Lower	st	: staining
cer	: cerussite	lst	: limestone	sur	: surface
chpy	: chalcopyrite	med	: medium	tet	: tetrahedrite
crys	: crystals	Pal	: Palaeozoic	tr	: trace
crysln	: crystalline	py	: pyrite	unid	: unidentified
Dev	: Devonian	pymor	: pyromorphite	v	: very
		qz	: quartz	?	: doubtful

The information for Moorbath's Irish specimens, Nos. M 84 - 100, is taken directly from his thesis (1959b) with a few minor alterations. The form of presentation of information is slightly different, but is self-evident. Donors of specimens are given in brackets.

IRELAND.

DONEGAL (OBrien, p.14)

1. Keeldrum. 1 in. 9, 6 in. Donegal 33 NE. (No. 437). Brecciated vein traversing Dalradian quartzite, mica schist and basic sills. Sample: mainly quartzite with sur coating of small gal crys. Assn: cer and/or angl, pymor (?), (Cole, p.91).

2. Faymore. 1 in. 10, 6 in. Donegal 26 SE. Large qz vein traversing quartzite inter-bedded with other metamorphic rocks of the Dalradian. Sample: fine to med gr gal. Assn: qz, alt prods.

3. Glentogher (Carrowmore). 1 in. 5, 6 in. Donegal 20 SE. Gal with sph occurred down 25° dip of brecciated and current-bedded silty quartzites interbedded with mica schists. The sulphides occurred as fillings between quartzite grains, and also as films on joints and bedding planes and in a few qz veinlets. Sample: med gr isolated gal crys. Assn: qz, sph, Fe ox (OBrien, p.14; Cole, p.91).

4. Ardaturr. 1 in. 10, 6 in. Donegal 44 SW. Geological setting as for No. 6 and in fact adjoining same fault as that passing the site of No. 6. Sample: fine gr gal. Assn: qz, cc, chpy.

5. Knockybrin. 1 in. 10, 6 in. Donegal 53 NE. Thin irregular vein traversing quartzites presumed Dalradian. Sample: slightly corroded gal crys on joint. Assn: qz, cc (Cole, p.92).

6. Glenaboghil (Fintown). 1 in. 16, 6 in. Donegal 58 NE. (No. 405). Vein cutting Dalradian quartzites, schists and lst bands with basic sills. Sample: massive crysln gal. Assn: sph, cc, greenockite, alt prods, Fe st. (Cole, p.92).

Note on Nos. 4 and 6: These samples are from the scattered small occurrences with similar mineral assemblages of finely intergrown gal, sph and a little ba which occur on minor fractures within 100 yd. of the fault running NE-SW for 20 m. S of Donegal main granite. The sulphides occupy veinlets, breccias, quartzite pores or replace thin impure lsts. (OBrien, p.14; Pitcher and Read, 1960).

SLIGO-LEITRIM

7. Rosses Upper. 1 in. 43, 6 in. Sligo 8 SW. Irregular veinlets in Carb lst ca. 300 ft. above junction with metamorphic rocks of presumed Moine age. Sample: massive crysln gal. Assn: v tiny veinlets of unid mineral traversed some gal crys.

8. Twigspark. 1 in. 43, 6 in. Leitrim 7 SE and SW. From irregular fracture in dolomitic Carb lst possibly 500 ft. above unconformable junction over metamorphic rocks of probable Moine age. Ca. ¼ m. N of major fault on which the Carb rocks are downthrown against the exposed Moine metamorphics of Ox Mts.. Ore was argentiferous. Sample: coarsely crysln gal. Assn: cc, py, sph, qz. (Cole, p.93).

9. Lugawarry. 1 in. 55, 6 in. Sligo 20 NW. From irregular breccia vein traversing Lr Carb lst, ca. 250 yd. from major normal fault which brings beds against Moinian schists. Sample: coarsely crysln gal, intimately mixed with gangue. Assn: py, sph, cc, Fe st.

10. Abbeytown A (Ballysadare). 1 in. 55, 6 in. Sligo 20 NW. From "index bed"

calcareous sst in Lr Carb lst, 275 ft. above unconformable junction over metamorphic rocks of probable Moine age. Sample: fine gr gal disseminated sparsely in sample (5% gal). Assn: sph, py, chpy, some marcasite, cc, qz (tr) (Cole, p.95; Dennison and Varvill, 1952).

General Note on Abbeytown (OBrien, p.13): Sph exceeds gal in irregular sulphide replacements which are mainly in and near top of 24 ft. thick calcareous sst ("index bed"), but which have been quarried and mined also from the gently dipping lst beds above and below. The mine area is between two big E-W faults, but is not known to extend to either of them. The lst is always dolomitized in the vicinity of the ore.

11. Abbeytown B. From lst 50 ft. below "index bed". Sample and assn: as for No. 10.

12. Abbeytown C. From "lower grit bed" ca. 120 ft. below "index bed". Sample and Assn: as for No. 10.

13. Abbeytown D. From same horizon as No. 10, i e. top of "index bed", but a different plan position (see below). Sample: med gr gal. Assn: as for No. 10.

14. Abbeytown E. From the mineralised lst 75 ft. below top of "index bed". Sample: massive gal (slightly corroded). Assn: as for No. 10.

15. Abbeytown F. From the mineralised lst 105 ft. below top of "index bed". Sample: coarsely crysln gal. Assn: as for No. 10.

16. Abbeytown G. From "lower grit bed" ca. 130 ft. stratigraphically below top of "index bed". Sample: coarsely crysln gal. Assn: as for No. 10.

Note on Nos. 10-16 from Abbeytown: These specimens are all from the mine itself or from boreholes within it. The first specimens studied were Nos. 10-12 from the "L.O.B.1 Area". When more specimens from these horizons were requested, they were unobtainable, but Nos. 13-16 are their counterparts from the "L.O.B.2 Area" which lies ca. 400 ft. to SE. Nos. 13 and 16 are from the same stratigraphical horizons respectively as Nos. 10 and 12. Nos. 13-15 are taken from the same vertical pillar, but No. 16 is offset ca. 100 ft. to the rise (NE).

MONAGHAN (Cole, p.96; OBrien p.14).

17. Derryleedigan. 1 in. 58, 6 in. Monaghan 8 NE. (No. 445). From brecciated and steeply inclined vein cutting gently dipping Carb lst, in part

dolomitic and impure, probably ca. 500 ft. above basement of Lr Pal seds. Sample: fine gr, irregularly shaped gal crys (v little in gangue matrix). Assn: cc, sph. (OBrien, p.14).

18. Lisdrumgormley. 1 in. 59, 6 in. Monaghan 15 NW. (No. 456). Geological setting similar to No. 19. The lode, 2-9 ft. wide, has a N trend. Sample: med gr gal. Assn: cc, qz. (Cole, p.99).

19. Coolartra (Bond Mine). 1 in. 59, 6 in. Monaghan 14 NE, (No. 467). From irregularly brecciated vein traversing silty sst of Lr Pal age (presumed Sil) which are strongly folded and of great thickness. Sample: massive gal. Assn: qz, cc, sph. (Cole, p.97).

MAYO AND N. GALWAY

20. Tullyduff. 1 in. 85, 6 in. Mayo 118 SE. From small vein in Lr Carb lst, probably 1000 ft. above unconformable junction with Lr Pal basement. Sample: massive gal. Assn: sur alt prods.

21. Ballykine Lower. 1 in. 95, 6 in. Mayo 120 NW. From bedding plane in Lr Carb lst, probably 500 ft. above unconformable junction with Lr Pal basement. Sample: massive crysln gal. Assn: sph, cer (?).

22. Grallagh. 1 in. 93, 6 in. Galway 22 SW. Small vein cutting Omey granite near its margin. Sample: med gr gal. Assn: chpy, qz, cc, cer.

23. St. MacDara's Island. 1 in. 103, 6 in. Galway 76 SW. Thin qz vein cutting granite. Sample: fine gr crysln gal. Assn: qz, fl, chpy (tr), sph (tr).

CLARE AND S. GALWAY

24. Tynagh (Carhoon). 1 in. 116, 6 in. Galway 117 NW. Veinlets traversing Lr Carb lst, probably 250 ft. above conformable junction with Dev sst, 2 m. S of fault paralleling Silvermines, Co. Tipperary, fault. Sample: massive crysln gal. Assn: Fe st, sur alt prods (Cole, p.116; OBrien, p.12).

25. Ailwee. 1 in. 114, 6 in. Clare 6 NW. From N-S vein cutting Lr Carb lst, probably 1000 ft. above unconformable junction over Galway granite. Sample: massive crysln gal. Assn: fl, sph, sur alt prods (cer and/or angl ?). (Cole, p.117).

26. Knockaphreaghaun (Crowhill). 1 in. 133, 6 in. Clare 34 NE. Geological setting as for No. 27. Sample: fine to med gr gal. Assn: chpy, sph, py, cc, Co minerals. (Cole, p.118).

27. Milltown A. 1 in. 133, 6 in. Clare 35 NW. From replacement in Carb lst, probably ca. 1000 ft. above conformable junction with Dev sst. Ore was argentiferous and scattered through irregular replacement of cc. Sample: massive crysln gal. Assn: cc, sph (more frequent than gal). (Cole, p.118).

28. Milltown B. Geological setting presumably as for No. 27 (dump material from same mine). Ore was argentiferous (see Appendix IV). Sample: coarsely crysln gal. Assn: cc. (Gal separated by supplier and presented as crushed powder).

29. Kilbreckan (Monanoe). 1 in. 133, 6 in. Clare 34 SW. Geological setting as for No. 27. Ore was highly argentiferous. Sample: massive crysln gal. Assn: sph, arspy, a Pt-Sb sulphide, sur alt prods, carbonates (Zn and Cu?) (Cole, p.119; OBrien, p.15).

30. Ballyhickey. 1 in. 133, 6 in. Clare 34 SE. Geological setting as for No. 27. Ore was low in silver and occurred in large cc veins. Sample: med gr gal crys. Assn: cc, sph, chpy, arspy. (OBrien, p.13; Cole, p.119).

SILVERMINES (Cole, p.121; OBrien, p.13; Rhoden, 1958).

31. Shallee (Coughlan). 1 in. 134, 6 in. Tipperary 26 NW. From vein in brecciated siltstone and sst of presumed Dev age ca. 500 ft. above unconformity over Lr Pal slates and 50 ft. below the conformable base of Carb lst. Sample from shaft pocket of King Shaft of the Silvermines Lead and Zinc Co. These ssts could, possibly, be basal Carb ssts. Sample: med gr crysln gal. Assn: qz, cc. (Cole, p.122; Rhoden, 1958).

32. Gortconadiha. 1 in. 134, 6 in. Tipperary 26 SW. Gal with tr of chpy from within or close to fissure of main Silvermines fault. (From old mine dumps). Mine is in Lr Carb shale on N of fault. Sample: fine gr gal disseminated in gangue. Assn: py, chpy, qz. (Cole, p.123; Rhoden, 1958).

33. Ballynoe. 1 in. 134, 6 in. Tipperary 26 SE. From within or close to fissure of main fault. (From old mine dumps). Sample: fine and med gr gal. Assn: qz, py, chpy, sph. (Cole, p.122; Rhoden, 1958).

34. Knockanroe A. 1 in. 134, 6 in. Tipperary 26 SE. From boulder (evidently ice-transported from N) of gal with sst breccia fragment found in excavation in boulder clay $\frac{1}{4}$ m. S of E end of Silvermines mineralisation. Material similar to No. 35, both being characteristic of Knockanroe mine. Sample: med gr gal. Assn: qz, py(tr), chpy(tr). (Cole, p.122; Rhoden, 1958).

35. Knockanroe B. From near base of oxidised zone of a large replacement ore

body in Carb dol. From dumps of Sulphur Shaft which lies 20-30 yd. N of main fault. Sample: fine and coarse gr gal. Assn: qz, cc, py, goe, sph, cer, calamine (hemimorphite and smithsonite).

36. Gortshanroe A. 1 in. 134, 6 in. Tipperary 26 SE. From breccia-filled fracture cutting Sil siltstone. (From old mine dump at Upper Gortshanroe). Sample: fine gr gal disseminated through gangue. Assn: ba, sid, qz. (Cole, p.122; Rhoden, 1958).

37. Gortshanroe B. The replacement type material with sph contrasts with breccia-filling type ore of No. 36.* (From a superficial boulder from same dump as No. 36). Sample: v fine gr gal (v little). Assn: sph (mainly) qz, Fe ox.

* (The contrast was sufficient to raise some doubt whether the source block of Nos. 37, 38 could have been transported to Gortshanroe from another part of the Silvermines district by ice or during prospecting and mining).

38. Gortshanroe C. Duplicate of No. 37 taken from same block of ore.

39. Garrane. 1 in. 135, 6 in. Tipperary 21 SE. In veinlets in brecciated Sil siltstones. (From old mine shaft debris). Sample: fine gr gal disseminated in country rock. Assn: qz, cc, chpy (tr), py(tr). (Rhoden, 1958).

S. OF SILVERMINES.

40. Killeen. 1 in. 144, 6 in. Tipperary 38 NW. Vein traversing Sil seds of great thickness 8 m. S of Silvermines fault. Sample: fine gr crysln gal. Assn: chpy, ba, py, sid, sph, tet (Cole, p.38).

41. Oolahills. 1 in. 154, 6 in. Limerick 24 SE. Vein parallel to Silvermines fault and 15 m. S of it cutting Lr Carb lst. Ore was moderately argentiferous. The ba gangue was plentiful in vertical veins. Sample: fine to med gr gal. Assn: ba, py, qz, chpy, goe. (Cole, p.124; OBrien p.12).

S. KERRY AND S. W. CORK

42. Ross Island. 1 in. 173, 6 in. Kerry 66 NE. From irregular replacement in strongly cleaved lst (here almost flat lying) $\frac{1}{2}$ m. N of large fault by which Dev sst is steeply overthrust against Carb lst. At Ross Is. mineralisation is probably in lsts ca. 500 ft. above the conformable junction with Dev sst. Sample: fine gr mixture of gal and gangue. Assn: sph, chpy, py, tet, Fe ox. (Cole, p.39).

43. Muckross. 1 in. 184, 6 in. Kerry 74 NE. Geological setting as for No. 42 except that distance above Dev sst may be only 200 ft. Gal v rare. Sample: v fine gr gal intimately mixed with gangue. Assn: chpy, py, sph cc, Co-As mineral. (Cole, p.40).

44. Shanagarry (Caher West). 1 in. 184, 6 in. Kerry 93 NE. Geological setting similar to No. 45. Closer than No. 45 to Carb-Dev boundary. Ore was argentiferous. Sample: med gr gal crys. Assn: massive sph, and as for No. 43. (Cole, p.127).

45. Cloontoo (Ardtully). 1 in. 184, 6 in. Kerry 93 NE. Brecciated vein in recrystallised and cleaved Carb lst of the Kenmare Syncline. These tightly folded rocks are probably only 200 ft. above the Dev sst. Sample: coarsely crysln gal. Assn: cc, qz, chpy (?). (Cole, p.127).

46. Cahermore (Kilkinnin West). 1 in. 198, 6 in. Cork 127 SW. From narrow vein cutting silty slates approximately at conformable junction of Upper Dev or base of Carb. (From old mine dump). Sample: med gr gal. Assn: qz, chpy, arspy (or lollingite?). (Cole, p.128; OBrien, p.10).

47. Killaveenoge (Bantry Lead Mine), 1 in. 199, 6 in. Cork 117 SE. Geological setting similar to No. 48. Ore was argentiferous. Sample: med gr gal. Assn: chpy, qz, sid, arspy, sph. (Cole, p.128).

48. Duneen. 1 in. 201, 6 in. Cork 144 NE. Steeply inclined vein almost coinciding with dip of Upper Dev sst. Mined for ba and chpy. Sample: fine to med gr gal. Assn: ba, chpy, py, Fe ox, arspy, qz. (Cole, p.128; OBrien, p.16).

S. E. IRELAND.

49. Templeyvrick. 1 in. 178, 6 in. Waterford 24 SE. From Trawnastrella lode, which is one of westernmost of the several Bonmahon lodes outcropping on the sea cliffs. Nos. 50 and 51 are also from the Bonmahon Copper Mining Area (also known as Knockmahon). The lodes cut Ord seds and volcanics and their v numerous dykes and sills. The lodes are not known to be themselves cut by intrusives, but there is good evidence that one of them (the Stage lode) is cut off by the unconformity above which lie the Upper O.R.S. conglomerates. The Ord seds (mainly argillaceous but some calcareous) and volcanics are steeply folded (strong pre-Dev as well as strong Hercynian folding) and NE-SW trending. Chpy is virtually devoid of accompanying sulphides and occurs in and especially at margins of large steep-dipping qz veins running SE-NW at right angles to strike of country rock. Sample: coarsely crysln gal. Assn: qz, chpy. (OBrien, p.9; Cole, p.41; Capewell, 1956).

50. Tankardstown A. 1 in. 178, 6 in. Waterford 25 SW. From thin vein in wide qz-veined breccia zone lying between two qz-chpy veins (Tankardstown and

Rowes) cutting across chloritized Ord volcanics, pyroclastics and slates. Sample: fine gr crysln gal (only ½% gal in sample). Assn: qz, Fe ox st. (Cole, p.42).

51. Tankardstown B (Foilaneena Cove). 1 in. 178, 6 in. Waterford 25 SW. From narrow qz-cc fissure vein cutting chloritized Ord volcanics. Sample: med gr crysln gal. Assn: qz, chpy, cc.

52. Barrystown. 1 in. 169, 6 in. Wexford 45 NE. Vein cutting Lr Pal seds of considerable thickness. Lodes trended E-W in country rock similar to that of No. 54. Gal was argentiferous. Sample: coarsely crysln gal intimately mixed with gangue. Assn: sph (mainly), qz, sid, chpy (?), sur alt prods. (Cole, p.125; OBrien, p.14).

53. Brownsford. 1 in. 157, 6 in. Kilkenny 33 SW. From vein in SW margin of the Caledonian Dublin-Wicklow granite which is in line with and ca. 1 m. from a similar vein in mica schists of its aureole. This vein, which is probably continuous from vein to aureole, is similar in character to the Glendalough, Co. Wicklow, veins (No. 58). The mica schist aureole is developed in Lr Pal seds. Sample: coarsely granular gal. Assn: qz, sph, Fe ox.

54. Caim (Ballyhighland). 1 in. 158, 6 in. Wexford 19 SW. From qz-carbonate fissure veins in Ord strata. (From old mine dumps). Caim is 10 m. SE of Leinster granite and midway between Avoca and Bonmahon but does not share major characteristics of either deposit. The Lr Pal rocks are silty mud-stones and the mineralised fractures ramify irregularly through these. Sample: med gr gal, closely mixed with gangue. Assn: qz, chpy, sph, cer, Cu st. (Cole, p.125; OBrien, p.14).

WICKLOW

55. Ballintemple. 1 in. 139, 6 in. Wicklow 40 NW. From qz-carbonate fissure vein cutting chloritic schists of Ord age - ca. 1 m. off strike of Avoca mineral belt. Lode runs some 30°N. of W. Sample: massive crysln gal. Assn: qz, carbonate (dol?). (Cole, p.115).

56. Kilmacoo A. 1 in. 130, 6 in. Wicklow 35 NE. Fine gr gal-sph-py-chpy mixture ("Kilmacooite" or "bluestone") from a replacement lode at NE end of Avoca mineral belt. Sample: exceedingly fine gr mixture of gal, sph, py, chpy with no separate grains of any of these minerals detectable except under high magnification. (Cole, pp. 33, 144; G. J. Murphy, 1959).

57. Kilmacoo B. Coarse grained dissemination in silicified schists. Sample: similar to No. 56 but not as fine gr.

58. Brockagh (E. Foxrock Lode, Glendalough). 1 in. 130, 6 in. Wicklow 23 NW. Vein cutting Caledonian granite ca. 200 yd. from its margin. SE margin of Leinster granite batholith is cut by a large number of steep-dipping narrow rectilinear veins mostly in sets running N-S and NE-SW. Other veins cutting granite have been worked at Ballycorus (No. 59), Glenmalure to SW (No. M 83) and Inistioge, Co. Kilkenny (opposite flank of granite). Sample: massive crysln gal. Assn: sph, py, chpy, qz, ser (?). (Cole, p.109; OBrien, p.12).

DUBLIN

59. Ballycorus. 1 in. 121, 6 in. Dublin 26 SW. Veincutting Caledonian granite ca. ¼ m. from its margin. Sample: med crysln gal. Assn: qz, Fe ox, sph, ser. (OBrien, p.12; Cole, p.107).

60. Corbally. 1 in. 111, 6 in. Dublin 21 SE. From small irregular vein cutting diorite intruded into Ord slates and near aureole at NW end of Dublin granite. (Sample from de Selby Quarry). Sample: coarsely crysln gal. Assn: alt prods (large amt - cer and/or angl), pymor, chpy (tr), py(tr).

61. Clontarf. 1 in. 112, 6 in. Dublin 19 NW. From vein in Carb lst. Sample: massive crysln gal. Assn: qz, py(tr), Fe st. (Cole, p.105).

NORTHERN IRELAND

62. Slieve Binian A. 1 in. 60, 6 in. Down 53 NW. (From tunnel through Mourne Mts. under Slieve Binian, 1482 yd. from Silent Valley end, N wall, 35 yd. E of Peg 39). The hydrothermal veins occur only in the Aplitic Variety of the granite (Type 3; Richey, 1928). The granite is chloritized for a width of 2-4 in. along the margins of a few rather open joints. One of these fissure veins contains gal as a film up to 3 mm. thick; gal is also finely disseminated throughout the central part of the vein. Assn: sph, chpy, covelline. (Robbie, 1955).

63. Slieve Binian B. Gal sample for isotopic analysis taken from opposite end of 6 in. hand specimen of vein material to No. 62.

MOORBATH'S IRISH GALENA SPECIMENS

M84. Castleward, Co. Down. (A. Fowler). 1 in. 49, 6 in. Down 31 SE. Gal from vein in Sil seds (Cole, p.94).

M85. Conlig Mine, Co. Down. (A. Fowler). 1 in. 37, 6 in. Down 6 NW. Gal from vein in Ord or Sil seds. (Cole, p.94; Fowler, 1959).

M86. Creggan, Co. Armagh. (A. Fowler). 1 in. 70, 6 in. Armagh 31 NW. Gal from crush-breccia of Lr Pal Grit, associated with ba. (Cole, p.101; Fowler, 1959).

M87. Glendalough, Co. Wicklow; Ruplagh Mine. (F. W. Dunning). 1 in. 130, 6 in. Wicklow 17 SW. Gal from vein traversing margin of Leinster Granite. (Cole, p.110).

M88. Glenmalure, Co. Wicklow. (F. W. Dunning). 1 in. 130, 6 in. Wicklow 23 SW. From vein traversing marginal part of Leinster Granite. (Cole, p.113)

M89. Barrystown, Co. Wexford. (F. W. Dunning). 1 in. 169, 6 in. Wexford 45 NE. From vein cutting Lr Pal sediments of considerable thickness. (Cole p.125).

M90. Avoca Mine, Co. Wicklow. (G. J. Murphy) 1 in. 139, 6 in. Wicklow 35 NW. Specimen No. 271. Gal from South Lode facies, showing relatively coarse-textured Pb-Zn-Cu-Fe sulphides, with qz (Cole, pp. 30, 84, 139, 144; G. J.Murphy, 1959).

M91. Avoca Mine, Co. Wicklow. (G. J. Murphy). Specimen No. DP 21. Gal from typical South Lode facies; see No. 90.

M92. Avoca Mine, Co. Wicklow. (G. J. Murphy). Specimen No. 3C. Gal from Pond Lode facies, v fine-grained dense aggregate of Pb-Cu-Fe-Zn sulphides without qz and with general banded distribution. Also known as "Kilmacooite" facies or "Bluestone".

M93. Avoca Mine, Co. Wicklow. (G. J. Murphy). Specimen No. B8A, 548 ft. From a small borehole core in Pb-Zn rich portion of Pond Lode facies.

M94. Abbeytown, Ballysadare, Co. Sligo. (J. A.V. Douglas). 1 in. 55, 6 in. Sligo 20 NW. From replacement in Carb 1st, ca. 250-300 ft. above unconformable junction with metamorphic rocks of probable Moine age. (Cole, p.95).

M95. Sheeffry Mine, Co. Mayo (Dr. K. C. Burke). 1 in. 84, 6 in. Mayo 107 SW. From N-S lode traversing Lr Pal seds. Ore is said to be highly argentiferous (Cole, p.101).

M96. Clements Mine, Carrowgarriff, Co. Galway (Dr. K. C. Burke). 1 in. 94, 6 in. Galway 39 NW. Locality is 2 m. SE of Maum and ¼ m. N of the most westerly prolongation of Lough Corrib. Gal from vein traversing Connemara schists, associated with py, chpy. (Cole, p.102).

M97. Glengowla Mine, nr. Oughterard, Co. Galway. (Dr. K. C. Burke). 1 in. 95, 6 in Galway 54 SW. Locality is S of the road from Oughterard to Clifden in Glengowla townland, 2 m. W of Oughterard. From vein in Connemara schists, associated with cc, ba, sph, fl. (Cole, p.102).

M98. Gloosh Mine, Oughterard, Co. Galway. (F. W. Dunning). 1 in. 105, 6 in. Galway 54 SW. Ca. 1½ m. S of Oughterard. Gal from vein traversing Connemara schists, associated with ba. (Cole, p.103).

M99. O'Flaherty's Shaft, Oughterard, Co. Galway. (S. Moorbath) 1 in. 105, 6 in. Galway 54 NW. Ca. 1 m. WSW of Oughterard. Small veins and pockets of gal in Oughterard Granite, very near its margin with the schist.

M100 Lough Corrib shore, Oughterard, Co. Galway. (S. Moorbath). 1 in. 105, 6 in. 54 NE. 1 m. NE of Oughterard. Gal from 2-3" wide N-S cc vein, traversing Carb lst. The vein actually cuts large fossil clusters (corals, bryozoa, etc.). The basement granite is estimated at 200-300 ft. below the surface.

FRANCE (These notes translated from the French).

64. Pierreville, Manche, Normandie (No. 9688α). Mine 6 km. from Les Pieux, 12 km. from Briquebec. This mine was worked in the 18th century and was the subject of some enterprise in 1913-14. Prof. Kerforne of Rennes did investigate it in 1920's, but little to no information is available on its geological setting. According to the geological map of Normandie, the mineralisation occurs in Dev seds. Sample: massive gal. Assn: sph, py, cer, angl(?).

65. Huelgoat, Finistère (No. 263α). Mine 4 km. ESE of Huelgoat, ca. 1 km. due SW of hamlet of La Bruguec. Dev and earlier sedimentary country rock complex consists of shales with Spirifer, shales with laumonite, green beds, grauwacke (calc shales) and graphite shales, all with veins of qz porphyry. The Huelgoat granite with which this qz porphyry is associated is post-Dev and is referred by structural analogy to the Namurian. Three qz seams occur in the direction N 20°W and cut the Dev and Dinantian shales. Sample: massive gal. Assn: qz, py, chpy, native Ag, sph, pymor, cer, angl, Pb phosphate (?), cerargyrite, bromargyrite.

66. Poullaouen, Finistère (No. 699β). 1 km. NNW of Poullaouen, 11 km. NNW of Carhaix, 4.5 km. E of Huelgoat mine (No. 65). Geological setting as for No. 65. The main lode trends N 20°W. The lodes are only contained within Dinantian shales and sst (shales of Chateaulin). Sample: massive gal. Assn: sur alt prods.

67. Trémuson, Côtes-du-Nord (No. 4989α). 7 km. W of St. Brieuc, 2 km. N 60°E of Trémuson. The country rock consists in general of shales with

diorite and 2-mica gneiss. These are all cut by a system of dolerite dykes with NNW and, to a lesser extent, ENE trends. Gal occurs in perpendicularly-intersecting NNW and ENE veins, the latter being predominant and in the vicinity of a ENE dolerite dyke, although no proof is given of any connection between the veins and dykes. The country rock of veins, shales and diorite were all folded by Hercynian movements. In the range of important fractures there are more than 100 veins and veinlets in the complex of green rocks (quartzic and feldspathic amphibolites, banded crushed doleritic gabbros, quartzic diorite and compact quartzites (leptynites?). Mineralisation occurs in the vicinity of outcrops of diorite with qz gangue. Sample: massive gal. Assn: qz, sur alt prods.

68. Le Hinglé, Côtes-du-Nord (No. 719 β). At village of Hervé-en-Bruslivy, 10 km. S of Dinan, at the boundary of communes of Le Hinglé and Bruslivy (no mine). Qz vein in direction N 25°E which cuts mica schists and granulitic gneiss to S, and 2-mica granite (granulite) of massif of Dinan to N. Iron hat ("chapeau de fer") with argentiferous gal and associated minerals. No detailed research made of this deposit. Sample: med gr gal (v little) in decomposed gangue. Assn: qz, Fe ox, cer, pymor, py.

69. La Touche A, Ille-et-Vilaine (633 β). At Vieux-Vy-sur-Couesnon, 30 km. NNE of Rennes at confluence of the Minette and the Couesnon. The deposit is probably connected with granite massif of Fougères - a granite rick in biotite and perhaps of Precambrian age. The qz vein runs N 160°E, accompanied by a 2-mica granite. Folding is NW-SE. Sample: massive gal. Assn: qz, sph, py (with radiating structure), stibnite (less frequent), sur alt prods.

70. La Touche B, Ille-et-Vilaine. Location and geology as for No. 69. Sample: massive gal. Assn: py, qz.

71. Pont-Péan, Ille-et-Vilaine (No. 10288 α). 10 km. S of Rennes. Emplaced within a series of shales cut by nearly vertical dolerite dykes, running approx. N 20°W, with gal vein in lower side of the dolerite adjacent to the shales. On the grounds that the dolerites elsewhere cut the Hercynian granites, they are referred to the Permian. There is no evidence for Tertiary mineralisation. Sample: coarsely crysln gal. Assn: qz, sph, py, marcasite (small).

72. La Chapelle St. Melaine A, Ille-et-Vilaine (No. 8352 α). 12 km. ENE of Redon. Vein in direction N 65°E cutting obliquely the slaty beds of the Middle and Lr Ord directed N 110°E. The complex vein is quartzose and ramified, with py dominating and gal only in small amt. Sample: med gr gal. Assn: qz, py, sph, chpy, covellite.

73. La Chapelle St. Melaine B, Ille-et-Vilaine. Location and geology as for No. 72. Sample and Assn: as for No. 72.

74. St. Pierre Montlimart, Maine-et-Loire (No. 9056∝). Mine of La Bellière (gold mine), 40 km. E of Nantes, 14 km. S of Ancenis. A group of parallel veins stretch over a distance of 2 km. in E-W direction, and are emplaced in Precambrian shales. The veins are cut by many transverse faults which are referred to the Hercynian orogeny and go back at least as far as the mineralisation. Gal is rare. Sample: fine gr gal. Assn: qz, py, mispickel, chpy (small), sph(rare), grains of gold free and in the mispickel.

REFERENCE SAMPLES

75. Lambriggan, Perranzabuloe, Cornwall: 1 in. geol, 346, 6 in. Cornwall 48/SW. This sample was obtained as the same Pb S precipitate which Moorbath used for his mass spectrometric determinations of its Pb isotopic composition. This is No. 6 in Moorbath's thesis (1959b).

76. N. B.S. Reference Sample No. 200. Gal from Ivigtut, Greenland. 100 mg. supplied as powder sealed in vacuum in Pyrex tube.

77. N.B.S. Reference Sample No. 200 a. Lead iodide from gal (presumably also from Ivigtut, although not stated) - supplied as for No. 76.

APPENDIX III

SEPARATION OF PURE GALENA SAMPLES

A micropanner, a copy of that described by Muller (1958), was used for separating very pure galena samples from as much as 95% contamination for trace element analysis. A weired type of aluminium deck was fitted. The techniques developed are outlined briefly below:-

After crushing, samples were sized into two fractions (-80, +120 and -120, +200 mesh) for individual treatment on the panner, which required well-sorted samples for efficient separation. No more than 3 g. sample was handled on the panner at once. Tests showed that water was less suitable as a wash liquid than bromoform, double-distilled samples of which were used throughout. Light gangue grains (e.g. quartz, calcite) were floated off in a preliminary bromoform washing before adding to the pan. Clean separations were obtained at the maximum motor rate (650 longitudinal vibrations/min. and 36 transverse rockings/min.) by adjusting the longitudinal slope of the deck and the rate of flow of the bromoform as required by the individual behaviour of each sample. Clean "heads" of galena were removed with dropping pipettes into evaporating dishes.

The most difficult separations occurred when the alteration products anglesite and cerussite were present. Their small density differences from galena made it necessary to remove only the very tip of the material column on the pan. during each of a large number of separate panning operations.

Once sufficient galena had been separated, it was washed twice with benzene (Analar grade). Supernatant benzene was decanted off and the sample dried under an infra-red lamp. Examination under a binocular microscope revealed the presence of any contaminating grains, in which case the separation was repeated.

This method was successfully applied to 60 galena specimens. It was unsuccessful in only two cases, both specimens coming from Kilmacoo, Co. Wicklow, Eire, in which there was such a fine-grained mixture of galena with pyrite, chalcopyrite and sphalerite that separate galena grains did not exist in even the smallest crushed sample.

Contamination was carefully avoided by thorough cleaning of the micro-panner between operations, the reservation of a special agate mortar and pestle for crushing, and the use of the purest available bromoform and benzene.

The use of this separation procedure for even the visually cleanest galenas was justified by the invariable observation of some contamination separating out on the micropanner. This was presumably due to small amounts of surface contamination and alteration on the cleavage planes of the galena.

APPENDIX IV

TRACE ELEMENT CONTENT OF GALENAS BY NEUTRON ACTIVATION ANALYSIS.

IV. (1) INTRODUCTION

Cahen et al. (1958) studied the isotope and trace element composition of some galenas from Africa and Europe. Emission spectrographic techniques were used for the trace element analyses. They found that when the lead model age was normal, the silver content was high; when the model age was older than the host formation (B-type galenas), silver content was low. The aim of this study was to analyse for trace element content some of the British galenas whose model ages have been determined by Moorbath and the author, included among which is a number of B-type galenas, notably from the Scottish Highlands and Western Ireland.

Emission spectrographic analysis is a rapid and convenient technique for detecting variations in trace elements in the large number of samples necessary for an adequate study of this nature, but it suffers from a low absolute accuracy. El Shazly et al. (1956), in the only concerted study of the trace element content of British galenas, claimed 20-50% precision for their emission spectrographic techniques, but their figures are also liable to considerable systematic errors. On the other hand, neutron activation analysis can possess a high degree of accuracy, precision and sensitivity, but the production of results is generally slow. It was intended to combine the advantages of each technique by analysing a suite of galenas for silver by neutron activation and using these samples as accurate reference standards for the later emission spectrographic analysis. At the same time as analysing for silver by neutron activation, the samples were also to be analysed for thallium (its invariable

presence in galenas has been noted in the mass spectrometry) and gold. No figures are available for the content of gold in galenas. Emission spectrographic analysis for thallium is hampered by its low spectral sensivity of 10 p.p.m. (Fleischer, 1955; el Shazly et al., 1956).

The nine galenas selected for analysis comprised four from each of the Northern and Southern Pennines mineralised areas provided by Moorbath (geological details given in his thesis, 1959 b), and one supplied by D. F. C. Morris as a reference sample (from Milltown, Co. Clare, Ireland - No. 28 in Appendix II of this thesis), for which he had determined the silver content after originally developing the methods used in this study (Morris and Killick, 1959; Specimen 2 G).

This study is not yet complete because no B-type galenas have been analysed, but the techniques used and the results obtained so far are briefly reported in this Appendix. The principles, applications and limitations of neutron activation analysis are given in many review articles (e.g. Jenkins and Smales, 1956) and are not discussed here.

IV. (2) EXPERIMENTAL TECHNIQUES.

Only those parts of the methods which were developed in this work are reported here.

Mineralogically pure galena samples were separated from the specimens provided by the methods described in Appendix III. The reference sample from Milltown was provided in the powdered form. All samples were ground very fine before sealing ca. 100 mg. of each in silica tubes before irradiation for three days in a neutron flux of ca. 10^{12} neutrons/cm.^{2}/sec. in the Harwell BEPO pile.

The solution of the irradiated galena was effected with aqua regia. After addition of inactive carriers (30 mg. gold foil, 2 ml. each of silver and

thallium standard solutions containing ca. 20 mg. of each element), solution was boiled nearly to dryness, 3 ml. conc. HCl added and cooled. The residue contained silver and some lead and the supernate contained gold and thallium and remaining lead. The supernate was heated nearly to boiling and 2-3 ml. 10% alcoholic solution of hydroquinone added to precipitate metallic gold. The new supernate was again heated nearly to boiling and SO_2 passed for several minutes to reduce Tl^{3+} to Tl^{+}, the excess boiled off and solution cooled before precipitation of thallium and lead with 5 ml. 6 M HCl. After standing overnight, this residue was combined with that from the silver chloride precipitation step, and boiled repeatedly with water to dissolve out lead and thallous chlorides, leaving residue of silver chloride. The washings were boiled until clear and 1 ml. of hold-back carrier (containing 1 mg. each of Ca, Ba, Sr, Ni, Mn) added, followed by 5 ml. 10% K_2CrO_4. The washed residue was warmed very gently with 10 ml. 3M NaOH to dissolve out lead chromate, leaving thallous chromate as a residue.

With the metallic gold, silver chloride and thallous chromate now separated from other major elements, the radiochemical purification steps were taken up at the appropriate stages as outlined by:-

(a) Gold: Method of Vincent and Crocket (1960), except that very dilute gold solutions in strong acid were used as irradiation standards.

(b) Silver and thallium: Method of Morris and Killick (1959, 1960) with modifications of D. B. Adams (1960). Adams reports satisfactory half-life and absorption characteristics determinations. All the methods described were found satisfactory. At least 10,000 counts were taken in all activity measurements. The paralysis correction proposed by Klug and Alexander (1954) was applied.

viz. $N = \frac{N_o}{(1 - N_o t)}$

N = true counting rate
N_o = observed " "
t = resolving time (= dead time)

This was tested thoroughly with a uranium standard, and was found to provide excellent corrections up to 10,000 c.p.m. for both dead time settings (800 and 300 μsec.) on the Panex Type D 54 counting and scaling unit used.

Morris and Killick (1959) claim that silver iodate shows no self-absorption characteristics. An investigation of this possible source of error was undertaken with Adams, which will be more fully reported in his B.Sc. thesis (1961). Samples of silver iodate of the same specific activity but differing weights were prepared and counted on two occasions, two months apart. Both series of results showed a linear relation between specific activity and precipitate weight, the specific activity being distinctly lower for higher weights. The magnitude of the effect was 0.47% decrease in specific activity per mg. increase of precipitate weight for the first count, and 0.34% for the second; the average of 0.4% was used for correction purposes. This significant correction was applied to calculate the specific activity of each sample at zero precipitate weight.

IV. (3) RESULTS.

(a) Gold: The analyses for gold were not very successful, only three samples remaining after the separation procedure for the following reasons:-

(i) The initial separation of gold by precipitation with alcoholic hydroquinone also caused reduction of some thallium and its precipitation as the chloride. Much gold was mechanically lost in the subsequent purifying steps.

(ii) The difficulty of precipitating and plating out gold in a finely divided form was never completely overcome.

(iii) The very low gold contents of the galenas resulted in low counts above background.

(iv) The gold standards used, although extremely dilute (e.g. 3.35 μg. Au irradiated, diluted to 500 ml., 5 ml. aliquots taken), were very highly active (e.g. 41,000 c.p.m., giving specific activity 1,227,000 c.p.m./μg. Au)

Nevertheless these difficulties could be overcome with further work, for which the following suggestions are made:-

(i) A longer irradiation is necessary.

(ii) Even more dilute standard solutions should be used.

(iii) The acid concentration must be very low before precipitation of the gold with hydroquinone.

The following preliminary results are only semi-quantitative, but they do at least indicate the level of gold in these galenas.

Sample	Gold Content (p.p.m.)
Millclose, Derbyshire	0.002
Wheels Rake, Derbyshire	0.001
Riber, Derbyshire	0.004

(b) Thallium (Table 41): After consideration of the invariable appearance of thallium in the mass spectra of lead from galenas and reports of many high thallium-containing galenas (Fleischer, 1955), the level of thallium found in these galenas was unexpectedly low. Counting rates for samples were very low (e.g. 15 c.p.m. above background) and susceptible to considerable error from background corrections, particularly as the background count at the time of this work was unusually variable (9 - 16 c.p.m.). The accuracy of the results quoted is unlikely to be better than 20%, although duplicates agreed remarkably well considering the low activities. Nevertheless, these figures are adequate for the purpose of detecting significant regional variations.

(c) Silver (Table 41): Satisfactory levels of activity, more reliable radiochemical separations and general close agreement between duplicates make a 5% accuracy estimate for the results quoted not unreasonable. The agreement

TABLE 41.

Thallium and Silver Contents of Galenas

Sample Location	Tl Content (p.p.m.)	Ag Content (p.p.m.)
NORTHERN PENNINES		
Barbary	1.0	50
Rotherhope Fell	1.3	60
Settlingstone	1.2	37
Sedling	0.5	165
SOUTHERN PENNINES		
Millclose	0.3	20
Moletrap	1.2	17
Wheels Rake	0.5	13
Riber	0.6	15
REFERENCE SAMPLE		
Milltown, Co.Clare, Eire	1.6	920

(Morris & Killick (1959) : 1100)

obtained with Morris and Killick's figure for the reference sample was not close, but their figure was uncorrected for self-absorption effects. If self-absorption corrections are not made, the 920 p.p.m. figure is increased to 1080 p.p.m. which is very close to Morris and Killick's figure.

The thallium and silver results quoted in Table 41 are the means of duplicate determinations.

IV. (4) DISCUSSION.

The thallium results do not demonstrate any significant variation between the Northern and Southern Pennines groups.

But with the silver results a significant difference between the two areas is immediately apparent. The Southern Pennines figures group so closely together that an average value for these four samples of 16 p.p.m. is meaningful. The Northern Pennines galenas have considerably higher silver contents than the Southern Pennines galenas. The high figure for the Sedling galena would make an overall average somewhat unrepresentative, but it is significant that the average of the other three Northern Pennines galenas (49 p.p.m.) is three times greater than that of the four Southern Pennines galenas, with a large gap between the highest Southern figure and the lowest Northern figure.

It is interesting to note that el Shazly's (1956) spectrographic analyses give an average of 65 p.p.m. silver for nine Northern Pennines galenas, and 25 p.p.m. for four Southern Pennines galenas - in reasonable agreement with this work. Also Moorbath's (1959) lead isotope studies of the same samples analysed in this study give mean model age values of 280 m.y. for Northern Pennines and 180 m.y. for Southern Pennines, an experimentally significant difference. The interesting possibility thus appears of being able to

associate together characteristic groupings of normal model ages and silver contents for particular lead deposits.

The sensitive techniques used here would allow distinctions to be drawn between lead deposits with low silver contents.

With this in mind, the data of el Shazly have been re-examined to select deposits which were definitely sampled both by el Shazly and Moorbath, and correlations have been sought between the former's trace element figures and the latter's model ages.

The results are given below:-

No. Specimens	Model Ages (m.y.)	Mean Ag Content (p.p.m.)	Mean Sb Content (p.p.m.)
7	420 - 470	1600	1600
4	340 - 370	100	350 ≠
8	240 - 310	180*	330
5	150 - 220	60	330 ≠

* Including one specimen of 1000 p.p.m. Ag. Exclusion of this would reduce mean Ag content to 65 p.p.m.

≠ Sb contents quoted for three specimens only.

Except perhaps for tin, other trace element figures quoted by el Shazly are insufficient for any comparison. Despite the limitations of these comparisons, they do provide considerable encouragement for the possible success of full-scale joint isotope and trace element studies of mineralisation in the British Isles.

In addition to indicating the value of further work in this field, the analyses reported here have provided a series of galenas for use as independent standards for emission spectrographic analysis of galenas for silver. The galenas themselves provide a range of concentrations from 13 to 165 p.p.m. with one of 920 p.p.m.; intermediate values could be obtained from quantitative mixtures of the galenas.

APPENDIX V

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R.P.C.P.

COMPUTER PROGRAMMES, DATA AND RESULTS

(for Chapter 7)

TABLES 14, 16, 17, 18, 19, 23, 24
25, 26, 27, 28, 29, 30.

These are bound in the following pages facing the opposite way to the preceding text and tables, because the margin left by the teleprinter is too small to allow binding on the left-hand side.

The typewritten notes are in red to distinguish them clearly from the teleprinting.

TABLE 14.

Data for Mass Spectrometer Calculation Programmes.

```
RUN P204 GORTSHANROE IS57 1ST DETN RPCP
26
-3
197  200  235  129  129.5  231  196  190
190  195.5  227  123.5  122  219  184.5  178.5
177  179.5  209  114  111.5  200  167.5  160
155.5  157  194  109  107  *191  163.5  158
155.5  158.5  183  100  98.5  175  148  142.5
141  143.5  167.5  90  88  157.5  134  128.5
127.5  129.5  151  81.5  81  145  122  117.5
-4
116.5  118.5  138  152  150  133  111.5  108.5
107  109  12*7  141  136  120  101.5  98
96.5  99  116  127  126  112  94  90
90  91.5  106  116.5  115  102.5  86  83
-3
182  184.5  216  117  115.5  206  173.5  166
163  168  196  106  105  187  158  153.5
152  154.5  180  97  96.5  174  147  142.5
142.5  144.5  168.5  92.5  91  162  136  130
-4
129.5  132  153  166  165  146  123  118.5
118  119.5  138  152.5  149  132  112  108.5
108  109  127  140  138  123.5  104.5  100
100  103  120  130.5  131  116  97.5  94
94  96.5  113  123  122.5  108.5  91  89
-3
167  171  197  106.5  105  188.5  159  152
150.5  152  176  95  94  168  140.5  134
133  135  157  85  83  149  125  120
-4
119  121  140.5  153  150.5  133.5  112.5  107.5
107  108  124.5  136  132  117  98  94
94  96  111.5  122.5  120  106  91  87.5
>
```

Title of run
No.of scans (N)

Range factor code no.applying to all following scans until next code no.

New range factor code no.

Peak heights in mm (1 scan per line)

Peak heights are printed in order of appearing on chart, thus

Isotope :	208	207	206	204	204	206	207	208
Symbol for Peak Height:	a_o	b_o	c_o	d_o	d_1	c_1	b_1	a_1

CHARTER0

A>8

100)Q=0

1)600(1)

JUMP1,I=27

620(1)

3)600(1)

JUMP99,I=30

630(1)

JUMP3

99)600(1)

620,0

630,14

620,27

620,14

630,5

620,23

620,0

620,14

620*,27

620,16

630,11

620,0

620,14

620,27

620,8

630,20

620,19

620,0

620,30

620,13

READ(N)

PRINT(N)2,0

630,30

620,13

M=N+Q

I=1(1)M

3)READ(A)

JUMP4,A>0

PRINT(A)2,0

Q=Q+1

M=N+Q

620,30

620,13

J=1(1)8

READ(AJ)

REPEAT

JUMP99

4)A1=A

J=2(1)8

READ(AJ)

REPEAT

99)J=1(1)8

JUMP5,210.5>AJ

PRINT(AJ)3,2

JUMP23

TABLE 16 (2

Programme for Correction for Recorder Non-Linearity.

Read and print title at head of data.

Add "NEW PK HTS" to data.

Read and print number of scans in data.

Read first number in line.

If positive, jump to 4).

If negative, print it (range factor code number).

Count number of negative numbers.

Add Q to N.

New line.

Read the 8 peak heights in the scan.

Jump into correction sequence.

Set first no. in line (positive) to A_1.

Read remaining 7 numbers in line.

Start of correction sequence.

If number is less than 210.5, jump to 5).

If " "greater " " , print it and jump to 23).

(TABLE 16, 2nd page)

```
5)JUMP6,180>AJ
PRINT(1.001AJ)3,2
JUMP23
6)JUMP7,160>AJ
PRINT(1.002AJ)3,2
JUMP23
7)JUMP8,150>AJ
PRINT(1*.003AJ)3,2
JUMP23
8)JUMP9,140>AJ
PRINT(1.004AJ)3,2
JUMP23
9)JUMP10,130>AJ
PRINT(1.005AJ)3,2
JUMP23
10)JUMP11,120>AJ
PRINT(1.006AJ)3,2
JUMP23
11)JUMP12,110>AJ
PRINT(1.007AJ)3,2
JUMP23
12)JUMP13,100>AJ
PRINT(1.008AJ)3,2
JUMP23
13)JUMP14,90>AJ
PRINT(1.009AJ)3,2
JUMP23
14)JUMP15,80>AJ
PRINT(1.01AJ)3,2
JUMP23
15)JUMP16,70>AJ
PRINT(1.012AJ)3,2
JUMP23
16)JUMP17,60>AJ
PRINT(1.013AJ)3,2
JUMP23
17)JUMP18,50>AJ
PRINT(1.015AJ)3,2
JUMP23
18)JUMP19,40>AJ
PRINT(1.017AJ)3,2
JUMP23
19)JUMP20,30>AJ
PRINT(1.02AJ)3,2
JUMP23
20)JUMP21,20>AJ
PRINT(1.024AJ)3,2
JUMP23
*21)JUMP22,10>AJ
PRINT(1.028AJ)3,2
JUMP23
*22)PRINT(1.033AJ)3,2
23)REPEAT
620,30
620,13
REPEAT
JUMP100
CLOSE
****
```

If number is less than 180, jump to 6).
If " " greater " 180, multiply it by 1.001 (correction factor), print it and jump to 23).

Continue until correct interval found for number. Multiply by appropriate correction factor, print corrected number and jump to 23).

Repeat correction sequence for all 8 numbers in each line.

New line.

Repeat complete sequence, i.e. start at 3)

At end of one set of data restart whole programme for new set of data.

TABLE 17.

Results of Programme for Correction for Recorder Non-Linearity

(Using data of Table 14).

RUN P204 GORTSHANROE IS57 1ST DETN RPCP NEW PK HTS

26
-3

197.2	200.2	235.0	129.8	130.3	231.0	196.2	190.2
190.2	195.7	227.0	124.2	122.7	219.0	184.7	178.9
177.4	179.9	209.2	114.8	112.3	200.2	167.8	160.3
156.0	157.5	194.2	109.9	107.9	191.2	163.8	158.5
156.0	159.0	183.2	100.8	99.4	175.3	148.6	143.1
141.6	144.1	167.8	90.8	88.9	158.0	134.7	129.3
128.3	130.3	151.5	82.3	81.8	145.6	122.7	118.3

-4

117.3	119.3	138.7	152.5	150.4	133.7	112.3	109.4
107.9	109.9	127.8	141.6	136.7	120.7	102.3	98.9
97.4	99.9	116.8	127.8	126.8	112.8	94.8	90.8
90.8	92.3	106.8	117.3	115.8	103.3	86.9	83.8

-3

182.2	184.7	216.0	117.8	116.3	206.2	173.8	166.3
163.3	168.3	196.2	106.8	105.8	187.2	158.5	154.0
152.5	155.0	180.2	97.9	97.4	174.3	147.6	143.1
143.1	145.1	168.8	93.3	91.8	162.3	136.7	130.6

-4

130.3	132.7	153.5	166.3	165.3	146.6	123.7	119.3
118.8	120.3	138.7	153.0	149.6	132.7	112.8	109.4
108.9	109.9	127.8	140.6	138.7	124.2	105.3	100.8
100.8	103.8	120.7	131.2	131.7	116.8	98.4	94.8
94.8	97.4	113.8	123.7	123.2	109.4	91.8	89.9

-3

167.3	171.3	197.2	107.4	105.8	188.7	159.5	152.5
151.0	152.5	176.4	95.9	94.8	168.3	141.1	134.7
133.7	135.7	157.5	85.8	83.8	149.6	125.7	120.7

-4

119.8	121.7	141.1	153.5	151.0	134.2	113.3	108.4
107.9	108.9	125.2	136.7	132.7	117.8	98.9	94.8
94.8	96.9	112.3	123.2	120.7	106.8	91.8	88.4

Isotope	208	207	206	204	204	206	207	208
Symbol for Peak Height	a_o	b_o	c_o	d_o	d_1	c_1	b_1	a_1

These results are in exactly the same form as the data of Table 14, and can be used directly in the mass spectrometer calculation programmes (e.g. Table 18).

TABLE 18 (8 pages)

Lead Mass Spectrometer Calculation Programme B

```
TITLE
LEAD MASS SPECTROMETER/REDUCED PRINTING/RPCP/SAT
                    (Specimen data in Table 17 was
CHAPTER 1           applied to this programme to
A→30                give results in Table 19).
B→30
C→30
D→30
E→30
£→30
W→30          Programme will accept up to a
X→30
Y→30            maximum of 31 scans in each
Z→30
F→30            set of data for calculation.
G→30
V→30          Queries must be suppressed in running programme.
U→30
H→30
7)X10(500,68) Read range factors: store in location 500.
HALT
1)600(I)      Read and print title
JUMP1,I≠27.
630(I)          on data type, starting
2)600(I)
630(I)          with Letter Shift and
JUMP2,I≠30
620,13          ending with Carriage Return.
620,13
READ(N)       Read and print number of
PRINT(N)2,0     scans in run (N).
NEWLINE
I=1(1)N       Count and print
PRINT(I)2,0     scan number (I).
READ(R)       Search for range factor
JUMP3,0>R       code number -R,
A0vR            identified by minus sign.
JUMP4
3)Mv-R
READ(A0)      Read peak heights in scan
4)READ(B0)
READ(C0)        in order of appearance in
READ(D0)
READ(DI)        data and assign them these
READ(CI)
READ(BI)        symbols (see Tables 14, 17).
READ(AI)
X6(496+4M)G1,4 Bring relevant range factors from store.
Lv0
J=0(31)93     Calculate mean total peak heights in
L=L+1           order of isotopes 208, 207, 206, 204.
K=I+J
AK=AJ+AK
AK=0.5AKGL
REPEAT
```

TABLE 18

Key Linking the Symbols used in Pages 85 & 86 and the Computer Variables used in this Programme

Symbol	Quantity	Programme Variable	Prog. Var. Found in this Table on :
x_i	206/204 for Scan i	CI	2nd page, line 21
y_i	207/204 " " "	BI	" " " 20
z_i	208/204 " " "	AI	" " " 22
P_i	Model age for Scan i	VI	3rd page, line 2
L_i	L.H.S. of H-H equation for Scan i	FI	2nd " , last line
R_i	R.H.S. of H-H equation for Scan i	GI	3rd " , line 6
V_i	U^{238}/Pb^{204} for Scan i	UI	3rd page, line 27
K_i	Th^{232}/U^{238} " " "	HI	" " " 33
a_{ic}	Corrected % 208 abundance for Scan i	WI	2nd page, line 9
$\bar{a}$	Mean % 208 abundance	Wn/R	(6th " " 16 (7th " " 3
σ_i	Deviation of a_{ic} from $\bar{a}$	WI	6th " " 16
r	Number of non-rejected scans	R	5th " " 29
S_a	Twice standard error of $\bar{a}$	2W/R	7th " " 4

Table 18 (2nd page)

```
£I=AI+BI+CI+DI
£I=1/£I
J=0(31)93
K=J+1
WK=100AK£I
REPEAT
£I=1.01WI+1.007XI+1.005YI+ZI
£I=*1/£I
WI=101WI£I
XI=100.7*XI£I
YI=100.5YI£I
ZI=100ZI£I
NEWLINE
PRINT(WI)3,2
PRINT(XI)3,2
PRINT(YI)3,2
PRINT(ZI)3,3
NEWLINE*
DI=1**/DI
BI=1.007BIDI
CI=1.005CIDI
AI=1.01AIDI
YI=100/YI
DI=XIYI
EI=WIYI
J=0(31)124
K=1+J
PRINT(AK)3,2
REPEAT
YI=100/YI
PRESERVE
DOWN1/2
RESTORE
**REPEAT
ACROSS1/3
CLOSE
```

Calculate total of mean peak heights and its reciprocal.

Calculate % isotope abundances in order % 208, % 207, % 206, % 204.

Correct % isotope abundances for mass discrimination and print them.

Calculate isotope ratios 207/204, 206/204 208/204, correcting for mass discrimination at the same time.

Calculate isotope ratios 207/206 x 100, 208/206 x 100, corrected for mass discrimination.

Print isotope ratios.

Go to Chapter 2, Instruction 1).

Return here from end of Chapter 2.

Repeat for next scan.

When all scans finished, go to Chapter 3 to calculate totals and means.

```
CHAPTER 2
VARIABLES 1
3)I=1
BI=Bn/R
AI=An/R
CI=Cn/R
NEWLINE
NEWLINE
620,27
620,3
620,8
620,5
620,3*
620,11
1)****B=CI-9.50
A=BI-10.36
A=137.8A
?FI=B/A
```

Enter here from Chapter 5 for calculation of check values of P, V, K using final mean values of isotope ratios.

Print "CHECK".

Enter here from Chapter 1.

Calculate L.H.S. of Holmes-Houtermans equation (FI) from isotope ratios (see p.85).

Table 18 (3rd page).

```
J=0(1)300
VI=-500+10J
X=XEXP(0.0001541VI)
X=2.0006-X
Y=XEXP(0.000972VI)
?GI=XDIVIDE(X,79.3604-Y)
JUMP4,J>0
400(GI)
430(FI)
410,32
200,33+
210(S)
JUMP5
4)400(GI)
430(FI)
410,32
200,33+
260(S)
290(5)
JUMP2
5)REPEAT
2)NEWLINE
620,27,
620,16
620,0
PRINT(VI)4,0
UI=B/X
NEWLINE
PRINT(UI)2,2
C=AI-29.49
V=XEXP(0.0000499VI)
HI=XDIVIDE(A,1*.2517-V)
HI=HIC/B
NEWLINE
PRINT(HI)1,2
NEWLIN*E
Fn=200
X7(Fn+I)FI,1
X7(Fn+I+N)GI,1
X7(Fn+I+2N)VI,1
X7(Fn+I+3N)UI,1
X7(Fn+I+4N)HI,1
UP
XEXP
XDIVIDE
CLOSE
```

Model age (VI) is given trial values from -500 to +2500 m.y. in increments of 10 m.y..

Calculate R.H.S. of equation (GI) using trial values of VI.

For each value of VI

check value of (GI - FI).

Check the sign of this

function. Record the value

of VI for which this function

is a minimum, i.e. when the sign

changes. This is solution of equation.

Print "P".

Print solution of equation (model age in m.y.).

Calculate geochemical ratio U^{238}/Pb^{204}

and print it (see p.85).

Calculate geochemical ratio Th^{232}/U^{238}

and

print it. (see p.86).

Transfer these variables to auxiliary store.

Return to Chapter 1.

```
CHAPTER 3
VARIABLES 1
1)Anvo
Bnvo
Cnvo
Dnvo
Envo
Fnvo
Gnvo
Hnvo
Unvo
Vnvo
Wnvo
Xnvo
Ynvo
Znvo
X6(201)F1,N
X6(201+N)G1,N
X6(201+2N)V1,N
X6(201+3N)U1,N
X6(201+4N)H1,N
I=1(1)N
An=An+AI
Bn=Bn+BI
Cn=Cn+CI
Dn=Dn+DI
En=En+EI
Vn=Vn+VI
Un=Un+UI
Hn=Hn+HI
Wn=Wn+WI
Xn=Xn+XI
Yn=Yn+YI
Zn=Zn+ZI
REPEAT
W=Wn/N
X=Xn/N
Y=Yn/N
Z=Zn/N
NEWLINE
N*EWLINE
PRINT(W)3,2
PRINT(X)3,2
PRINT(Y)3,2
PRINT(Z)3,3
Q=0
I=1(1)N
E=XMOD(WI-W)
JUMP2,E>0.40
F=XMOD(XI-X)
JUMP2,F>0.40
G=XMOD(YI-Y)
JUMP2,G>0.40
H=XMOD(ZI-Z)
JUMP2,H>0.04
JUMP4
2)NEWLINE
```

Set these variables to zero.

Read these variables from store.

Calculate totals of all % isotope abundances and ratios and P, V, K values for each scan.

Calculate temporary mean values of % 208, % 207, % 206, % 204 and print them.

Examine deviation of each set of % isotope abundances from their respective temporary means.

If for a particular scan, either % 208 or % 207 or % 206 are more than 0.40 from their temporary means or % 204 is more than 0.040 from its temporary mean, reject all the values for that scan by JUMP 2.

```
620,27.
620,18
620,5          Print "REJECT".
620,10
620,5
620;3
620,20
620,0
620,14
PRINT(I)2,0    Print number of each scan rejected.
Q=Q+1          Count total number of rejected scans.
Wn=Wn-WI
Xn=Xn-XI
Yn=Yn-YI       Subtract all values of % isotope
Zn=Zn-ZI
An=An-AI         abundances and ratios and P, V, K
Bn=Bn-BI
Cn=Cn-CI         for each rejected scan from
Dn=Dn-DI
En=En-EI         their respective temporary totals.
Vn=Vn-VI
Un=Un-UI
Hn=Hn-HI
J=0(31)434     Put rejected
K=I+J
AKv0             scans to zero.
REPEAT
4)REPEAT       Repeat examination for next scan.
R=N-Q          R = No. of remaining (i.e. non-rejected) scans.
NEWLINE
620,27,
620;13
620,5
620,1          Print "MEANS".
620*,14
620,19
620;0
P=1(1)20
620,14
REPEAT
620,27.
620,19         Print "S".
620,5
NEWLINE*
ACROSS1/4      Go to Chapter 4.
xMOD
xSQRT
CLOSE
```

```
CHAPTER4
VARIABLES1
1)Avo
Bvo
Cvo
Evo
Dvo
Uvo
Vvo
Wvo
Xvo
Yvo
Zvo
I=1(1)N
JUMP2,WI=0
WI=WI-Wn/RCalculate deviation of each %208 value from final
WI=WIWI                                                    mean.
W=W+WI      Calculate square of each %208 deviation.
XI=XI-Xn/RProgressively sum the squares of all %208
XI=XIXI                                          deviations.
X=X+XI
YI=YI-Yn/R
YI=YIYI
Y=Y+YI
ZI=ZI-Zn/RCalculate the sum of squares of
ZI=ZIZI
Z=Z+ZI        deviations of all other calculated
AI=AI-An/R
AI=AIAI       values from their final means,
A=A+AI
BI=BI-Bn/R    similarly to above.
BI=BIBI
B=B+BI
CI=CI-Cn/R
CI=CICI
C=C+CI
DI=DI-Dn/R
DI=DIDI
D=D%+DI
EI=EI-En/R
EI=EIEI
E=E+EI
VI=VI-Vn/R%
VI=VIVI
V=V+VI
UI=UI-Un/R
UI=UIUI
U=U+UI
HI=HI-Hn/R
HI=HIHI
H=H+HI
2)REPEAT    Repeat above procedure for next scan.
W=xSQRT(W)
X=xSQRT(X)
Y=xSQRT(Y)
Z=xSQRT(Z) Calculate square roots of sums of
A=xSQRT(A)   squares of deviations of
B=xSQRT(B)
C=xSQRT(C)   all calculated values.
D=xSQRT(D)
E=xSQRT(E)
V=xSQRT(V)
U=xSQRT(U)
H=xSQRT(H)
ACROS%S1/5Go to Chapter 5.
xSQRT
CLOSE
```

```
CHAPTER5
VARIABLES1
1)PRINT(Wn/R)4,2
PRINT(2W/R)14,2
NEWLINE
PRINT(Xn/R)4,2
PRINT(2X/R)14,**2
NEWLINE
PRINT(Yn/R)4,2
PRINT(2Y/R)14,2
NEWLINE
PRINT(Zn/R)4,3
PRINT(2Z/R)14,3
NEWLINE
PRINT(Bn/R)4,2
PRINT(2B/R)14,2
NEWLINE
PRINT(Cn/R)4,2
PRINT(2C/R)14,2
NEWLINE
PRINT(An/R)4,2
PRINT(2A/R)14,2
NEWLINE
PRINT(Dn/R)4,****2
PRINT(*2D/R)14,2
NEWLINE
PRINT(En/R)4,1
PRINT(2E/R)14,1
NEWLINE
PRINT(Un/R)4,2
PRINT(2U/R)14,2
NEWLINE
PRINT(Hn/R)4,2
PRINT(2H/R)14,2
NEWLINE
620,27.
620***,16
Vn=0.5+0.1Vn/R
Vn=XINTPT(Vn)
PRINT(10Vn)3,0
V=0.5+0.2V/R
V=XINTPT(V)
PRINT(10V)18,0
NEWLINE
DOWN3/2
ACROSS1/1*
CLOSE
*
```

Calculate the final means of all % isotope abundances and ratios and P, V, K values, and twice the standard errors of these means, and print them in table (see Table 19, 3rd page).

Round final mean value of model age and twice the standard error of this mean to nearest 10 m.y. before printing them.

Go to Chapter 2, Instruction 3) for check calculations.

Go to beginning of Chapter 1 for next set of data.

```
 CHAPTERo
VARIABLESı
ACROSS7/ı
CLOSE

→
**********
200   100   100   10
200   100   100   4
100   40    40    4
100   40    40    2
40    20    20    2
40    20    20    1
40    10    10    1
20    10    10    1
200   100   200   10
200   100   200   4
100   40    100   4
100   40    100   2
100   40    20    2
100   20    40    2
40    20    40    2
40    20    40    1
40    10    20    1

→
**********
```

Steering tape

Start calculation.

Range Factors Groups

These are arranged in order from R = - 1 to - 17 (see Table 13).

TABLE 19 (3 pages).

Results of Programme B, using Data of Table 17.

)

LEAD MASS SPECTROMETER/REDUCED PRINTING/RPCP/SAT Prog.title

RUN P204 GORTSHANROE IS57 ,1ST DETN RPCP NEW PK HTS Title of data.

26 Total no. of scans.
1 Scan no.
52.26 21.33 25.02 1.390 % Isotope abundances.
37.61 15.35 18.01 85.23 208.87 Isotope ratios.
P 220 Model age in m.y.
8.80 V_P
3.83 K_P
2
52.11 21.43 25.08 1.381
37.73 15.51 18.15 85.46 207.81
P 320
9.11
3.84
3
52.06 21.40 25.15 1.388 % Isotope
37.50 15.42 18.12 85.10 207.00 abundances and
P 230 ratios are
8.93 all corrected
3.73 for mass
4 discrimination
52.01 21.19 25.37 1.427
36.46 14.86 17.78 83.53 205.02
P 330
7.89
3.30
5
52.25 21.43 24.93 1.385 For each
37.72 15.47 18.00 85.97 209.62 scan,
P 390 % isotope
9.05 abundances
3.92 appear in
6 the order
52.15 21.45 25.02 1.373 (L.to R.) of:
37.98 15.62 18.22 85.74 208.44
P 410 % 208
9.32 % 207
3.94 % 206
7 % 204
52.19 21.38 25.06 1.377
37.90 15.53 18.20 85.33 208.28
P 310
9.14
3.90
8
52.30 21.31 25.01 1.384
37.80 15.40 18.08 85.19 209.09
P 230
8.89
3.89

9
52.13 21.43 25.04 1.395
37.36 15.36 17.95 85.56 208.17
P 280
8.83
3.75
10
51.90 21.46 25.25 1.393
37.25 15.40 18.13 84.97 205.50
P 200
8.90
3.61
11
52.11 21.43 25.07 1.384
37.65 15.48 18.12 85.46 207.84
P 310
9.05
3.82
12
52.11 21.38 25.13 1.386
37.59 15.42 18.13 85.08 207.39
P 220
8.93
3.77
13
52.11 21.42 25.08 1.384
37.65 15.48 18.12 85.41 207.73
P 300
9.05
3.81
14
52.27 21.37 24.99 1.370
38.15 15.60 18.24 85.53 209.15
P 370
9.28
4.00
15
52.10 21.40 25.10 1.396
37.32 15.33 17.98 85.28 207.61
P 220
8.77
3.71
16
52.23 21.40 25.00 1.374
38.01 15.57 18.19 85.61 208.97
P 370
9.23
3.96
17
52.35 21.40 24.87 1.379
37.95 15.51 18.03 86.06 210.51
P 420
9.13
4.02
18
52.14 21.43 25.05 1.381
37.75 15.52 18.14 85.57 208.17
P 340
9.12
3.86

For each scan, isotope ratios appear in the order (L.to R.) of:
208/204
207/204
206/204
207/206 x 100
208/206 x 100

Isotope and model parameter results for scans 9 - 18.

```
19
  52.92     21.49     25.30      1.388
  37.42     15.49     18.26     85.31    206.07
P  290
  9.07
 3.69
20                                                  Isotope and
  52.08     21.37     25.16      1.385
  37.61     15.43     18.17     84.94    207.04     model
P  210
  8.96                                              parameter
 3.79
21                                                  results
  52.10     21.49     25.03      1.376
  37.88     15.62     18.19     85.89    208.21     for
P  430
  9.32                                              Scans 19-25.
 3.91
22
  52.18     21.38     25.06      1.379
  37.83     15.50     18.17     85.35    208.24
P  300
  9.09
 3.88
23
  52.11     21.41     25.10      1.380
  37.77     15.52     18.20     85.29    207.56
P  300
  9.12
 3.84
24
  52.16     21.42     25.04      1.378
  37.85     15.54     18.17     85.53    208.26
P  350
  9.18
 3.89
25
  52.18     21.43     25.01      1.379
  37.83     15.53     18.13     85.68    208.65
P  370
  9.16
 3.90
26
  52.16     21.52     24.94      1.381
  37.77     15.58     18.06     86.30    209.16
P  480
  9.26
 3.93


  52.14     21.41     25.07      1.384Temporary mean % abundances.
REJECT   4                              No. of each scan rejected.
MEANS                    E             Final means & twice the standard
  52.15                  0.04                % 208          error
  21.42                  0.02                % 207        of each.
  25.06                  0.03                % 206
   1.383                 0.003               % 206
  15.49                  0.03              207/204
  18.12                  0.03              206/204
  37.73                  0.09              208/204
  85.47                  0.13              207/206 x 100
 208.1                   0.4               208/206 x 100
   9.07                  0.06              V_P
   3.85                  0.04              K_P
P 310                    30          (T)   Model Age to nearest 10 m.y

CHECK                Check values computed using final mean isotope
P  320               Model age (P_o)                          ratios.
  9.07               V_P
 3.85                K_P
```

TITLE

TABLE 23.

LEAD MODEL AGE TABLE ONE PROGrG / RPCP / GM2

(Results for data attached below are given in Table 21)

```
CHAPTERo
A=o
J=o
F=o.5              1st value of F = 0.5
READ(B)
READ(C)
READ(D)            Read values of
READ(E)
PRINT(B)3,2          physical constants and
NEWLINE
PRINT(C)1,5          parameters given in data
NEWLINE
PRINT(D)1,5          for use in calculations
NEWLINE
PRINT*(E)1,5         and print them.
NEWLINE
NEWLINE
NEWLINE
NEWLINE
PRINT(F)1,3 Print 1st value of F. (L.H.S.of equation).
U=-1250     U = 1st trial value of V in m.y.
2)V=U+A     V progressively increases by 0.5 m.y. until
W=xEXP(CE)                                  solution found.
X=xEXP(o.oo1CV)Evaluate R.H.S. of Holmes-Houtermans
X=W-X
X=BX               equation (G) using trial value of V
Z=xEXP(DE)
Y=xEXP(o.oo1DV)  (see introduction to Table 21).
Y=****Z-Y
G=Y/X
H=G-F            Check difference between R.H.S. and L.H.S.
JUMP3,H≥oWhen difference 1st becomes non-negative, jump to 3).
AvA+o.5  If difference is negative, add 0.5 m.y.to A, i.e.to V.
JUMP2,6ooo≥V Jump to 2),unless V has increased to 6000 m.y.
3)Vn=*xINTPT(V)Round solution of equation (V) to nearest m.y.
PRINT(Vn)4,o  Print V (model age in m.y.)
U=V Set new 1st trial value of V = last solution of equation.
*FvF+o.oo1     Increase F by 0.001 for new calculation.
JvJ+1
A=o              Set A to zero for new calculation.
JUMP8,J≠5        Instructions for printing results
NEWLINE            and every 5th value of F in the
PRINT(F)1,3        forms of Tables 21, 22.
J=o
8)JUMP2,2.5≥F  Jump to 2), for new calculation, until F = 2.5.
xEXP
xINTPT
END
CLOSE
**************************
```

Data

```
137.8      U238/U235
0.1541     λ238 x 10^9 yr^-1.
0.972      λ235 x 10^9 yr^-1.
4.50       Age of earth
$
```

(Programme variable : B)
(" " : C)
(" ")
( )

TITLE

TABLE 24

LEAD MODEL AGE TABLE ONE PROG11 / RPCP / GM2

(Results for data attached below are given in Table 20,IV)

```
CHAPTERo
A=o
J=o
F=o.5
READ(B)
READ(C)
READ(D)
READ(E)
PRINT(B)3,2
NEWLINE
PRINT(C)1,5
NEWLINE
PRINT(D)1,5
NEWLINE
PRINT*(E)1,5
NEWLINE
NEWLINE
NEWLINE
NEWLINE
PRINT(F)1,2
U=-1250
2)V=U+A
W=XEXP(CE)
X=XEXP(o.oo1CV)
X=W-X
X=BX
Z=XEXP(DE)
Y=XEXP(o.oo1DV)
Y=****Z-Y
G=Y/X
H=G-F
JUMP3,H≥o
AvA+o.5
JUMP2,5ooo≥V
3)Vn=*XINTPT(V)
PRINT(Vn)4,o
U=V
*FvF+o.o1
JvJ+1
A=o
JUMP8,J≠5
NEWLINE
PRINT(F)1,2
J=o
8)JUMP2,2.5≥F
XEXP
XINTPT
END
CLOSE
**********************
```

The method of calculation of this programme is identical to that of Table 23, except that F is increased here in increments of 0.01 and so produces only 1/10th of the number of solutions produced by Table 23.

```
139
o.154
o.98
4.486
>
```

TABLE 25.

```
TITLE

LEAD MODEL AGE  TABLE TWO PROG 2D /**RPCP / GM2


CHAPTERo

J=o
V=-1500          1st value of V (in m.y.) for substitution
READ(B)            in R.H.S. of Holmes-Houtermans equation.
READ(C)
*READ(D)
READ(E)          Read values of
PRINT(B)3,2
NEWLINE            physical constants and
PRINT(C)1,5
NEWLINE            parameters given in data
PRINT(D)1,5
NEWLINE            for use in calculations
PRINT(E)1,5
NEWLINE            and print them.
*NEWLINE
NEWLINE
NEWLINE
NEWLINE
PRINT(V)4,o      Print 1st value of V.
2)W=xEXP(CE)
X=xEXP(o.oo1CV)  Evaluate R.H.S. of Holmes-Houtermans
H=W-X
H=BH               equation using given value of V.
Z=xEXP(DE)
Y=xEXP(o.oo1DV)    (see introduction to Table 20).
U=Z-Y
F=U/H
PRINT(F)1,5      Print value of R.H.S. to 5 decimals.
VvV+1            Add 1 m.y. to V. for next evaluation.
JvJ+1
JUMP4,J≠5        Instructions for printing results and
NEWLINE            every 5th value of V in table form
PRINT(V)4,o        similar to Tables 20-22.
J=o
4)JUMP2,5000≥V   Jump to 2), for next evaluation, until V =
xEXP                                                5000 m.y.
END
CLOSE
**********************
```

Data.

```
137.8
o.1537           As given in Table 23. Any values may be
o.9722             used for these constants and parameters.
4.50
→
*
→
```

TABLE 26 (3 pages)

```
TITLE
CALCULATION OF P,V,K FROM LEAD ISOTOPE RATIOS/PROG3C/RPCP/GM2

CHAPTER1
B→4*
C→1
D→2                    Set
E→1                    variables.
**W→6
X→2
Y→2
Z→7
1)Av0                  Set A to zero.
2)V=U+A                V is trial model age value.
W0=xEXP(B1B4)
W1=xEXP(0.001B1V)      Evaluate R.H.S. of Holmes-Houtermans
W1=W0-W1                 equation (G) using trial value of V
W2=B0W1                  (see introduction to Table 20).
W3=xEXP(B2B4)
W4=xEXP(0.001B2V)
W4=W3-W4
G=W4/W2
H=G-F                  Check difference between R.H.S. and L.H.S.
JUMP3,H≥0 When difference 1st becomes non-negative, jump to 3).
Av A+0.5   If difference is negative, add 0.5 m.y.to A,i.e.to V.
JUMP2,500>A            Jump to 2), if A has not increased to 500 m.y.
3)V=xINTPT(V)          Round solution to equation (V) to nearest m.y.
620,27                 Print  " P = "
620,16
620,0
620,10
PRINT(V*)4,0           Print V (model age in m.y.).
Vn=xINTPT(0.1V+0.5)    Round V to rearest 10 m.y.
Vn=10Vn                  for ensuing calculations.
W5=xEXP(0.001B1Vn)
W5=W0-W5               Evaluate geochemical ratio U238/Pb204(Vp).
W6=X2/W5
620,27
620,22                 Print  " V = "
620,0
620,10
PRINT(W6)2,2           Print value of Vp
Z2=Z0-29.49
Z3=Z2/X2
Z4=xEXP(B3B4)
Z5=xEXP(0.001B3Vn)     Evaluate geochemical ratio Th232/U238(Kp).
Z6=Z4-Z5
*Z7=W*5/Z6
Z7=Z3Z7
620,27                 Print  " K = "
620,11
620,0
620,10
PRINT(Z7)2,2           Print value of Kp
ACROSS2/0              Go to Chapter 0.
*xEXP
xMOD
xINTPT
CLOSE
```

```
CHAPTERo
VARIABLESı
ı)READ(Bo)
READ(Bı)
READ(B2)
READ(B3)
READ(B4)
PRINT(Bo)3,2
NEWLINE
PRINT(Bı)ı,5
NEWLINE
PRINT(B2)ı*,5
NEWLINE
PRINT(B3)ı,5
NEWLINE
PRINT(B4)ı,5
NEWLINE
NEWLINE
NEWLINE
READ(M)
J=ı(ı)M
READ(N)
READ(Xo)
READ(Xı)
READ(Yo)
READ(Yı)
READ(*Zo)
READ(Zı)
READ(U)
620,27.
620,14
620,15
PRINT(N)4,0
620,27.
620,24
620,0
620,10
PRINT(Xo)***3,2
620,0
620,5
PRINT(Xı)ı,2
620,0
620,6
620,14
620,27.
620,25
620,0
620,10
PRINT(Yo)3,2
620,0
620,5
PRINT(Yı)ı,2
620,0
620,6
620,14
620,27.
620,26
620,0
620,10
```

Read values of physical constants and parameters used in calculations and print them.

Read total number of sets of data.

Read sample number.

Read values of isotope ratios and errors (see Table 27).

Read estimated lower limit to model age.

Print sample number, and isotope ratios and errors with distinguishing symbols (see Table 28).

```
P*RINT(Z0)3,2
620,0
620,5
PRINT(Z1)1,2
620,0
620,6
620,30
620,13
620,14
620,27
620,6
620,0
620,10
Y2=Y0-10.36          Evaluate L.H.S. of Holmes-Houtermans
X2=X0-9.50             equation (F) from isotope ratios
F=Y2/X2                (see introduction to Table 23).
F=X INTPT(1000F+0.5)  Round F to
F=0.001F                 nearest 0.001.
PRINT(F)1,3           Print value of F.
ACROSS1/1             Go to Chapter 1.
2)620,0
620,30
620,13
620,13
620,13
REPEAT
X SQRT
END
CLOSE
**********************
→
```

TABLE 27

Data for Programme 3C (Table 26)

137.8	U^{238}/U^{235}	(Programme variable : B_0)
0.1541	$\lambda 238 \times 10^9$ yr.$^{-1}$	(" " : B_1)
0.972	$\lambda 235 \times 10^9$ yr.$^{-1}$	(" " : B_2)
0.0499	$\lambda 232 \times 10^9$ yr.$^{-1}$	(" " : B_3)
4.5	Age of earth	(" " : B_4)

6 Number of sets of data. (Prog. variable : M)

Isotope Data: No.	$\frac{206}{204}$	Error	$\frac{207}{204}$	Error	$\frac{208}{204}$	Error	U	(Error refers to preceding ratio.)
1	18.14	0.06	15.40	0.05	37.41	0.11	100	
2	18.02	0.08	15.39	0.07	37.44	0.16	200	
3	17.82	0.07	15.25	0.06	37.61	0.14	160	
4	18.05	0.06	15.47	0.05	37.79	0.11	280	
5	18.45	0.06	15.39	0.05	38.15	0.12	-150	
6	18.16	0.04	15.43	0.04	37.67	0.09	130	

Prog. Variable: N	X_0	X_1	Y_0	Y_1	Z_0	Z_1	U	(U is lower limit for model age.)

Data for Programme 3D (Table 29)

137.8	U^{238}/U^{235}	(Programme variable : B_0)
0.1541	$\lambda 238 \times 10^9$ yr.$^{-1}$	(" " : B_1)
0.972	$\lambda 235 \times 10^9$ yr.$^{-1}$	(" " : B_2)
0.0499	$\lambda 232 \times 10^9$ yr.$^{-1}$	(" " : B_3)
4.5	Age of earth	(" " : B_4)

6 Number of sets of data. (Prog. variable : M)

Isotope Data: No.	%204	Error	%206	Error	%207	Error	%208	Error	U
1	1.390	0.004	25.21	0.03	21.40	0.03	52.00	0.04	100
2	1.392	0.006	25.08	0.03	21.42	0.02	52.11	0.03	200
3	1.395	0.005	24.86	0.03	21.28	0.04	52.47	0.05	160
4	1.383	0.004	24.97	0.03	21.39	0.03	52.27	0.04	280
5	1.370	0.004	25.28	0.03	21.09	0.03	52.27	0.04	-150
6	1.384	0.003	25.13	0.02	21.36	0.02	52.13	0.04	130

Prog. Variable: N	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	U

Note: Error refers to preceding abundance. U is lower limit for model age

TABLE 28

Results of Programme 3C (Table 26) (using Data of Table 27)

CALCULATION OF P,V,K FROM LEAD ISOTOPE RATIOS/PROG 3C/RPC P/GM2

```
 137.80
0.15410        Constants used
0.97200          in calculations
0.04990          copied direct
4.50000          from data

NO    1  X= 18.14 ( 0.06 ) Y= 15.40 ( 0.05 ) Z= 37.41 ( 0.11 )
 F= 0.583  P=  176  V= 8.88  K= 3.67

NO    2  X= 18.02 ( 0.08 ) Y= 15.39 ( 0.07 ) Z= 37.44 ( 0.16 )
 F= 0.590  P=  256  V= 8.88  K= 3.75

NO    3  X= 17.82 ( 0.07 ) Y= 15.25 ( 0.06 ) Z= 37.61 ( 0.14 )
 F= 0.588  P=  234  V= 8.63  K= 3.92

NO    4  X= 18.05 ( 0.06 ) Y= 15.47 ( 0.05 ) Z= 37.79 ( 0.11 )
 F= 0.598  P=  344  V= 9.03  K= 3.92

NO    5  X= 18.45 ( 0.06 ) Y= 15.39 ( 0.05 ) Z= 38.15 ( 0.12 )
 F= 0.562  P=  -80  V= 8.84  K= 3.83

NO    6  X= 18.16 ( 0.04 ) Y= 15.43 ( 0.04 ) Z= 37.67 ( 0.09 )
 F= 0.585  P=  199  V= 8.93  K= 3.79
```

Note: Figures in brackets are errors of preceding ratios

Symbols: X = 206/204, Y = 207/204, Z = 208/204
P = model age (m.y.), V = V_p , K = K_p.
F - see Table 28.

```
TITLE
CALC OF P,V,K FROM LEAD ISOTOPE ABUNDANCES/PROG3D/RFC P/GM2


CHAPTER R1 :
A→7 .
B→4                          Set
C→29
D→6                          variables.
E→5
W→6
X→2
Y→2
Z→7 .                        Enter at 1) from end of Chapter 0.
1)Xo=A2/Ao                   Calculate ratio 206/204.
Xo=XINTPT(100Xo+0.5)         Round ratio off to nearest 0.01
Xo=0.01Xo                     for future calculations.
620,27 .
620,24                       Print  " X = " .
620,0
620,10
PRINT(Xo)2,2                 Print rounded-off value of 206/204 .
Co=A2A1 :
Co=CoCo                      Calculate error in 206/204
C1=AoA3                        from errors in % 206 and
C1=C1C1 :
C2=Co+C1                       % 204 read from data, using
C2=XSQRT(C2)
C3=AoAo                        formula on p.94.
C4=C2/C3
C4=XINTPT(100C4+0.5)
X1=0.01C4                    Round error off to nearest 0.01.
620,
620,14
620,5
PRINT(X1)1,2                 Print error in 206/204 with
620,0                          enclosing brackets.
620,14
620,6
620,14
Yo=A4/Ao                     Calculate ratio 207/204.
Yo=XINTPT(100Yo+0.5)
Yo=0.01Yo
620,27 .
620,25
620,0                        Remainder
620,1***0
620,14                         as for
PRINT(Yo)2,2
C5=A4A1                        206/204.
C5=C5C5
C6=AoA5
C6=C6C6
C7=C5+C6
C7=XSQRT(C7)
C8=C7/C3
C8=XINTPT(100C8+0.5)
Y1=0.01C8
```

```
620,0
620,5
PRINT(Y1)1,2
620,0
620,6
620,14
Z0=A6/A0                    Calculate ratio 208/204.
Z0=XINTPT(100Z0+0.5)
Z0=0.01Z0
620,27,
620,26
620,0
620,10
PRINT(Z0)2,2                Remainder
C9=A6A1
C9=C9C9
C10=A0A7,                     as for
C10=C10C10
C11=C9+C10
*C11=XSQRT(C11)               206/204.
C12=C11/C3
C12=XINTPT(100C12+0.5)
Z1=0.01C12
620,0
620,5
PRINT(Z1)1,2
*620,0
620,6
620,30
620,13
620,14
ACROSS1/2                   Go to Chapter 2.
XSQRT
CLOSE


CHAPTER2
VAR*IABLES1
1)E0=A0/A2                  Calculate ratio 204/206 x 100
E0=100E0
E0=XINTPT(*1000E0+0.5)      Round ratio off to nearest 0.001.
E0=0.001E0
620,27,
620,7,
620,0
620,10
PRINT(E0)2,3
C13=A0A3
C13=C13C13                  Calculate error in 204/206 x 100
C14=A2A1
C14=C14C14                    as for preceding ratios, except
C15=C13+C14                   that error is rounded off to
C15=XSQRT(C15)                nearest 0.001.
C16=A2A2
C17=C15/C16
C17=100C17,
C18=XINTPT(1000C17+0.5)
E1=0.001C18
I1=0.01C0
```

```
620,0
620,*5
PRINT(E1)1,3
620,0
620,*6
620,14
E2=A4/A2                    Calculate ratio 207/206 x 100
E2=100E2
E2=XINTPT(100E2+0.5)
*E2=*0.01E2
620,27
620,8
620,*0
620,10
PRINT(E2)3,2                Remainder as above.
C19=A4A3
C19=C19C19
C20=A2A5
C20=C20C20
C21=C19+C20
C21=*X*SQRT(C21)
C23=C21/C16
C23=100C23
C24=XINTPT(100C23+0.5)
E3=0.01C24
620,0
620,5
PRINT(E3)1,2
620,0
620,6
620,14
E4=A6/A2                    Calculate ratio 208/206 x 100
E4=100E4
620,27
620,9
620,0
620,10
PRINT(E4)3,1                Remainder as above.
C25=A6A3
C25=C25C25
C26=*****A2A7
C26=C26C26
C27=C25+C26
C27=XSQRT(C27)
C28=C27/C16
C28=100C28
C29=XINTPT(100C28+0.5)
E5=0.01C29
620,0
620,5
PRINT(E5)1,1
620,0
620,14
620,6
620,30
620,13
620,14
ACROSS1/3                   Go to Chapter 3.
XSQRT
CLOSE
```

```
CHAPTER3
VARIABLES1
1)Y2=Yo-10.36        Calculate experimental value for L.H.S. of
X2=Xo-9.50             Holmes-Houtermans equation (F) from ratios
F=Y2/X2                207/204 (Yo) and 206/204 (Xo) calculated
F=XINTPT(1000F+0.5)    in Chapter I, and round F off to
F=0.001F               nearest 0.001 for following calculation.
620,27
620,6                  Print " F = " .
620,0
620,10
PRINT(F)1,3            Print value of F.
Ev0
2)V=U+E
Wo=XEXP(B1B4)          Method of solution of equation
W1=XEXP(0.001B1V)
W1=Wo-W1                 for the model age (V) is
W2=BoW1
W3=XEXP(B2B4)            identical to that outlined in
W4=XEXP(0.001B2V)
W4=W3-W4                 the notes to Table 23. V is
G=W4/W2
H=G-F                    estimated to the nearest m.y.
JUMP3,H≥0
EvE+0.5                  (see also p.85).
JUMP2,500>E
3) V=X INTPT(V)
620,27
620,16                 Print " P = " .
620,0
620,10
PRINT(V)4,0            Print value of model age.
Vn=XINTPT(0.1V+0.5)    Round value of model age off to nearest
Vn=10Vn                  10 m.y. for calculation of geochemical
W5=XEXP(0.001B1Vn)     Calculate geochemical ratio     (ratios.
W5=Wo-W5                 U238/Pb204 using formula on p.85 and
W6=X2/W*5                same programme method as in Table 18,
620,27                                                Chapter 2.
620;22                 Print " V = " .
620,0
620,10
PRINT(W6)2,2           Print value of U238/Pb204.
Z2=Zo-29.49            Calculate geochemical ratio Th232/U238
Z3=Z2/X2                 using formula on p.86 and same
Z4=XEXP(B3B4)
Z5=XEXP(0.001B3Vn)       programme method as in Table 18,Chapter 2.
Z6=Z4-Z5
Z7=W5/Z6
Z7=Z3Z7
620,27
620,11                 Print " K = " .
620,0
620,10
PRINT(Z7)2,2           Print value of Th232/U238.
ACROSS2/0              Go to Chapter 0, instruction 2).
xSQRT
*xEXP
xMOD
CLOSE
```

```
CHAPTERo
VARIABLESI
I)READ(Bo)
READ(BI)
READ(B2)
READ(B3)
READ(B4)
PRINT(Bo)3,2
NEWLINE
PRINT(BI)I;5
NEWLINE
PRINT(B2)I;5
NEWLINE
PRINT(B3)I;5
NEWLINE
PRINT(B4)I;5
NEWLINE
NEWLINE
NEWLINE
READ(M)
J=I(I)M
READ(N)
READ(Ao)
READ(AI)
READ(A2)
READ(A3)
READ(A4)
READ(A5)
REA*D(A6)
READ(A7)
READ(U)
620,27
620,I4
620,I5
PRINT(N)4,o
620,o
620,I4
620,27
620,I
620,o
620,Io
PRINT(Ao)I,3
620,o
620,*5
PRINT(AI)I,3
620,o
620,6
620,I4
620,27
620,2
620,o
620,Io
PRINT(A2)2,2
620,o
620,5
PRINT(A3)I,2
```

Read values of constants and parameters for use throughout calculations from these data, and print them. See Table 27, second half, where programme variables are given.

Read number of sets of data.

For each set of data, read all the figures and assign these variables to them. (see Table 27).

Print the figures for each set of data with appropriate identifying symbols (see Table 30).

```
620,0
620,6
620,30
620,I3
620,I4
620,I4
620,I4
620,I4
620,I4
620*,I4
620,I4
620,I4
620,I4
620,I4
620,I4
620,27
620,3
620,0
620,I0
PRINT(A4)2,2
620,0
620,5
PRINT(A5)I,2
620,0
620,I4
620,6
620,I4
620,27
620,4
620,0
620,I0
PRINT(A6)2,2
620,*0
620,5
PRINT(A7)I,2
620,6
620,30
620,I3
620,I4
**ACROSSI/I
2)620,0
620,30
620,I3
620,I3
620,I3
REPEAT
END
CLOSE
```

Printing and

tabulating instructions

to reproduce figures

of each set of data

in the form of Table 30.

Go to Chapter 1.
Enter from end of Chapter 3.

3 new lines.

Repeat for new set of data; i.e go to
$J = 1^{(1)} M$ in Chapter 0 (5th page).

****

TABLE 30.

Results of Programme 3D (Table 29) (Using Data of Table 27)

CALC OF P,V,K FROM LEAD ISOTOPE ABUNDANCES/PROG3 D/RFC P/GM2

```
 137.80
 0.15410
 0.97200
 0.04990
 4.50000
```

Constants used in calculations copied direct from data.

```
NO    1   A= 1.390  ( 0.004 ) B= 25.21  ( 0.03 )
          C= 21.40  ( 0.03  ) D= 52.00  ( 0.04 )
 X= 18.14   ( 0.06  ) Y= 15.40  ( 0.05 ) Z= 37.41  ( 0.11 )
 G=  5.514  ( 0.017 ) H= 84.89  ( 0.16 ) I= 206.3  ( 0.3  )
 F= 0.583  P=  176  V=  8.88  K=  3.67
```

Note : Figures in brackets are errors of preceding numbers.

```
NO    2   A= 1.392  ( 0.006 ) B= 25.08  ( 0.03 )
          C= 21.42  ( 0.02  ) D= 52.11  ( 0.03 )
 X= 18.02   ( 0.08  ) Y= 15.39  ( 0.07 ) Z= 37.44  ( 0.16 )
 G=  5.550  ( 0.025 ) H= 85.41  ( 0.13 ) I= 207.8  ( 0.3  )
 F= 0.590  P=  256  V=  8.88  K=  3.75
```

Symbols: A = % 204, B = % 206, C = % 207, D = % 208

```
NO    3   A= 1.395  ( 0.005 ) B= 24.86  ( 0.03 )
          C= 21.28  ( 0.04  ) D= 52.47  ( 0.05 )
 X= 17.82   ( 0.07  ) Y= 15.25  ( 0.06 ) Z= 37.61  ( 0.14 )
 G=  5.611  ( 0.021 ) H= 85.60  ( 0.19 ) I= 211.1  ( 0.3  )
 F= 0.588  P=  234  V=  8.63  K=  3.92
```

Symbols: X = 206/204, Y = 207/204, Z = 208/204.

```
NO    4   A= 1.383  ( 0.004 ) B= 24.97  ( 0.03 )
          C= 21.39  ( 0.03  ) D= 52.27  ( 0.04 )
 X= 18.05   ( 0.06  ) Y= 15.47  ( 0.05 ) Z= 37.79  ( 0.11 )
 G=  5.539  ( 0.017 ) H= 85.66  ( 0.16 ) I= 209.3  ( 0.3  )
 F= 0.598  P=  344  V=  9.03  K=  3.92
```

Symbols: G = 204/206 x 100, H = 207/206 x 100, I = 208/206 x 100.

```
NO    5   A= 1.370  ( 0.004 ) B= 25.28  ( 0.03 )
          C= 21.09  ( 0.03  ) D= 52.27  ( 0.04 )
 X= 18.45   ( 0.06  ) Y= 15.39  ( 0.05 ) Z= 38.15  ( 0.12 )
 G=  5.419  ( 0.017 ) H= 83.43  ( 0.15 ) I= 206.8  ( 0.3  )
 F= 0.562  P=  -80  V=  8.84  K=  3.83
```

Symbols: P = model age (m.y.), V = V_p , K = K_p (F- see Table 29).

```
NO    6   A= 1.384  ( 0.003 ) B= 25.13  ( 0.02 )
          C= 21.36  ( 0.02  ) D= 52.13  ( 0.04 )
 X= 18.16   ( 0.04  ) Y= 15.43  ( 0.04 ) Z= 37.67  ( 0.09 )
 G=  5.507  ( 0.013 ) H= 85.00  ( 0.10 ) I= 207.4  ( 0.2  )
 F= 0.585  P=  199  V=  8.93  K=  3.79
```

TABLES 20, 21, 22

R.P.C. Pockley Thesis

TABLE 20

R.P.C. POCKLEY

SHORTER LEAD MODEL AGE TABLES I - IV.

R.P.C. POCKLEY.

SHORTER LEAD MODEL AGE TABLES I - IV.

The enclosed tables provide solutions for the Holmes-Houtermans equation relating the isotopic composition and "model" age of lead deposits (1), which in general form is:

$$\frac{y - y_o}{x - x_o} = F = \frac{1}{B} \cdot \frac{\exp(DE) - \exp(0.001\,DP)}{\exp(CE) - \exp(0.001\,CP)} \quad - \quad (i)$$

where:
- y = experimental 207/204 ratio
- y_o = primeval " "
- x = experimental 206/204 "
- x_o = primeval " "
- B = U^{238}/U^{235} now
- C = $\lambda_{238} \times 10^9$ yr.$^{-1}$
- D = $\lambda_{235} \times 10^9$ yr.$^{-1}$
- E = age of the earth in 10^9 yr.
- P = model age of sample in 10^6 yr. (i.e. millions of years)

For a particular sample, the value of F is calculated by subtraction of the primeval from the experimental isotope ratios. For Tables I, II and III, Patterson's values (2) for x_o and y_o should be used;

viz. $x_o = 9.50$
$y_o = 10.36$

$$\therefore \quad F = \frac{y - 10.36}{x - 9.50}$$

For Tables I and II, the value of E has been calculated, to the nearest 0.01, by substitution of Patterson's values (3) for x and y for modern lead from ocean sediments;

viz. $x = 18.93$
$y = 15.73,$

giving $F = \overset{0.569}{\cancel{1.756}}$ for $P = 0$ m.y.

Substitution of chosen values for B, C and D in equation (i) allows E to be calculated by trial and error. For the constants used in Tables I and II, the best value of E is 4.50 for both sets of constants, and this was then used with the other constants in computing values for P.

Values of P are given in the tables to the nearest million years for particular values of the experimentally determined ratio F, increasing in increments of 0.01. It is not claimed that the experimental method and the Holmes-Houtermans theory give model ages accurate to one million years, but their quotation in these tables to this accuracy allows rounding-off to any desired accuracy without incurring calculation errors.

Table I has been computed with the constants used by Moorbath (4) in his work in this laboratory on the isotopic composition of lead from British deposits.

Table II has been computed with the values of B, C and D used by Russell and Farquhar throughout their monograph (5), but the value of E has been calculated by the author as described above.

In the low age range in particular, interpolations over wide intervals are necessary if P values are to be obtained to, say, the nearest 10 m.y., using F values calculated to the 3rd decimal place. So Tables I and II have also been computed with the same constants, but with F increasing in increments of 0.001, and are presented under separate covers as Tables V and VI; these avoid the necessity of interpolations.

Table III has been calculated to check that given by Russell and Farquhar ((5), p.47). The same physical constants are used as in Table II, but these authors use E = 4.5106, which they claim to give the same values of P as originally obtained from Houtermans' charts*. The values obtained for these constants are almost exactly the same as those published by Russell and Farquhar. In 15 cases the values quoted in Table III differ from Russell and Farquhar's by only 1 m.y. In 3 cases a much larger difference is observed, viz:

F	Russell & Farquhar Values for P.	Pockley Values for P.
0.55	-372	-327
0.58	1	61
1.36	3701	3710

These cases are clearly typographical errors in Russell and Farquhar's table, as can be checked by simple interpolation. In the remaining 132 cases, the agreement between the two tables is exact, indicating that the two methods of computation are closely comparable.

Table IV has been computed with the constants originally used by Houtermans (1), with which Russell and Farquhar claim their tables give agreement. However, in using Table IV, the values originally used by Houtermans for x_o and y_o should be used in calculating the experimental ratio, F,

viz. $x_o = 9.41$

$y_o = 10.27$

$$\therefore \quad F = \frac{y - 10.27}{x - 9.41}$$

The tables have been very thoroughly checked by also computing the values of F for particular values of P in equation (i), using the different constants as in the tables. F was calculated to 5 decimal places for values of P increasing in increments of 1 m.y. In every case the 2 sets of values agreed exactly. The check tables are not reproduced here owing to their bulk and comparative difficulty of use.

However, the possibility of typographical error still exists, and the author would greatly appreciate being informed of any such mistakes which may be noticed by others.

* This value for E has not been determined as for Tables I and II. The differences between Tables II and III are simply due to the differences in the value of E.

References

(1) F.G. Houtermans ; Nuovo Cimento 10, 1623 (1953)
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LEAD MODEL AGE TABLE I

R.P.C. POCKLEY

CONSTANTS USED

B = 237.8
C = 0.1541
D = 0.978
E = 4.50

AS USED BY S. MOORBATH

VALUES OF MODEL AGE, P, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.00	0.01	0.02	0.03	0.04
0.50	-1023	-847	-682	-526	-378
0.55	-238	-105	21	141	256
0.60	366	471	573	669	762
0.65	851	937	1020	1100	1176
0.70	1253	1325	1395	1463	1529
0.75	1593	1655	1716	1774	1833
0.80	1887	1941	1994	2046	2096
0.85	2145	2193	2240	2286	2330
0.90	2374	2417	2459	2500	2540
0.95	2580	2618	2656	2693	2730
1.00	2766	2801	2835	2869	2903
1.05	2935	2968	2999	3030	3061
1.10	3091	3121	3150	3179	3207
1.15	3235	3262	3289	3316	3342
1.20	3368	3394	3419	3444	3468
1.25	3493	3516	3540	3563	3586
1.30	3609	3631	3653	3675	3697
1.35	3718	3739	3760	3781	3801
1.40	3821	3841	3861	3880	3899
1.45	3918	3937	3956	3974	3992
1.50	4010	4028	4046	4063	4081
1.55	4098	4115	4132	4148	4165
1.60	4181	4197	4213	4229	4245
1.65	4261	4276	4291	4306	4322
1.70	4336	4351	4366	4380	4395
1.75	4409	4423	4437	4451	4465
1.80	4479	4492	4506	4519	4532
1.85	4545	4559	4572	4584	4597
1.90	4610	4622	4635	4647	4659
1.95	4672	4684	4696	4708	4720

LEAD MODEL AGE TABLE II

R. P. C. POCKLEY

CONSTANTS USED

B = 137.8
C = 0.1537
D = 0.9722
E = 4.050

} AS USED BY RUSSELL AND FARQUHAR
} AS CALCULATED BY R. P. C. P.

VALUES OF MODEL AGE, P, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.00	0.01	0.02	0.03	0.04
0.50	-1063	-885	-719	-561	-413
0.55	-273	-138	-11	120	226
0.60	336	442	544	641	734
0.65	824	911	994	1075	1153
0.70	1228	1301	1371	1440	1506
0.75	1570	1633	1693	1752	1810
0.80	1866	1920	1973	2025	2076
0.85	2125	2173	2220	2266	2311
0.90	2355	2398	2440	2481	2522
0.95	2561	2600	2638	2675	2712
1.00	2748	2783	2818	2852	2885
1.05	2918	2950	2982	3013	3044
1.10	3074	3104	3133	3162	3190
1.15	3218	3246	3273	3300	3326
1.20	3352	3378	3403	3428	3453
1.25	3477	3501	3524	3548	3571
1.30	3593	3616	3638	3660	3682
1.35	3703	3724	3745	3766	3786
1.40	3806	3826	3846	3865	3885
1.45	3904	3923	3941	3960	3978
1.50	3996	4014	4032	4049	4066
1.55	4084	4101	4117	4134	4151
1.60	4167	4183	4199	4215	4231
1.65	4247	4262	4277	4293	4308
1.70	4323	4337	4352	4367	4381
1.75	4395	4410	4424	4438	4451
1.80	4465	4479	4492	4506	4519
1.85	4532	4545	4558	4571	4584
1.90	4596	4609	4622	4634	4646
1.95	4658	4671	4683	4695	4706

Xo

LEAD MODEL AGE TABLE III

R.F.C. POCKLEY

CONSTANTS USED

B = 137.8
C = 0.1537
D = 0.9742
E = 4.5106

AS USED BY RUSSELL AND FARQUHAR

VALUES OF MODEL AGE, P, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.00	0.01	0.02	0.03	0.04
0.50	-1130	-951	-780	-622	-470
0.55	-327	-191	-62	61	178
0.60	290	398	500	599	694
0.65	785	873	957	1039	1117
0.70	1194	1267	1338	1407	1474
0.75	1539	1603	1664	1723	1781
0.80	1838	1893	1946	1999	2050
0.85	2099	2148	2195	2242	2287
0.90	2331	2375	2417	2459	2499
0.95	2539	2578	2617	2654	2691
1.00	2727	2763	2798	2832	2866
1.05	2899	2931	2963	2995	3026
1.10	3056	3086	3115	3145	3173
1.15	3201	3229	3256	3283	3310
1.20	3336	3362	3387	3412	3437
1.25	3461	3485	3509	3533	3556
1.30	3579	3601	3623	3645	3667
1.35	3689	3710	3731	3752	3772
1.40	3792	3812	3832	3852	3871
1.45	3890	3909	3928	3947	3965
1.50	3983	4001	4019	4036	4054
1.55	4071	4088	4105	4122	4139
1.60	4155	4171	4187	4203	4219
1.65	4235	4250	4266	4281	4296
1.70	4311	4326	4341	4355	4370
1.75	4384	4399	4413	4427	4441
1.80	4454	4468	4482	4495	4508
1.85	4522	4535	4548	4561	4574
1.90	4586	4599	4611	4624	4636
1.95	4648	4661	4673	4685	4697

LEAD MODEL AGE TABLE IV

R.P.C. POCKLEY

CONSTANTS USED

B = 139
C = 0.154
D = 0.98
E = 4.486

} AS ORIGINALLY USED BY HOUTERMANS

VALUES OF MODEL AGE, P, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.00	0.01	0.02	0.03	0.04
0.50	-1192	-1010	-839	-678	-526
0.55	-381	-245	-115	9	127
0.60	239	347	450	549	643
0.65	736	824	909	991	1070
0.70	1146	1220	1291	1360	1427
0.75	1493	1556	1617	1677	1735
0.80	1791	1846	1900	1952	2003
0.85	2053	2102	2149	2195	2241
0.90	2285	2328	2371	2412	2453
0.95	2493	2533	2570	2608	2645
1.00	2681	2716	2751	2786	2819
1.05	2852	2885	2917	2948	2979
1.10	3009	3039	3069	3098	3126
1.15	3154	3182	3209	3236	3262
1.20	3289	3314	3340	3365	3389
1.25	3414	3438	3461	3485	3508
1.30	3531	3553	3575	3597	3619
1.35	3640	3662	3683	3703	3724
1.40	3744	3764	3784	3803	3822
1.45	3842	3860	3879	3898	3916
1.50	3934	3952	3970	3987	4005
1.55	4022	4039	4056	4072	4089
1.60	4105	4122	4138	4154	4169
1.65	4185	4200	4216	4231	4246
1.70	4261	4276	4291	4305	4320
1.75	4334	4348	4363	4376	4390
1.80	4404	4417	4431	4444	4457
1.85	4471	4484	4497	4509	4522
1.90	4535	4547	4560	4572	4585
1.95	4597	4609	4621	4633	4645

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TABLE 21

R.P.C. POCKLEY

LONGER LEAD MODEL AGE TABLE V.

R.P.C. POCKLEY.

LONGER LEAD MODEL AGE TABLE V.

The enclosed table provides solutions for the Holmes-Houtermans equation relating the isotopic composition and "model" age of lead deposits (1), which in general form is:

$$\frac{y - y_o}{x - x_o} = F = \frac{1}{B} \cdot \frac{\exp(DE) - \exp(0.001\,DP)}{\exp(CE) - \exp(0.001\,CP)} \quad \text{- (i)}$$

where:
- y = experimental 207/204 ratio
- y_o = primeval " "
- x = experimental 206/204 "
- x_o = primeval " "
- B = U^{238}/U^{235} now
- C = $\lambda_{238} \times 10^9$ yr.$^{-1}$
- D = $\lambda_{235} \times 10^9$ yr.$^{-1}$
- E = age of the earth in 10^9 yr.
- P = model age of sample in 10^6 yr. (i.e. millions of years)

For a particular sample, the value of F is calculated by subtraction of the primeval from the experimental isotope ratios. For this table, Patterson's values (2) for x_o and y_o should be used;

viz. $x_o = 9.50$
$y_o = 10.36$

$$\therefore F = \frac{y - 10.36}{x - 9.50}$$

For this table, the value of E has been calculated, to the nearest 0.01, by substitution of Patterson's values (3) for x and y for modern lead from ocean sediments;

viz. $x = 18.93$
$y = 15.73$

giving $F = \frac{0.569}{1.756}$ for P = 0 m.y.

Substitution of chosen values for B, C and D in equation (i) allows E to be calculated by trial and error.

The values of B, C and D used in computing this table have beeen those used by Moorbath (4) in his work in this laboratory on the isotopic composition of lead from British deposits. For these values, E = 4.50.

Values of P are given in the table to the nearest million years for particular values of the experimentally determined ratio F, increasing in increments of 0.001. It is not claimed that the experimental method and the Holmes-Houtermans theory give model ages accurate to one million years, but their quotation in the table to this accuracy allows rounding-off to any desired accuracy without incurring calculation errors. The increment in P for a given increment in F is very small in the higher age range, but all values are reproduced here for completeness.

Another similar table (Table VI) has been computed using slightly different values for C and D, as used by Russell and Farquhar (5), and is bound under a separate cover. Also under another cover are bound four shorter tables with F values increasing in increments of only 0.01 to allow more ready comparison of the effect of use of different constants.

This table has been very thoroughly checked by also computing the values of F for particular values of P in equation (i) using the same constants as in this table. F was calculated to 5 decimal places for values of P increasing in increments of 1 m.y. In every case the two sets of values agreed exactly. The check table is not reproduced here owing to its bulk and comparative difficulty of use.

However, the possibility of typographical error still exists, and the author would greatly appreciate being informed of any such mistakes which may be noticed by others.

References

(1) F.G. Houtermans ; Nuovo Cimento 10, 1623 (1953)
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LEAD MODEL AGE TABLE V

R.P.C. POCKLEY

CONSTANTS USED

B = 137.8
C = 0.1541
D = 0.972
E = 4.50

} AS USED BY S. MOORBATH

VALUES OF MODEL AGE, F, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.000	0.001	0.002	0.003	0.004
0.500	-1023	-1005	-987	-969	-951
0.505	-934	-916	-899	-881	-864
0.510	-847	-830	-813	-796	-780
0.515	-763	-747	-730	-714	-698
0.520	-682	-666	-650	-634	-618
0.525	-603	-587	-572	-556	-541
0.530	-526	-510	-495	-480	-465
0.535	-451	-436	-421	-407	-392
0.540	-378	-364	-349	-335	-321
0.545	-307	-293	-279	-266	-252
0.550	-238	-225	-211	-198	-184
0.555	-171	-158	-145	-131	-118
0.560	-105	-92	-80	-67	-54
0.565	-41	-29	-16	-4	9
0.570	21	33	45	58	70
0.575	82	94	106	118	130
0.580	141	153	165	176	188
0.585	199	211	222	234	245
0.590	256	267	279	290	301
0.595	312	323	334	344	355
0.600	366	377	387	398	409
0.605	419	430	440	450	461
0.610	471	481	492	502	512
0.615	522	532	542	552	562
0.620	572	582	592	601	611
0.625	621	630	640	650	659
0.630	669	678	687	697	706
0.635	716	725	734	743	752
0.640	762	771	780	789	798
0.645	807	816	824	833	842
0.650	851	860	868	877	886
0.655	894	903	912	920	929
0.660	937	946	954	962	971
0.665	979	987	996	1004	1012
0.670	1020	1028	1036	1044	1053
0.675	1061	1069	1077	1084	1092
0.680	1100	1108	1116	1124	1132
0.685	1139	1147	1155	1162	1170
0.690	1178	1185	1193	1200	1208
0.695	1215	1223	1230	1238	1245

0.700	1253	1260	1267	1275	1282
0.705	1289	1296	1303	1311	1318
0.710	1325	1332	1339	1346	1353
0.715	1360	1367	1374	1381	1388
0.720	1395	1402	1409	1416	1423
0.725	1429	1436	1443	1450	1456
0.730	1463	1470	1476	1483	1490
0.735	1496	1503	1509	1516	1523
0.740	1529	1536	1542	1548	1555
0.745	1561	1568	1574	1580	1587
0.750	1593	1599	1606	1612	1618
0.755	1624	1631	1637	1643	1649
0.760	1655	1661	1667	1673	1680
0.765	1686	1692	1698	1704	1710
0.770	1716	1722	1727	1733	1739
0.775	1745	1751	1757	1763	1769
0.780	1774	1780	1786	1792	1797
0.785	1803	1809	1815	1820	1826
0.790	1831	1837	1843	1848	1854
0.795	1860	1865	1871	1876	1882
0.800	1887	1893	1898	1904	1909
0.805	1914	1920	1925	1931	1936
0.810	1941	1947	1952	1957	1963
0.815	1968	1973	1978	1984	1989
0.820	1994	1999	2005	2010	2015
0.825	2020	2025	2030	2036	2041
0.830	2046	2051	2056	2061	2066
0.835	2071	2076	2081	2086	2091
0.840	2096	2101	2106	2111	2116
0.845	2121	2126	2130	2135	2140
0.850	2145	2150	2155	2160	2164
0.855	2169	2174	2179	2184	2188
0.860	2193	2198	2202	2207	2212
0.865	2217	2221	2226	2231	2235
0.870	2240	2244	2249	2254	2258
0.875	2263	2267	2272	2277	2281
0.880	2286	2290	2295	2299	2304
0.885	2308	2313	2317	2322	2326
0.890	2330	2335	2339	2344	2348
0.895	2352	2357	2361	2365	2370
0.900	2374	2378	2383	2387	2391
0.905	2396	2400	2404	2408	2413
0.910	2417	2421	2425	2430	2434
0.915	2438	2442	2446	2451	2455
0.920	2459	2463	2467	2471	2475
0.925	2480	2484	2488	2492	2496
0.930	2500	2504	2508	2512	2516
0.935	2520	2524	2528	2532	2536
0.940	2540	2544	2548	2552	2556
0.945	2560	2564	2568	2572	2576
0.950	2580	2584	2587	2591	2595
0.955	2599	2603	2607	2611	2614
0.960	2618	2622	2626	2630	2634
0.965	2637	2641	2645	2649	2653
0.970	2656	2660	2664	2667	2671
0.975	2675	2679	2682	2686	2690
0.980	2693	2697	2701	2704	2708
0.985	2712	2715	2719	2723	2726
0.990	2730	2733	2737	2741	2744
0.995	2748	2751	2755	2759	2762

1.000	2766	2769	2773	2776	2780
1.005	2783	2787	2790	2794	2797
1.010	2801	2804	2808	2811	2815
1.015	2818	2822	2825	2828	2832
1.020	2835	2839	2842	2846	2849
1.025	2852	2856	2859	2863	2866
1.030	2869	2871	2876	2879	2883
1.035	2886	2889	2893	2896	2899
1.040	2903	2906	2909	2912	2916
1.045	2919	2922	2926	2929	2933
1.050	2935	2939	2942	2945	2948
1.055	2951	2955	2958	2961	2964
1.060	2968	2971	2974	2977	2980
1.065	2983	2987	2990	2993	2996
1.070	2999	3002	3005	3009	3012
1.075	3015	3018	3021	3024	3027
1.080	3030	3033	3036	3040	3043
1.085	3046	3049	3052	3055	3058
1.090	3061	3064	3067	3070	3073
1.095	3076	3079	3082	3085	3088
1.100	3091	3094	3097	3100	3103
1.105	3106	3109	3112	3115	3118
1.110	3121	3124	3127	3130	3132
1.115	3135	3138	3141	3144	3147
1.120	3150	3153	3156	3159	3161
1.125	3164	3167	3170	3173	3176
1.130	3179	3181	3184	3187	3190
1.135	3193	3196	3199	3201	3204
1.140	3207	3210	3213	3215	3218
1.145	3221	3224	3227	3229	3232
1.150	3235	3238	3240	3243	3246
1.155	3249	3251	3254	3257	3260
1.160	3262	3265	3268	3270	3273
1.165	3276	3279	3281	3284	3287
1.170	3289	3292	3295	3297	3300
1.175	3303	3305	3308	3311	3313
1.180	3316	3319	3321	3324	3327
1.185	3329	3332	3334	3337	3340
1.190	3342	3345	3348	3350	3353
1.195	3355	3358	3360	3363	3366
1.200	3368	3371	3373	3376	3378
1.205	3381	3384	3386	3389	3391
1.210	3394	3396	3399	3401	3404
1.215	3406	3409	3411	3414	3416
1.220	3419	3421	3424	3426	3429
1.225	3431	3434	3436	3439	3441
1.230	3444	3446	3449	3451	3454
1.235	3456	3459	3461	3463	3466
1.240	3468	3471	3473	3476	3478
1.245	3481	3483	3485	3488	3490
1.250	3493	3495	3497	3500	3502
1.255	3505	3507	3509	3511	3514
1.260	3516	3519	3521	3524	3526
1.265	3528	3531	3533	3535	3538
1.270	3540	3542	3545	3547	3549
1.275	3553	3554	3556	3559	3561
1.280	3563	3566	3568	3570	3572
1.285	3575	3577	3579	3582	3584
1.290	3586	3588	3591	3593	3595
1.295	3598	3600	3602	3604	3607

I.300	3609	3612	3613	3616	3618
I.305	3620	3622	3625	3627	3629
I.310	3631	3634	3636	3638	3640
I.315	3642	3645	3647	3649	3651
I.320	3653	3656	3658	3660	3663
I.325	3664	3667	3669	3671	3673
I.330	3675	3677	3680	3682	3684
I.335	3686	3688	3690	3693	3695
I.340	3697	3699	3701	3703	3705
I.345	3708	3710	3712	3714	3716
I.350	3718	3720	3722	3724	3727
I.355	3729	3731	3733	3735	3737
I.360	3739	3741	3743	3745	3748
I.365	3750	3752	3754	3756	3758
I.370	3760	3762	3764	3766	3768
I.375	3770	3772	3774	3777	3779
I.380	3781	3783	3785	3787	3789
I.385	3791	3793	3795	3797	3799
I.390	3801	3803	3805	3807	3809
I.395	3811	3813	3815	3817	3819
I.400	3821	3823	3825	3827	3829
I.405	3831	3833	3835	3837	3839
I.410	3841	3843	3845	3847	3849
I.415	3851	3853	3855	3857	3859
I.420	3861	3863	3865	3866	3868
I.425	3870	3872	3874	3876	3878
I.430	3880	3882	3884	3886	3888
I.435	3890	3892	3894	3895	3897
I.440	3899	3901	3903	3905	3907
I.445	3909	3911	3913	3915	3916
I.450	3918	3920	3922	3924	3926
I.455	3928	3930	3931	3933	3935
I.460	3937	3939	3941	3943	3945
I.465	3946	3948	3950	3952	3954
I.470	3956	3958	3959	3961	3963
I.475	3965	3967	3969	3970	3972
I.480	3974	3976	3978	3980	3981
I.485	3983	3985	3987	3989	3991
I.490	3992	3994	3996	3998	4000
I.495	4002	4003	4005	4007	4009
I.500	4010	4012	4014	4016	4018
I.505	4019	4021	4023	4025	4026
I.510	4028	4030	4032	4034	4035
I.515	4037	4039	4041	4043	4044
I.520	4046	4048	4049	4051	4053
I.525	4055	4056	4058	4060	4062
I.530	4063	4065	4067	4069	4070
I.535	4072	4074	4076	4077	4079
I.540	4081	4082	4084	4086	4088
I.545	4089	4091	4093	4094	4096
I.550	4098	4100	4101	4103	4105
I.555	4106	4108	4110	4111	4113
I.560	4115	4117	4118	4120	4122
I.565	4123	4125	4127	4128	4130
I.570	4132	4133	4135	4137	4138
I.575	4140	4142	4143	4145	4147
I.580	4148	4150	4152	4153	4155
I.585	4157	4158	4160	4162	4163
I.590	4165	4166	4168	4170	4171
I.595	4173	4175	4176	4178	4180

1.600	4181	4183	4184	4186	4188
1.605	4189	4191	4192	4194	4196
1.610	4197	4199	4201	4202	4204
1.615	4205	4207	4209	4210	4212
1.620	4213	4215	4217	4218	4220
1.625	4221	4223	4224	4226	4228
1.630	4229	4231	4232	4234	4236
1.635	4237	4239	4240	4242	4243
1.640	4245	4247	4248	4250	4251
1.645	4253	4254	4256	4257	4259
1.650	4261	4262	4264	4265	4267
1.655	4268	4270	4271	4273	4274
1.660	4276	4278	4279	4281	4282
1.665	4284	4285	4287	4288	4290
1.670	4291	4293	4294	4296	4297
1.675	4299	4300	4302	4303	4305
1.680	4306	4308	4309	4311	4312
1.685	4314	4316	4317	4319	4320
1.690	4322	4323	4324	4326	4327
1.695	4329	4330	4332	4333	4335
1.700	4336	4338	4339	4341	4342
1.705	4344	4345	4347	4348	4350
1.710	4351	4353	4354	4356	4357
1.715	4359	4360	4361	4363	4364
1.720	4366	4367	4369	4370	4372
1.725	4373	4375	4376	4377	4379
1.730	4380	4382	4383	4385	4386
1.735	4388	4389	4390	4392	4393
1.740	4395	4396	4398	4399	4400
1.745	4402	4403	4405	4406	4408
1.750	4409	4410	4412	4413	4415
1.755	4416	4418	4419	4420	4422
1.760	4423	4425	4426	4427	4429
1.765	4430	4432	4433	4434	4436
1.770	4437	4439	4440	4441	4443
1.775	4444	4446	4447	4448	4450
1.780	4451	4453	4454	4455	4457
1.785	4458	4459	4461	4462	4464
1.790	4465	4466	4468	4469	4470
1.795	4472	4473	4475	4476	4477

1.800	4479	4480	4481	4483	4484
1.805	4485	4487	4488	4490	4491
1.810	4492	4494	4495	4496	4498
1.815	4499	4500	4502	4503	4504
1.820	4506	4507	4508	4510	4511
1.825	4512	4514	4515	4516	4518
1.830	4519	4520	4522	4523	4524
1.835	4526	4527	4528	4530	4531
1.840	4532	4534	4535	4536	4538
1.845	4539	4540	4542	4543	4544
1.850	4545	4547	4548	4549	4551
1.855	4552	4553	4555	4556	4557
1.860	4559	4560	4561	4562	4564
1.865	4565	4566	4568	4569	4570
1.870	4572	4573	4574	4575	4577
1.875	4578	4579	4581	4582	4583
1.880	4584	4586	4587	4588	4589
1.885	4591	4592	4593	4595	4596
1.890	4597	4598	4600	4601	4602
1.895	4603	4605	4606	4607	4609
1.900	4610	4611	4613	4614	4615
1.905	4616	4617	4619	4620	4621
1.910	4622	4624	4625	4626	4627
1.915	4629	4630	4631	4633	4634
1.920	4635	4636	4637	4639	4640
1.925	4641	4642	4643	4645	4646
1.930	4647	4648	4650	4651	4652
1.935	4653	4655	4656	4657	4658
1.940	4659	4661	4662	4663	4664
1.945	4666	4667	4668	4669	4670
1.950	4672	4673	4674	4675	4677
1.955	4678	4679	4680	4681	4683
1.960	4684	4685	4686	4687	4689
1.965	4690	4691	4692	4693	4695
1.970	4696	4697	4698	4699	4701
1.975	4702	4703	4704	4705	4707
1.980	4708	4709	4710	4711	4713
1.985	4714	4715	4716	4717	4718
1.990	4720	4721	4722	4723	4724
1.995	4725	4727	4728	4729	4730

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TABLE 22

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LONGER LEAD MODEL AGE TABLE VI.

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LONGER LEAD MODEL AGE TABLE VI.

The enclosed table provides solutions for the Holmes-Houtermans equation relating the isotopic composition and "model" age of lead deposits (1), which in general form is:

$$\frac{y - y_o}{x - x_o} = F = \frac{1}{B} \cdot \frac{\exp(DE) - \exp(0.001\,DP)}{\exp(CE) - \exp(0.001\,CP)} \quad - (i)$$

where:
- y = experimental 207/204 ratio
- y_o = primeval " "
- x = experimental 206/204 "
- x_o = primeval " "
- B = U^{238}/U^{235} now
- C = $\lambda_{238} \times 10^9$ yr.$^{-1}$
- D = $\lambda_{235} \times 10^9$ yr.$^{-1}$
- E = age of the earth in 10^9 yr.
- P = model age of sample in 10^6 yr. (i.e. millions of years)

For a particular sample, the value of F is calculated by subtraction of the primeval from the experimental isotope ratios. For this table, Patterson's values (2) for x_o and y_o should be used;

viz. $x_o = 9.50$
$y_o = 10.36$

$$\therefore \quad F = \frac{y - 10.36}{x - 9.50}$$

For this table, the value of E has been calculated, to the nearest 0.01, by substitution of Patterson's values (3) for x and y for modern lead from ocean sediments;

viz. $x = 18.93$
$y = 15.73$,

giving $F = \frac{0.569}{\cancel{1.256}}$ for P = 0 m.y.

Substitution of chosen values for B, C and D in equation (i) allows E to be calculated by trial and error.

The values of B, C and D used in computing this table have been those used by Russell and Farquhar throughout their monograph (5), but the value of E has been calculated by the author as described above. For these values, E = 4.50. This differs from the value E = 4.5106 used by Russell and Farquhar in computing their table ((5), p.47) which was chosen to give ages equal to those originally obtained from Houtermans' charts which were constructed using different constants.

Some typographical errors exist in Russell and Farquhar's table, and so this Table VI should be compared with the calculation of Russell and Farquhar's table repeated by the author and reproduced as Table III under a separate cover. Three other shorter tables, with F values increasing in increments of only 0.01 to allow more ready comparison of the effect of use of different constants, are bound with Table III.

Another table (Table V), similar to this Table VI, has been computed using slightly different values for C and D, as used by Moorbath (4) in his work in this laboratory on the isotopic composition of lead from British deposits, and is bound under another cover.

Values of P are given in the tables to the nearest million years for particular values of the experimentally determined ratio F, increasing in increments of 0.001. It is not claimed that the experimental method and the Holmes-Houtermans theory give model ages accurate to one million years, but their quotation in these tables to this accuracy allows rounding-off to any desired accuracy without incurring calculation errors. The increment in P for a given increment in F is very small in the higher age range, but all values are reproduced here for completeness.

This table has been very thoroughly checked by also computing the values of F for particular values of P in equation (i) using the same constants as in this table. F was calculated to 5 decimal places for values of P increasing in increments of 1 m.y. In every case the two sets of values agreed exactly. The check table is not reproduced here owing to its bulk and comparative difficulty of use.

However, the possibility of typographical error still exists, and the author would greatly appreciate being informed of any such mistakes which may be noticed by others.

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February 1961.

LEAD MODEL AGE TABLE VI

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CONSTANTS USED

B = 137.8
C = 0.1537
D = 0.9742
E = 4.50

} AS USED BY RUSSELL AND FARQUHAR
} AS CALCULATED BY R.P.C.P.

VALUES OF MODEL AGE, P, IN MILLIONS OF YEARS, FOR PARTICULAR VALUES OF RATIO, F.

F	0.000	0.001	0.002	0.003	0.004
0.500	-1063	-1044	-1026	-1008	-990
0.505	-973	-955	-937	-920	-903
0.510	-885	-868	-851	-834	-817
0.515	-801	-784	-768	-751	-735
0.520	-719	-702	-686	-670	-655
0.525	-639	-623	-608	-593	-577
0.530	-561	-546	-531	-516	-501
0.535	-486	-471	-456	-443	-427
0.540	-413	-398	-384	-370	-355
0.545	-341	-327	-313	-299	-286
0.550	-272	-258	-244	-231	-217
0.555	-204	-191	-177	-164	-151
0.560	-136	-125	-112	-99	-86
0.565	-74	-61	-48	-36	-23
0.570	-11	1	14	26	38
0.575	50	62	75	86	98
0.580	110	122	134	146	157
0.585	169	180	192	203	215
0.590	226	237	248	260	271
0.595	282	293	304	315	326
0.600	336	347	358	369	379
0.605	390	400	411	421	432
0.610	442	453	463	473	483
0.615	493	504	514	524	534
0.620	544	553	563	573	583
0.625	593	602	612	622	631
0.630	641	650	660	669	679
0.635	688	697	707	716	725
0.640	734	744	753	762	771
0.645	780	789	798	807	815
0.650	824	833	842	851	859
0.655	868	877	885	894	902
0.660	912	919	928	936	945
0.665	953	961	970	978	986
0.670	994	1003	1011	1019	1027
0.675	1035	1043	1051	1059	1067
0.680	1075	1083	1091	1099	1106
0.685	1114	1122	1130	1138	1145
0.690	1153	1160	1168	1176	1183
0.695	1191	1198	1206	1213	1221

0.700	1228	1235	1243	1250	1258
0.705	1265	1272	1279	1287.	1294
0.710	1302	1308	1315	1322	1329
0.715	1336	1343	1350	1357.	1364
0.720	1371	1378	1385	1392	1399
0.725	1406	1413	1419	1426	1433
0.730	1440	1446	1453	1460	1466
0.735	1473	1480	1486	1493	1499
0.740	1506	1512	1519	1525	1532
0.745	1538	1545	1551	1558	1564
0.750	1570	1577.	1583	1589	1595
0.755	1602	1608	1614	1620	1627.
0.760	1633	1639	1645	1651	1657.
0.765	1663	1669	1675	1681	1687.
0.770	1693	1699	1705	1711	1717.
0.775	1723	1729	1735	1741	1747.
0.780	1752	1758	1764	1770	1776
0.785	1781	1787.	1793	1799	1804
0.790	1810	1816	1821	1827.	1832
0.795	1838	1844	1849	1855	1860
0.800	1866	1871	1877.	1882	1888
0.805	1893	1899	1904	1909	1915
0.810	1920	1926	1931	1936	1942
0.815	1947.	1952	1958	1963	1968
0.820	1973	1979	1984	1989	1994
0.825	1999	2005	2010	2015	2020
0.830	2025	2030	2035	2040	2045
0.835	2050	2055	2061	2066	2071
0.840	2076	2081	2085	2090	2095
0.845	2100	2105	2110	2115	2120
0.850	2125	2130	2135	2139	2144
0.855	2149	2154	2159	2163	2168
0.860	2173	2178	2183	2187.	2192
0.865	2197.	2201	2206	2211	2215
0.870	2220	2225	2229	2234	2238
0.875	2243	2248	2252	2257.	2261
0.880	2266	2270	2275	2280	2284
0.885	2289	2293	2297.	2302	2306
0.890	2311	2315	2320	2324	2329
0.895	2333	2337.	2342	2346	2350
0.900	2355	2359	2361	2368	2372
0.905	2376	2381	2385	2389	2394
0.910	2398	2402	2406	2411	2415
0.915	2419	2423	2427.	2432	2436
0.920	2440	2444	2448	2452	2456
0.925	2461	2465	2469	2473	2477.
0.930	2481	2485	2489	2493	2497.
0.935	2501	2505	2509	2513	2518
0.940	2522	2525	2529	2533	2537.
0.945	2541	2545	2549	2553	2557.
0.950	2561	2565	2569	2573	2577.
0.955	2581	2584	2588	2592	2596
0.960	2600	2604	2608	2611	2615
0.965	2619	2623	2627.	2630	2634
0.970	2638	2642	2645	2649	2653
0.975	2657.	2660	2664	2668	2672
0.980	2675	2679	2683	2686	2690
0.985	2694	2697.	2701	2705	2708
0.990	2712	2715	2719	2723	2726
0.995	2730	2733	2737.	2741	2744

I.000	2748	2751	2755	2758	2762
I.005	2765	2769	2773	2776	2780
I.010	2783	2787.	2790	2793	2797.
I.015	2800	2804	2807.	2811	2814
I.020	2818	2821	2825	2828	2831
I.025	2835	2838	2842	2845	2848
I.030	2852	2855	2858	2862	2865
I.035	2868	2872	2875	2878	2882
I.040	2885	2888	2892	2895	2898
I.045	2902	2905	2908	2911	2915
I.050	2918	2921	2924	2928	2931
I.055	2934	2937.	2941	2944	2947.
I.060	2950	2953	2957.	2960	2963
I.065	2966	2969	2973	2976	2979
I.070	2982	2985	2988	2991	2995
I.075	2998	3001	3004	3007.	3010
I.080	3013	3016	3019	3023	3026
I.085	3029	3032	3035	3038	3041
I.090	3044	3047.	3050	3053	3056
I.095	3059	3062	3065	3068	3071
I.100	3074	3077.	3080	3083	3086
I.105	3089	3092	3095	3098	3101
I.110	3104	3107.	3110	3113	3116
I.115	3119	3122	3124	3127.	3130
I.120	3133	3136	3139	3142	3145
I.125	3148	3151	3153	3156	3159
I.130	3162	3165	3168	3171	3173
I.135	3176	3179	3182	3185	3188
I.140	3190	3193	3196	3199	3200
I.145	3204	3207.	3210	3213	3216
I.150	3218	3221	3224	3227.	3229
I.155	3232	3235	3238	3240	3243
I.160	3246	3249	3251	3254	3257.
I.165	3260	3262	3265	3268	3270
I.170	3273	3276	3278	3281	3284
I.175	3287.	3289	3292	3295	3297.
I.180	3300	3302	3305	3308	3310
I.185	3313	3316	3318	3321	3324
I.190	3326	3329	3331	3334	3337.
I.195	3339	3342	3344	3347.	3350
I.200	3352	3355	3357.	3360	3362
I.205	3365	3368	3370	3373	3375
I.210	3378	3380	3383	3385	3388
I.215	3390	3393	3396	3398	3401
I.220	3403	3406	3408	3411	3413
I.225	3416	3418	3421	3423	3426
I.230	3428	3430	3433	3435	3438
I.235	3440	3443	3445	3448	3450
I.240	3453	3455	3457.	3460	3462
I.245	3465	3467.	3470	3472	3474
I.250	3477.	3479	3482	3484	3486
I.255	3489	3491	3494	3496	3498
I.260	3501	3503	3506	3508	3510
I.265	3513	3515	3517.	3520	3522
I.270	3524	3527.	3529	3531	3534
I.275	3536	3538	3541	3543	3545
I.280	3548	3550	3552	3555	3557.
I.285	3559	3562	3564	3566	3568
I.290	3571	3573	3575	3578	3580
I.295	3582	3584	3587.	3589	3591

I.300	3593	3596	3598	3600	3603
I.305	3605	3607	3609	3611	3614
I.310	3618	3621	3620	3623	3625
I.315	3627	3629	3632	3634	3636
I.320	3638	3640	3643	3645	3647
I.325	3649	3651	3653	3656	3658
I.330	3660	3662	3664	3667	3669
I.335	3671	3671	3675	3677	3679
I.340	3682	3684	3686	3688	3690
I.345	3692	3694	3697	3699	3701
I.350	3703	3705	3707	3709	3711
I.355	3714	3716	3718	3720	3722
I.360	3724	3726	3728	3730	3733
I.365	3735	3737	3739	3741	3743
I.370	3745	3747	3749	3751	3753
I.375	3755	3757	3759	3762	3764
I.380	3766	3768	3770	3772	3774
I.385	3776	3778	3780	3782	3784
I.390	3786	3788	3790	3792	3794
I.395	3796	3798	3800	3802	3804
I.400	3806	3808	3810	3812	3814
I.405	3816	3818	3820	3822	3824
I.410	3826	3828	3830	3833	3834
I.415	3835	3838	3840	3842	3844
I.420	3846	3848	3850	3852	3854
I.425	3856	3858	3859	3861	3863
I.430	3865	3867	3869	3871	3873
I.435	3875	3877	3879	3881	3883
I.440	3885	3886	3888	3890	3892
I.445	3894	3896	3898	3900	3902
I.450	3904	3906	3907	3909	3911
I.455	3913	3915	3917	3919	3921
I.460	3922	3924	3926	3928	3930
I.465	3932	3934	3936	3937	3939
I.470	3941	3943	3945	3947	3949
I.475	3950	3952	3954	3956	3958
I.480	3960	3961	3963	3965	3967
I.485	3969	3971	3973	3974	3976
I.490	3978	3980	3982	3983	3985
I.495	3987	3989	3991	3992	3994
I.500	3996	3998	4000	4001	4003
I.505	4005	4007	4009	4010	4012
I.510	4014	4016	4017	4019	4021
I.515	4023	4025	4026	4028	4030
I.520	4032	4033	4035	4037	4039
I.525	4040	4042	4044	4046	4047
I.530	4049	4051	4053	4054	4056
I.535	4058	4060	4061	4063	4065
I.540	4066	4068	4070	4072	4073
I.545	4075	4077	4078	4080	4082
I.550	4084	4085	4087	4089	4090
I.555	4092	4094	4096	4097	4099
I.560	4101	4102	4104	4106	4107
I.565	4109	4111	4112	4114	4116
I.570	4117	4119	4121	4123	4124
I.575	4126	4128	4129	4131	4133
I.580	4134	4136	4137	4139	4141
I.585	4142	4144	4146	4147	4149
I.590	4151	4152	4154	4156	4157
I.595	4159	4161	4162	4164	4165

1.600	4167.	4169	4170	4173	4174
1.605	4175	4177.	4178	4180	4182
1.610	4183	4185	4186	4188	4190
1.615	4191	4193	4195	4196	4198
1.620	4199	4201	4203	4204	4206
1.625	4207.	4209	4210	4212	4214
1.630	4215	4217.	4218	4220	4222
1.635	4223	4225	4226	4228	4229
1.640	4231	4233	4234	4236	4237.
1.645	4239	4240	4242	4244	4245
1.650	4247.	4248	4250	4251	4253
1.655	4254	4256	4257.	4259	4261
1.660	4262	4264	4265	4267.	4268
1.665	4270	4271	4273	4274	4276
1.670	4277.	4279	4280	4282	4284
1.675	4285	4287.	4288	4290	4291
1.680	4293	4294	4296	4297.	4299
1.685	4300	4302	4303	4305	4306
1.690	4308	4309	4311	4312	4314
1.695	4315	4317.	4318	4320	4322
1.700	4323	4324	4326	4327.	4329
1.705	4330	4332	4333	4334	4336
1.710	4337.	4339	4340	4342	4343
1.715	4345	4346	4348	4349	4351
1.720	4352	4354	4355	4356	4358
1.725	4359	4361	4362	4364	4365
1.730	4367.	4368	4370	4371	4373
1.735	4374	4375	4377.	4378	4380
1.740	4381	4383	4384	4385	4387.
1.745	4388	4390	4391	4393	4394
1.750	4395	4397.	4398	4400	4401
1.755	4402	4404	4405	4407.	4408
1.760	4410	4411	4412	4414	4415
1.765	4417.	4418	4419	4421	4422
1.770	4424	4425	4426	4428	4429
1.775	4431	4432	4433	4435	4436
1.780	4438	4439	4440	4442	4443
1.785	4445	4446	4447.	4449	4450
1.790	4451	4453	4454	4456	4457.
1.795	4458	4460	4461	4463	4464

I.800	4465	4466	4468	4469	4471
I.805	4473	4473	4475	4476	4477
I.810	4479	4480	4481	4483	4484
I.815	4485	4487	4488	4490	4491
I.820	4492	4494	4495	4496	4498
I.825	4499	4500	4502	4503	4504
I.830	4506	4507	4508	4510	4511
I.835	4513	4514	4515	4516	4518
I.840	4519	4520	4522	4523	4524
I.845	4526	4527	4528	4529	4531
I.850	4532	4533	4535	4536	4537
I.855	4539	4540	4542	4543	4544
I.860	4545	4546	4548	4549	4550
I.865	4552	4553	4554	4556	4557
I.870	4558	4559	4561	4562	4564
I.875	4565	4566	4567	4568	4570
I.880	4571	4572	4574	4575	4576
I.890	4584	4585	4586	4588	4589
I.895	4590	4591	4593	4594	4595
I.900	4596	4598	4599	4600	4602
I.905	4603	4604	4605	4607	4608
I.910	4609	4610	4612	4613	4614
I.915	4615	4617	4618	4619	4620
I.920	4622	4623	4624	4625	4627
I.925	4628	4629	4630	4631	4633
I.930	4634	4635	4636	4638	4639
I.935	4640	4641	4643	4644	4645
I.940	4646	4647	4649	4650	4651
I.945	4652	4654	4655	4656	4657
I.950	4658	4660	4661	4662	4663
I.955	4665	4666	4667	4668	4669
I.960	4671	4672	4673	4674	4675
I.965	4677	4678	4679	4680	4681
I.970	4683	4684	4685	4686	4687
I.975	4689	4690	4691	4692	4693
I.980	4695	4696	4697	4698	4699
I.985	4701	4702	4703	4704	4705
I.990	4706	4708	4709	4710	4711
I.995	4712	4714	4715	4716	4717