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On the Evolution of the Lunar Magma Ocean

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and

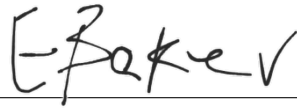
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HILARY 2021

Declaration

I declare that the whole of this thesis is my own work, except where otherwise cited. The views and opinions expressed herein are mine and not necessarily those of any other person or body unless so attributed.



Signature

21.05.2021

Date

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Abstract

The Earth and the Moon are observed to be almost indistinguishable over a range of refractory isotopes systems. This thesis aims to test the hypothesis that the lunar magma ocean (LMO) possessed the same elemental composition as that of the terrestrial mantle. In particular, I explore whether the LMO's differentiation would result in liquid and crystal phases that can reproduce the Apollo observations of the lunar surface. To achieve this, I have conducted a detailed series of experiments which track the evolution of a hypothetical lunar magma ocean of terrestrial mantle composition. I have broken the differentiation of the LMO into discrete steps, with the bulk composition of the next step taken as the melt composition of the previous step. The final experimental liquid, representing $\sim 98\%$ crystallisation of the LMO, is highly enriched in Fe (>30 wt.%) and Ti (~ 3 wt.%). To explore the petrogenesis of the mare basalts and the Ferroan Anorthosite Suite (FAS), I have simulated the remelting of the lunar cumulate mantle using the MELTS program. By recombining experimental phases and melts in different proportions, I am able to prove that the Apollo observations are compatible with a LMO of terrestrial mantle composition. The mafic crystals present in the ferroan anorthosite suite are best matched to experimentally produced crystals rather than melt, indicating inefficient flotation rather than trapped melt has contributed to the ferroan anorthosite suite.

Mineral/melt Rare Earth element (REE) partitioning occurring throughout the evolution of the lunar magma ocean has been experimentally determined, and predict heavy REE depletion of final liquids, due to high-temperature pyroxene crystallisation. Consequently, the 'bow shaped' trend witnessed in the mare basalts results from a lunar mantle possessing pyroxene enriched in heavy REE and a light REE enriched KREEP basalt. I explore the implications of different compositions on the lunar moment of inertia, finding that an overturn of the lunar mantle is more significant than any conceivable change in composition.

It is possible, if not likely, that the refractory element composition of the lunar mantle reflects that of the bulk silicate Earth and hence reconciles geochemical and dynamical models of lunar origin. A terrestrial composition can reproduce the observations of the surface of the Moon and is robust to different initial conditions imposed by the Moon-forming giant impact.

Extended Abstract

The Earth and Moon are identical across a range of refractory isotope systems, but lunar samples are depleted in a number of light volatile isotopes. These observations, alongside the angular momentum of the Earth-Moon system, can be explained by a giant impact occurring between the proto-Earth and a Mars-sized body. Models predict that following the giant impact the newly accreted Moon will, inevitably, be molten. However, the contribution of terrestrial and impactor material to the Moon is not unconstrained by these dynamical models. Furthermore, the ferroan anorthosite suite (FAN) and the mare basalts are compositionally and texturally unlike terrestrial rocks, leading some authors to suggest a bulk lunar composition dissimilar to Earth's mantle. However, this suggestion is contrary to the observed refractory element isotopic similarities between the two bodies. In this thesis, I explore the refractory isotope similarity by asking: **'Is it conceivable that silicate Earth and silicate Moon are identical in refractory element composition?'**

While the mode of a lunar magma ocean crystallisation remains uncertain, this work assumes that crystallisation was fractional.

The canonical model for the crystallisation and evolution of the LMO forms olivine and pyroxene, and after 70% crystallisation, plagioclase. After plagioclase crystallises, the melt becomes enriched in Fe and Ti and densifies, such that late crystallising dense phases are found at the top of the mineral cumulate pile. Then, a density-driven overturn of the lunar mantle forms melts, which are extruded to form the mare basalts.

To test this model, I have broken the fractional crystallisation of a terrestrial pyrolytic lunar magma ocean into 11 equal steps. Such an approach enables the concentration of any element to be accurately predicted (<1 % rel. error) in melt or mineral phases, assuming the mineral/melt is partition coefficient <2 . My ex-

perimental program simulates a fractional crystallisation by crystallising 9 wt. % crystal and measuring the melt composition, the melt composition of the previous melt is used as the bulk composition for the next experiment. A total of 118 experiments were conducted in a Boyd-England type piston-cylinder apparatus, with a graphite capsule and CaF_2 or $BaCO_3/SiO_2$ pressure medium. Experimental conditions ranged from 0.5 to 2 GPa and 850 to 1675 °C, at one log unit above the iron-wüstite ($Fe - FeO$) buffer. Of note, the experimentally produced liquid line of descent differs from that predicted by the *phMELTS* modelling package, which stabilises pyroxene on the liquidus significantly earlier than in my experiments. The final liquid is enriched in Fe, >30 wt.%, and Ti, ~3 wt.%, consistent with the refractory element enrichment required to produce the mare basalts. Comparison between the experimentally produced phases and petrogenetic studies of the mare basalts finds olivines and pyroxenes with the similar MgFe ratios at appropriate depths throughout the lunar cumulate mineral pile. In addition, the spread in Fe/Mg and Anorthite content of the lunar highland forming feldspars matches those sampled by the Apollo missions.

The petrogenesis of the mare basalts and picritic glasses do, however, require secondary remelting of the initial lunar cumulate mantle. To explore these remelting relationships further, the experimentally produced cumulate layers have been computationally remelted to low degree (5 wt.%) using the *phMELTS* thermodynamic modelling package. These melts are recombined, and the proportions are varied, to reproduce the groups of mare basalts and picritic glasses sampled by the Apollo missions. The recombination models require partial melting of the earliest, most Mg rich cumulates, which are found deep in the lunar mantle. Mare and picritic compositions are reproduced very accurately, with few exceptions, requiring the whole lunar mantle to be involved in a density-driven lunar mantle overturn.

In contrast to the mare basalts, the ferroan anorthite suite is primary, directly

derived from the lunar magma ocean. The ferroan anorthosite suite is dominantly composed of feldspar, with a small number of mafic crystals like pyroxene, but it is not clear if such 'mafic' represent trapped crystal or melt. To constrain this, the petrogenesis of the ferroan anorthite suite was modelled by combining the experimental produced phases present when plagioclase is on the liquidus. The 'mafic' present in the ferroan anorthosite suite are shown to be trapped crystals, rather than melt.

All experiments were doped with rare earth elements (REE), allowing REE partitioning between minerals and melt to be tracked throughout the crystallisation of the LMO. I show that the 'bow shaped' rare Earth element trends (i.e., depletion in light and heavy REEs relative to the middle of the lanthanide series) observed in the mare basalts can be explained by heavy REE compatibility in high-temperature pyroxene, and the light REE enrichment of the KREEP basalts. REE enrichment observed in the ferroan anorthosite suite indicates that the Moon has a pyrolytic, and hence, chondritic, inventory of REEs.

Models of the internal density profile of the Moon agree with the measured moment of inertia (MOI); however, the change in MOI arising from the overturn of the lunar mantle is greater than that arising from the various bulk compositional models of proposed, including changes in the core composition. Therefore, a wide variety of core or bulk silicate compositions could be accommodated with reasonable assumptions on the efficiency of lunar mantle overturn, and hence MOI observations do not provide enough fidelity to explore bulk lunar compositions. Therefore, only limited insight can be gained from the moment of inertia or density measurements of the Moon without constraint on the Moon's density profile, from better seismic or gravimetric data.

Overall, the chemical observations of the surface of the Moon are entirely compatible with a bulk silicate Moon of a volatile depleted terrestrial pyrolytic compo-

sition. **It is conceivable, if not likely, that silicate Earth and silicate Moon are identical in refractory element composition,** with the implication that the majority of the Moon originated from the mantle of the terrestrial proto-Earth, with minimal contributions from the Moon-forming impactor.

Table of Common Terms

Element Groups

FAS Ferroan Anorthosite Suite, An Iron rich group of Anorthosites which are a major component of the light colour lunar highlands.

HPE Heat Producing Elements

HREE Heavy Rare Earth Element

KREEP A lunar rock rich in incompatibles, Potassium (K) Rare Earth Elements (REE) and Phosphorus (P)

LREE Light rare Earth Element

PGE Platinum Group Elements

REE Rare Earth Element

Phases and Compositions

CPX Clinopyroxene

Fa Fayalite olivine

Fo Forsterite olivine

LMO Lunar Magma Ocean

MORB Mid Ocean Ridge Basalt

Mg# $\frac{XMgO}{XMgO+XFeO}$

OPX Orthopyroxene

Physical, Analytical and Experimental

BSE Back Scattered Electron, typically refers to an image created by measuring back scattered electrons

EPMA Electron Probe Micro Analyser

LA-ICP-MS Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry

MELTS/phMELTS A thermodynamic modelling program. Used to simulate magma crystallisation and melting paths.

MIF Mass Independent Fractionation, isotopic fractionation that doesn't scale with relative isotopic mass

MOI Moment of Inertia, an objects resistance to changing its turning moment

SEM Scanning Electron Microscope

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1 Introduction

The first artificial object to touch down on the Moon was the Soviet craft, Luna 2. The first crewed mission to the Moon was Apollo 11, which landed at 20:17 GMT on the 20th of July 1969. The Luna and Apollo missions returned a total of 382 kg of material, in over 110,000 individual samples (Nasa, 2016). Later Apollo missions deployed seismographs, which collected some limited seismic data, detecting Moonquakes (~ 7000) and some small meteorite impacts (~ 1800) (Wieczorek, 2009).

Following the Apollo missions (fig. 1.1), which ended in 1972, geophysical orbiter missions have been launched, including: the Gravity Recovery And Interior Laboratory (GRAIL) in 2011, the Lunar Reconnaissance Orbiter (LRO) in 2009, and the Lunar PrOspector (LPO) in 1998. These later geophysical missions have provided compositional maps of the surface and gravimetric data for the interior of the Moon. Most recently, in 2020, the Chang'e 5 lander returned ~ 1.7 kg of regolith. In addition, all the astronauts that have been to the Moon were given geological training in order to select samples, which have been analysed on Earth. These returned samples along with the geophysical observations of the Moon form the basis for our current understanding of the Moon.

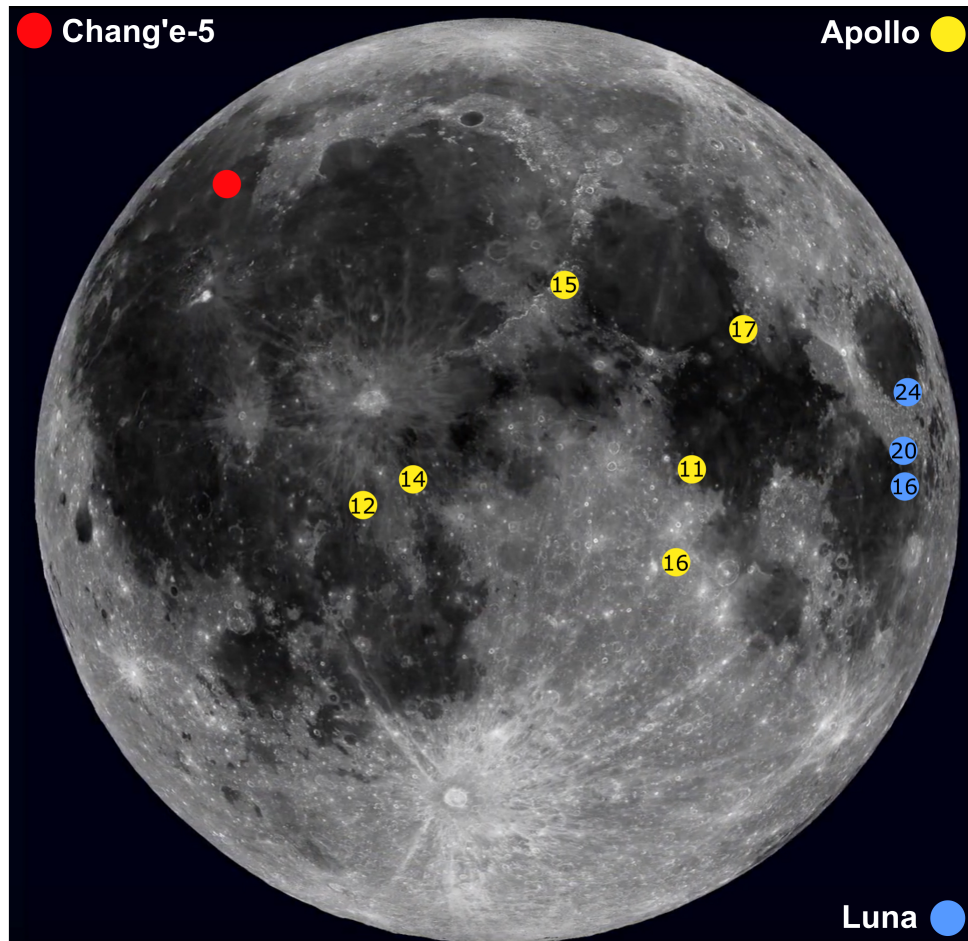


Figure 1.1: Photo shows the nearside of the Moon (NASA). The lunar return sites are all found on the near side of the Moon. The dark mare are smooth volcanic plains, which erupted effusively; principally, the mare basalts pool in impact craters. The raised lighter highlands are older and are scarred by many large impact craters.

1.1 Theories of Lunar Formation

Lunar creation myths are abundant in ancient cultures, the Moon being the left eye of Ra according to the Ancient Egyptians and the ‘white’ of a world egg in Finnish pre-history. Recently, the data collected has allowed the development and testing of natural theories.

Four principal hypotheses for the origin of the Moon have been advanced. The first theory invokes a resonance between solar tides and the slowest free oscillation of the Earth, estimated by George Darwin in 1879 to have a period of 2 hours (Darwin, Stratton, & Jackson, 2009). This hypothesis suggested that the amplitude of the resultant oscillation, if large enough, could have ejected material from Earth to form the Moon. The hypothesis was discounted by Jeffreys (1930) who showed that the friction of Earth’s mantle would preclude such an extreme tidal effect; in addition, the departing Moon would have been within the Roche limit of the Earth (18,400 km radius) and therefore unable to coalesce. The second theory is that the Moon was a wandering object, gravitationally captured as it passed close to the Earth (Gerstenkorn, 1955). However, gravitational capture requires an unknown mechanism to dissipate the kinetic energy of the captured Moon and predicts an independent formation history for the Earth and the Moon. The third theory, proposed by Roche (1873), produces the Moon from a ring of protoplanetary material, analogous to Saturn’s rings. The issue in this case is that if the Moon and the Earth accreted from the same material, it is difficult then to explain the low lunar density, and hence low metallic iron content, of the Moon when compared to the Earth and other terrestrial planets. In addition, rings are typically produced from Moons inside the Roche radius, where celestial bodies are broken down due by the tidal forces of the planet. The final theory, which contains elements of the first three, invokes an impactor colliding with the proto-Earth, forming the Moon from the resulting debris cloud (Hartmann & Davis, 1975). It is this latter hypothesis

that has the majority of the scientific support and observational evidence.

1.1.1 Massive Impact Modelling

Models of a giant impact between a proto-Earth and another planetary-sized body are able to recreate the current angular momentum and mass distribution of the Earth-Moon system. These models employ a range of impactor masses, from roughly equally sized bodies to highly energetic and off-centre collisions with more unequally sized bodies. Smooth particle hydrodynamic (SPH) simulations are able to recreate these collisions (Benz, Cameron, & Melosh, 1989; Cameron, 1997; Cameron & Benz, 1991; Kokubo, Ida, & Makino, 2000). Some disagreement between models is found in the predicted energy of collision which is important in predicting the degree of mixing between the two planetary bodies. Specifically, a collision with enough energy to vaporise silicate will also enable nearly complete mixing between the two bodies (S. Lock et al., 2016). In addition to more thorough initial mixing, a molten disk will mix over longer timescales of between 100s or 1000s of years (Pahlevan & Stevenson, 2007). Material generated during the giant impact that is ejected beyond the Roche radius and with enough energy to enter orbit is available to form the Moon. This material is predicted to accrete rapidly, forming the Moon within ~ 10 years (Canup & Esposito, 1996). SPH models are able to discern the heritage of material that goes on to form the Earth and the Moon by tracking the movement of individual particles. However, the degree of mixing cannot be constrained by SPH models which are dependent on the input parameters, particularly the material properties, of the simulation.

Elsewhere in the solar system, giant impacts are considered to be important in Moon formation, for example for the formation of the Moons of Pluto: Charon, Nix, and Hydra (Canup, 2005, 2011).

1.1.2 Impact Complications

The simple model for deriving the Moon from an impact with an unknown degree of mixing is further complicated by the later addition of material. The Moon's surface area to volume ratio is greater than the Earth's, and any later added material will therefore constitute a greater amount of the Moon's total mass.

The postulated late heavy bombardment, a period of enhanced meteoritic bombardment seen on Earth, was likely initiated by the migration of the gas-giant planets like Jupiter. This migration, known as the 'Grand tack', perturbed the orbits of large meteorites and occurred ~ 700 Ma after the formation of the solar system (Gomes, Levison, Tsiganis, & Morbidelli, 2005). Approximately 0.01 % of the Earth's mass could have been delivered in the late heavy bombardment (Gomes et al., 2005), if similar amounts were received by the Moon it could be 0.1–1 % the mass of the Moon. The added mass is more important for particular elements such as volatiles or siderophiles.

1.1.3 Degree of Mixing Between the Impactor and Proto-Earth

Samples returned by the Apollo missions (1969–1972) established a strong genetic link between the Earth and the Moon, which essentially rules out the capture hypothesis. Initially, this 'genetic link' was based on oxygen-isotope measurements, which show that both lunar and terrestrial rocks lie on the same $O^{16,17,18}$ terrestrial fractionation line (fig. 1.2). Since the oxygen-isotope composition of silicates varied radially in the early solar system, the similarity in the Moon and the Earth's signatures means they likely both formed in the same region of the evolving solar system (Yurimoto & Kuramoto, 2004), or have been mixed. In addition, terrestrial and lunar rocks were shown to have similar ratios of refractory lithophile elements, and more recently virtually identical ratios of the stable isotopes of a number of refractory elements, notably Cr, Ti, and W in addition to O (table 1.1) (Kleine et

al., 2009; Qin, Alexander, Carlson, Horan, & Yokoyama, 2010; U. Wiechert et al., 2001; Zhang, Dauphas, Davis, Leya, & Fedkin, 2012). Given the observed variations in the isotopic ratios of these elements in other solar system bodies, the genetic link between the Earth and the Moon is now confirmed. The implication is that the Moon is predominantly made of terrestrial material, a requirement reinforced by the super-chondritic ratios of Hf/W and isotopic W_{182}^{183} (table 1.1). Since these two ratios are controlled by partitioning into metallic phases during planetary growth, the close similarity between the silicate Earth and the silicate Moon would be most readily explained if the Moon were a fragment of the early Earth’s mantle ejected by resonance (a theory largely discounted) or more probably, by a giant impact, with the majority of lunar material originating from the Earth (Wade & Wood, 2016). Other isotope systems do show a difference between the Earth and the Moon. For example, K, a more volatile element, is depleted in lighter isotopes in the Moon: consistent with volatile loss in a high-temperature silicate vapour, formed from an energetic collision (Wang & Jacobsen, 2016). Volatile loss from the nascent Moon has been examined through different isotope systems, the Cr isotope systematics are consistent with a lower temperature (1800 K) early Moon. (Sossi, Moynier, & Van Zuilen, 2018). This lower-temperature-isotopic modification can be easily explained if it occurred on the Moon once it has accreted and began to cool. In general, the isotopic literature is strongly supporting the conclusion that there was complete mixing between the proto-Earth and the impactor.

Some recent work finds a correlation between the Ti content of lunar materials with the $\delta^{18}O$ (Cano, Sharp, & Shearer, 2020). If the Ti concentration is meaningful, it could point to isotopically different lunar reservoirs. In this case a separate deeper reservoir would be required, a relic of the impactor.

In the round, the weight of evidence points towards a genetic link between the Earth and Moon.

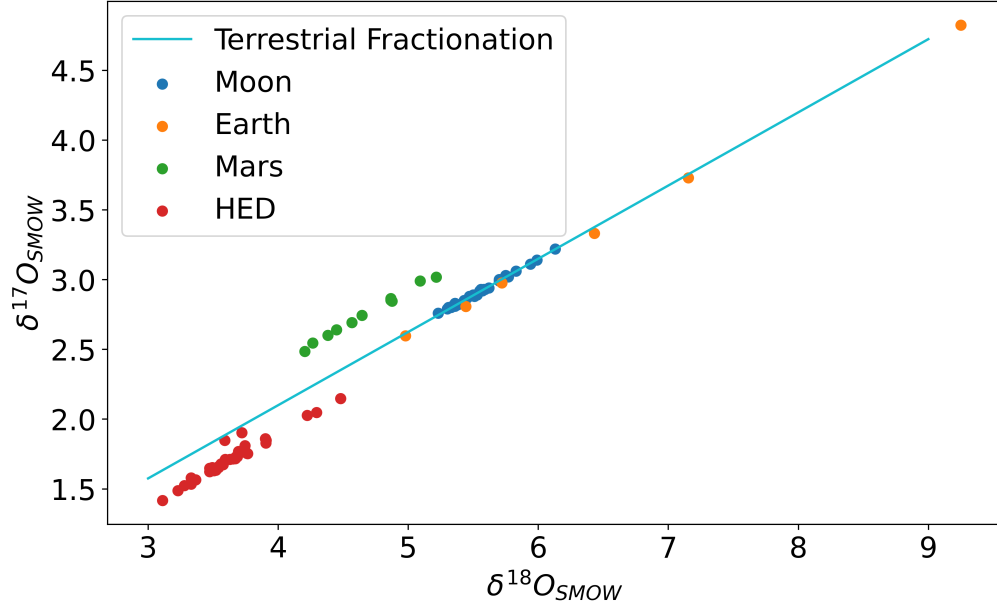


Figure 1.2: Oxygen isotope mass dependent fractionation lines of inner solar system bodies. The terrestrial fractionation line from Ahn et al. (2012) is plotted for comparison. This fraction line falls through the data from the Moon (U. Wiechert et al., 2001; Xiong et al., 2001) and the Earth (Franchi et al., 1999) and is indistinguishable within the measurement precision of the analysis. Samples from Mars (Franchi et al., 1999) and the HED group of meteorites (U. H. Wiechert et al., 2004) are plotted as examples of inner solar system objects that are significantly different from the Earth–Moon line.

	Earth	Moon	Mars	HED	CI	Reference
Hf/W	17 ±5	26 ±2			0.6–1.8	(Kleine et al., 2009)
FeO (wt.%)	8.05	9–12.5	17.9			(Mcdonough & Sun, 1995; O’Neill, 1991; Wanke & Dreibus, 1988; Warren, 2005)
ε182W	1.9 ±0.1	1.9 ±0.1			0	(Kleine et al., 2009)
ε50Ti	0 ±0.01	-0.03 ±0.04	-0.3 ±0.20	-0.44 ±0.42	1.74 ±0.05	(N. H. Williams, 2015; Zhang et al., 2012)
δ54Cr	0.11 ±0.06	0.07 ±0.06	-0.15 ±0.05	-0.67 ±0.14	1.62 ±0.07	(Qin et al., 2010; Trinquier, Birk, & Allegre, 2007)
Δ17O	-0.01 ±0.13	-0.001 ±0.005	0.43 ±0.16	0.41 ±0.09	0.41 ±0.04	(Clayton & Mayeda, 1983, 1999; Franchi et al., 1999; Young et al., 2016)
ε62Ni	0.01 ±0.04		0.04 ±0.05		0.14 ±0.07	(Tang & Dauphas, 2014)
δ30Si	-0.27 ±0.01	-0.27 ±0.02	-0.49 ±0.03	-0.41 ±0.03	-0.44 ±0.03	(Zambardi et al., 2013)

Table 1.1: Compositional values for major inner solar system bodies.

1.2 Lunar Magma Ocean Physics

Following an energetic Moon forming collision, the newly accreting Moon will be hot, inviscid and convecting rapidly. For crystals to settle, the settling velocity, equivalent to the terminal velocity, must exceed the convective velocity. Whether or not these conditions are satisfied in the lunar magma ocean (LMO) has not been resolved. The conditions which would enable a fractional, rather than equilibrium crystallisation, are set out in eq. (1.1) and eq. (1.2). Equation (1.1) calculates the Rayleigh number: values above 1 indicate that buoyant, convective forces dominate whereas values below 1 refer to systems where viscous forces dominate. Lower Rayleigh numbers will make crystal settling more likely. Equation (1.2) computes the Stokes falling velocity (V_{fall}), an approximate solution to a sphere falling through a viscous fluid. If V_{fall} exceeds the convective velocity crystal settling may occur. The density settling of a fluid with multiple crystal phases is more complex due to energy transfer between different crystals during collisions (Suckale & L.T. Elkins-Tanton, 2011). A higher crystal fraction increases the number of collisions, which could reduce the efficiency of crystal sorting and settling. Experimental studies which explore crystal settling suggest that even in the case of large convective velocities, boundary regions where the characteristic length scale is reduced, are important and will allow crystals to settle (Martin & Nokes, 1988). Numerical models find that if crystals are large enough (>1 mm) and crystal fractions are low enough (< 13 vol. %) crystal settling will occur throughout the magma ocean (Suckale, Elkins Tanton, & Sethian, 2012; Suckale, Sethian, Yu, & Elkins Tanton, 2012). Other studies suggest that crystal sizes of up to 1 m in diameter can be suspended in a LMO, and that the viscosity in the convection cell is the major factor controlling crystal settling (Tonks & Melosh, 1990). The work presented here does not explore these arguments in detail but is conditional on the fractional nature of the LMO. Thus, this study assumes that the physical conditions to enable settling must be

present, however there are multiple sets of physical conditions that could give rise to a fractionally crystallised ocean.

It is important to note that only the volume of the magma ocean that can sustain extant crystals is able to differentiate: if adiabatic melting recombines crystals and melt, differentiation cannot proceed. On Earth, the steep pressure gradient prevents particularly deep magma oceans from differentiating as a single body because the depths over which crystals could exist, that is the physical distance between the liquidus and solidus, is small (10–100s of Km, see fig. 1.3). On the Moon, because the pressure gradient is much smaller, the adiabatic gradient is much lower enabling a deeper magma ocean (fig. 1.3). Thus, if the LMO were to evolve fractionally, it would enable greater enrichment in the incompatible elements than seen on Earth. The characteristic convecting velocity of a fluid is most strongly controlled by the characteristic length scale, in this case the depth of the LMO. For a LMO with a depth of 1000 km the convective velocity could be as high as 100 ms⁻¹ (Suckale, Sethian, et al., 2012).

$$Ra = \frac{\alpha \cdot g \cdot \Delta T \cdot D^3}{\kappa \cdot \nu} \quad (1.1)$$

Equation 1.1: The Rayleigh Number (Ra), dimensionless. Ra for a lunar ocean is dependent on the depth of the ocean cubed. This would suggest fast convection velocities and a turbulently convecting ocean. The length scale of convection is the dominant factor and the turbulence would likely be much higher than on Earth. α = Coefficient of thermal expansion, g = Gravity, ΔT = Temperature difference between the two boundaries, κ = Thermal conductivity, ν = Kinematic viscosity

$$V_{fall} = \frac{2 \cdot (\rho_1 - \rho_2) \cdot g \cdot a^2}{9 \cdot \rho_1 \cdot \nu} \quad (1.2)$$

Equation 1.2: Stokes falling velocity, ms⁻¹. The dominant control on the falling velocity (Vfall) is the size of the crystal. The density difference and the strength of gravity are smaller factors. Viscosity is also an important control, but this also influences the turbulence and speed of convection, so may not be significant. ρ_1 = Density of crystal, ρ_2 = Density of the liquid, ν = Viscosity of the liquid, a = characteristic length scale of crystal, g = Acceleration due to gravity

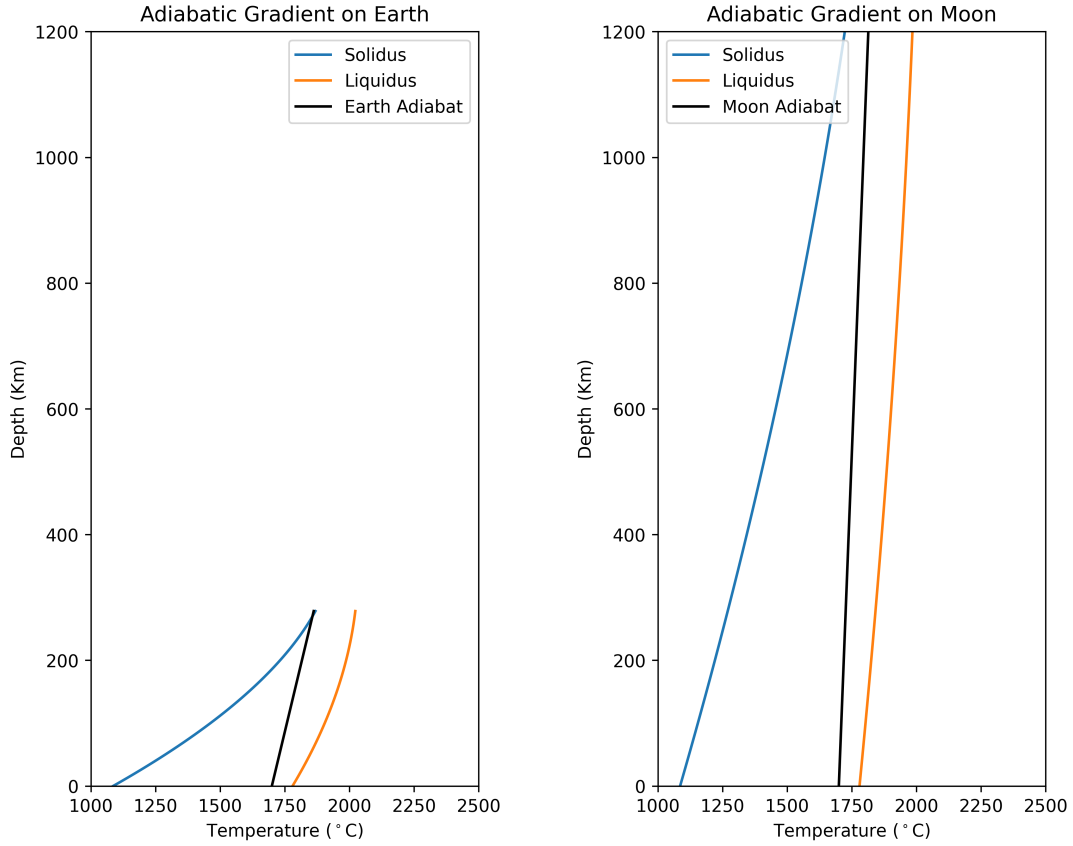


Figure 1.3: Adiabats on the Earth and the Moon, using a potential temperature of 1700 °C for both the lunar and terrestrial mantle. Solidus and liquidus lines are taken from (Katz et al., 2003), with pressure converted to depth using g of 9.8 and 1.6 ms^{-2} for the Earth and the Moon, respectively. Earth's adiabat assumes a $0.6 \text{ }^{\circ}\text{Ckm}^{-1}$ gradient, which is converted to a lunar gradient using the lunar value of g (1.6 ms^{-2}). All discrete mineralogical transitions have been omitted to allow comparison. Because of the significantly lower lunar gravity, the Moon's adiabat lies between the lunar mantle's liquidus and solidus over a greater range of depths when compared to that of the Earth

Oxide	N-MORB	D-MORB	E-MORB	A 11 high K	A 11 low-K	A 17 Low-K	A 12 pi-geonite	A 15 pi-geonite	A 12 Olivine	A 15 Olivine	A 12 Ilmenite
<i>SiO₂</i>	50.42	50.39	50.58	40.5	40.7	38.7	46.4	48.1	44.2	44.9	43.3
<i>TiO₂</i>	1.53	1.51	1.53	11.6	10.1	12.5	3.5	1.8	2.6	2.4	4.3
<i>Al₂O₃</i>	15.13	14.93	14.94	8.8	10.3	8.9	10.5	9.3	8	8.8	8.4
<i>Cr₂O₃</i>				0.4	0.3	0.5	0.5	0.5	0.6	0.7	0.5
<i>FeO</i>	9.81	10.15	9.64	19.1	18.7	18.6	19.8	20.1	21.2	22.3	21.4
<i>MnO</i>	0.171	0.178	0.165	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
<i>MgO</i>	7.76	7.82	7.37	7.4	6.9	9.1	7.6	8.9	14.3	10.2	11.9
<i>CaO</i>	11.35	11.49	11.18	10.7	11.7	10.8	11.2	10.5	8.5	9.8	9.4
<i>Na₂O</i>	2.83	2.71	2.72	0.5	0.4	0.4	0.3	0.3	0.2	0.3	0.3
<i>K₂O</i>	0.14	0.096	0.394	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Table 1.2: Average compositions of mare basalt groups (Jolliff et al., 2006) and mid ocean ridge basalts (Gale et al., 2013) N-MORB is average Mid Ocean Ridge Basalt, found more than 500 km away from a mantle hotspot. D-MORB is MORB depleted in incompatible elements. E-MORB is MORB enriched in incompatible elements.

1.3 Geophysical Observations

The only direct way to collect data on the interior of the Moon is through geophysical observations. The Apollo 12, 14, 15, 16 missions deployed seismographs as part of the science package, which were able to collect data until 1977. These seismographs are the only source of seismic data on the Moon. The physical deployment of seismic sensors on the Moon was hampered by a thick layer of dusty regolith, which inhibited seismic coupling, and consequently, reduced data quality.

1.3.1 Crustal

GRAIL The Gravity Recovery And Interior Laboratory survey mission to the Moon was launched on the 10th of September 2011. The mission used two spacecraft, ‘Ebb’ and ‘Flow’, which orbited in formation. GRAIL found the crust to be 2550 kgm^{-3} on average, with 12% porosity to a depth of at least a few km. The lateral variations in crustal porosity correlate with impact craters and the crustal density variations are controlled by composition. GRAIL constrained the crustal thickness to 34–43 km. However, in some places the crust is drastically thinned, as little as 1 km thick on the far side of the Moon in the Moscoviense basin (Wieczorek et al., 2013).

Surface compositional measurements The lunar prospector and the lunar reconnaissance orbiter missions produced elemental maps of the lunar surface. These maps find an inverse correlation between FeO and Al_2O_3 and an average lunar surface Mg# of ~ 60 , $Mg\# = \frac{[MgO]}{[MgO][FeO]}$. A Neutron Activation Analysis (NAA) study performed by (Wolf & Anders, 1980) revealed that the Moon possesses a trace element content¹ ~ 2.6 % of Earth’s, across a range of elements of variable volatility. Volatilisation or partitioning into metal phases could explain the observed deple-

¹Elements in the study are: siderophiles (Os Ir Re Ni Pd Au) and volatiles (Sb Ge Se Te Ag Zn Sn In Br Cd Bi Tl)

tion, such conditions come with implications for the conditions immediately after the Moon-forming impact.

Magnetism Samples of the Moon’s crust have been analysed for remnant magnetism, they exhibit a brief period of high palaeomagnetic intensity, 100 μT compared to the baseline of 10 μT , for lunar rocks aged 3.9–3.6 Ga. The reason for the temporary nature of the lunar magnetic field is unknown. In addition, the high strength of the Moon’s field (the Earth’s is 30–60 μT) is difficult to achieve with the small expected size of a lunar core (Wieczorek et al., 2006b).

A possible explanation that has been advanced for the late and intense lunar dynamo involves material with high concentrations of heat-producing elements, descending through the lunar mantle to the core-mantle boundary. The heat-producing elements lower the thermal gradient across the core/mantle boundary, which prevents core convection, slowing any dynamo effect. The material later partially melts to contribute to the mare basalts, removing the ‘blocking effect’ on a core dynamo and initiating a short period of intense convective activity (Stegman, Jellinek, Zatzman, Baumgardner, & Richards, 2003). The concentration of magnetic anomalies in ejecta deposits and a correlation of the antipodes of meteorite impacts with stronger magnetic anomalies has led to suggestions that impactors are important (Halekas et al., 2001). Hood and Artemieva (2008) suggested that plasma produced from impactors goes around the Moon to the antipode of the impact, locally intensifying the magnetic field.

1.3.2 Mantle

Seismic stations on the Moon have approximately 8 years of data, gathered between the Apollo 12 and 16 missions. The recorded Moonquakes are primarily composed of 1800 meteorite impacts, 28 shallow Moonquakes and approximately

7000 deeper (> 100 km) Moonquakes (Wieczorek, 2009). The deeper Moonquakes are correlated with tidal forcing from the Earth and not found on the far side, although the far side could suffer from stronger attenuation at depth, preventing detection of far-side Moonquakes (Bulow, Johnson, Bills, & Shearer, 2007; Nakamura, 2003). The seismogenic regions are 300 ‘nests’ that are continually reactivated, and correlated with Earth-tides. These nests could represent magma-filled cracks that accommodate tidal forces from Earth, the small s-wave components could suggest small amounts of melt (Nakamura, 2005; Wieczorek, 2009). If these ‘nests’ do represent pockets of melt, radioactively heated, they could be consistent with late dense KREEP like liquids descending to the core-mantle boundary (Mallik, Ejaz, Shcheka, & Garapic, 2019).

The observed difference in magmatic activity and crustal thickness between the near and far side of the Moon means that their mantle structures may also be different. From the limited seismic tomography, inversions of gravity, and electrical conductivity measurements, the mantle is inferred to be composed dominantly of orthopyroxene and olivine with limited clinopyroxene and garnet. However, these inversions are non-unique and limited by paucity of electrical conductivity lab measurements (Kuskov & Kronrod, 2009).

1.3.3 Core

As the Moon passes through the Earth’s magnetic ‘tail’, an artefact of the interaction of the Earth’s magnetic field and the solar wind, electrical currents are induced inside the Moon. Magnetotelluric measurements of the Moon’s interior imply the existence of a high-electrical-conductivity core with a radius of about 340 km (Hood, Mitchell, Lin, Acuna, & Binder, 1999) consistent with seismic inversions. Laser ranging measurements indicate that energy is being dispersed - there is a liquid solid interface - at approximately the same radius (J. G. Williams, Boggs, Yoder,

Ratcliff, & Dickey, 2001). Together these measurements suggest at least a semi-liquid core-mantle boundary. The physical state and composition of the core is very poorly constrained, the liquid outer core implies a light element component, likely S (Weber, Lin, Garnero, Williams, & Lognonné, 2011). Unfortunately, none of the well-defined ray paths pass through the core so seismic velocity cannot be used to constrain the state of the core (Jolliff et al., 2006). The density is consistent with a pure iron or iron sulphide core. As a measure of the limitations of our understanding of the lunar core, the current measurements of the lunar core are compatible with a Fe- and Ti- rich silicate (Wieczorek, 2009).

1.4 Geochemical Data

1.4.1 Primary Crust

Ferroan Anorthosite Suite (FAS) The most striking feature of the FAS is that it is nearly mono-mineralic, > 95 % plagioclase by mass (N. J. Dygert, Lin, Marshall, Kono, & Gardner, 2017). Very few FAS rocks contain more than 10% mafic minerals, and this observation combined with the coarse grain size and texture means that the FAS is likely a cumulate deposit. In addition to the high feldspar content, the FAS has low Mg# (40-80 Ohtake et al., 2012) minerals. Typically, as feldspar evolves from calcic to sodic the mafic minerals become more ferric, however high iron contents are found across the FAS (Jolliff et al., 2006). The depth of emplacement can be estimated from inferred cooling rates, none of the samples studied indicate emplacement depths greater than 25 km (Mccallum & O'Brien, 1996).

Sm-Nd isochrons indicate ages for the FAS between 4.54-4.29 Ga, suggesting that the FAS is primary formation, extracted directly from the lunar magma ocean. An age as late as 4.29 Ga could indicate a suite of rocks that has remained hot for up to 200 Ma, which would suggest a slow solidification of the LMO, alternatively the geochronometer could have been reset. The FAS is most abundant at the Apollo

16 site, 9.18 kg out of 9.47 kg collected, much of the FAS data is from the Apollo 16 site (fig. 1.1). The Apollo 16 site is not found to be representative of the broader FAS dominated crust as observed by the lunar reconnaissance orbiter, with greater Fe (5.5 vs 4.5 wt. % FeO) and Th (1.8 ppm vs <1 ppm Th), than the average highlands. This difference is largely due to mafic impact melt (Wieczorek et al., 2006b).

It is possible, if not likely, that the whole crust is not represented well by the surface, and some craters which excavate deep into the crust show a systematic decline of feldspar with depth (Ryder & Wood, 1977).

South Pole Aitkins Terrain The South Pole Aitken Terrain is found in the largest impact crater in the surface of the Moon, with a diameter of 2600 km. The crater exposes deep material within the lunar crust, excavating about 12 km into the crust. The crater is not filled by any mare basalts despite the impact occurring early in the Moon's history (Jolliff, Gillis, Haskin, Korotev, & Wieczorek, 2000). The deeper more central region has a higher FeO content (~ 10 wt.%) than the sides ($\sim 4-5$ wt.%) which represent more shallow sections of the lunar primary crust

Magnesium Suite The Mg suite rocks are pristine lunar rocks, dominated by feldspar, but with higher Mg#’s ($Mg\# = \frac{XMg}{XMg + XFe}$) than the FAS, between 0.6 and 0.95. Generally, the Mg# decreases with An number, from An_{98} to An_{84} but there are a number of sub groups which appear unrelated. The Mg Suite may be consistent with Mg rich melts intruding the FAS rich anorthosite crust. However, the brecciated grains that represent the Mg suite are small and the bulk composition of these small samples may not be representative of the whole rock.

Isotopic dating indicates that there is overlap in age between some Mg suite rocks and the FAS; some of the oldest Mg suite rocks (<4.3 Ga Jolliff et al., 2006) are nearly as old as the oldest FAS rocks (4.4 Ga - Nemchin et al., 2009). The

ages suggest that the petrogenesis is more complicated than simply intruding and hybridising with the FAS.

A study on an Mg suite rock with clinopyroxene, orthopyroxene and chromium spinel (Herzberg & Baker, 1980), found these rocks to be equilibrated at 800-900 °C at pressures of 220-250 MPa, which corresponds to 42-50 km in depth. However, this is only one sample and, again, may not be representative of the Mg suite at large.

Alkali Suite Represented by only 14.3 grams, the alkali suite is the smallest of the highland lithologies. Most Mg#’s are between 0.6-0.4. The distinguishing feature of the alkali suite is the high Na_2O content, averaging about 1.6 wt.%, which is not necessarily accompanied by high levels of K_2O . Snyder, Neal, Taylor, and Halliday (1995); Shervais and McGee (1999) report a relationship between the alkali suite and the Mg suite: KREEP fractionation is suggested to be able to produce both the Mg suite and Alkali suite. This hypothesis has been challenged as the two rocks types are not found in the same place. Another characteristic of the alkali suite is their very high Eu concentrations, 3-8 ppm (av. 6 ppm), which is much higher than that of the FAS (~ 0.8 ppm) and Mg Suite (~ 1.2 ppm) (B. L Jolliff et al., 2006). The Alkali suite dates from 4.3 to 3.8 Ga, although the younger cut off could result from the absence of deep impact basins that expose the lowermost lunar crust. Very little is known about the abundance of the alkali suite on the Moon. It is possible that the alkali suite represents small melt rich pods trapped or larger intrusions in the shallow crust. The Alkali suite is more abundant in the western landing sites, Apollo 12 14 and 15, suggesting they made be confined to the KREEP terrain and it has been proposed that they were emplaced at shallow depths, within 2 km of the surface (Jolliff et al., 2006).

1.4.2 KREEP Basalts

The KREEP basalts are rich in incompatible elements such as K, the REEs, P, U and Th. These incompatible and heat producing elements are not compatible in most silicate minerals and so typically concentrated within the melt phases. The core-rim compositional profiles, seen in the pyroxenes and plagioclase found in this group of basalts, are consistent with olivine fractionation. The REE concentrations are more than 150 times chondritic, indicating that KREEP forms from highly incompatible enriched material with much material removed from the starting composition. The Apollo 15 KREEP basalts are similar to one another, and distinct from those collected by Apollo 17, which are more ferroan (0.6 compared to 0.5 Mg#) and less enriched in incompatibles, half or a third as rich. The Apollo 15 KREEP basalts were extruded from 3.82-3.68 Ga, shortly after the Imbrium impact event (Ryder, 1994). Apollo 17 KREEP basalts are older, from 3.93-4.08 Ga (Shih, Nyquist, Bansal, & Wiesmann, 1992).

1.4.3 Mare basalts

The Mare basalts are volcanic rocks, formed from partial melting of the lunar mantle. These melts, once formed, are extruded onto the lunar highland crust and typically pool in meteorite impact craters, forming the *mare*. The mare basalts are dated, using crater counting statistics and some absolute dating techniques, from 3.93 to 1.2 Ga, the youngest of the mare are found on the *Oceanus Procellarum* (Hiesinger, Head, Wolf, Jaumann, & Neukum, 2003). The variety of mare basalts has generated several different classification schemes to group them and allow genetic relationships to be established. For the purpose of this thesis, the C. R. Neal and Taylor (1992) method is used (see fig. 1.4). More detailed, group specific, petrogenetic descriptions of the mare basalt groups are found in Chapter 3.

Mare basalts are chronologically separated from the primary crust as their liq-

uid melts continued to extrude after the formation of the primary crust (Taylor, 1982). The chemical data set suggests a bimodal distribution of the Ti content of mare basalts (section 1.4.3). However, this could be a sampling artefact, remote sensing data of Ti contents of mare lithologies shows a smooth continuous distribution (Giguere, Taylor, Hawke, & Lucey, 2000). Recent work by (Kato et al., 2017), suggests that there is a significant step change in the compositions and associated timing of the mare basalt eruption, linked to radiogenic heating or lunar mantle overturn (figs. 1.5 and 1.8). If true, it would suggest that any apparent bimodality is a real consequence of a discrete change in the driving mechanism of eruption.

The mare basalts are dissimilar to common terrestrial basalts (table 1.2); perhaps most obviously that the mare basalts are significantly richer in Fe and Ti. However, the Fe and Ti enrichment is not witnessed by all the mare samples, with significantly more variability than found in terrestrial MORB. This dissimilarity has led many studies to suggest that the bulk silicate Moon is significantly enriched in Fe and/or refractory elements compared to Earth. It is this observation, that the bulk silicate Moon is refractory element and Fe enriched compared to Earth, that is at odds with the isotopic and trace element similarities between the bulk silicate Moon and Earth. Chemically, the mare basalts are most easily differentiated by their Ti content, which varies from < 1 wt. % to > 19 wt. % (Heiken, Vaniman, & French, 1991)

The whole spectrum (K , Na and H_2O , Cl) of volatile elements are depleted in the mare basalts compared to terrestrial rocks, by approximately $2/3^{rds}$ (Wetherill, 1971), based on the K/U and isotopic Pb ratios.

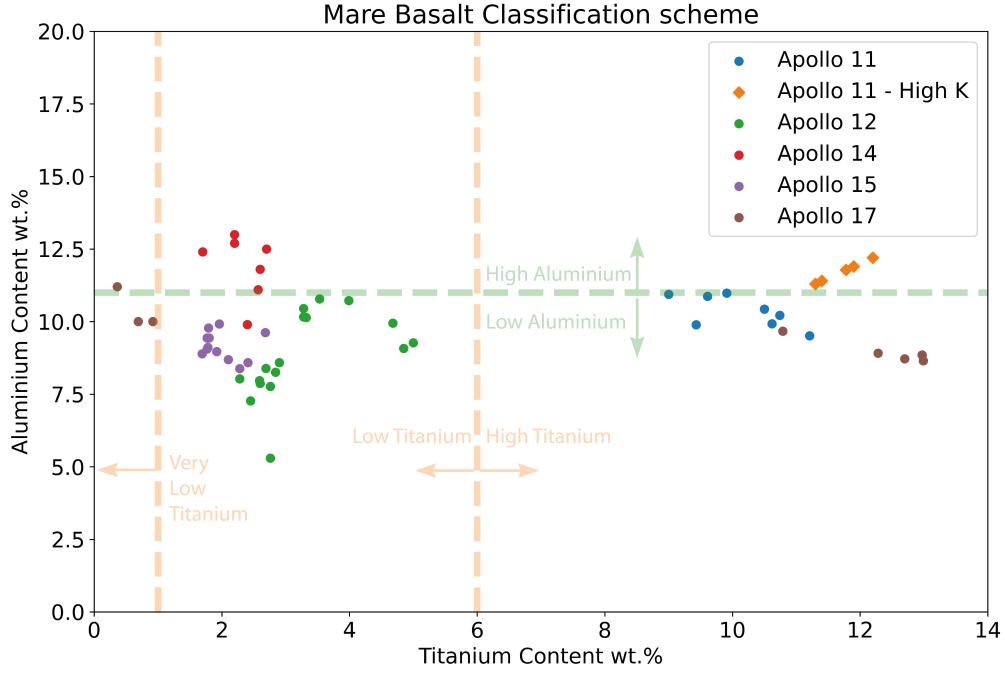


Figure 1.4: Mare basalt classification diagram according to (C. R. Neal & Taylor, 1992). Ti and Al content of bulk mare basalts, coloured by their respective mission. The Al and Ti content are the major characteristics used to classify the basalts. After classification by Al and Ti, K content is used. 2000 ppm is the boundary of the high and low K basalts.

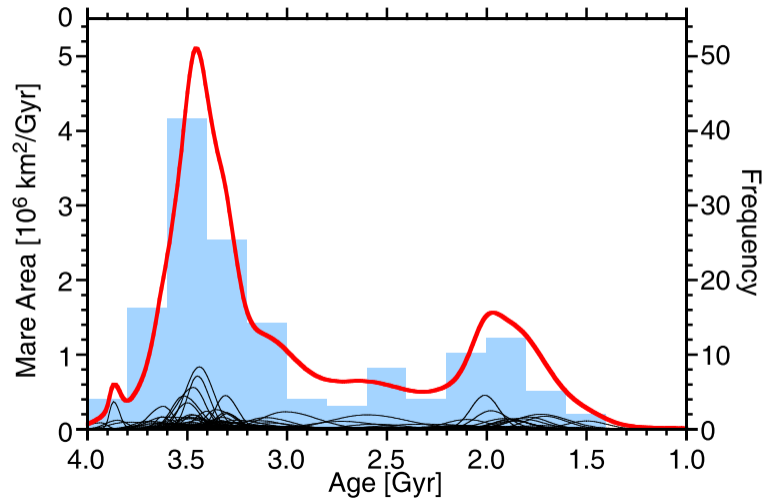


Figure 1.5: Mare basalt age distribution. Figure from Kato et al. (2017). Dated mare basalt flows are plotted as Gaussian distributions, with the width determined by the age uncertainty and the height by the area of flow. Red line is sum of the distributions.

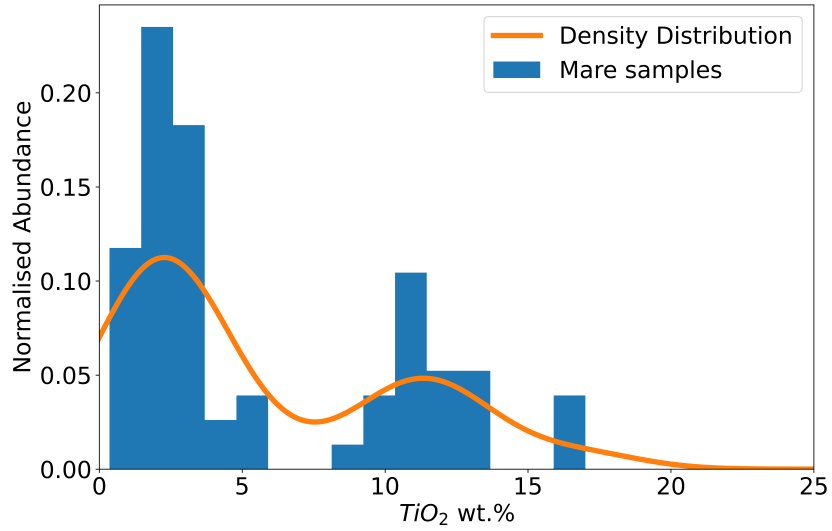


Figure 1.6: Density distribution of TiO_2 content of mare basalts. Density plot is bimodal. Data from Jolliff et al. (2006)

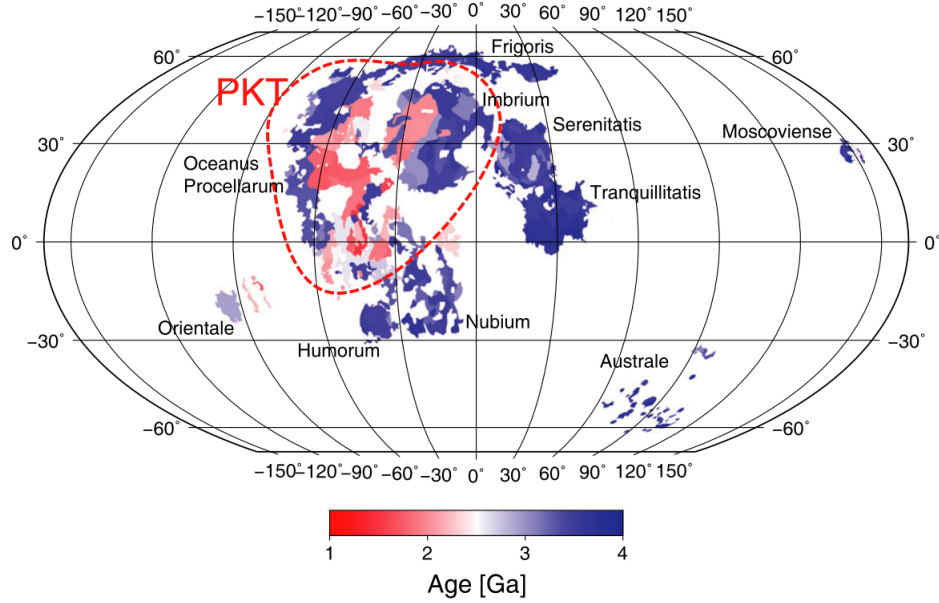


Figure 1.7: Age distribution of mare basalts, figure from Kato et al. (2017). Significant concentration of younger basalt flows in the Procellarum KREEP Terrane (PKT)

1.5 Models of the Bulk Composition of the Moon

There have been multiple attempts to constrain the bulk composition of the Moon. Broadly these investigations consider important observations of parts of the surface of the Moon to constrain the composition of the lunar mantle. The initial state of the Moon is of primary importance in these models, for instance, any giant impact results in rapid lunar accretion, the resultant proto-Moon being totally molten. In contrast if all the gravitational potential energy is conserved, the Moon can only melt to a depth of 500 km, assuming an initial temperature of 800 °C (A. E. Ringwood, 1976).

A summary of proposed lunar compositions is found in table 2. Many of the compositions can be nearly reconciled with subtraction of Forsterite, which could simply be a function of the depth of the lunar magma ocean, see table 1.3. What follows is a brief overview of the main lunar compositional models which have been proposed by various authors.

1.5.1 Taylor-Jakes

Taylor and Jakes (1974) estimated the bulk silicate Moon to be 50% enriched in refractory elements compared to the Earth. Their approach used orbital measurements to establish elemental ratios in the lunar crust. For example, orbital measurements of the Th concentration of yields average crustal concentration to be 1500 ppb, for both Mare and Highlands. With an assumed crustal thickness of 60 km, 10% of the Moon, this measurement can be used to calculate the Th concentration of the whole Moon (150 ppb); which compares to 79.5 ppb for terrestrial pyrolite (McDonough & Sun, 1995) and is four times that of chondrites (35 ppb). Th, as a refractory incompatible lithophile, should be strongly partitioned into the lunar crust and is used as a proxy for other refractory elements. Heat flow data from the Apollo scientific payload was used to estimate that the U concentration in

the bulk Moon, which is 4-7 times the chondritic value. These values for U and Th were then combined to develop a silicate Moon model in which refractory lithophile elements are enriched by a factor of 5 relative to chondrites, thus setting the abundances of Al, Ca and Ti. The FeO content was set at 10.5% to satisfy magnetic and density constraints (Dyal, Parkin, & Daily, 1974). Finally, a chondritic Si/Mg ratio was used to constrain Mg and Si.

1.5.2 Ringwood

A. E. Ringwood (1976) experimentally evaluated the Taylor and Jakes model lunar composition by investigating melting and crystallization at high pressures and temperatures. He simulated the fractional crystallization sequence of the lunar magma ocean and developed models of the partial melting behaviour of potential cumulate layers. Although the Taylor-Jakes composition is capable of producing an anorthositic crust of approximately the correct thickness (~ 60 km) Ringwood found that the potential source region of the Mare basalts, a pyroxene-rich layer at ~ 200 km depth would be incapable by partial melting of generating the low- Al_2O_3 , low CaO basalts which are common in the Mare regions. He therefore argues that the Taylor-Jakes composition is too rich in CaO and Al_2O_3 , perhaps by a factor of 2, and that these should be reduced and replaced by enhanced concentrations of Mg, Si and Fe. Indeed he states “The lunar bulk composition would then approach that of the Earth’s mantle”.

A. E. Ringwood, Seifert, and Wänke (1987), expanded on this suggestion by showing that breccias from the Apollo 16 landing site lie on a mixing line between highland anorthosite and komatiite. They then assumed that the lunar mantle can be represented by a mixture of the inferred komatiite composition and its liquidus olivine, in an analogous manner to some models of the Earth’s mantle. The next step was to add sufficient olivine (22-44%) to the komatiite such that the Mg/Si

ratio of the mantle lies in the range between that of CI chondrite and that of the Earth. The resultant composition (table 1.3) is similar to that of Earth’s mantle but again enriched in Fe and impoverished in alkalis.

1.5.3 Jones-Delano

Jones and Delano (1988) constructed a bulk Moon composition (table 1.3) from a mixture of 3 end-members. They assumed that the early Moon differentiated into an olivine-rich residuum of $\sim$ Fo90 composition and an *FeO*-rich magma ocean. They then allowed the magma ocean to differentiate to form an olivine ($>$ Fo80) + orthopyroxene cumulate and a hypothetical liquid precursor (PPG) to the lunar mafic glasses. The 3 end members, PPG, cumulate and residual olivine were mixed to yield a model Moon composition constrained to have CI chondritic Mg/Al.

1.5.4 O’Neil

O’Neill (1991) developed a chemical model of the Earth and Moon which is based on the giant impact hypothesis. Due to the low concentrations of weakly siderophile elements in Earth’s mantle he argued that the first 90% of Earth’s accretion was under highly reducing conditions such that elements such as V, Cr and, to a lesser extent, Si were partitioned into the core. Most of Earth’s Fe, and all of the more strongly siderophile elements such as Ni, Co, W and the Pt-group entered the core during this phase. The second stage involved impact of an oxidized body of $\sim$ 11% of Earth’s mass, which supplied oxidized Fe Ni, Co and W to the Earth’s mantle and ejected debris which was a mixture of mantle and impactor. The ejected material was assumed to consist of all the impactor and 50% of Earth’s mantle and would have been a mixture of liquid and vapour. Most of this material was re-accreted to Earth with a small-volatile depleted fraction forming the Moon. Finally, a “late veneer” of 0.5-1% H-chondrite-like material is proposed to have been added

to Earth with 4% of similar material providing all of the Moon’s volatile elements. Note that much more recent data on highly siderophile element abundances (e.g. Day and Walker, 2015) indicate that there was proportionally much less “late veneer” added to the Moon than to the Earth. The important point of the approach, however, is that it addresses the chemical similarities between Earth and Moon in a holistic way while providing a rational means of explaining small differences between the two bodies.

1.5.5 Warren

Warren (2005) re-interpreted bulk lunar Th content derived from the Lunar Prospector gamma-ray data to argue for bulk lunar Th of ~ 0.07 ppm. Assuming chondritic ratios of refractory elements, including Th leads to a bulk lunar Al_2O_3 content of 3.8%. He then uses data on highland regolith to argue for a high Mg endmember which, extrapolated to 3.8% Al_2O_3 would have MgO/FeO of ~ 3.9 . The Mn/Mg ratio was then used to infer the MgO/SiO_2 ratio (0.77). From these constraints the composition of the whole silicate Moon was calculated. As with several of the other estimates, the result is only slightly enriched in FeO relative to Earth’s mantle (table 1.3).

1.5.6 Longhi

Longhi (2003) investigated the fractionation of a hypothetical lunar magma ocean formed either from the Lunar Primitive Upper Mantle (LPUM) of (Hart & Zindler, 1986b) or the Taylor Whole Moon (TWM) enriched in refractory elements (Taylor, 1982). He used 3 bulk compositions 1. Ferroan Anorthosite Parent (FP), a composition designed to produce the crystals found in the Ferroan suite. 2. Ferroan Residual (FR), designed to mimic late stage melts after plagioclase crystallization and 3. A ‘Taylor Bence series’ (TB) designed to map out the olivine and orthopy-

roxene crystallization sequence under lunar conditions. The lunar mantle contains too much Al_2O_3 to generate the source regions of the low Ti mare basalts and green glasses, and that the LPUM composition (table 1.3) is a better model provided it undergoes fractional crystallization until plagioclase appears.

Wt. %	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO	Reference
Warren	0.05	36	3.87	46.8	3.06	0.18	0.44	0.13	9.24	(Warren, 2005)
Taylor Heavy Moon	0.09	32.7	6.14	44.4	4.6	0.31	0.61	0.15	10.9	(Taylor, 1982)
Ringwood et al	0.06	36.85	3.72	43.24	3.03	0.3	0.32	0.16	12.24	(A. E. Ringwood et al., 1987)
O'Neill	0.05	35.1	3.9	44.6	3.3	0.17	0.47	0.17	12.4	(O'Neill 1991)
Jones and Delano	-	37.1	3.7	42.6	3	0.19	-	0.19	13.6	(Jones & Delano, 1988)
Longhi	0.05	38.3	3.93	46.1	3.18	0.17	0.5	0.13	7.62	(Longhi, 2003, 2006)
Terrestrial mantle	0.36	37.8	4.45	45	3.55	0.2	0.38	0.14	8.05	(McDonough & Sun, 1995)
Experimental Starting composition (B)	0.15	34.32	5.47	45.87	4.36	0.25	0.47	0.16	8.96	This work

Table 1.3: Compositions of the bulk silicate Moon according to different authors. The major changes are different degrees of refractory element enrichment, inferred from thickness and composition of bulk crust and the amount of iron enrichment required in the bulk Moon, required to produce enough iron enrichment in the mare basalts.

1.6 Lunar Mantle Overturn

During the crystallisation and solidification of the lunar magma ocean, after plagioclase begins to crystalize, the density of the melt begins to increase. Dense metals like Fe and Ti concentrate in the melt, in the final 5% of crystallisation, forming dense phases like rutile (4250 kgm^{-3}) and ilmenite (4786 kgm^{-3}) (Robie & Bethke, 1962). The lunar mantle overturn hypothesis postulates a dense descending lithology, which is able to transport Fe and Ti rich phases down into the deep lunar mantle. (Elkins Tanton, Van Orman, Hager, & Grove, 2002) conduct numerical models of the density and viscosity of the layer of Fe and Ti rich minerals in the lunar upper mantle. The FeTi phases are sufficiently dense only when cool, temperatures which satisfy the density constraint produce a prohibitive viscosity. However, three possible mechanisms would allow the dense FeTi phases to sink (Elkins Tanton et al., 2002).

1. **Remelting of FeTi ilmenite rich zone** Ilmenite and clinopyroxene, at 100 km deep in the Moon, melt in a roughly 2:1 ratio. The liquid produced from this is dense and will percolate into the deeper lunar mantle. The speed of descent will be from $0.4\text{-}9 \text{ cm yr}^{-1}$ depending on the porosity and grain size. Once at the correct depth for petrogenesis the liquid can mix with other melts, to form the correct composition. In this model, heat for melting can be radiogenic or from impacts.
2. **Addition of olivine** If olivine is added to the solidus assemblage of: an FeTi phase and clinopyroxene (and feldspar) the FeTi phase becomes spinel, rather than ilmenite, and the solidus temperature increases from 1150°C to 1250°C . At higher temperature, the viscosity reduces by a factor of 30 and solid diapirs are much more likely to form eqs. (1.3) and (1.4).
3. **Dense late stage liquids** Recent work from (Zhao, de Vries, van den Berg,

Jacobs, & van Westrenen, 2019) agree that solid high density cumulates have too high viscosity to efficiently separate but argue that Fe and Ti densify the melt enough that it can sink, without remelting. Depending on the initial lunar composition and the crystallisation model used, FeTi phases are found on the liquidus after 89-95% of crystallisation.

$$t = \frac{6.5 \cdot \mu_2^{2/3} \cdot \mu_1^{1/3}}{\Delta\rho \cdot h \cdot g} \quad (1.3)$$

Equation 1.3: t = The timescale of Rayleigh-Taylor instability. This describes the characteristic length of time that a Rayleigh-Taylor instability would take to destabilise and reorganise as a function of density. The timescale is found to be 10-100 thousand years. (Hess & Parmentier, 1995). μ_1 : The viscosity of layer 1, μ_2 : The viscosity of layer 2, assumed to be $\mu_2 \gg \mu_1$. 10^{19} is taken to be a reasonable minimum value, (silicates near melting point), $\Delta\rho$: The density difference between layer 1 and 2, g : Local acceleration due to gravity, h : Thickness of layer

$$\lambda = 2.9h \cdot \frac{\mu_1^{1/3}}{\mu_2} \quad (1.4)$$

Equation 1.4: The length scale (wavelength) of instability. $\mu_1/\mu_2 \sim 0.1$ would give a length scale of 120 km, lead to 80 km diameter diapirs sinking through the lunar mantle about 2000 diapirs of this size would be needed. (Hess & Parmentier, 1995)

1.7 Global Asymmetry

The Moon is observed to have a major nearside-far side asymmetry: this is apparent in the topography (3.2 km higher - Kaula, Schubert, Lingenfelter, Sjogren, & Wollenhaupt, 1974); the crustal thickness (8 km thicker - Zuber, Smith, Lemoine, & Neumann, 1994); mare basalt volumes (Head & Wilson 1992); incompatible heat producing elements (~ 4 times less - Jolliff et al., 2000); and elevated Mg# (nearside 40-68, farside 50-75 - Ohtake et al., 2012).

To explain this asymmetry, two main hypotheses have been proposed, different in the timing of the asymmetry.

1. Earth 'Glow' and tilted convection: The early Moon was significantly closer to the Earth than it is currently, As a result 'Earth Shine' from a nearby hot planet would cause differential heating of the lunar nearside, especially near the equator. This effect is compounded by a Coriolis induced tilted convection that would concentrate the feldspar 'icebergs' on the far side. (Loper & Werner, 2002).
2. Hydrodynamic instabilities arising from convection due to the Rayleigh-Taylor instability of the late Ilmenite layer: The mantle convection caused by the dense ilmenite layer drives mode one convection concentrating the buoyant felspar on one side of the Moon (Zhong, Parmentier, & Zuber, 2000).

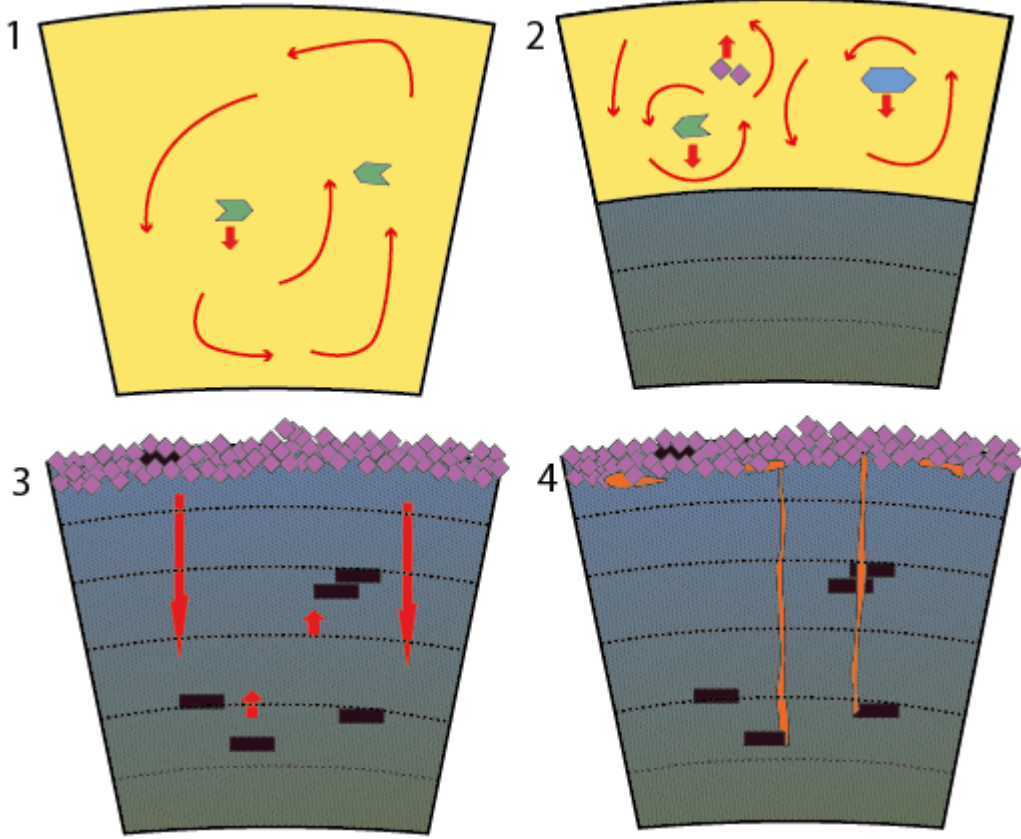


Figure 1.8: A generalised scenario for the crystallisation and overturn of the lunar magma ocean.

1.8 The Current Model

While multiple scenarios and compositions have been proposed for lunar crystallisation, a generalised model for the solidification of the lunar mantle can be drawn, fig. 1.8. This model has been built from the same observations use to construct the models (section 1.5)

1. The first crystals formed are denser than the bulk LMO, these crystals are entrained in the circulation of the turbulently convecting lunar mantle. Once the crystals enter the boundary layer, the characteristic convective length scale drops (eq. (1.1)), reducing the convective velocity. Dense crystals settle to at the bottom of the LMO. These crystals build up to form cumulate layers, compressing and squeezing some interstitial liquid out of the pores.

2. Later on in crystallisation, multiple crystal phases are present on the liquidus. These crystals sort according to their density, dominantly fall from the bottom boundary layer to add to the cumulate pile. Once plagioclase, a buoyant crystal, is present on the liquidus the lunar primary crust begins to form. The plagioclase is removed from circulation in the LMO at the top boundary layer, forming a pure (>95 vol.%) (N. J. Dygert et al., 2017)) anorthite primary crust. After multiple phases are on the liquidus, the efficiency of sorting decreases due to collisions, which transfer energy between crystals (Suckale, Elkins Tanton, & Sethian, 2012).
3. Following the formation of the lunar highlands, and the solidification of the LMO, 4.417 Ga (~ 100 Ma after lunar formation (Nemchin et al., 2009)). Some of the densest phases to precipitate after lunar crystallisation are found at shallow depths in the lunar mantle. Through one of the possible mechanisms (discussed above), the lunar mantle is mixed, driven by phases rich in Fe and Ti.
4. A combination of radioactive heating and release of gravitational potential energy partially melts the lunar cumulate stack. The melts produced ascend through the Moon, extruding onto the surface to form the lithologies we observe. Some melts which fail to extrude are emplaced below meteorite impact craters, forming mascons. (Konopliv, Asmar, Carranza, Sjogren, & Yuan, 2001)

2 Thermodynamic and Physical Modelling

Experimental and observational data are difficult to generate and expensive to come by. As a consequence, physical and computational models using theoretically derived equations are used to further our understanding of physical systems. In this chapter, physical modelling is used to:

- 1) determine parameters that are required for the series of experiments in future chapters;

- 2) generate a fractional liquid line of descent, using the phMELTS (Connolly, 2005; Smith & Asimow, 2005) modelling package. This line of descent will be compared with experimentally-derived profiles from Chapter 3;

- 3) Finally, different bulk lunar compositions are tested against the density and moment of inertia they predict. The structure of the chapter is set out in the way described above.

2.1 Intensive Parameters Through the Moon

The primary objective of this work is to test, experimentally, if the observed lunar lavas can likely be generated by a terrestrial bulk composition. Thus, it is imperative that the experimental parameters chosen be applicable to the differentiation of the lunar magma ocean. Below, I detail how I chose the Pressure, Temperature and Oxygen fugacity (fO_2) for the experiments detailed in Chapter 3. These parameters are also required for the physical and thermodynamic calculations described in this chapter.

2.1.1 Lunar Pressure gradient

Unfortunately, the observations of density, and so pressure, through the Moon are poor (see section 2.3 and fig. 2.7). In the absence of a compelling density or pressure profile the most simple must be assumed. Due to the lack of robust estimates of pressure in the Moon I assume that the Moon is a homogeneous body, with a mass of $7.34 \times 10^{22} kg$, a mean density of $3344 kgm^{-3}$, and radius of $1738 km$ (Nasa, 2016). Equation (2.1) describes the pressure gradient through a spherical homogeneous body.

The relationship described by eq. (2.1) is likely to be an underestimation of the true pressure because after the solidification of a LMO, the Lunar mantle over-turn would rearrange the mantle, by density (Elkins Tanton et al., 2002). If the Lunar mantle has undergone density-driven rearrangement, the actual pressure at a given depth will be less than that predicted by eq. (2.1), (Kuskov, Kronrod, & Hood, 2002).

The pressure gradient through a spherical homogeneous body is described by eq. (2.1). However, the Moon is neither homogeneous nor spherical, so eq. (2.1) is an approximation. Unfortunately, the observations of density, and so pressure, through the Moon are poor so in the absence of a compelling density/pressure profile the

most simple must be assumed. Therefore, in this study the pressure through the Moon is assumed to perfectly follow that of a homogeneous body, of the correct mass ($7.34 \times 10^{22} kg$), density and radius. This rule is likely to be an underestimation of the true pressure because after the solidification of a LMO, the Lunar mantle overturn would rearrange the mantle, by density. In the case of a vertical profile through the Moon that is sorted by density, the pressure will be less than the homogeneous profile predicted by eq. (2.1), (Kuskov et al., 2002).

$$P = P_0 \cdot \{1 - (\frac{R - d}{R})^2\} \quad (2.1)$$

Equation 2.1: Pressure, P , as a function of depth from the lunar surface taken from Kuskov (1997). Where P_0 is the initial pressure at the centre of the Moon, R is the maximum radius of the Moon (1738 km), and d is the depth below the lunar surface (km). P_0 (4.71 GPa) is derived theoretically by integrating the mass and acceleration (g) through the radius of the Moon and assuming a mean density $3344 kgm^{-3}$ throughout the calculation.

2.1.2 Temperature Profile

Temperature models for the Moon are critical as they allow you to interpret seismic tomography as well as understand the distribution of Heat Producing Elements (HPEs) in the lunar mantle. In this thesis the current temperature profile is important for setting the conditions of the moment of inertia calculations (section 2.3).

Multiple temperature models for the Moon have been derived, in most cases the temperature models produce similar outcomes (fig. 2.1).

Two measurements are commonly used in order to infer temperature:

1. Magnetotelluric measurements. Measurements of the magnetic field produced from electrical currents within the Moon. These measurements leverage the effect of the Moon travelling through the ‘tail’ of Earth’s magnetic field and interacting with the solar wind. The electrical conductivity at depths through the Moon is measured by orbiting satellites. This is related to the temperature and composition through laboratory measurements of conductivity of a given mineral, which is a function of temperature.
2. Seismic measurements of P and S wave speeds directly measure the shear and young’s moduli of lunar rocks, both of which are dependent on temperature.

In addition to these measurements, heat flux was directly measured by the Apollo surface geophysics equipment. Measurements found the heat flux to be $2.2 \times 10^{-2} \text{ Jm}^{-2}\text{s}^{-1}$ and $1.6 \times 10^{-2} \text{ Jm}^{-2}\text{s}^{-1}$ at the Apollo 15 and Apollo 17 landing sites, respectively (Kuskov et al., 2014). The heat flux measurements can be inverted to find lunar geotherms (selenotherms). The heat flux measurements are modelled by Kuskov et al. (2014) to be above the average value expected for the average lunar mantle’s heat producing element inventory; this is attributed to the choice of landing sites. The landing sites (see fig. 1.1) are all on the lunar nearside and, for engineering

reasons, located no more than 30 degrees North or South of the equator, mainly sampling mare rich in KREEP and therefore, heat producing elements, fig. 1.7.

In fig. 2.1 I compare different selenotherms. While there is divergence between models, there is broad agreement that the lunar mantle temperature is below the pyrolite solidus and only increasing gradually from the surface. The major difference between the Kuskov et al. (2014); Kuskov and Kronrod (1998) models is the sophistication of the thermodynamic system used to invert the seismic data, a 5 verses an 8 component system in the more recent study. eq. (2.2) was chosen as the relationship is calibrated for the whole lunar mantle. eq. (2.2) is combined with eq. (2.1) to make a PT path for the density modelling of this work.

$$T = 435 + 800 \cdot (1 - e^{-0.0035(d-58)}) \quad (2.2)$$

Equation 2.2: The temperature (T, °C) through the Moon as a function of depth from the lunar surface (d, km). Model I from (Kuskov & Kronrod, 1998)

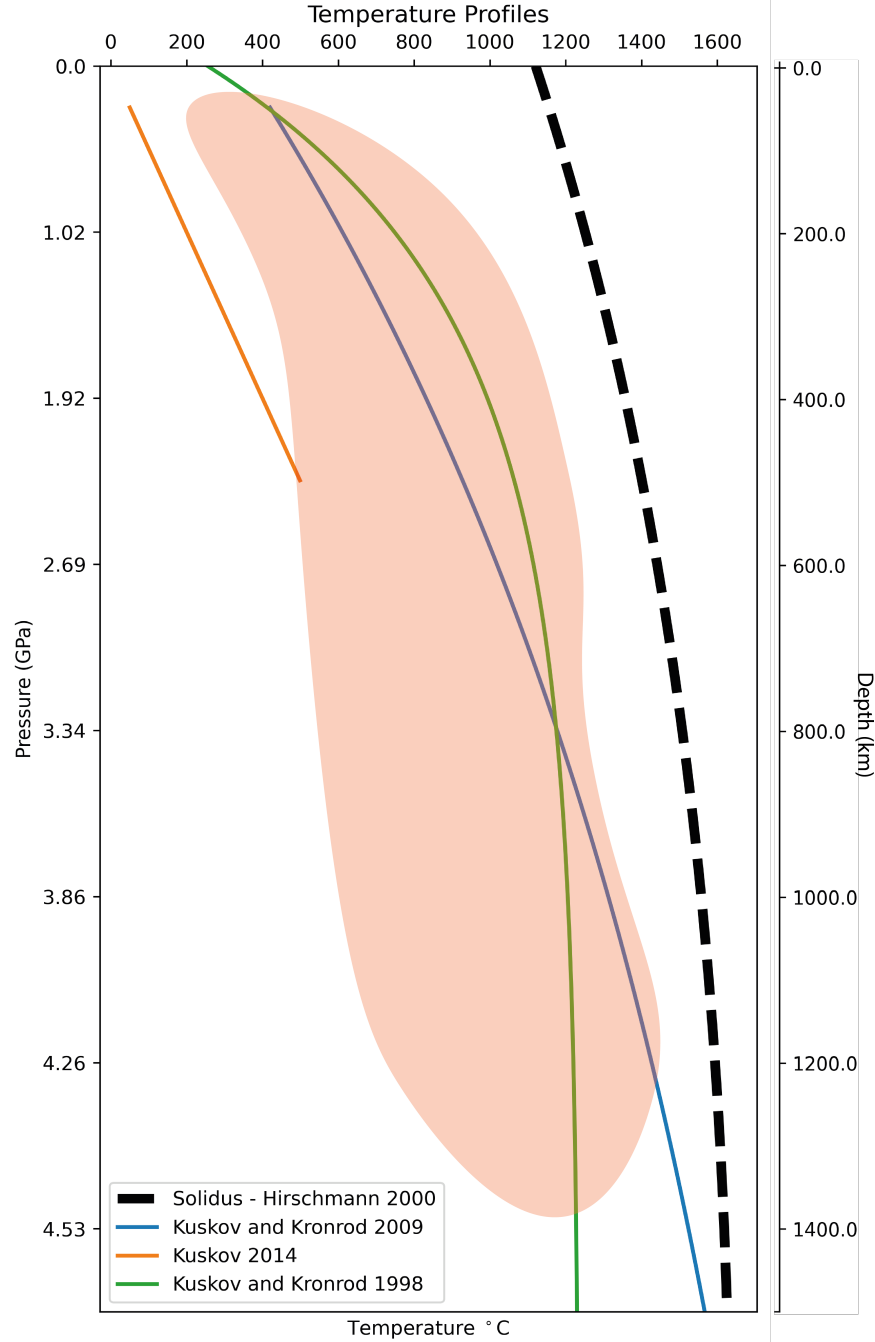


Figure 2.1: Modelled selenotherms. T-depth relations are taken from (Kuskov & Kronrod, 1998; Kuskov et al., 2014). The right-hand y-axis is depth in (km). In addition to the analytical relations, 'inverse sampling' research created multiple possible distributions, based on magnetotelluric (Khan, MacLennan, et al., 2006; Khan, Connolly, et al., 2006) and seismic data (Gagnepain-Beyneix et al., 2006). Inverse sample studies calculate multiple possible temperature profiles within the bounds set by the author, all of these possible temperature profiles are plotted to find the most common temperature profile and the probability distribution around it. These possible distributions have been generalised for simplicity (Red shaded area). For comparison, the solidus temperature of pyrolite mantle is plotted from (Hirschmann, 2000).

2.1.3 Oxygen Fugacity

In silicate magmas the fugacity of oxygen (fO_2) controls the speciation of multi-valent ions and can be altered by de-volatilization and crystallisation; as well as changing with temperature and pressure. This variability means that fO_2 is normally discussed relative to a buffer like iron-wustite (IW) or Nickel-Nickel oxide (NNO). Unfortunately, the fO_2 of the lunar mantle is not unambiguously sampled by any lithology on the surface of the Moon. Measurements of lunar fO_2 have been made on pristine mare basalts recovered by the Apollo missions (figs. 2.2 and 2.3). These measurements find the mare basalts to be more reduced than Earth's mantle, which sits between FMQ and IW (Ballhaus, Berry, & Green, 1990). However, it is not known how representative the mare basalts are of the lunar mantle. In addition, despite the large number of samples, many of the Apollo rocks are breccias and soils, which contain meteorite derived material.

Degassing during and immediately before an eruption could reduce the basalts (Jolliff et al., 2006). These mechanisms are: the degassing of sulphur (Brett, 1976) or carbon monoxide (Nicholis & Rutherford, 2009). Some research on the pressure dependence of fO_2 in lunar glasses suggests an fO_2 as high as the FMQ buffer at depth (Delano, 1990; Wieczorek et al., 2006a). However, this high value is the result of extrapolating a single Apollo 17 glass sample. In general, figs. 2.2 and 2.3, the fO_2 of the lunar mantle likely lies between IW+1 and IW-3 (Jolliff et al., 2006).

To account for eruption related reduction and to allow the use of a graphite (C) capsule, a higher fO_2 than the values measured from basalts (IW-2 – IW) was chosen, IW+1. A graphite capsule, as used in my experiments, will buffer the sample below the C-CO buffer which lies just above the IW buffer over the range of pressures relevant to my experiments (Médard et al., 2008) (Chapter 3 - fig. 3.1). In volatile-absent experiments, and in the 11-component system I have used in all experiments and models, fO_2 is not a decisive factor. The most redox-sensitive

element in the 11-component ($SiO_2 - TiO_2 - Al_2O_3 - Cr_2O_3 - FeO - MnO - MgO - NiO - CaO - Na_2O - K_2O$) system is Fe. The speciation of Fe around the IW buffer has been experimentally described by Kress and Carmichael (1991). The $XFe_2O_3/XFeO$ varies from 1.9 % to 0.7 % at one log unit above and below the IW buffer for a pyrolite composition (Mcdonough & Sun, 1995). To allow fair comparison, the same fO_2 value (IW+1) was used throughout this thesis.

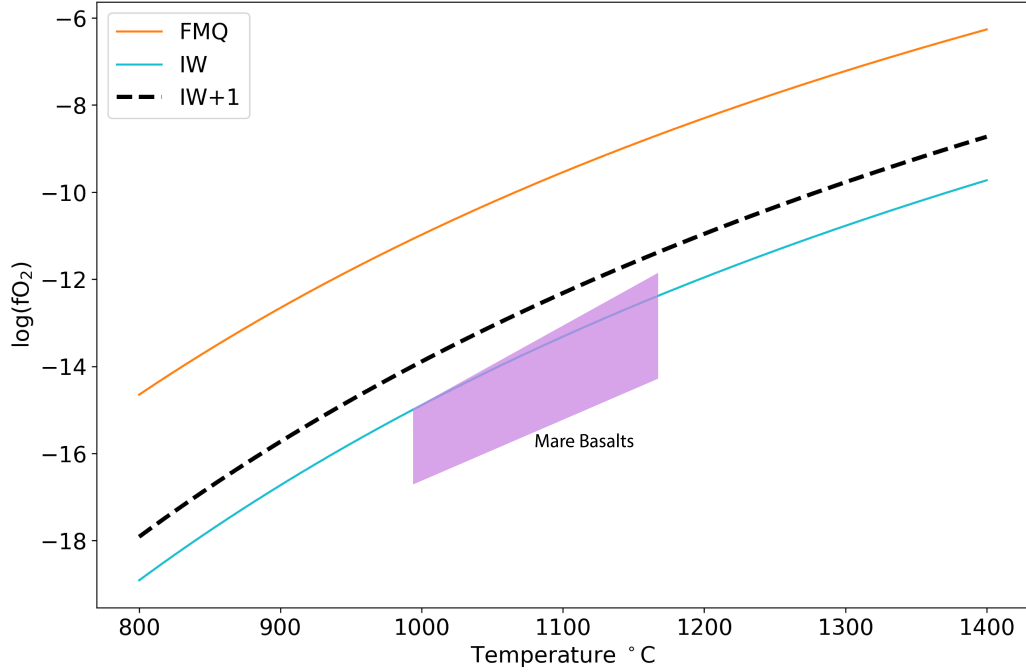


Figure 2.2: fO_2 plotted with temperature. Top, generalised fO_2 values of mare basalts compared to fO_2 buffers. FMQ= Fayalite-Magnetite-Quartz, IW=Iron-Wüstite. Reference curves for fO_2 buffers were calculated from thermodynamic data at 1 bar atmospheric pressure (Deines et al., 1976). Most mare basalts plot below the IW buffer at low pressure.

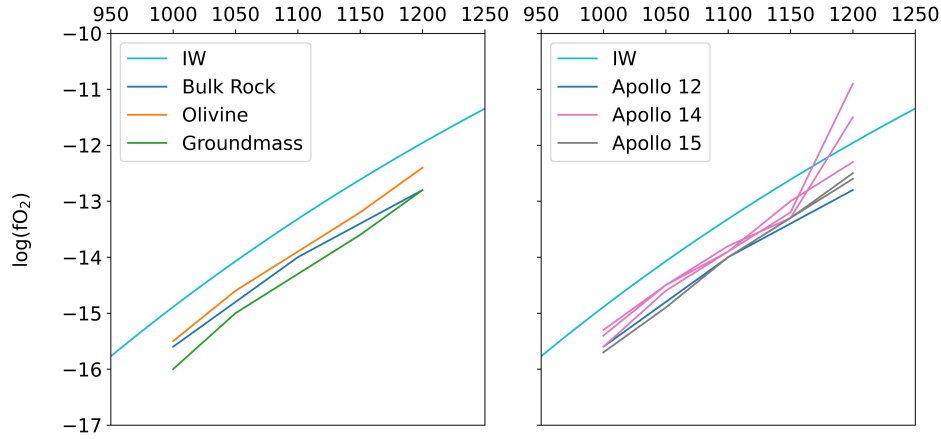


Figure 2.3: Bottom left, fO_2 of different phases in the Apollo 12 mare basalts (Sato et al., 1973). The mineral phases in the Apollo samples have higher fO_2 's than the bulk rock, indicating that some reducing process occurred towards the end of petrogenesis. Bottom right, the fO_2 of lunar samples determined by incremental heating of a collection of Apollo 12, 14, and 15 samples (Sato et al., 1973; Sato, M., Hickling, N. L., McLane, 1973).

2.2 Computational Crystallisation

The experimental fractional crystallisation, chapter 3, is complemented by a computational fractionation, performed on the phMELTS modelling program (Connolly, 2005; Smith & Asimow, 2005). The MELTS group of thermodynamic modelling programs (Asimow, Dixon, & Langmuir, 2004; Smith & Asimow, 2005) are widely used across disciplines in the Earth sciences, with different versions optimized for specific pressures, temperatures, and compositions. The MELTS thermodynamic model is based on a large database of primarily terrestrially-relevant experimental data, and is widely used by geochemists. Thus, it is instructive to compare my experimental results to the MELTS model output.

Gibbs Minimisation Algorithms In any system, the phase proportions and compositions seek to minimise the Gibbs free energy of the whole system. A system at equilibrium has minimised its Gibbs free energy. Likewise, Gibbs minimisation algorithms modify the system to find the state with the minimum Gibbs free energy (G). In addition to minimising G , modelling programs must conserve mass. Therefore, the algorithm used in to find the optimal configuration of phases and phase compositions iterates between changing the compositions phases to reduce the free energy and then conserving mass by calculating the least 'expensive', in terms of ΔG , arrangement that keeps the composition constant.

In practice, the number of possible configurations of minerals and compositions are too great to all be computed and compared. The algorithm starts with the configuration of the previous step and adds a small amount of a new phase into the assemblage, updating the composition and computing the ΔG . The process is continued until no phase when added reduces the free energy of the system.

Mineral Solution Models The process described above is sufficient for minerals of set composition (e.g., quartz), however, many minerals have solid solutions between endmembers (e.g., olivine). In the case of a phase with a range of possible compositions, a solution model is required to describe the relationship between mineral composition and ΔG . A first-order approximation of a solution model is ‘ideal mixing’ where the composition is expressed as a sum of the endmembers, ΔG is assumed to vary linearly between the two endmembers. For a more accurate model, experimental data is used to find more accurate mixing parameters. A curve can then be fit to these data. Algorithms for conserving mass and minimising Gibbs free energy all seek the same end state, the main difference between thermodynamic modelling programs are the solution models for phases. Decisions about the data used or the ideality of a solid solutions introduce variation.

2.2.1 Methods

Choice of Modelling Program and System I have chosen the phMELTS version of MELTS. This version is specialised for pressures from 1-3 GPa and peridotite or pyroxenite compositions. The specialisation comes from the choice of experiments to use to calibrate the solid-solution models. The MELTS group of models are calibrated using experiments selected from the online Library of Experimental Phase Relations (LEPR - (Hirschmann et al., 2008)). The phMELTS version has been calibrated for peridotite or pyroxenite bulk compositions between 1 and 3 GPa.

The MELTS program, like most magmatic modelling programs, is calibrated to recreate melting relationships for magmas of terrestrial composition. As total melting and crystallisation of the Moon evolves the melt composition far away from terrestrial compositions, the accuracy of the program may suffer. In addition, it is well known that MELTS over-stabilises orthopyroxene (Hirschmann, Ghiorso, Wasylenzi, Asimow, & Stolper, 1998).

Starting Composition The Null hypothesis of this thesis is: **Is it conceivable that silicate Earth and silicate Moon are identical in refractory element composition?** To assess this hypothesis the bulk starting composition for the thermodynamic modelling must be the same as for the experimental series: an estimate of terrestrial pyrolite (Mcdonough & Sun, 1995) (table 2.1).

Table 2.1: Estimate of the composition of terrestrial pyrolite (Mcdonough & Sun, 1995) used as the starting composition for the MELTS modelling.

Elemental Oxide	wt.%
<i>SiO₂</i>	45.01
<i>TiO₂</i>	0.2
<i>Al₂O₃</i>	4.45
<i>Fe₂O₃</i>	0.35
<i>Cr₂O₃</i>	0.38
<i>FeO</i>	7.74
<i>MnO</i>	0.13
<i>MgO</i>	37.8
<i>NiO</i>	0.25
<i>CaO</i>	3.55
<i>Na₂O</i>	0.12
<i>K₂O</i>	0.01
<i>P₂O₅</i>	0.02
Total	100

Starting and continuation conditions Following the hypothesised giant impact, the Moon is widely expected to have been molten (Canup & Asphaug, 2001; S. J. Lock et al., 2018), indeed it is likely that the lunar core is molten today ((Weber et al., 2011; J. G. Williams et al., 2001). For this reason, it is logical to use a superliquidus starting temperature.

The pressure at the centre of the Moon is 4.71 GPa, (eq. (2.1)) (D. R. Williams, 2020). The pressure at which crystals are removed from equilibrium within the LMO will also vary during crystallisation. In order to choose a pressure which best represents most of the mass of the crystallisation I use the median value. The median value is the pressure at that the middle amount of Moon material experienced,

i.e. the mass of material which experienced lower and higher pressure is the same. A Moon with a core 5% the mass of the Moon has a median silicate pressure of 1.55 GPa. If the lunar core is more dense than the silicate, which is likely, the median pressure will be slightly lower. A single value of 1.5 GPa is taken to be representative of the bulk silicate Moon. The shallow pressure gradient through the Moon minimises the impact of this simplification on the modelled crystallisation. Simulations were run with a -1 °C temperature increment.

In the case of fractional crystallisation, the non-liquid phases are discarded after each step, reducing the total system mass. In a batch or equilibrium system, the crystal phases are conserved. In both cases, the configuration of the previous step is used as the starting configuration for the next step, this reduces the computation time required to achieve equilibrium.

2.2.2 Results

The mode of crystallisation of the lunar magma ocean is debated (see chapter 1 for detailed discussion) but to capture both end member scenarios, both fractional and equilibrium models have been run. The difference in the evolved liquid compositions is stark. For example, in the case of fractional crystallization, FeO concentration of the liquid increases to more than 35 wt.%, compared to no more than 10 wt.% in the case of equilibrium crystallisation (fig. 2.4). The mass fraction of crystals and liquid at the same temperature is similar in both crystallisation modes (fig. 2.5), but the composition of the liquid varies significantly. The compositional variation in the liquid must result in a significant difference in the composition of the minerals precipitated. The MELTS liquid line of descent is compared to the experiments in Chapter 3.

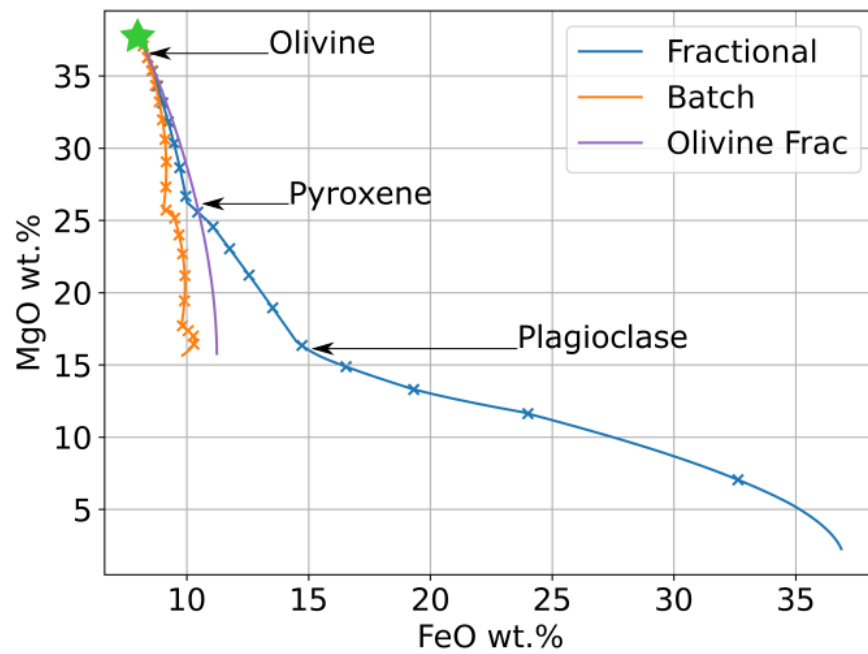


Figure 2.4: Liquid evolution paths, plotted as FeO vs MgO . Starting composition, table 2.1, plots towards to the top of the graph, green star. FeO enrichment in the liquid predicted by Batch and Fractional crystallisation models vary significantly. Major liquidus phases are added at point of first appearance. Each 'x' represents a further 5 wt. % crystallisation.

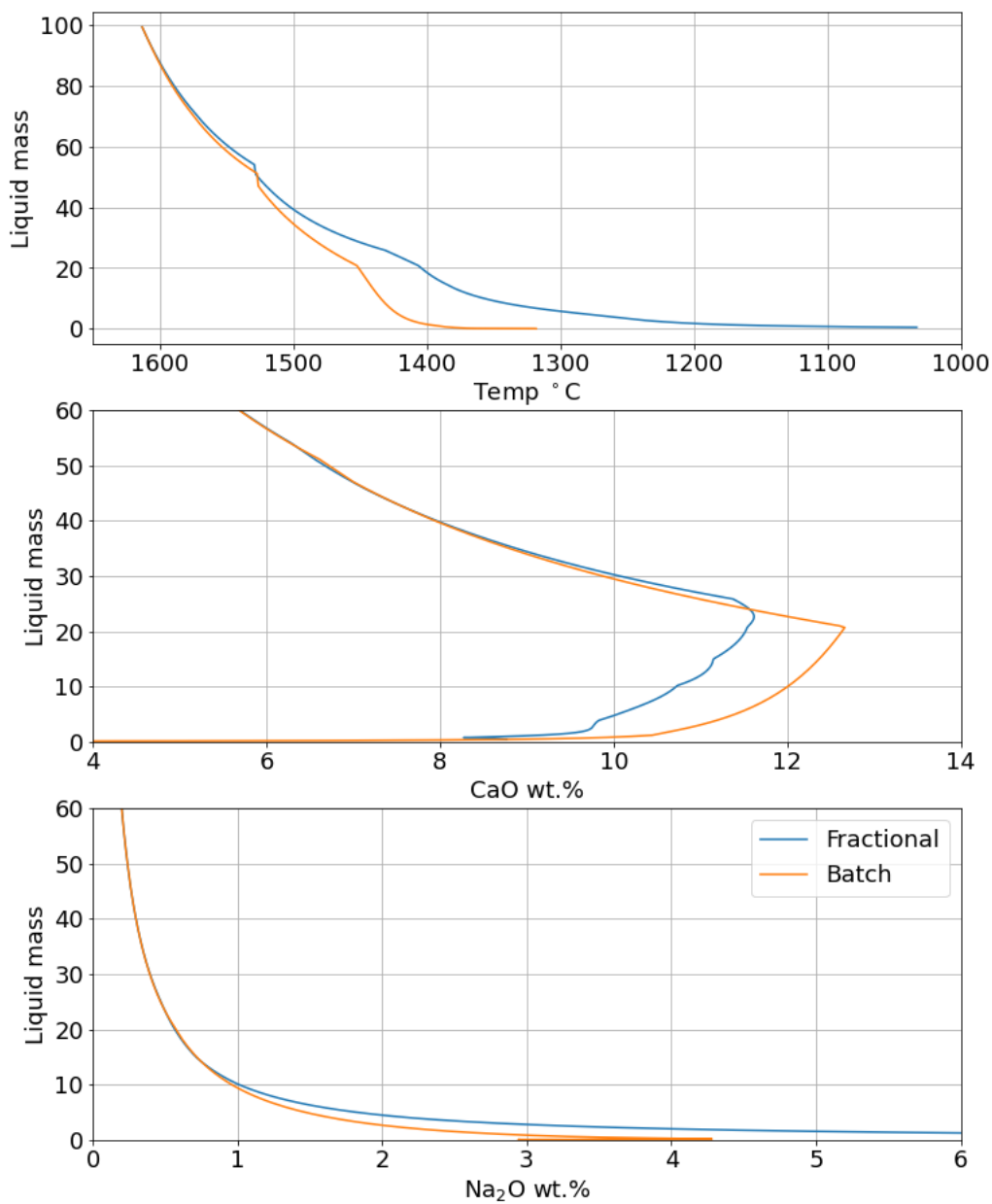


Figure 2.5: The mass fraction of liquid as a function of a) temperature b) Ca concentration in the liquid during crystallisation. c) Na concentration. A batch crystallisation mode loses liquid more quickly than a fractional mode. Y axis truncated to 60% in b) and c) as no divergence before. The absence of plagioclase in the equilibrium trend, and small differences in pyroxene composition responsible for divergence in Ca and Na concentration.

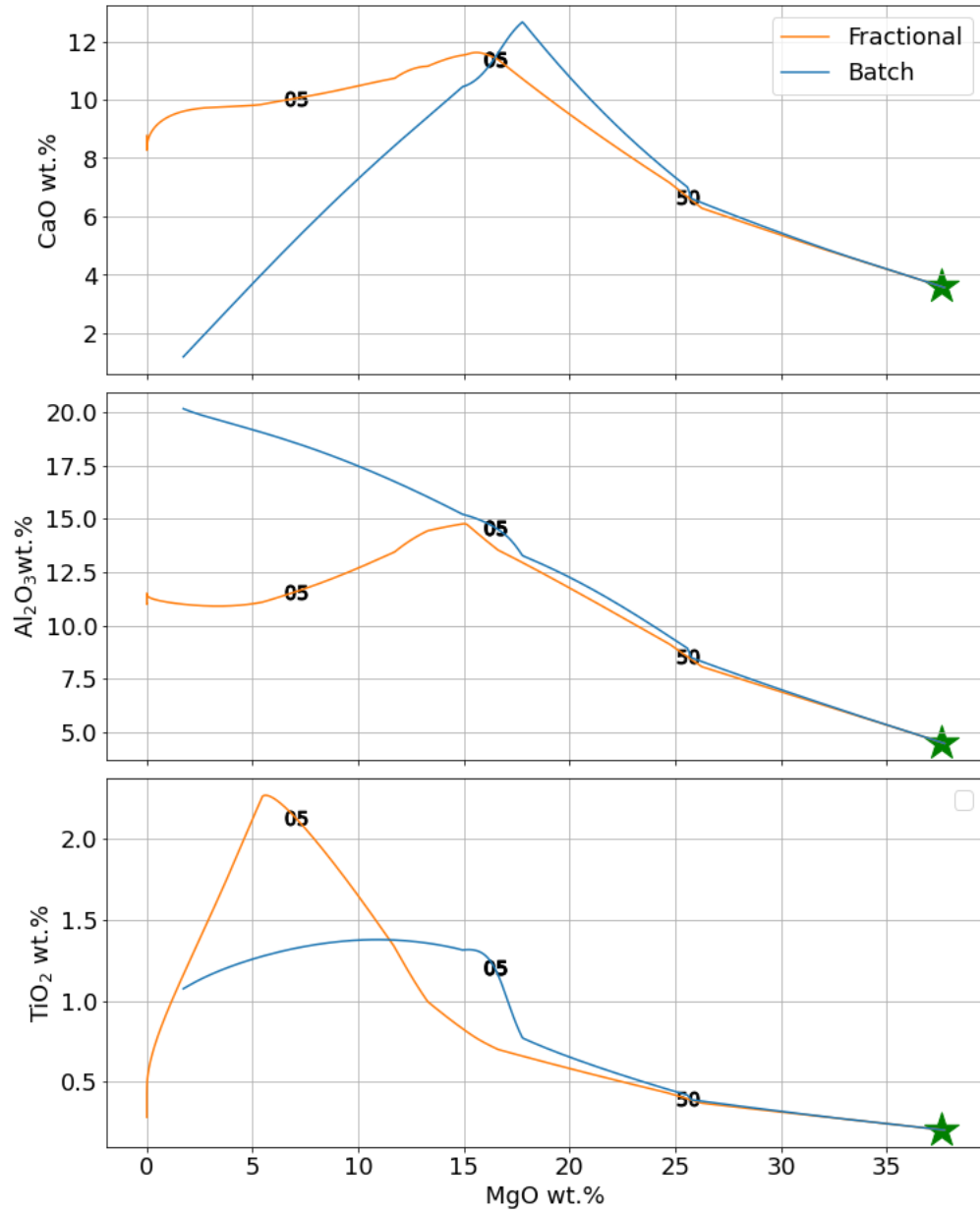


Figure 2.6: The evolution of Ca, Al and Ti plotted with MgO, the amount of liquid remaining is labelled onto the lines. For most of the liquid line of descent the two liquids are similar in Ti, Al and Ca concentration.

The concentration of Fe in the two liquid lines of descent is controlled by the liquidus phases. Figure 2.4 shows that the degree of Fe enrichment increases much more rapidly once pyroxene and then plagioclase begin to crystallise. With respect to the Ca and Na evolution, fig. 2.5, there is only a small difference in the liquid compositions. The trends in Ca and Al concentration, fig. 2.6, only diverge in the last few percent of crystallisation, after plagioclase becomes stable in the fractional but not the equilibrium trend. In the last stages of crystallisation, multiple phases are present on the liquidus. Multiple liquidus phases are likely to reduce the efficiency of fractionation (section 1.2), if true, the fractional trend in Ca, Al and Ti could more closely follow the equilibrium trend at the very end of crystallisation.

2.3 Density Through the Moon

The Moon’s mass, size and moment of inertia can be measured to high precision. For this reason, testing the models against these precise observations is useful.

The density through the lunar mantle is a function of the mineral phases, pressure, and temperature. Thus, to estimate the density of the Moon as a function of depth; the pressure, temperature, and composition must be determined. The temperature-depth profile and pressure structure have been defined above. The chemical composition is more complex: after the crystallisation of the lunar magma ocean the mantle is likely to be chemically stratified. However, it is not known how much of the chemical stratification, from the crystallisation of the lunar magma ocean remains. The density of the solid and liquids, predicted by *phMELTS*, (see above) are plotted in fig. 2.8. The lithologies we observe on the Moon require the lunar mantle to be heterogeneous, even in the case of a Moon without a lunar magma ocean, (Heiken et al., 1991; Cano et al., 2020; Hallis et al., 2010). However, without a preconceived notion of compositional structure, a homogeneous lunar mantle has been assumed.

The P-T path from eq. (2.2) and eq. (2.1) along with a constant composition can be fed into a thermodynamic modelling program to compute phase proportions and densities. In order to understand how different bulk compositions will affect the density profile through the Moon two differing bulk compositions were used (table 2.2). The two chosen compositions represent an Earth-like end member (Mcdonough & Sun, 1995) and a refractory enriched end member (Warren, 2005).

The limited lunar seismic data has allowed a very preliminary reference seismic model for the Moon to be created (Garcia et al., 2011). plotted in fig. 2.7. Garcia et al. (2011) stress that the paucity of lunar data makes this model ‘very preliminary’ and valid only for the lunar nearside. The seismic and geodesic data are not consistent so two models have been developed.

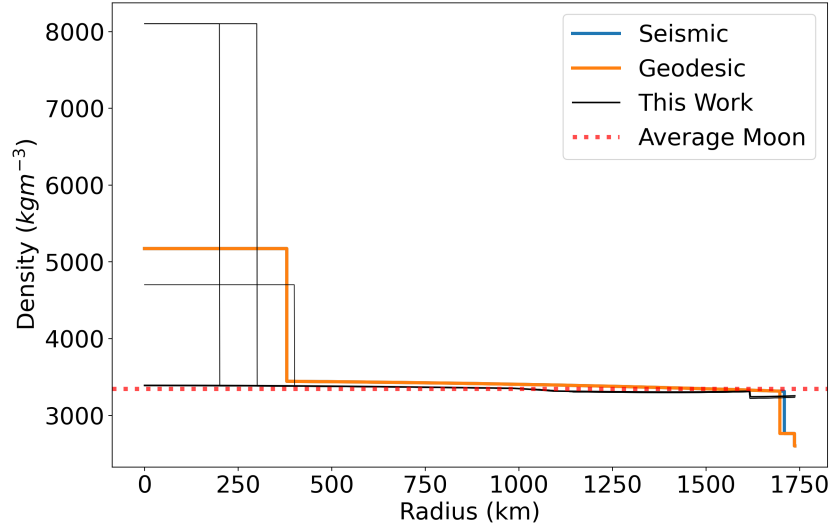


Figure 2.7: The VPREMOON preliminary seismic and geodesic model from Garcia et al. (2011), the possible density profiles considered in these calculations, section 2.3, straddle the VPREM model for the Moon.

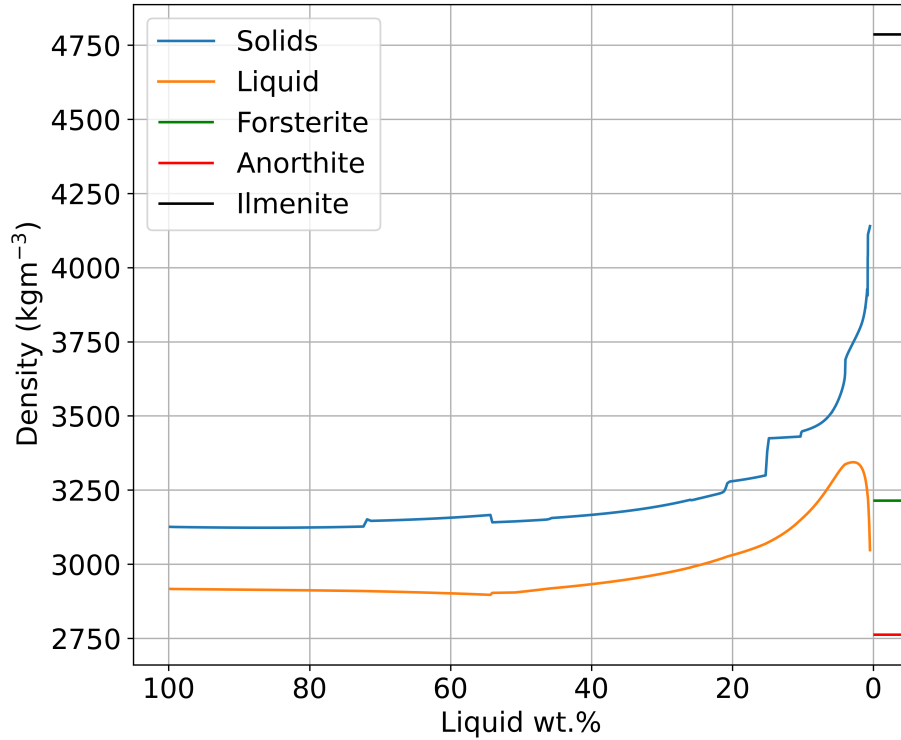


Figure 2.8: The density of the liquid and solid that evolves from the primary crystallisation of the lunar magma ocean as modelled by pHMELTS. The increase in solid density with depth, if left unperturbed, would give an MIF (Moment of Inertia Factor) above 0.4. The layers of minerals produced by the crystallising LMO is referred to as the 'cumulate pile'. For reference the density of Forsterite, Anorthite and Ilmenite has been plotted (Robie & Bethke, 1962)

2.3.1 Methods

Perple_X For liquid-absent thermodynamic minimisation, the Perple_X minimisation program was used. Perple_X does not have an inbuilt set of thermodynamic solution models or thermodynamic data; the models used are chosen by the user. I have chosen the stx11 group (Stixrude & Lithgow-Bertelloni, 2011), based on the system $Na_2O - MgO - Al_2O_3 - SiO_2 - CaO - FeO$. The stx11 models were chosen as they have been calibrated for the whole pressure range considered for the Moon, with particular focus on predicting seismic properties, including density.

Table 2.2: Bulk end-member compositions for refractory enriched (Warren, 2005) and terrestrial pyrolite (Mcdonough & Sun, 1995) LMO. The compositions have been renormalized for the six-component system: $Na_2O-MgO-Al_2O_3-SiO_2-CaO-FeO$.

Component (wt. %)	(Mcdonough & Sun, 1995)	(Warren, 2005)
Na_2O	0.36	0.35
MgO	38.1	36.62
Al_2O_3	4.49	4.31
SiO_2	45.36	43.59
CaO	3.58	3.44
FeO	8.11	11.7
Total	100	100

2.3.2 Lunar Moment of Inertia

The moment of inertia of the Moon can be calculated using a radial density profile (eq. (2.3)). In order to compare different planetary bodies, the moment of inertia is converted to the Moment of Inertia Factor (MIF, (eq. (2.4))). The MIF of the Moon, measured by doppler radar, is 0.394 (D. R. Williams, 2020). For reference the Earth’s MIF is 0.3308, (D. R. Williams, 2020), which is far lower than the Moon’s. Earth’s MIF is significantly lower because Earth has large and dense core. A MIF value of 0.4 indicates an entirely homogeneous body with respect to density, which is close to the value for the Moon (0.394). Thus, it is possible that the Moon is genuinely homogeneous with respect to density. Alternatively, the lunar

mantle could be homogeneous at large scale (100s km) but layered at smaller scale, analogous to the dunite channels observed in mid ocean crust. These different scales cannot be analysed using a blunt measurement like moment of inertia.

The crystallisation of the LMO is widely expected to lead to a gravitationally unstable mantle because the precipitation of feldspar densifies the melt significantly (Charlier et al., 2018; Heiken et al., 1991; Jolliff et al., 2006; Longhi, 2006). If the cumulate pile (immediately following the crystallisation of the LMO) remained (fig. 2.8), the MIF would be greater than 0.4. If the cumulate pile was perfectly sorted by density, the MIF would be far below 0.4. An intermediate value indicates that neither of these end-member situations is true. (Médard, Schmidt, & Schiano, 2004)

An additional complication is the size and composition of the lunar core, The Moon's core is smaller than Earth's and will have a smaller effect on the Moon's MIF. For comparison multiple core sizes and compositions are plotted figs. 2.9 and 2.10.

$$MoI = \int_0^R M(r)R^2 dr \quad (2.3)$$

Equation 2.3: The general equation for the moment of inertia of a spherical object.

$$MIF = \frac{I}{MR^2} \quad (2.4)$$

Equation 2.4: Moment of inertia factor is calculated by dividing the moment of inertia by the maximum moment of inertia, the mass multiplied by the maximum radius squared. $MoI = I$ = Moment of inertia, MIF = Moment of inertia factor, $M(r)$ = Mass as a function of radius, r = Radius, R = Maximum radius, M = Total mass.

2.3.3 Results

I have calculated the MOI resulting from a wide range of possible density profiles (figs. 2.7 and 2.9). The results clearly show that the size of the lunar core has a smaller effect than a big change in bulk lunar composition. However, as shown in

fig. 2.10, the difference between the Moon's MIF and that predicted from the density profile is within the expanded error of a remobilised dense layer. The uncertainty comes from a dense layer sinking through the Moon and being replaced by deeper material of the same density of forsterite olivine.

In detail, the change in moment of inertia of a 20 km thick region of ilmenite rich material (450 kgm^{-3} denser than prevailing lunar mantle (Elkins Tanton et al., 2002)) at a depth of 40 km in the Moon is shown by the dotted red lines fig. 2.10 . The effect in change of moment of inertia of the lunar mantle overturn is greater than any reasonable change in the bulk composition of the Moon. Therefore, the efficiency with which any lunar mantle overturn is able to reorganise the lunar mantle into the most density stratified configuration is the main factor controlling the MOI. These results demonstrate that any change in the core size or composition, coupled with any suggested bulk silicate composition can be reconciled by changing the efficiency of lunar mantle overturn. For the moment inertia to be used with average density to constrain the structure of the Moon, the amount of late crystallised dense material that has sunk into the mantle must be constrained.

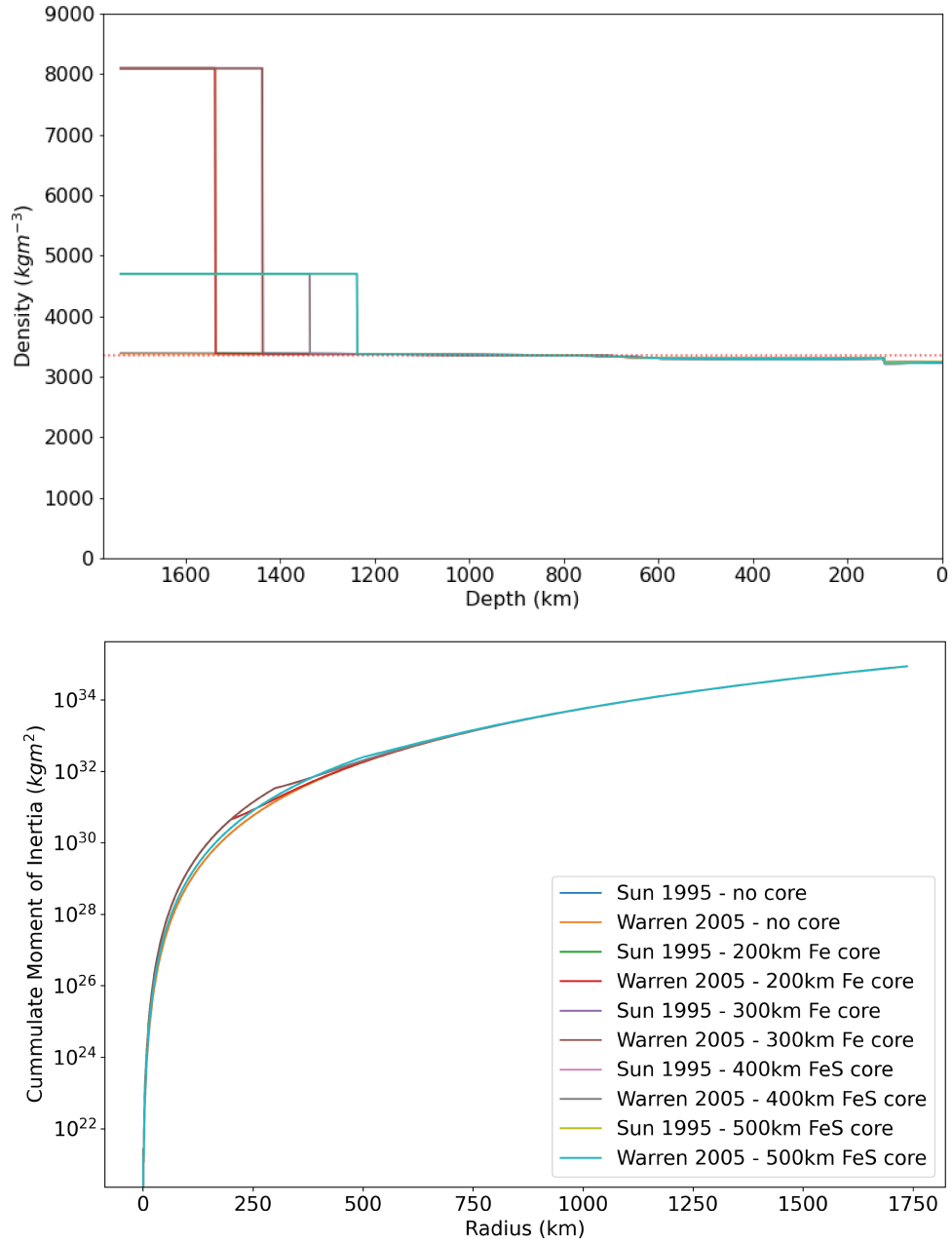


Figure 2.9: Top: The calculated moments of inertia, increasing with density. Bottom: the density profiles used to calculate the moments of inertia, multiple different core sizes and compositions are plotted to cover the range of possible core and mantle compositions.

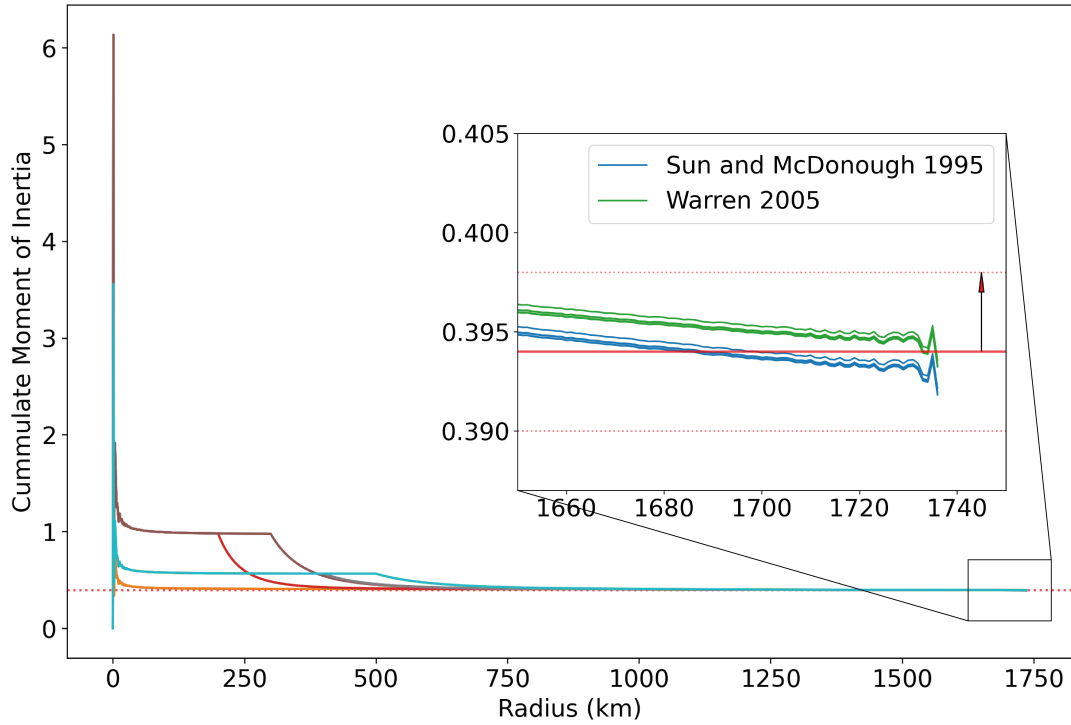


Figure 2.10: The calculated moment of inertia factor as a function of radius. Higher values closer to the middle of the Moon are because the average density was used to convert from moment of inertia to MIF, and the high-density core has a higher MIF than possible for the average density. A zoom in of the final calculated MIF, with the different bulk compositions coloured separately. The dotted red lines are from the maximum change in MIF of lunar mantle overturn. The error of measurement for the Lunar MIF is less than the thickness of the solid red line.

2.4 Discussion

2.4.1 Thermodynamic Modelling of the LMO

Careful calibration of ΔG crystallisation models enables precise prediction of magma evolution. igneous rocks found on the Moon are dissimilar to those found on Earth, the concentration of Ti and Fe are higher than anything found on Earth and the abundance of REEs can be hundreds of times higher. For this reason, the calibration may not recreate experiments accurately.

fig. 2.4 demonstrates the difference between a batch and fractional crystallisation of the LMO. The fractional crystallisation model produces a substantial enrichment in FeO concentration in the liquid, >35 wt.%; this compares to <11 wt.% for the batch crystallisation scenario. Both models end up with a melt almost entirely depleted in MgO, so the Mg# of the melt would decrease in both cases. The liquid fraction for a batch crystal is always lower than fractional crystallisation for the same temperature (fig. 2.5), crystallising at a faster rate for the same drop in temperature. fig. 2.5 shows the Na/Ca evolution of the modelled melt. The precipitation of olivine, which does not contain much Na or Ca, results in no difference between the batch and fractional crystallisation schemes. Once a clinopyroxene phase is on the liquidus the two modes enrich the melts by different amounts of Ca and Na.

2.4.2 Density Profile

The present day density profile of the Moon, inferred from seismic data, controls the moment of inertia of the Moon, which can be accurately measured. The difficulty in applying the seismic density profile to the whole Moon is that the seismic stations are clustered within $<35^\circ$ of each other (Grayzeck, 2003). The lunar crust is observed to differ from the near-side to far-side of the Moon. If the lunar mantle varies similarly to the crust then seismic sampling is insufficient to draw meaningful

conclusions about the density structure of the lunar mantle.

In lieu of comprehensive seismic information about the density structure, chemical reservoirs of known density are compared to the measured moment of inertia. The major unknown which prevents quantitative treatment of the density structure of the Moon is the distribution of late crystallising dense phases such as ilmenite and spinel. I have shown that these phases would have a larger effect on the moment of inertia than a doubling of core radius if they are found at shallow depths in the Moon, as discussed above.

A reorganisation of the density structure of the Moon, the ‘lunar magma overturn’, is most physically probable when the Fe- Ti- rich phases are combined with olivine (Elkins Tanton et al., 2002), it is possible that the lunar mantle is not sorted by density. Isolated pockets of purer Fe- Ti- phases could remain at shallow depths in the Moon with other larger pods able to sink further down. The simplest explanation for a planetary MIF close to 0.4 is an average density profile close to constant.

2.5 Conclusions

1. The investigation of the interior structure of the Moon through the Moon’s moment of inertia is limited, even in the case of a predetermined bulk composition because of the density redistribution mechanism. Before lunar density is able to be used to constrain the composition of the lunar mantle, better constraints on the lunar core, mantle and overturn are required.
2. The possible presence of pockets of melt in the deep lunar mantle, if confirmed by a more comprehensive study of lunar seismicity, would constrain the se-lenotherm in the deep Moon. Such a constraint would help the understanding of lunar mantle evolution by locating heat producing elements.

3. Thermodynamic modelling suggests that fractional and equilibrium crystallisation liquids chemically diverge. Such difference illustrates the importance of a fundamental understanding of the mode of differentiation of the molten Moon. The timing of divergence will change the depth at which Mg# enriched or depleted crystals are found in the lunar mantle. In turn, the distribution of Fe enriched material will impact the composition of any later derived melts.

3 Major Element Experimental Series

Following the hypothesised giant impact, the Earth and Moon are expected to have melted to a significant degree (Canup, 2004), following the collision, the Moon is likely to have accreted in fewer than 10 years (Canup & Esposito, 1996). Combined, these two statements mean that the nascent Moon will be largely molten. Once formed, this magma ocean will cool and crystallise, the mode of crystallisation determines how the bulk magma ocean composition evolves. In this chapter I will describe how the lunar magma ocean would crystallise, and how this could produce the lithologies we observe on the surface of the Moon.

3.1 Starting and Continuation Conditions

In the introduction I pose the question: 'Is it conceivable that silicate Earth and silicate Moon are identical in refractory element composition?'. To explore this question I have taken the peridotitic mantle of McDonough and Sun (1995), reducing the alkali content by $\frac{2^{rds}}{3}$, following Wetherill (1971)'s observations of lunar depletion in volatile alkalis and Pb relative to the Earth.

McDonough and Sun (1995), calculate the bulk composition of Earth's mantle, pyrolite, through comparison with chondritic meteorites. After re-evaluating the average composition of CI Chondrites they select 160 peridotie samples, xenoliths and massifs, and plot their major element compositions. The Major element arrays are extrapolated to the refractory element ratios found in CI Chondrites. Assuming all Al in Earth is found in the Mantle, the Bulk silicate Earth composition is calculated through mass balance. McDonough and Sun (1995) note that there have been multiple attempts to find the average composition of Earth's mantle (e.g., Ringwood, 1966; Jagoutz et al., 1979; Palme & Nickel, 1985; Sun, 1982; Wanke, Dreibus, & Jagoutz, 2002; Hart & Zindler, 1986a) and that: *"These models show remarkable similarity to one another and to the original pyrolite model"*. For this reason the choice of pyrolite composition is not decisive.

An initial magma ocean depth of 600 km is assumed, corresponding to a pressure of 2.6 GPa given by eq. (2.1). 600 km was chosen because it is an intermediate depth for the models discussed in Chapter 1. Additionally, a 600 km deep ocean is 78% the volume of a 1000 km deep ocean.

Once formed, the magma ocean will inevitably cool, to simulate this I have cooled and crystallised my putative starting composition in a stepwise manner. The temperature for each step is found experimentally: the temperature which corresponds to the correct mass of crystal. The crystals produced at each stage of LMO crystallisation sink to the bottom, reducing the depth of the magma ocean.

The quantity of crystals produced was added to the bottom of the ocean, and change in LMO depth was calculated. The corresponding pressure drop could be found using eq. (2.1).

I first calculated the evolution of the starting composition using MELTS (see Chapter 2) (Ghiorso, Hirschmann, Reiners, & Kress, 2002; Smith & Asimow, 2005), fractionally crystallising the initial melt composition until orthopyroxene joined olivine on the liquidus. This took place at 25% fractional crystallisation in ph-MELTS. MELTS is known to overestimate orthopyroxene stability (Hirschmann et al., 1998), even so, to ensure that the starting composition is in the olivine field, a conservative 20 wt.% olivine fractionation was chosen. Therefore, the starting composition was calculated by fractionating 20 wt.% olivine from my hypothetical lunar mantle composition manually, using the temperature-insensitive exchange coefficient, K_d given by (Matzen et al., 2011; Matzen, Baker, Beckett, & Stolper, 2013): $K_{Fe-Mg}^{Ol/Gl} = \frac{FeO^{Ol}/MgO^{Ol}}{FeO^{Gl}/MgO^{Gl}} = 0.33$. A calculation error led to 2 wt.% too much Cr being added to the starting composition, EB11 - table 3.3. As ~ 2 wt.% Cr spinel was produced in the first experiment, and the additional Cr did not affect the crystallisation sequence (fig. 3.11-liquid still on the Olivine fractionation curve), no repeat experiment was required.

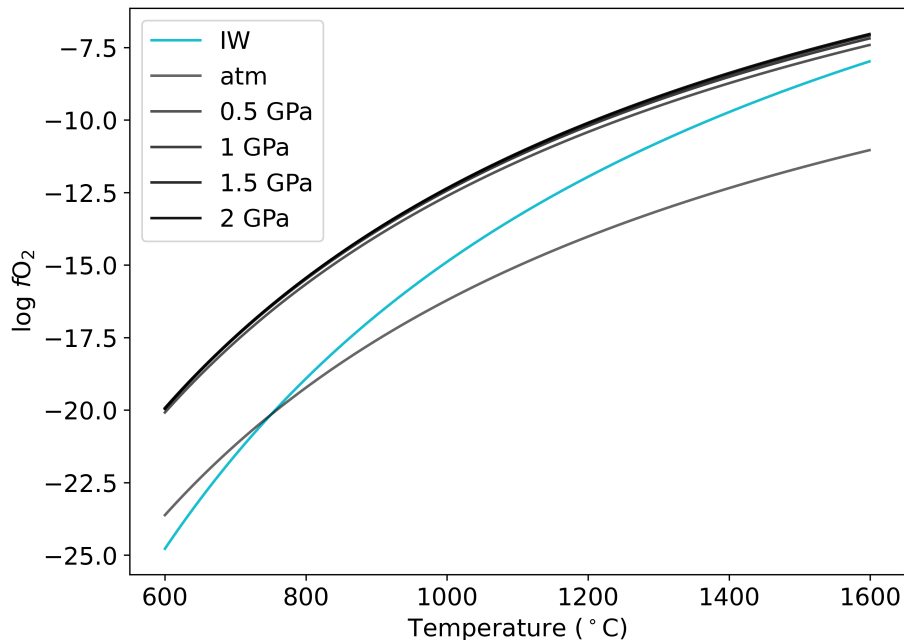
The conditions of each experiment are found in (table 3.2). Experimental simulations of fractional crystallisation require the process of fractional crystallisation to be broken down into several discrete steps. As the number of steps increases, the crystallisation more closely follows a fractional trend, with the caveat that very small extents of crystallisation are difficult to reproduce reliably. For crystal-liquid partition coefficients < 2 , 9% equilibrium crystallisation steps result in a liquid composition within 1 wt.% of that generated by the same amount of fractional crystallisation. For these reasons, 9 wt.% was chosen as a balance between precision and experimental practicalities. Experiments with 6-15 wt.% crystal fraction were there-

fore considered acceptable when determining the melt composition used to form the subsequent bulk composition. In the case of six steps of 15 wt.% fractionation in each step, the difference in liquid concentration is 6 wt.% between the stepwise and fractional liquid, after the same amount of fractionation. If too little crystal was present (less than the requisite 9 wt.%) and only a single major crystalline phase observed (as in experiments EB25 and EB44) then, the next bulk composition was calculated by further crystallisation of a small amount of that crystalline phase to bring it into line with the 9 wt.% crystal fraction (tables 3.3 to 3.6). In all other cases the melt phase from a successful experiment (in which large crystals were present and available to perform microanalysis), was used as the bulk composition for the next step. This process is continued to approximate the evolution of a LMO. Crystalline assemblages at each stage were regarded as potential source materials for further partial melting.

3.2 Experimental Methods

The perennial question asked by experimental petrologists is: what material should be used to contain the sample charge without altering it? For this series of experiments, I have chosen graphite capsules, as graphite should not chemically interact with the sample. In addition, the presence of graphite carbon acts to constrain the fO_2 of the system. At high pressure the CCO buffer is 1.5 to 3.5 log units below the FMQ oxygen buffer (Holloway, J.R., Pan, & Gudmundsson, 1992)(see Chapter 2). At pressure, the CCO buffer tracks the IW buffer (see fig. 3.1), an fO_2 relevant to the reduced lunar mantle, section 2.1.3. The control of other intensive and extensive parameters are discussed below. Experiments were performed in a Boyd-England end-loaded type piston-cylinder apparatus (Boyd & England, 1960).

Figure 3.1: The C-CO buffer plotted against the IW buffer. The CCO buffer is pressure and temperature dependent. Typically tracking near the IW buffer, the experimental assembly with a graphite capsule is stable up 4 log units below the CCO buffer (French & Eugster, 1965; Médard et al., 2008).



3.2.1 Pressure Calibration

In order to ensure all experiments were conducted at reliable known pressures, I first calibrated the Piston-Cylinder study to cover all (or most) of the pressures utilised during this study. In order to calibrate the true pressure; I performed salt melting experiments, using the well-constrained melting point of pure NaCl. These experiments use capsules filled with powdered NaCl, and a small Pt ball, 0.5 mm diameter, at the top and bottom. If, when the experiment is complete the balls are together at the bottom, then it has shown that experiment was above the liquidus of NaCl at a particular PT coordinate, defined by Clark (1959). Several repeat experiments were performed to constrain the PT coordinates at which the salt became liquid (fig. 3.2). Once compared to the known PT liquidus line, any deviations would signify a correction was required to future experiments.

The measured hydraulic at the face of the press is converted to sample pressure

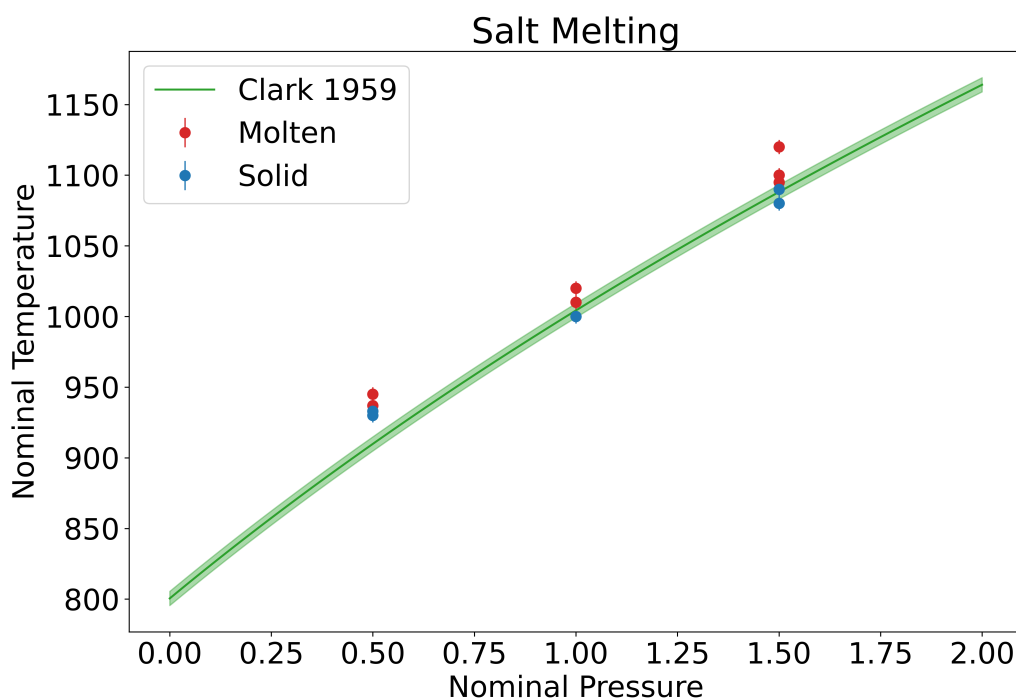


Figure 3.2: Pressure and Temperature conditions of salt melting experiments. The green line, with a 5 °C error margin, is a literature study on the melting of chlorides over a range of pressures up to 6.5 GPa. My set of experiments is done with 0.5 GPa increments. The temperature error come from uncertainty of the positioning of the thermocouple relative to the sample hotspot.

by the geometry of the press and anvils and piston. After the piston, the pressure can be amplified by an 'Anvil effect' - a consequence of the sample geometry - or reduced by friction between the sample cell and the inside of the bomb.

The 'anvil effect' focusses force onto the sample, effectively reducing the piston area, increasing the true pressure while the friction effect reduces the true pressure. The nominal pressure and temperature are the values measured by the Eurotherm temperature controller on the apparatus. The pressure correction is found to be 0 above 1 GPa and at 0.5 GPa the correction is found to be less than 0.1 GPa. For $BaCO_3/SiO_2$ sleeves a standard 12% pressure correction is used (Green, Ringwood, & Major, 1966).

3.2.2 Design of Experimental Assemblage

Experiments were conducted using a pressure medium of thick-wall CaF_2 or $BaCO_3/SiO_2$ sleeve for experiments which exceeded 1400 °C. See figure 2.2, for the experimental assembly. A ‘hot piston in’ approach was taken, where temperature was increased with pressure, to avoid overpressure experiments. Depending on the type of sleeve, the temperature was initially raised to 1400 °C or 1650 °C to ensure homogeneity, before cooling to the target equilibrium temperature. Low temperature, experiments were run for longer durations to ensure equilibrium had been met and also employed welded Pt outer capsules to prevent CaF_2 ingress. Where a Pt outer capsule is used, the MgO ring is filed to allow the Pt outer capsule to fit. The Pt capsules are made by arc welding tempered Pt tube which has been cut to size. Run times and conditions are found in table 3.2. The full sample assembly is in fig. 3.3.

3.2.3 Synthesising and Preparation of Reagent Mixture

My starting compositions were synthesised using powdered reagent grade oxides and carbonates. To produce a homogeneous, intimate, mix it was ground under acetone for 2 hours. To improve weighing accuracy, more than 5 g of starting material was synthesised. Rare Earth Elements (REEs) were then added as spec-pure acids, and the mixture was partially de-carbonated and de-nitrated in air at 800 °C overnight. Samples were then pressed into 500 mg pellets and held in an alumina crucible and reduced to an fO_2 of $(Fe-FeO + 1)$ in a 1-atmosphere $CO-CO_2$ gas-mixing furnace at sub-solidus temperatures for at least 24 h; for all but the final 3 compositions 1100 °C was used. For the final 3 compositions, with low melting point compositions, the fO_2 mixing furnace temperature was reduced to 900 °C, and the gas mix changed accordingly. Once the sample was reduced the alumina crucible containing the pelletised reagent was pulled incrementally out of the hotspot of the furnace to cool under reducing conditions, the sample was grey when removed, indicating Fe^{2+} over Fe^{3+} , and stored in a clean plastic tube in a 110 °C preparation oven.

3.2.4 Thermocouple Control of Temperature

Pressure and temperature were controlled in a Boyd-England-Type piston-cylinder apparatus (Boyd & England, 1960), using a type-C (W95Re5–W74Re26) thermocouple. The thermocouple is inserted through the crushable MgO spacer using a 4-bore alumina sheath, keeping the wires apart, and separated from the sample capsule by a 0.5 mm thick ceramic alumina disk, 6 mm O.D. To prevent thermocouple oxidation, a small stream of argon was passed over where the thermocouple wires exit the base plug, an argon line. The Argon line was necessitated as a slow increase in output power was detected in some early experiments (fig. 3.4), indicative of thermocouple oxidation, which was verified by inspecting the thermocouple

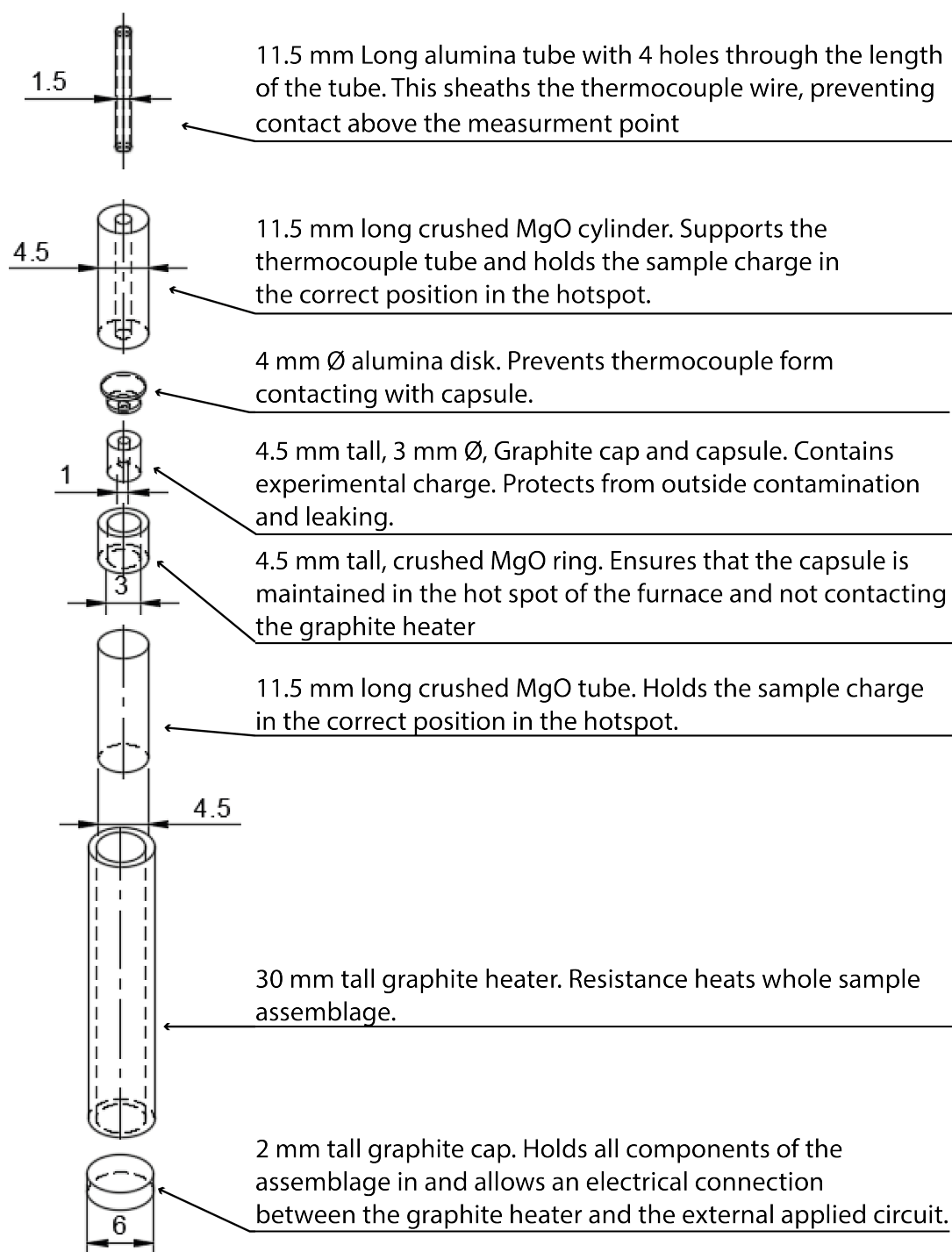


Figure 3.3: Experimental assembly. All dimensions in mm. Is encapsulated in a 32 mm tall, 6 mm I.D. 6.3 mm O.D., CaF_2 or $\text{BaCO}_3/\text{SiO}_2$ pressure medium. The purpose of the sample assembly and pressure medium is to ensure that the sample is held at the correct pressure with the sample in the 'hot spot' of the graphite furnace.

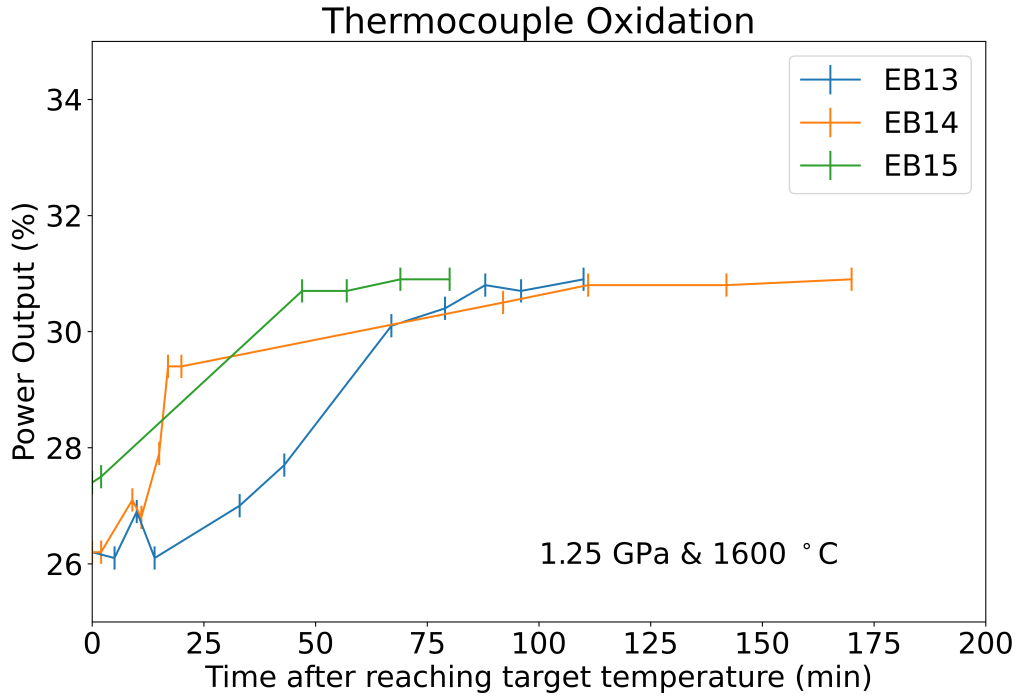


Figure 3.4: Power output of temperature control unit. The furnace apparatus is seen to increase in a few experiments at moderate pressure and high temperature. A successful experiment would have a maximum power deviation of 0.1%.

after quenching.

Because oxidation reduces the EMF generated by the thermocouple, reported temperatures reduce overtime forcing the power supplied to the furnace by the eurotherm controlled to increase. Actual temperatures will therefore be higher than reported.

3.2.5 Quenching

The experiment was quenched by turning off the power; typical quench rates are $>100\text{ }^{\circ}\text{C s}^{-1}$. Run times can be found in table 3.2. After the sample had been successfully extracted, the thermocouple wire was inspected for oxidation using an optical microscope. The quench times are fast enough that the quench texture can be easily identified in backscatter electron images.

3.3 Analytical Methods

Once cooled, the charge was carefully extracted from the experimental assembly by hand and the thermocouple is inspected. The primary analytical technique employed to analyse the experimental charges is the Electron Probe Micro Analyser (EPMA), commonly referred to as an electron microprobe. In this study I used the CAMECA SX5-FE electron microprobe, at the University of Oxford, Department of Earth Sciences. The principles of EPMA are outlined here:

1. An EPMA produces a beam of electrons at the source, which is then accelerated by a high potential difference ($15Kv_{acc}$) and focussed onto the charge.
2. Electron interactions in the sample include the displacement of inner shell electrons, in the case of this study k-shell X-ray lines are used. K-shell lines correspond to electrons falling to the innermost 'K' shell
3. Electrons from higher shells fall to fill vacancies in inner shells, producing 'X-ray's of characteristic frequency.
4. The X-rays which escape from the charge are Bragg-refracted by 'crystal's with known 'd' spacing.
5. The reflected X-rays are counted by proportional gas flow detectors.
6. X-ray counts are converted to compositional data using matrix correction algorithms, which require calibration. These algorithms account for effects such as X-ray absorption and secondary florescence that occurs in the matrix. Standards are used to convert these to fully quantified concentrations. Detection limits are typically ~ 100 ppm.

3.3.1 Mounting and Polishing

Once the charge is extracted the sample is mounted in epoxy resin and left to set for 12 h. Once mounted the experimental label (e.g. EB100) is inscribed on to the mount using an engraving tool. The sample is then carefully ground to expose the graphite capsule and the first part of the experimental charge. Once exposed, more epoxy resin is applied to the charge, and the sample is left in a vacuum bell jar. The low pressure draws any air out of the sample to be replaced with resin, so any subsequent polishing does not displace or remove grains. Epoxy is reapplied as required to ensure none of the experimental charge is lost. Once the second application of resin is complete, the sample is polished using different grades of diamond sandpaper, up to 0.1 nm.

3.3.2 Carbon Coating

Samples and standards were coated in 20 nm of carbon. To ensure a consistent coating of C, a brass chip is inserted, the apparent colour of the chip is highly sensitive to the thickness of the carbon coat. Before coating, the sample is cleaned with isopropanol and Kimtech fibreless wipes and placed in an ultrasonic agitator for 5 minutes, then air dried to ensure sample cleanliness.

Once polished and coated, the samples are photographed using a back scatter electron imaging sensor. Some example charges are found in figs. 3.5 and 3.6. All Images are taken at 15 Kv and 20 nA with a focussed beam. In the case of EB100 (fig. 3.6), the sample grinding was not flat so the sample charge appears shorter.

3.3.3 Standards

Primary Standards The primary standards are used by the EPMA software to calibrate the matrix correction algorithms. Calibrations are sensitive to externals such as room temperature, because the lattice spacing of the reflecting crystals are

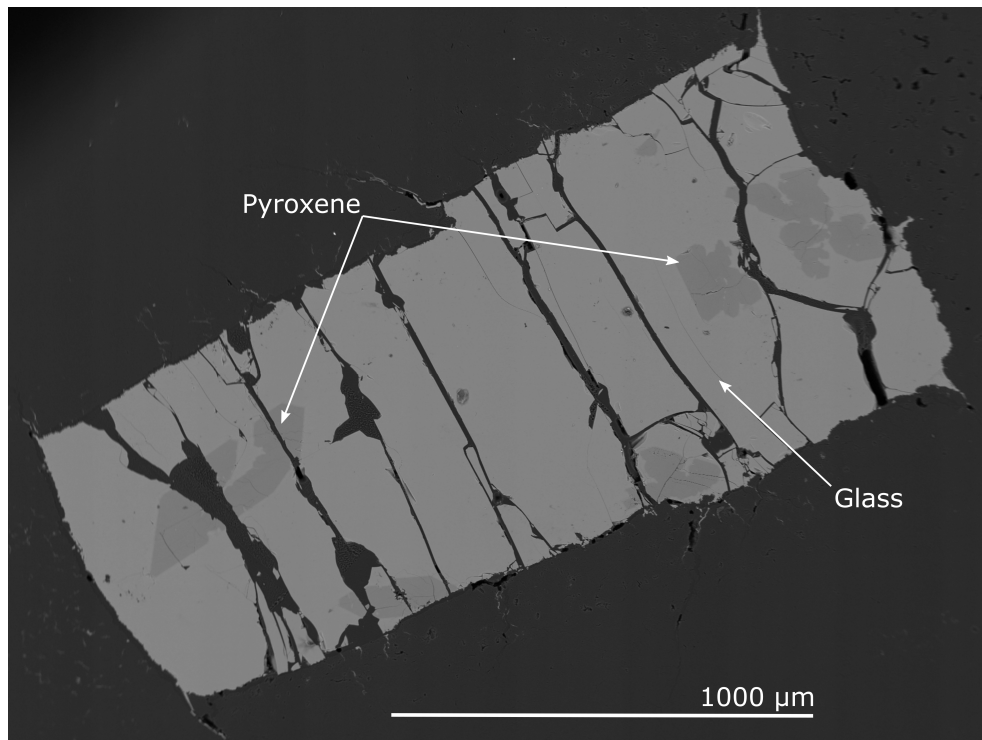


Figure 3.5: A BSE image of sample charge EB44

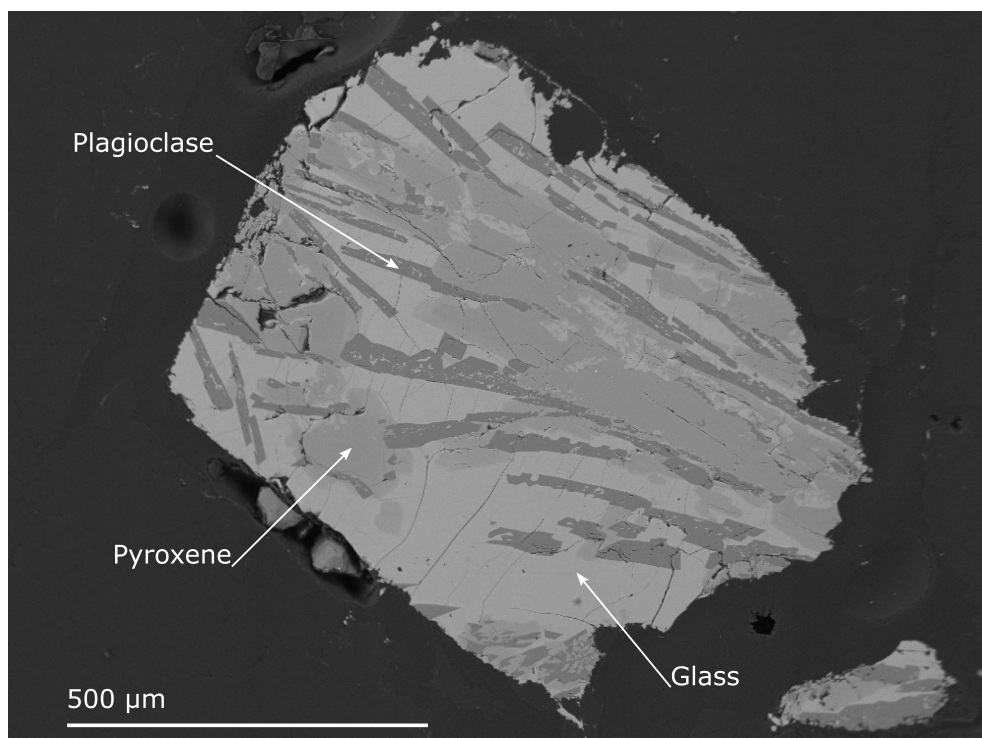


Figure 3.6: A BSE image of sample charge EB100

sensitive to temperature. The primary standards are rerun before each analytical session to ensure accuracy and are checked against a variety of secondary mineral and glass standards. Primary standards used can be found in table 3.1.

Table 3.1: Spectrometer Conditions

Element	Spec	crystal	Line	Bg 1	Bg 2	Primary Standard
Na	1	TAP	K α	-850	850	Albite
Mg	1	TAP	K α	-1750	1400	<i>MgO</i>
Ca	2	PET	K α	-800	800	Andradite
Ti	2	PET	K α	-1000	800	<i>TiO₂</i>
Cr	3	LLIF	K α	-1000	1000	Cr (metal)
Mn	3	LLIF	K α	-850	850	Mn (metal)
Al	4	TAP	K α	-650	800	Albite
Si	4	TAP	K α	-750	850	Albite
Fe	5	LLIF	K α	-1000	1000	Andradite
Ni	5	LLIF	K α	-1000	1000	Ni (metal)

Secondary Standards Secondary standards used include St John’s Island Olivine (Mg), Wollastonite, KN18 Rhyolite glass, Labradorite, and Albite. The secondary standards are used to check that the primary standard calibration is accurate. Secondary standards were re-analysed regularly during an analytical session to recognise instrument drift.

3.3.4 Background and Peak Positions

Accurate electron microprobe analysis calculates the elemental composition of a target by counting characteristic x-rays that are produced by interactions between incident electrons and inner shell orbitals.

Electronic transitions produced from these interactions are systematically named by the ‘Siegbahn notation’. The notation is codified in (Jenkins, Manne, Robin, & Senemaud, 1991). In this study, all lines used are ‘K α ’ lines, which signify transitions from the 2p orbital (L shell) to the 1s orbital (K shell).

Wavescans are run to target peaks, by comparison with known energies of

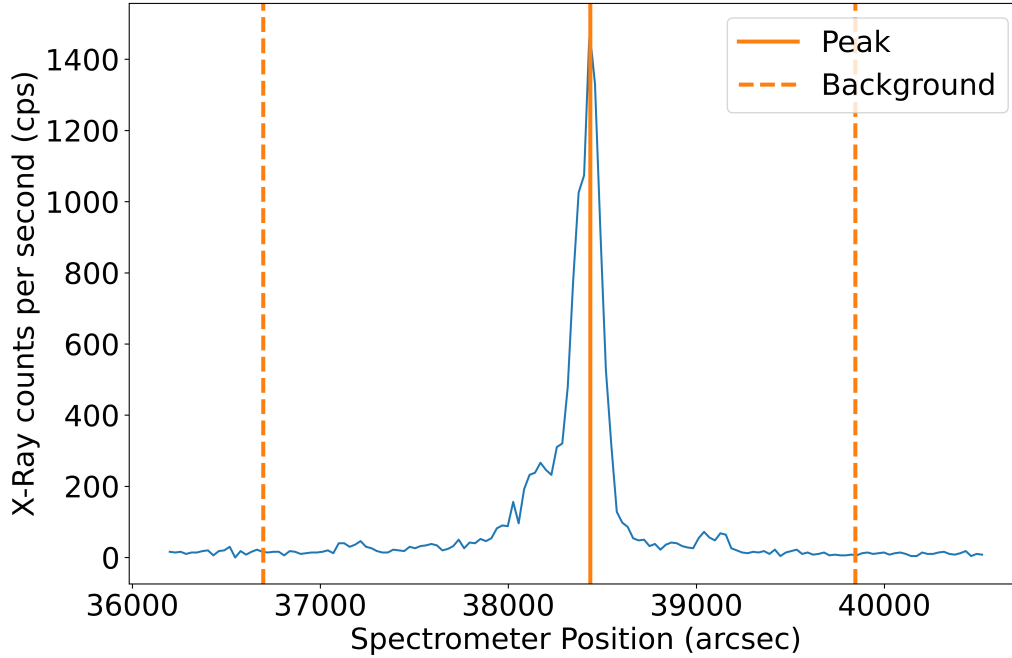


Figure 3.7: TAP crystal wavescan around the Mg K peak. Peak and background positions clearly visible. True background is lineally interpolated between the two peaks at +1400 and -1750 arcsin.

targeted transitions, and check that there is not any overlap with other peaks, particularly important when determining background positions. An example peak is the Mg K α peak, see fig. 3.7. Positions used in the analysis are highlighted in fig. 3.8. Two LLIF and TAP crystals are used in the standard setup, so these peak positions have 4 elements each.

3.3.5 Beam Setup

The electron beam must be set-up to correctly analyse the required phases without influence from adjacent phases. The interaction volume describes the volume of material that generates X-ray's which subsequently 'escape' and can be counted by the X-ray detectors. The interaction volume is regarded as the X-ray generating volume. The process of X-ray generation and absorption can be modelled compu-

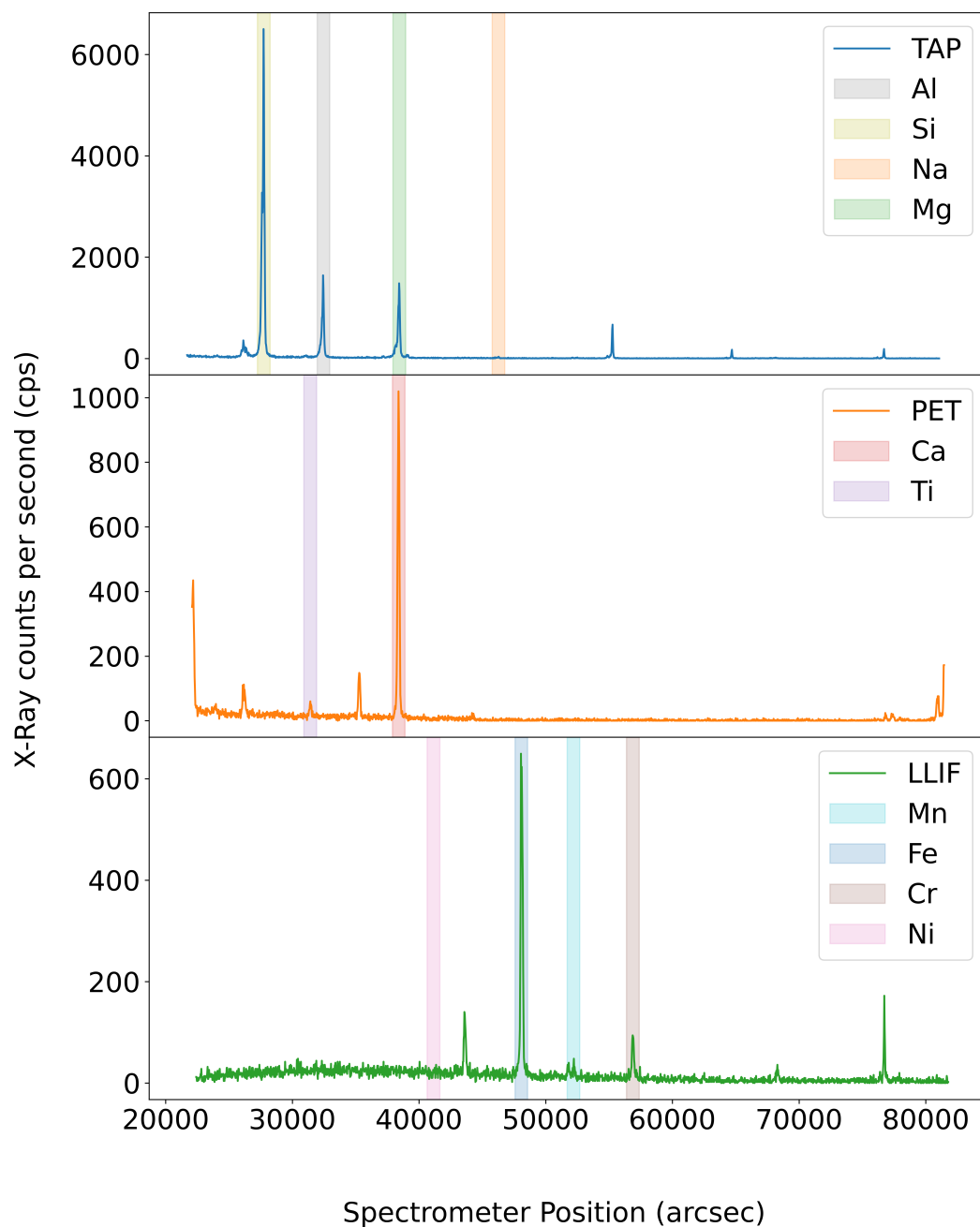


Figure 3.8: X-ray counts per second across all available crystal positions, on TAP, PET and LLIF crystals. The peaks used for each element of interest are highlighted. Some peaks are relatively small, e.g. Na, this is due principally to the low concentration in the sample.

tationally, see fig. 3.9. The beam size changes between phases to ensure that the interaction volume does not encroach into other phases. For glass phase analysis, a spot size of 10 μm is used because small, charged ions, such as the alkali metals are prone to migrating. As a result, their apparent concentration in the material changes with time. To mitigate this, these elements are analysed first, simultaneously with other major elements (e.g. Si). A defocused beam is also used to minimise the beam energy density, in addition counting times are kept short. The absence of light ion migration is checked by looking at the change in count rate with time – if light ion migration occurs, the count rate will drop after a short time known as the ‘incubation time’.

All phases were analysed with a 15 kV accelerating voltage and 15-20 nA current. Typical count times, on 5 WDS spectrometers, of 30-60 s for peaks and 15-30 for back ground were used, and totals of 98-101 % and 97-100 % for crystals and glasses respectively were allowed. The lower value for glass was chosen to accommodate a small amount of trace elements (see Chapter 4). Counts are converted to concentration using a $\phi\rho z$ algorithm (Bastin, Van Loo, & Heijligers, 1984).

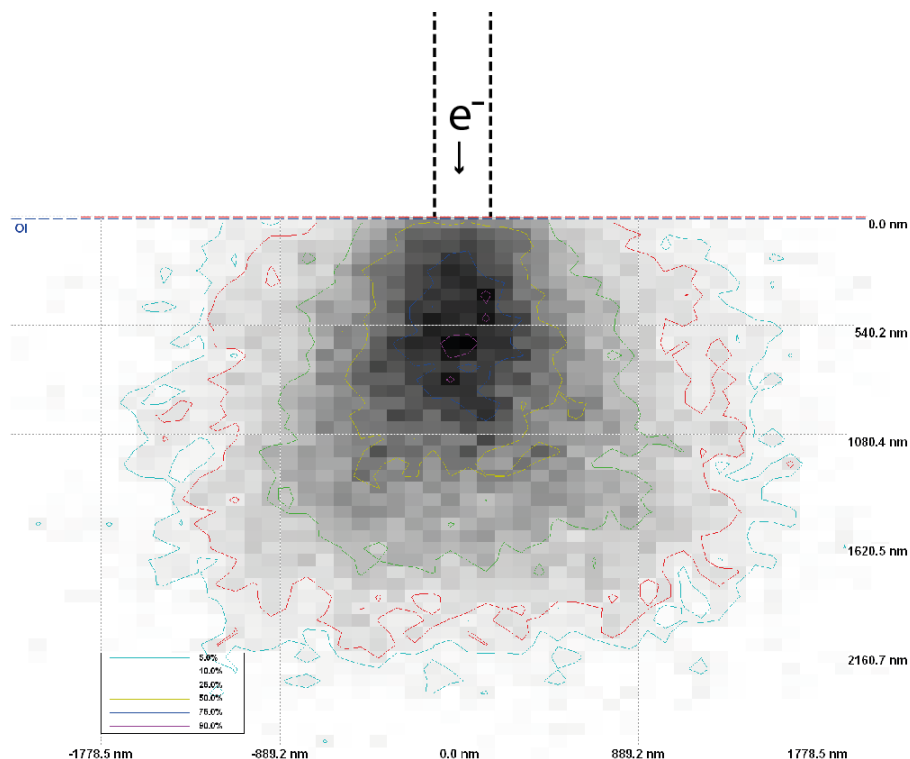


Figure 3.9: Interaction volume of 15 Kv, 1 μm spot size electron beam in a FeMgSiO_4 olivine. Figure generated in Casino 2D electron modelling software (Drouin et al., 2007). The 90 % interaction volume is approximately 3 μm across and 2 μm deep and is considered the ultimate spatial resolution with these analytical conditions

3.4 Results

A total of 118 experiments have been performed, yielding 11 experiments, which crystallised the correct quantity of crystalline phases. The conditions of each experiment are found in table 3.2 and fig. 3.10.

My experiments produce a range of iron-magnesium silicates, olivines and pyroxenes, with initially low Mg-numbers and become progressively more iron-rich as crystallisation proceeded (fig. 3.11). The 'melt's Fe and Mg content is initially controlled by the crystallisation of Olivine (Ol) which results in decreasing the Mg# of the melt. In addition, the melt is rapidly denuded in Cr, a consequence of the early formation of chrome spinel. Once clinopyroxene and plagioclase became stable on the liquidus (after around 80 % crystallisation), the melt was increasingly enriched in Fe, and consequently produced low Mg# phases. The most evolved melt

generated by the experiments contained in excess of 3 wt.% TiO_2 .

Of note, our liquid line of descent diverges from that predicted by phMELTS (fig. 3.11). In comparison to my experiments, phMELTS over-estimates the high-temperature stability of pyroxene (as observed by Hirschmann et al. (1998)). The composition of the most evolved liquid predicted by phMELTS is similar to my experimentally found liquid; FeO 30.9 wt.% in by my experiments and 31.5 in the phMELTS model, CaO 10.4 and 10.0, Al_2O_3 9.8 and 11.6 respectively, the Mg# is also similar; 31 and 28 in experiments and phMELTS respectively.

As will be shown, the consequence of this divergence between the experimental liquid line of descent and that from phMELTS is that the experiments predict Fe-rich olivine and pyroxene bearing silicates which will be emplaced at significantly shallower depths within the Moon than previously suggested.

Table 3.2: Experimental runs and conditions. Phases found on the liquidus, which control the evolution of the melt, are marked. Significant enrichment in Fe and Ti are found when clinopyroxene and plagioclase are on the liquidus.

Composition	P (GPa)	T (°C)	Hours		Spnl	Ol	Pyx	Plg
B	2	1675	2	EB11	y	y		
E3	1.25	1540	4	EB18	y	y		
F	1.1	1425	4	EB25	y	y		
J	1	1200	4	EB44			y	
K	0.9	1150	4	EB63			y	
N	0.9	1125	6	EB68			y	y
O	0.8	1125	8	EB84			y	y
P2	0.7	1120	8	EB100			y	y
Q	0.6	1050	50	EB115		y		
Q	0.6	1000	50	EB117			y	y
Q	0.6	850	51	EB118			y	y

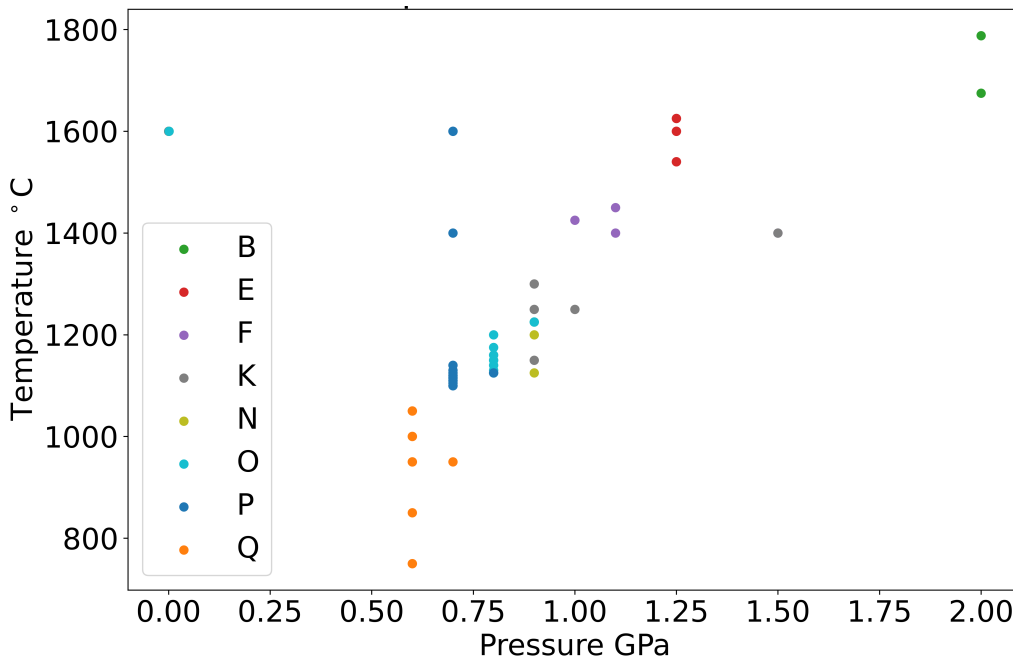


Figure 3.10: Experimental Conditions. Pressure and Temperature coordinates of each experimental run. Points are coloured by the bulk composition used in the experiment B-Q, see tables 3.3 to 3.6

The proportions of each phase are found in table 3.8. In the case of plagioclase, the volume produced equates to a thickness of anorthosite crust given in table 3.7. Estimates of crustal thickness for a given depth of LMO is complicated as the efficiency of plagioclase separation is unknown and the influence of lunar mantle overturn is unknown.

Table 3.3: Major Element datatable Experiments B-F

Comp	a	n	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO	NiO
B												
Bulk	na		0.15	33.41	5.33	44.66	4.25	0.24	2.79	0.16	8.72 (0)	0.3 (0)
Sp	0.02	5	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)		
Ol			0	16.93	8.24	0.39	0.09	0.15	66.44	0.1	7.55	0.11
			(0.01)	(0.54)	(0.92)	(0.12)	(0.03)	(0.05)	(1.17)	(0.06)	(0.16)	(0.01)
Gl	0.36	11	0.07	47.51	1.13	41.77	1.01	0.05	1.43	0.11	6.71	0.21
			(0.01)	(0.36)	(0.04)	(0.42)	(0.02)	(0.03)	(0.05)	(0.02)	(0.09)	(0.04)
	0.62	57/na	0.19	25.97	7.61	47.8	5.96	0.35	1.61	0.18	9.94	0.4
			(0.26)	(12.58)	(4.1)	(4.17)	(3.86)	(0.21)	(4.36)	(0.03)	(1.27)	(0.08)
Bulk	na		0.19	25.97	7.61	47.8	5.96	0.35	1.61	0.18	9.94 (0)	0.4 (0)
			(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)		
E												
Bulk	0.01	5	0	16.1	16.16	0.31	0.05	0.22	56.58	0.15	10.13	0.28
Sp			(0.02)	(0.41)	(0.81)	(0.05)	(0.03)	(0.04)	(1.01)	(0.1)	(0.55)	(0.06)
Ol	0.14	31	0	49.4	0.09	40.99	0.15	0	0.56	0.14	8.11	0.53
			(0.02)	(0.31)	(0.13)	(0.69)	(0.18)	(0.03)	(0.72)	(0.06)	(0.43)	(0.34)
Gl	0.85	14	0.29	20.84	9.11	48.47	9.1	0.48	1.54	0.25	9.77	0.15
			(0.37)	(0.89)	(1.04)	(1.15)	(0.23)	(0.12)	(0.56)	(0.07)	(0.44)	(0.05)
Bulk	na		0.29	20.84	9.11	48.47	9.1 (0)	0.48	1.54	0.25	9.77 (0)	0.15 (0)
			(0)	(0)	(0)	(0)		(0)	(0)	(0)		
F												
Bulk	0.01	5	0.01	15.68	16.43	0.6	0.33	0.26	54.88	0 (0)	11.59	0.21
Sp			(0.01)	(0.22)	(0.06)	(0.31)	(0.14)	(0.04)	(0.43)		(0.26)	(0.03)
Ol	0.09	28	0.01	48.7	0.13	40.06	0.32	0.01	0.84	0.15	9.36	0.42
			(0.01)	(0.52)	(0.15)	(0.73)	(0.02)	(0.01)	(0.5)	(0.02)	(0.06)	(0.02)
Gl	0.91	7	0.25	18.09	10.03	48.1	11.48	0.54	1.18	0.21	10.05	0.07
			(0.04)	(0.87)	(0.11)	(0.24)	(0.38)	(0.02)	(0.07)	(0.02)	(0.38)	(0.01)

Table 3.4: Major Element datatable Experiments J-N

Comp	a	n	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO	NiO
J*	na	18	0.33 (0)	13.97 (0)	11.29 (0)	50.65 (0)	12.99 (0)	0.64 (0)	0.01 (0)	0.21 (0)	9.92 (0)	0 (0)
			0.12	0.04 (0.01)	2.54 (0.16)	54.21 (0.17)	6.9 (0.43)	0.12 (0.01)	0.01 (0.01)	0.21 (0.01)	7.49 (0.15)	0 (0.01)
			0.88	0.37 (0.03)	12.19 (0.17)	50.14 (0.34)	13.76 (0.07)	0.71 (0.03)	0 (0.01)	0.21 (0.02)	10.22 (0.09)	-0.01 (0.02)
K*	na	39	0.42 (0)	9.32 (0)	14.19 (0)	49.32 (0)	15 (0)	0.82 (0)	0 (0)	0.21 (0)	10.71 (0)	-0.01 (0)
			0.24	0.13 (0.06)	9.56 (0.12)	48.73 (0.35)	19.56 (0.15)	0.52 (0.08)	0.02 (0.02)	0.14 (0.02)	6.19 (0.44)	0.01 (0.02)
			0.76	0.59 (0.05)	15.63 (0.5)	48.6 (0.27)	14.53 (0.65)	0.9 (0.05)	0 (0.01)	0.2 (0.02)	11.99 (0.61)	0 (0.02)
N	na	13	0.59 (0)	7.54 (0)	15.63 (0)	48.6 (0)	14.53 (0)	0.9 (0)	0 (0)	0.2 (0)	11.99 (0)	0 (0)
			0.27	0.23 (0.04)	12.65 (0.12)	46.31 (0.29)	19.71 (0.14)	0.74 (0.07)	0.07 (0.01)	0.18 (0.01)	7.55 (0.09)	0.01 (0.01)
			0.05	2.12 (0.1)	0.31 (0.02)	31.97 (0.29)	17.03 (0.17)	0.03 (0.01)	0 (0.01)	0.01 (0.01)	0.63 (0.05)	0 (0.01)
EB68	0.27	44	0.23 (0)	12.65 (0)	12.55 (0.36)	46.31 (0.29)	19.71 (0.14)	0.74 (0.07)	0.07 (0.01)	0.18 (0.01)	7.55 (0.09)	0.01 (0.01)
			0.05	2.12 (0.1)	0.31 (0.02)	31.97 (0.29)	17.03 (0.17)	0.03 (0.01)	0 (0.01)	0.01 (0.01)	0.63 (0.05)	0 (0.01)
			0.68	0.72 (0.03)	5.97 (0.44)	48.57 (0.13)	12.61 (0.22)	1.11 (0.09)	0 (0.02)	0.24 (0.01)	14.95 (0.21)	0.01 (0.01)

Table 3.5: Major Element datatable Experiments O-Q

Comp	a	n	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO	NiO
O	na		0.72 (0)	5.97 (0)	15.82 (0)	48.57 (0)	12.61 (0)	1.11 (0)	0 (0)	0.24 (0)	14.95 (0)	0 (0)
	0.18	23	0.16 (0.05)	12.38 (0.38)	8.62 (0.28)	47.48 (0.14)	17.19 (0.35)	0.79 (0.17)	0.06 (0.02)	0.22 (0.03)	13.09 (0.41)	0 (0.02)
	0.22	11	1.88 (0.08)	0.22 (0.05)	31.85 (0.24)	48.32 (0.38)	16.87 (0.26)	0.03 (0.02)	0 (0.01)	0.01 (0.01)	0.82 (0.15)	0 (0.02)
	0.6	6	0.67 (0.02)	4.33 (0.24)	13.06 (0.13)	45.48 (0.35)	13.02 (0.58)	1.9 (0.13)	0 (0.01)	0.25 (0.02)	21.3 (0.66)	-0.01 (0.01)
P	na		0.67 (0)	4.33 (0)	13.06 (0)	45.47 (0)	13.02 (0)	1.9 (0)	0 (0)	0.25 (0)	21.29 (0)	0 (0)
	0.32	9	0.17 (0.01)	7.9 (0.1)	11.28 (0.23)	44.24 (0.19)	18.41 (0.15)	2.14 (0.16)	0.29 (0.03)	0.24 (0.01)	15.33 (0.21)	0 (0.02)
	0.14	10	1.95 (0.05)	0.19 (0.01)	31.76 (0.27)	48.14 (0.28)	16.68 (0.14)	0.06 (0.01)	0.01 (0.01)	0.01 (0.01)	1.19 (0.02)	0.02 (0.02)
	0.54	5	0.55 (0.03)	2.35 (0.05)	9.83 (0.02)	42.34 (0.06)	10.41 (0.05)	3.28 (0.03)	0 (0)	0.34 (0)	30.9 (0.05)	0 (0)
Q	na		0.55 (0)	2.35 (0)	9.83 (0)	42.34 (0)	10.41 (0)	3.28 (0)	0 (0)	0.34 (0)	30.9 (0)	0 (0)
	0.28	3	0 (0)	13.47 (0.25)	0.08 (0.01)	32.91 (0.03)	0.71 (0.04)	-0.02 (0)	0.06 (0)	0.48 (0.01)	52.28 (0.4)	0.01 (0.01)
	0.72	3	1.13 (0.14)	1.99 (0.18)	16.08 (0.67)	46.28 (0.32)	11.75 (0.83)	0.01 (0.02)	0.01 (0)	0.26 (0)	22.48 (0.17)	0.01 (0)

Table 3.6: Major Element datatable Experiments ext

Comp		a	n	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	FeO	NiO
Q	Bulk	na		0.55 (0)	2.35 (0)	9.83 (0)	42.34 (0)	10.41 (0)	3.28 (0)	0 (0)	0.34 (0)	30.9 (0)	0 (0)
	OI	0.32	5	0.02 (0.05)	14.91 (0.61)	0.05 (0.02)	32.71 (0.22)	0.77 (0.06)	-0.01 (0.02)	0.05 (0.01)	0.48 (0.01)	50.99 (0.73)	0 (0.01)
	PI	0.56	5	0.2 (0.06)	3.92 (0.12)	11.97 (0.6)	43.03 (0.36)	17.51 (0.31)	0.02 (0.01)	0.07 (0.02)	0.29 (0.02)	22.99 (0.54)	0 (0.02)
	GI	0.12	4	2.68 (0.3)	0.19 (0.07)	28.26 (0.67)	50.64 (0.92)	14.97 (0.59)	0 (0.02)	0 (0.01)	0.05 (0.02)	3.2 (0.54)	-0.01 (0.01)
Q	Bulk	na		0.55 (0)	2.35 (0)	9.83 (0)	42.34 (0)	10.41 (0)	3.28 (0)	0 (0)	0.34 (0)	30.9 (0)	0 (0)
	OI	0.34	5	0 (0.05)	14.93 (0.33)	0.06 (0.02)	33.7 (0.31)	0.82 (0.04)	0 (0.02)	0.08 (0.01)	0.53 (0.02)	49.84 (0.45)	0 (0.02)
	PI	0.35	5	1.42 (0.09)	0.29 (0.04)	17.31 (0.47)	48.98 (0.69)	12.34 (1.01)	0.01 (0.01)	0.02 (0.01)	0.25 (0.02)	19.37 (1.92)	0 (0.01)
	GI	0.31	5	0.17 (0.06)	4.31 (0.31)	11.91 (0.26)	44.18 (0.11)	18.56 (0.33)	0.02 (0.02)	0.12 (0.02)	0.28 (0.02)	20.45 (0.68)	0.01 (0.02)

Table 3.7: Calculations of crustal thickness that corresponds to a 7.5 % volumetric production of feldspar from a magma ocean of different depths. Density of feldspar from (Robie & Bethke, 1962)

Depth of Ocean (km)	Thickness of Anorthite crust (km)
400	23.95
500	28.2
600	31.83
700	34.89
800	37.42
900	39.47
1000	41.09
1100	42.32
1200	43.23
1300	43.85
1400	44.25
1500	44.47

Table 3.8: The aggregated phase proportions from all successful experiments, weighted by the amount of crystallisation that occurred in each step.

Phase	Final Proportions (mass)
Spinel	0.02
Olivine	0.65
Clinopyroxene	0.24
Plagioclase	0.06
Fayalite	0.01
Glass	0.01

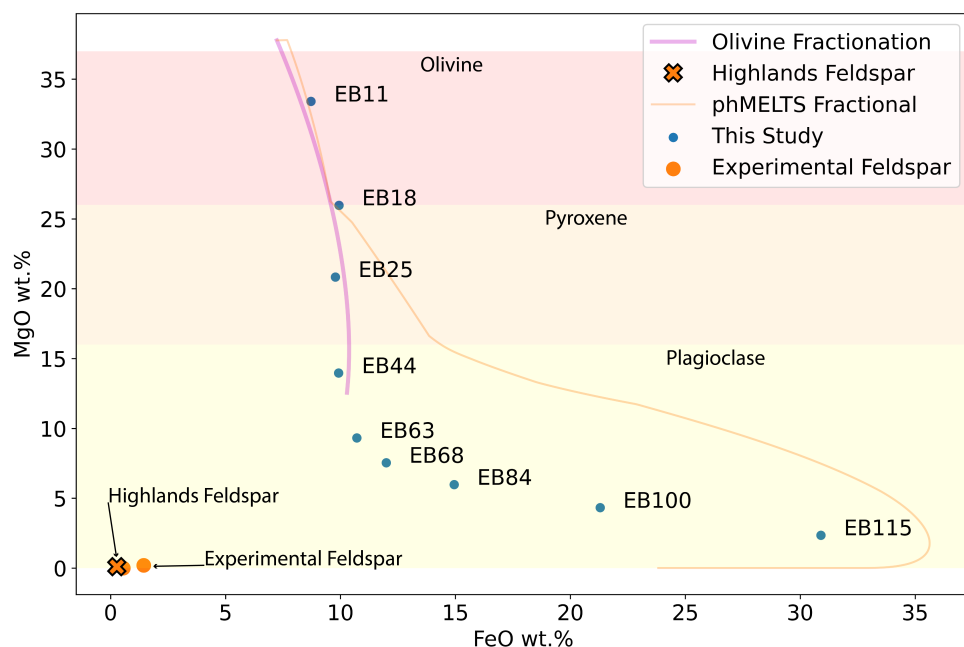


Figure 3.11: Liquid Compositions. The experimentally found liquid line of descent descends from the top left in a series of blue dots to the bottom right. The solid orange line is the liquid composition predicted by the phMELTS modelling program. Feldspar compositions are plotted in orange; orange crosses are from the FAS, orange dots are experimentally found, plotted in fig. 3.12. The pure olivine fractionation curve is plotted as a purple line using the exchange coefficient of 0.33 from Matzen et al. (2011)

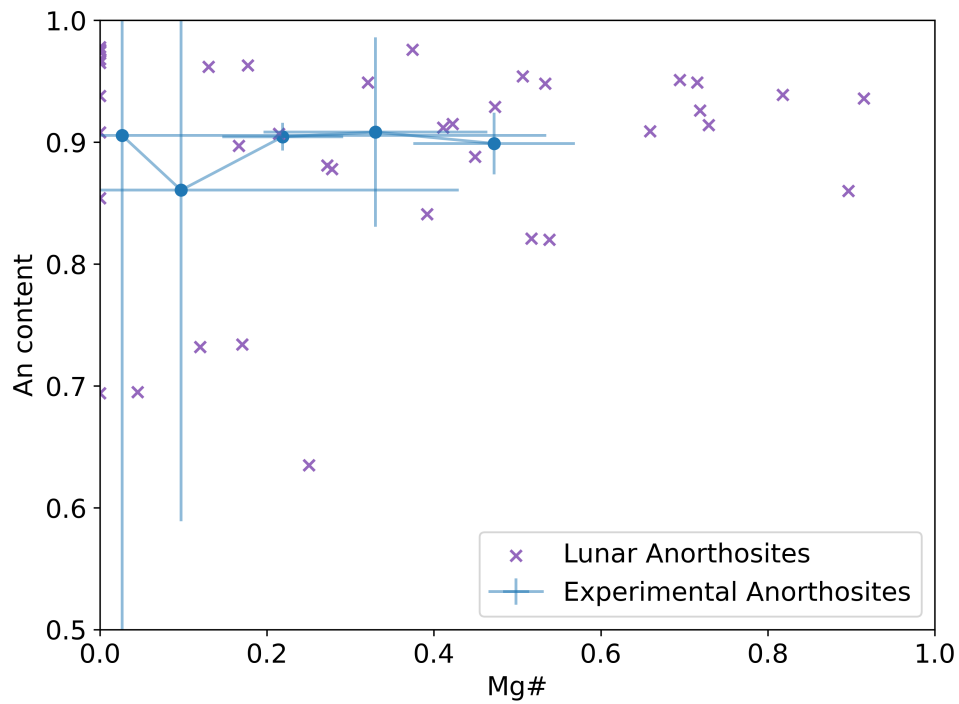


Figure 3.12: The Apollo anorthosites from Jolliff et al. (2006) plotted against experimentally produced anorthosites. The An and Mg# of experimental phases plot in the centre of the cloud of Apollo highland data from (Jolliff et al., 2006)

3.5 Cumulate remelting and recombination

The Moon's surface is divided into the 'primary crust', the light-coloured lunar highlands, and the darker mare basalts which are extruded on top of the primary crust. Convincing evidence for the distinction between the primary crust and the mare basalts arises from both dating and textural analysis. Whereby, the Ferroan Anorthosite Suite (FAS) dates to 4.3-4.5 Ga and is comprised of pristine igneous rocks, with large crystals. The younger mare basalts extruded from 4.2 to 2.7 Ga (Shearer & Papike, 1999b). The timing of mare basalt petrogenesis precludes a direct link between the lunar magma ocean, which solidified up to $\sim 80\%$ in less than 100 ma (Elkins Tanton, Burgess, & Yin, 2011; Nemchin et al., 2009). In addition to the age separation, the Eu anomaly seen in many mare basalt suites requires plagioclase extraction to pre-date its petrogenesis. To assess how well my experimentally produced cumulate stack, the layers of crystal phases produced in each experiment, can recreate the mare basalts and FAS I have recombined them. For the reasons above, the FAS and mare basalts are treated separately. See the top of each section for methods.

In the following discussion, I will compare the composition and mineral assemblages of known lunar samples and show, to a good degree, that my model of fractional crystallisation can accurately recreate these compositions and assemblages during the evolution of a lunar mare basalt from a terrestrial peridotite origin.

3.5.1 Petrogenesis of Primary Lunar Crust

The GRAIL survey mission estimated the thickness of the lunar crust to be 34 to 43 km (Wieczorek et al., 2013). However, the observed high porosity makes it difficult to estimate the chemistry of the primary crust with precision. Our experiments produce 7-8% feldspar by volume, combined with the GRAIL estimates of crustal thickness (34-43 km) maps to a LMO depth of 700-1400 km (table 3.7)(Wieczorek et

al., 2013). This calculation must be taken with caution, trapped melt and imperfect flotation of plagioclase decrease the accuracy of this estimation. It is possible, if not likely that the whole crust is not represented well by the surface, some craters which excavate deep into the crust reveal a systematic decline of feldspar with depth (Ryder & Wood, 1977).

Ferroan Anorthite Suite recombination methods An important constraint on the petrogenesis of the FAS is the presence of minor/trace amounts of mafic minerals, dominantly pyroxene, known as ‘mafics’. These mafics must have been produced or trapped alongside plagioclase. To investigate the origin of these mafic components, I have subtracted the feldspar component from the bulk FAS and determined if the mafics can be produced from the liquid or crystals, coexisting with feldspar. To achieve this, pure Anorthosite and Albite are used as mixing components. The SOLVER function, contained within Microsoft Excel, is used to remove the nominal feldspar contribution from the bulk rock composition. To achieve this, I used a range of FAS compositions, from the supplementary information of Jolliff et al. (2006) to pick out systematic relationships in the FAS samples (table A.1) and mixing components (table A.3). The amount of variation between the expected and observed composition produced by the optimised mixing of components is called the Sum Squared Misfit, SSQM. This SSQM is used to assess the accuracy of the fit, values below 1 are considered successful. Mixing outcomes are found in table A.2.

Ferroan-Anorthosite Suite (FAS) The FAS is nearly monomineralic in composition and comprises >95 wt% plagioclase, itself comprised of ~95 wt% anorthite. Very few FAS samples have more than 10% mafic minerals. The mineralogical purity and the coarse crystal size indicates a cumulate deposit that formed from the initial crystallisation of the magma ocean. (Jolliff et al., 2006; Shearer et al., 2006).

As the FAS is thought to be crystallised directly from the initial solidification

of the lunar magma ocean, the crystal and bulk rock compositions can be directly compared to those experimentally generated (fig. 3.11). Firstly, Lunar highland feldspars range between An_{70} to An_{98} (Vaniman & Papike, 1980), spanning the range of my experimentally generated feldspars (An_{81-91}). The samples of the FAS could cross the trapped-melt/trapped-crystal continuum. 20 FAS samples have been recreated by mixing experimentally produced anorthites with late-stage crystals and melts, produced concurrently with the feldspars. The samples (table A.3), are produced dominantly with trapped crystals, samples with larger mafic components require more trapped melt. (Mixing coefficients table A.2 The dominance of trapped crystals over trapped melt is clear in aggregate, with only 21% of mafic material fit to melt; the majority of that signal comes from only two samples.

3.5.2 Petrogenesis of Mare Basalts

Mare Basalts recombination methods The mare basalts are younger than the FAS (Shearer & Papike, 1999a) and require the re-melting and hybridisation of lunar cumulates and late-stage melts as evidenced by complimentary Eu anomalies, e.g. (Jolliff et al., 2006; Taylor, 1982) and highly variable Ti and Al concentrations. Cumulate phases produced at each experimental step are melted to 5 wt.% melt fraction, at the pressure of the corresponding experiment, in pHMELTS. The temperature used is that required to get 5 wt.% melt with a fO_2 fixed to IW+1. The pHMELTS 1.9 model, run from cmd.exe, is used for the melting calculations. An ilmenite and a rutile composition (Deer, Howie, & Zussman, 2013) are taken to represent a FeTi rich component. Mare Components are found in table A.6.

Using the same pressure in the pHMELTS model as the experiment implies no adiabatic component of melting. However, the relatively modest pressure gradient within the silicate Moon reduces the adiabatic component of melting. Additionally, ground-penetrating radar measurements depict that mare basalts represent 0.1-0.5

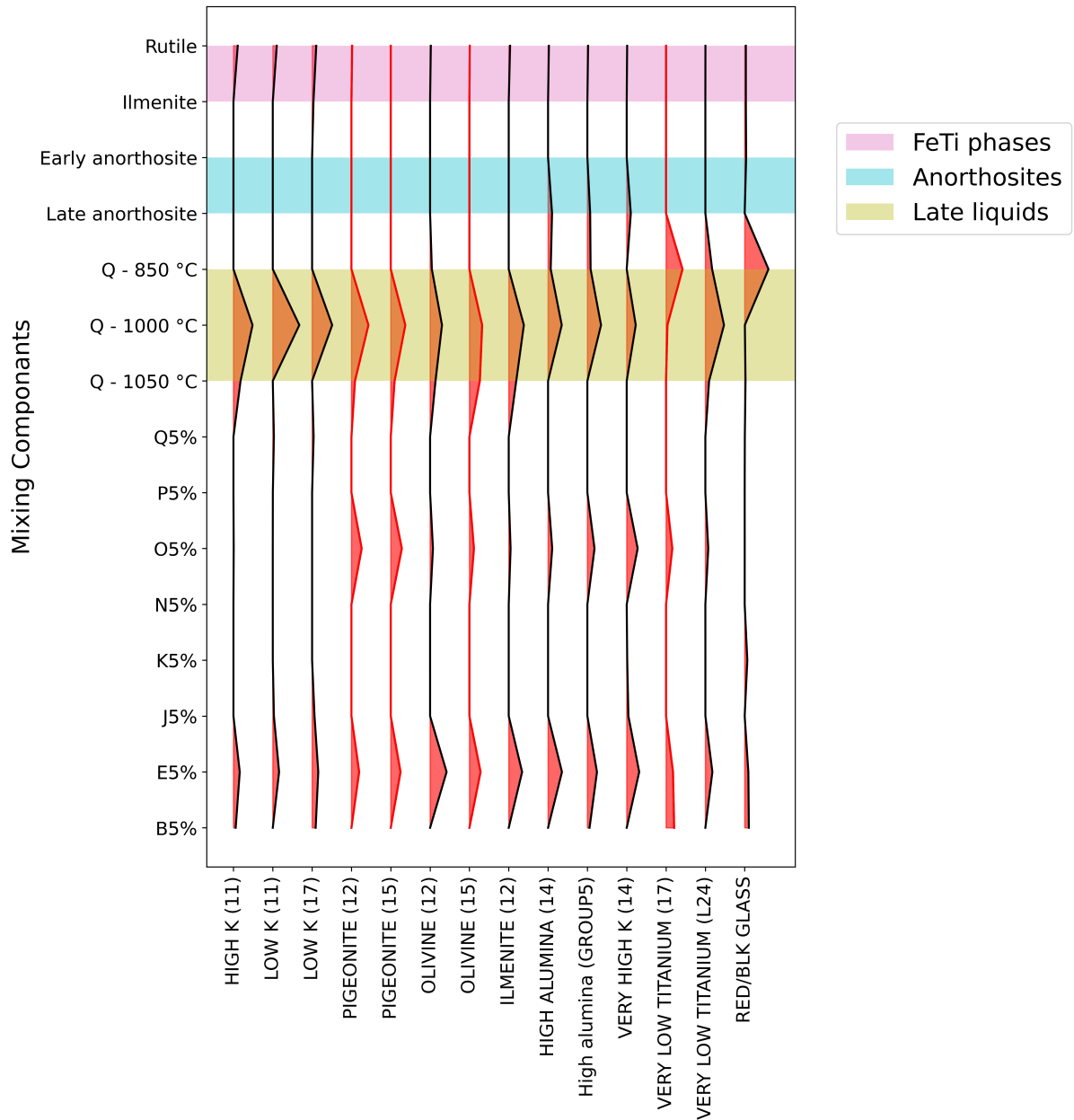


Figure 3.13: Here I plot the outcome of the mixing and recombination models. The amount of material derived from each cumulate layer or other phase, required to reproduce the observed bulk composition, is marked as red. Black lines are lines which accurately recreate the observed bulk compositions. Red lines do not accurately (more than 1 SSQM) recreate the observed lithologies. B5% refers to the 5 wt.% melt of the cumulate phases produced from composition B, as modelled by MELTS. Cumulate phases found in tables 3.3 to 3.6, mixing coefficients and target compositions found in tables A.4 to A.6.

vol% of the lunar crust (Head & Wilson, 1992; Jolliff et al., 2006). Furthermore, the lack of any large-scale compressional faults on the lunar surface precludes volumetrically significant melting. Therefore, it is predicted that melting of the lunar crust is restricted to $\leq 5\%$.

To constrain origin of the Mare basalt compositions (Mare target compositions, table A.4), these were fit with linear combinations of our experimentally found phases (Feldspar, Pyroxene, Fayalite and Melt, table A.6), using Excel's SOLVER, the solver function was run until no improvement in fit is possible. The degree of misfit is quantified as the sum of the squared error. The optimum mixing outcomes are found in table A.5 and fig. 3.13. The Melt compositions used for the mixing models are named by the crystals that make up the bulk composition, e.g. olivine derived melt is melt formed from olivine containing cumulates from our experimental sequence.

High Ti Low K The high Ti mare basalts found at the Apollo 11 landing site have variable K concentrations and represent at least 5 different magmatic events, dating from 3.6 to 4 Ga. (Guggisberg et al., 1979; Papanastassiou, Depaolo, & Wasserburg, 1977). The Apollo 17 high Ti mare basalts can be split by major element chemistry into three groups which is consistent with petrological studies. However, trace element studies have split these samples into 5 groups (C. Neal & Taylor, 1991).

While the Apollo 11 basalts generally have lower Ti contents than the Apollo 17 basalts, the major element concentrations are essentially the same. In all High Ti low K samples, Mg# decreases with increasing Al content, indicating that plagioclase was not on the crystallisation trend of either groups of basalts (Jolliff et al., 2006). The most pronounced 'bow shaped' REE trends (Depleted in heavy and light REEs compared to the middle) are found in the High Ti mare basalts, see fig. 4.1. This

indicates that much of the material is derived from late-stage melts, which have undergone both Ca, pyroxene, and Olivine/Orthopyroxene crystallisation.

Existing petrogenetic models invoke a source region containing pyroxene, olivine and ilmenite (Walker, Longhi, Stolper, Grove, & Hays, 1975) from the outer 150 km of the Moon. This suggests that the differences between Apollo 11 and 17 basalts can be reconciled by different degrees of partial melting. In this scenario, the variations in the alkalis can be attributed to metasomatism (Shih et al., 1992) et al., 1992), which allows 'hybridisation' with lunar granites without altering the characteristic REE pattern. This mechanism would, however, require significant free water content on the Moon, which is possible if volatiles can be concentrated on a volatile poor Moon (Wang & Jacobsen, 2016; Wetherill, 1971).

Using an averaged composition of the Apollo 17 high Ti basalts, Hughes, Delano, and Schmitt (1989) suggested a source region containing Olivine, Augite, plagioclase and ilmenite, melted to 15%. This degree of melting would have exhausted both clinopyroxene and plagioclase in the source to produce the source composition; this model used an averaged composition of the Apollo 17 high Ti basalts.

My mixing model finds that the High Ti basalts can be very accurately recreated from the mixing components, <0.1 SSQM error. The Apollo 11 high Ti basalts have a greater proportion of final stage liquid (68%), and less olivine generated melt. In contrast, the Apollo 17 High Ti basalts have only (51% from the final stage liquid). Both Apollo 11 and 17 high Ti basalts require significant rutile and ilmenite assimilation. The Ti phase assimilation is significant as it requires a lunar magma overturn and so is consistent with a younger date.

High Ti and K basalts The Apollo 11 'type A' basalts (C. R. Neal & Taylor, 1992) are defined by having high Ti contents, and variable K contents. The Apollo 11 basalts which contain relatively high concentrations of both K and Ti are also

relatively enriched in Hf and Ba compared to High Ti low K basalts (~ 8 and 16 ppm Hf). In general, they are similar to the Apollo 14 basalts which also containing relatively higher amounts of K. It is therefore likely that these suites have assimilated from a lunar granite (C. R. Neal, Taylor, Schmitt, Hughes, & Lindstrom, 1989). However, minor elements such as La and K fractionate towards KREEP (KREEP magmatism happens at the Apollo 17 site at 4.1 Ga) and is not compatible with the LREE depletion found in the type A basalts (C. R. Neal & Taylor, 1992).

My mixing model indicates that the best fit for the high K basalts are late stage liquids, (67 %), mixing with melts derived from olivine-rich cumulates (22 %) and late-stage FeTi phases (11 %). The total error for this mix is 0.96 SSQM, higher than for other high titanium basalts.

Low Ti high Al high K basalts By mass of sample, the rarest of the lunar basalts are the low Ti high Al Apollo 14 suite, defined by having more than 0.3 wt.% K_2O and high levels of Rb and Ba, K rich feldspars and a very large range of Fo olivine (and An plagioclase (75-95) (C. R. Neal et al., 1988, 1989). At least three separate basalt flows of VHK basalts are known.

Shervais, Taylor, and Laul (1984); Shervais, Taylor, Laul, Shih, and Nyquist (1985) conclude that the most probable petrogenetic model starts with a high alumina basalt, which shares the major element signature, assimilating lunar granites (up to 5 w.t %) during ascent. The lunar granites contribute the enriched K levels, and variable degrees of assimilation are able to account for the variation within the suite. Direct source melting models are not appropriate in this case as the high K concentrations are not consistent with high Ba/La and low $^{87}Sr/^{86}Sr$.

My mixing model is able to accurately recreate this group of basalts, (with 0.14 SSQM error), drawing from remelting of early cumulates and plagioclase bearing rocks. The mixing also calls for assimilation of anorthosites, which is consistent

with some of the existing petrogenetic models.

Low Ti high Al low K basalts Often called the high aluminium basalts, they were returned by the Apollo 14 and Luna 16 missions. Unfortunately, the high Al basalts are poorly sampled, found as clasts in breccias with Luna 16 only returning basalt fragments less than 100 mg. The high Al basalts are the oldest mare basalts, dated to 4.3 Ga, and have Al contents from 11-14 wt.%. In REE space, the High Al basalts appear to represent a single continuum, with a single source region (C. Neal & Taylor, 1991). The Luna 16 samples can be grouped into high (9-12 wt.%) and low (3-7 wt.%) *MgO*, the Mg-rich group being similar to the Apollo 14 samples.

Some of the trends of REE enrichment has been modelled to indicate KREEP assimilation (Dasch, Shih, Bansal, Wiesmann, & Nyquist, 1987). An assimilation and fractional crystallisation model from (C. R. Neal & Taylor, 1990) called for cycles of eruption and assimilation, these cycles would confuse any elemental trends and allow variable REE compositions to be found across different suits.

Two source petrology models from Dickinson et al. (1985) and Shervais et al. (1985) concluded that partial melting of olivine, orthopyroxene, clinopyroxene and very small amounts (<5%) of plagioclase can reproduce the High Al basalts however this is not compatible with the assimilation and crystallisation hypothesis. This is well defined in my mixing model, which is able to very accurately recreate the high alumina basalts. Therefore, olivine derived melts, and final stage liquids are both important, supplemented by late, plagioclase normative melts and some assimilation of late-stage plagioclase.

Low Ti low K and Low Al mare basalts Found at the Apollo 12 and 15 sites the Low Ti and low Al basalts are divided into 6 groups. The Apollo 12 basalts are divided into the Olivine, pigeonite, ilmenite and plagioclase basalts, with near-surface olivine fractionation responsible for the intra-group variation. Quartz

(QNB) and Olivine normative basalts (ONB) are found at the Apollo 15 site, dated to 3.3 and 3.2 Ga respectively. The ONBs in this instance have significant chemical diversity, dependent on the lava flow and degree of olivine fractionation. The low Ti basalts do not have strong Eu anomalies, and no bow-shaped REE pattern, rising continuously from La to Lu.

Apollo 15 mare 'basalts' within group variation can be accounted for by 15% olivine for the ONBs or pigeonite fractionation in the case of the QNBs (Rhodes & Hubbard, 1973). The closed system fractionation responsible for the intra-group variation requires longer cooling times, which require relatively thick flows, >30 m, which is difficult to achieve with the low viscosity of lunar magmas, requiring some sort of ponding or channelisation.

Various models of the source of the low Ti basalts have been proposed. (L. Nyquist, Bansal, Wooden, & Wiesemeyer, 1977; L. E. Nyquist, Shih, Wooden, Bansal, & Wiesmann, 1979), concluded that the REE and trace element patterns are compatible with an Olivine clinopyroxene and orthopyroxene source melted to 2-10%, if the source was, as part of a LMO, REE enriched. A different model by Vetter and Shervais (1989) calls for dynamic melting from a mantle source which is tapped more than once. The major element content is controlled by the composition of the mantle residuum, which was enriched in MgO and depleted in SiO_2 . The trace element abundances are modified by assimilation of earlier material, found in dikes and veins.

However, as my mixing model treats the different groups of low Al low K basalts separately, then in the case of the olivine normative basalts my model predicts that the dominant sources of melt are from the early olivine rich cumulate mixed with highly evolved liquid. The ilmenite normative basalts are similar, but supplemented with a small amount of FeTi rich material. The pigeonite normative basalts require melting from the mid-depth pyroxene bearing rocks, with just less than 30 wt.%

from pyroxene bearing cumulates.

Very Low Ti mare Basalts The VLT basalts have an Mg# of 75 and high Al and Ca concentrations compared to other mare basalts. The dominant compositional trend of increasing Al_2O_3 alongside decreasing Mg# is consistent with olivine fractionation. The target compositions used are in table A.4 (Jolliff et al., 2006). VLT mare basalts are found in two localities, the Apollo 17 drill core and the Luna 24 landing site. The Apollo 17 VLT basalts have low REE and incompatible trace element concentrations, with no bow shape and only a small Eu anomaly. However, the Luna 24 mare basalts do have a bow-shaped REE trend, and more Ca and Al. Therefore, a simple olivine fractional crystallisation process can relate all the samples within the Luna 24 subset (C. R. Neal & Taylor, 1992). Additionally, the VLT basalts are dominantly composed of clinopyroxene 60 % and plagioclase 30 %, with minor olivine 5 % and aluminium chromate (trace) (Jolliff et al., 2006).

Existing petrogenesis models have high-aluminium clinopyroxene on the liquidus, at 400 km, for both groups. High Al and Ca pyroxene is required to sufficiently enrich the melt with Ca and Al. (Papike, Hodges, Bence, Cameron, & Rhodes, 1976). A separate model finds that the source for the Apollo 17 VLT basalts is Consistent with 1-2 % partial melting of a 90-10 olivine-orthopyroxene cumulate or 4 % melting of 70-30 olivine-orthopyroxene cumulate. (Wentworth et al., 1979). A different model, which considers the Luna 24 group, finds that the higher alumina nature of the Luna 24 VLT basalts cannot be produced with just clinopyroxene on the liquidus and requires a plagioclase component (C. R. Neal & Taylor, 1992).

My mixing model finds different proportions of the same components for the two groups of VLT basalts. The Apollo 17 basalts are produced from olivine derived melts (39 %) mixing with final stage liquids (45 %), in contrast, the Luna 24 group

are produced from much less olivine derived melts (18 %) and correspondingly more final stage melt (74 %). Both groups are modelled to contain a similar proportion of plagioclase derived melt (14-16 %). The olivine derived melt is produced at up to 420 km and mixed with late-stage liquids, which is expected be found near the 'Moon's surface. The mismatch for the VLT Apollo 17 basalts is quite high, 5.18 SSQM, this could indicate a missing component or that one of the assumptions made, 5% melting or no change in-depth, is not valid in this instance. It may be more appropriate to consider the mixing as most likely before or contemporaneously with melting.

In contrast, my melting and mixing models is able to very accurately (0.35 SSQM) recreate the Luna 24 group of VLT basalts. Later stage melts, more dominant in the Luna 24 group, should produce a strong bow-shaped signature. Therefore, a process to neutralise this would be required to fully explain the Luna 24 samples.

Picritic Glasses The picritic glasses are morphologically different from the rest of the mare basalt suite, found as small, <1 mm Ø, glass spheres and found across the lunar landing sites. The smooth spherical shape requires the bead to solidify in a vacuum rapidly. The absence of large crystals indicates that the melt was extracted and erupted rapidly, which is in contrast to the crystalline mare basalts (Jolliff et al., 2006). The eruptive style, able to suspend the droplets for enough time for them to cool in a vacuum suggests that a gas phase, e.g. water, was present. The apparently rapid ascent and eruption of the picritic glasses can provide direct insight into the structure of the deep lunar mantle. In total 25 groups of picritic glasses have been described (Delano, 1986).

The picritic glasses have a wide range of REE concentrations, only united by a negative Eu anomaly. Like the mare basalts, the picritic glasses have an extensive

range of titanium concentration, 0.2-17 wt.% (Jolliff et al., 2006). With respect to other major elements the picritic glasses have high Mg#’s and lower concentrations of CaO and Al_2O_3 . Across the suites of glasses, the general trend of Mg# and SiO_2 concentration is attributed to olivine crystallisation or a pressure effect on melting (Grove & Lindsley, 1978; Steele, Colson, Korotev, & Haskin, 1992).

Longhi (2006), has generalised trends in the picritic glasses, and found that the picritic glasses share characteristic compositions and common parental magmas . In brief, Longhi (2006) found that that low titanium glasses, require a source region 700-1000 km deep, containing olivine and pyroxene. Further studies have indicated that at least some wall rock or other assimilation is required, Apollo 15 green glass group B and C (Elkins Tanton, Chatterjee, & Grove, 2003).

The parental melt of the picritic glasses can be produced by the polybaric melting of a dominantly olivine and pyroxene source region, sometimes including an alumina rich phase, at different depths is able to produce an accumulated melt parental to the picritic glasses, 'FF40' and 'FF30'; these along with 2 typical low and 1 average high titanium picric glass are used as target (table A.7) for my mixing model.

Results (table A.8) show that my mixing model, is able to accurately reproduce the picritic glasses (average of 0.2 SSQM) using the same components as the mare basalt (table A.6). This finding is supported by the (Longhi, 2006) model, whereby much of the melt is drawn from the early olivine bearing cumulates, with some limited contribution from later pyroxene and plagioclase bearing cumulates.

3.6 Conclusions

A model of lunar magma ocean fractional crystallisation has been created experimentally, demonstrating that Lunar Mare Basalts can originate from a magma ocean of terrestrial peridotitic composition. My model has then been compared to

observed samples. It has been shown, that to a good degree, the model can recreate the variation of compositions and mineral assemblages observed from a selection of Apollo and lunar suites. This model improves on previous models because it is entirely experimental and empirical in nature, and robust to different depths of magma ocean.

1. The large degree of Fe and Ti enrichment present in the final melt of a pyrolytic LMO is more than sufficient to produce the extra-terrestrial enrichments found in some of the mare basalts. In addition, fractional enrichment of Ti, $>3\%$ in the final melt, is sufficient to produce the FeTi rich phases, which are later required to hybridise and produce the Ti enrichment found in the high Ti mare basalts. Later the FeTi rich cumulates drive the density-driven overturn of the lunar magma ocean.
2. The modal phase in the Ferroan anorthite suite is plagioclase. My experimentally produced plagioclases have the same composition and are produced alongside MgFe silicates with the correct Mg#. The experimental plagioclase compositions are entirely consistent with the Apollo samples, fig. 3.12.
3. Within the FAS, the similarity of the mafics to experimentally produced crystals indicates that the final stages of crystallisation, at least with regards to the flotation of the plagioclase highlands, was not efficiently fractionated. Crystals are still removed from the melt, but the amount of crystal at equilibrium with the melt at any time is not small enough to allow efficient fractional crystallisation. Indeed, the change with composition with depth, detected in the deeply excavated south pole Atkins terrain, could be consistent with a falling efficiency in mineral separation, which is observed to become more ferrous with depth (Jolliff et al., 2000). The separation efficiency would drop with temperature as the viscosity and crystal fraction increases, getting closer to

an equilibrium crystallisation. In this case, the FAS is analogous to a poorly sorted sandy beach rather than a glacier trapping pockets of air.

4. My series of experiments fail to produce a KREEP like component; two hypotheses could be advanced to explain this. 1) The KREEP basalts observed on the Moon are not simply the product of fractional crystallisation. Hybridisation and crystal fractionation, over a long period of time has taken the original composition and evolved it far enough away to be unrecognisable. 2) Low-temperature liquid immiscibility, Hess, Rutherford, Guillemette, Rye, and Turekian (1975), proposed in low-temperature high Ti and high REE basaltic melts has significantly depleted the composition in Fe, Ca. Removing the melts from the fractional trend in a way not seen in my experiments. Such Fe liquid immiscibility was not found in this set of experiments, however, the absence of an increasing concentration of incompatible elements, e.g. P, would not suppress the liquidus sufficiently to be found in my experiments.
5. A high number of steps is required simulate the crystallisation of the LMO, to closely follow the trajectory of liquid enrichment. More crystallisation steps are also important for the timing of Fe enrichment and for precisely describing the composition of the cumulate mineral stack. The depth and conditions of melting on the cumulate stack will affect the composition of the liquids produced. More work is needed to calibrate thermodynamic models. These models will enable a precise understanding of the sensitivity of re-melting to de-pressurisation which is important for lunar relevant compositions.
6. The re-melting and re-combination models for the petrogenesis of the mare basalts and picritic glasses suggests that the deep lunar mantle is accessed via overturning fig. 3.13. Almost all the mare basalts compositions require a significant proportion of deep mantle-derived, high-Mg, liquids.

7. On Earth, the residence time in the crust is significant. Shallow emplacement modifies the composition of crustal melt significantly. The degree of shallow modification on the Moon is not well understood.

4 Rare Earth Elements

The lithologies observed on the surface of the Moon have a greater diversity of Rare Earth Element (REE) patterns compared to terrestrial igneous rocks. I experimentally track the enrichment of the REEs throughout the crystallisation of the LMO. The REE carrying phases are identified, partition coefficients are used to predict the REE abundance in lunar phases. A sound understanding of the distribution of REEs in the crystallised Moon is then be used to test the conclusions of Chapter 3.

4.0.1 ‘Bow-shaped’ Rare Earth element patterns

The Rare Earth Element (REE) profile for some lunar rocks can be described as ‘bow shaped’. The Apollo 11 high-K basalts, presented in (fig. 4.1), are one such example of this bow-shaped REE profile. The trend is characterised by increasing elemental concentrations from La to Gd and decreasing concentrations from Gd to Lu. The obvious Eu anomaly (fig. 4.1) results from the precipitation of plagioclase, as Eu is significantly more compatible than other REEs in plagioclase, due to its Eu^{2+} species. For comparison, the partition coefficient of Eu^{2+} is 0.9 compared to < 0.024 for Lu, (Aigner-Torres, Blundy, Ulmer, & Pettke, 2007). Examining the variation in REE content of rocks is important when assessing the petrogenesis of different groups of mare basalts because any petrological model must be holistic - predicting major elements and trace elements like REEs alike.

The question that emerges from comparing the REE trends of the mare basalts (fig. 4.1) with the KREEP group of basalts (fig. 4.2) is: if the bulk Moon has a chondritic REE profile, where does the Moon’s compliment of HREEs reside?

4.0.2 Rare Earth contents of Lunar Phases

REEs are not principally found in modally abundant phases such as olivine or pyroxene, they are dominantly found in accessory minerals: phosphates, zirconia, merellite and whitlockite. Phosphate tends to exhibit a flat REE trend (Andersen & Hinthorne, 1972), however, those accessory minerals with ‘bow-shaped’ REE profiles have much higher concentrations of REEs. The bulk rock trend, therefore, resembles the profiles found in the minerals containing the highest REE contents. In addition to the REEs, the accessory minerals are stabilised by other trace elements such as phosphorus (e.g. apatite), these accessory minerals are often the last minerals to precipitate from a melt.

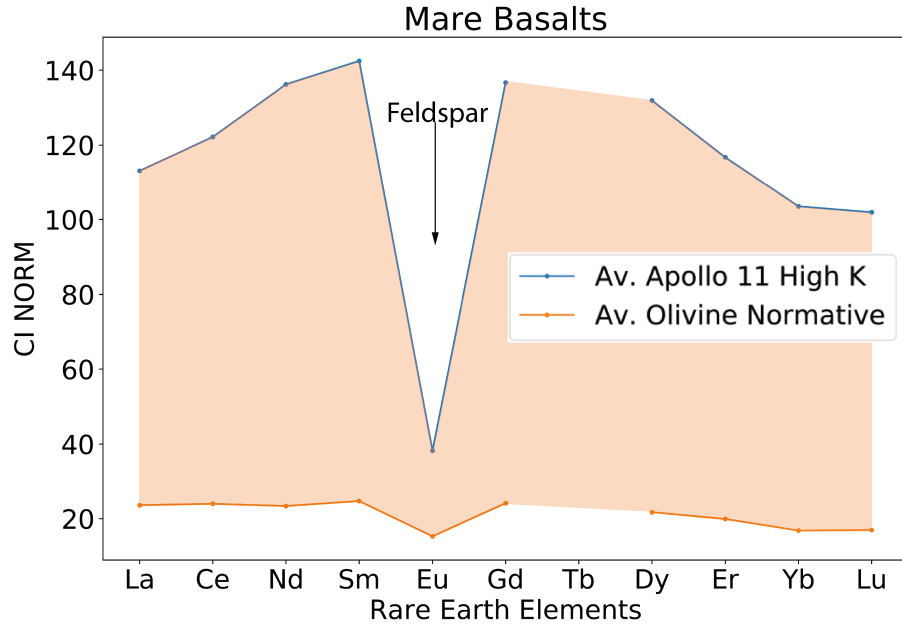


Figure 4.1: The chondritically-normalised concentrations of REEs in mare basalts. Concentration of mare basalts vary significantly between different studies is represented by the shaded region, between the olivine-normative basalts and the Apollo 11 high-potassium basalts. Data from Jolliff et al. (2006).

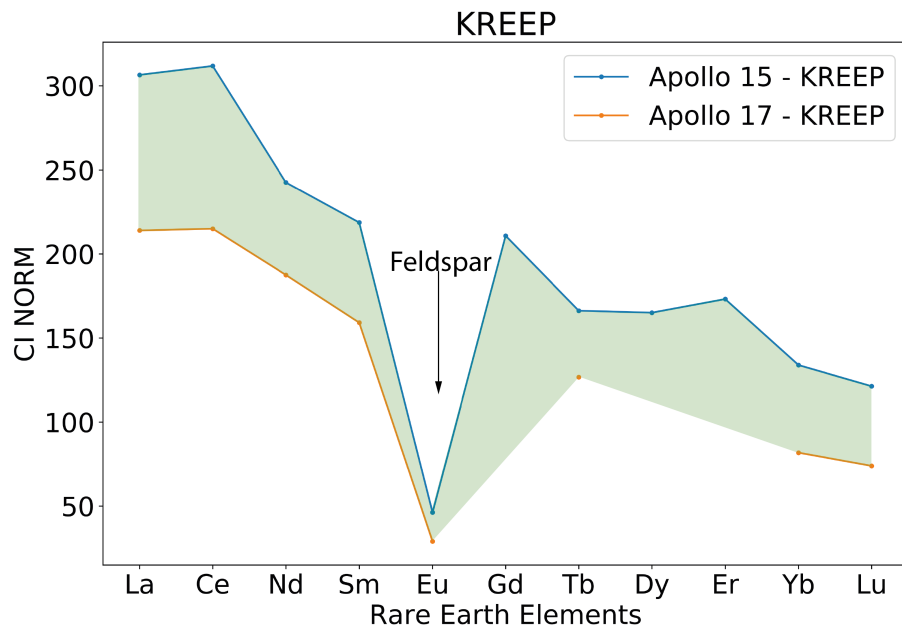


Figure 4.2: REE concentrations in KREEP basalts. Data from Jolliff et al. (2006). The concentration of REEs in KREEP basalts are much higher than the other mare basalts and, crucially, highly enriched in the lighter REEs, reflecting both REE incompatibility and the late stage crystallisation of KREEP.

Rare Earth Elements content of primary crust The ferroan-anorthosite suite (FAS) is the main rock type in the highlands of the Moon (section 1.4.1), dated from 4.4 Ga. The REE profile of the FAS is quite flat, with a pronounced positive Eu anomaly, see fig. 4.3. While flat, the REE profile still indicates substantial enrichment above chondritic levels.

Less is known about the magnesium suite (fig. 4.3) as only small fragments of the lithology have been collected. However the Mg suite is sample by lunar meteorites, which appear to cross the continuum between the FAS and Mg suite. The Mg suite has been broadly identified as a cumulate lithology (Jolliff et al., 2006) and therefore individual fragments are not necessarily representative. Despite the variation in bulk chemistry however, the enrichment in REEs remains clear. This enrichment is present in both olivine and orthopyroxene, phases likely to crystallise early, as well as late crystallising phases. Enrichment across the crystallisation sequence indicates that a systemic enrichment of REEs is a genetic feature of the precursor magma (Papike, Ryder, & Shearer, 1998; Warren, 1985).

The KREEP suite (fig. 4.2) of rocks is dominantly found in the Procellarium basin, inferred from Th contents measured by gamma ray spectroscopy, from the lunar prospector spacecraft (Binder, 1998); no KREEP rocks have been found on the lunar far side. The KREEP suite is highly enriched relative to chondrite, >100 times, substantially more enrichment of LREEs than HREEs.

REE content of Mare Basalt groups The mare basalts have a large variation in REE concentrations, correlated with their major element concentrations. The mare basalts also exhibit a nearly ubiquitous negative Eu anomaly, attributed to the source, since not all mare basalts are saturated in plagioclase (Longhi, 1992). Alternatively, hybridisation or pooling of a melt, containing a strong Eu anomaly, could account for the trend seen in mare basalts (Warren, 1990). McKay, Wagstaff,

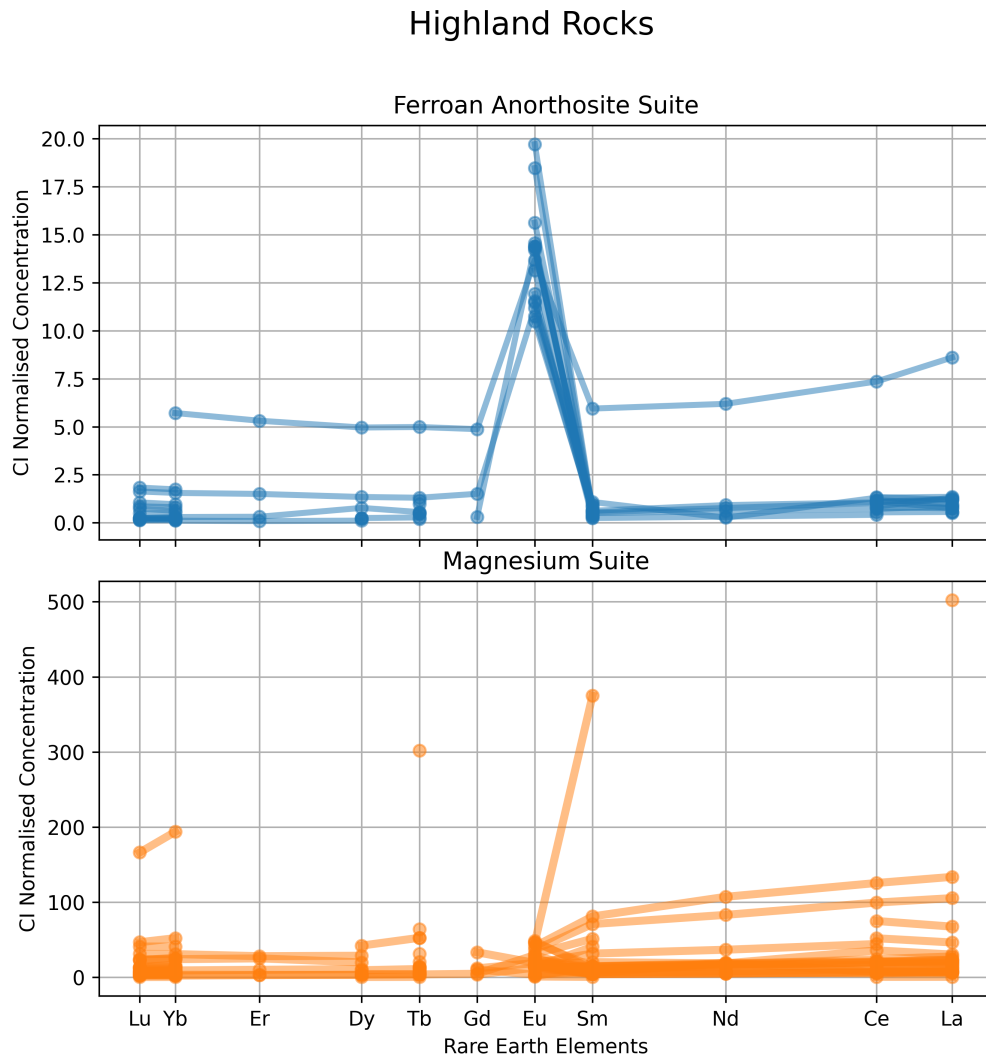


Figure 4.3: Rare Earth element plots of the two primary formations that are present in the lunar highlands. Note the large change in scale between the two plots. The Mg suite has much higher concentrations of REEs than the FAS. The Eu anomaly is clear in the FAS. Data from Jolliff et al. (2006)

and Le (1991) found that some low-Ti basalts may not require plagioclase on the liquidus, because clinopyroxene has particularly low Eu partition coefficients.

Picritic glasses The volcanic picritic glasses have high pressures of multiple saturation (Longhi, 2006), which is a proxy for the depth at which they equilibrated with the source rock. These elevated pressures indicate a deep source region, approximately 400 km below surface (Shearer & Papike, 1993; Longhi, 2006). Some of the very low titanium basalts, recovered by the Apollo missions, contain high concentrations of REEs, ~ 30 times the chondritic value. The REE profiles peak at La and slope down continuously to Lu, potentially indicating KREEP assimilation (Papike et al., 1998; Shearer & Papike, 1993).

4.0.3 Possible REE sinks in the Lunar mantle

In the lunar mantle, the most volumetrically significant minerals are olivine, pyroxene, and plagioclase. However, the size of REE ions precludes many rock-forming minerals from accepting REEs of any kind. The potential for the minerals of the lunar mantle to accommodate REEs is outlined below. In addition, I discuss garnet which has also been suggested as a potential REE carrying phase (Longhi, 1992).

Olivine Substitution of the major cations, Mg , Fe , and Si , for REEs in olivine requires substitution coupling in order to balance charge. The requirement to have coupled substitutions forces a more significant distortion of the lattice, compared with a single, isovalent, substitution. For this reason, this substitution is highly energetically unfavourable. In addition to the charge imbalance, the ionic radii of Mg and Fe (0.72–0.78 Å) are smaller than the radius of the smallest lanthanide (Lu, 0.98 Å). The T site of olivine (0.26 Å) (Shannon, 1976) is even smaller than the M1 and M2 sites and normally filled with Si^{4+} . In the case of a coupled substitution,

the T site must accommodate a misfitting Al ion with an ionic radius of 0.39 Å. For these reasons, olivine is expected to be a very poor sink for REEs.

Pyroxene At high temperature orthopyroxene and clinopyroxene become miscible in one another, enabling a greater range of Ca and Al concentrations across the cation sites. This miscibility, coupled with the large size of the calcium cation (1.12 Å, 6 coordination), makes the larger REEs relatively more compatible in clinopyroxene, especially at high temperature. Element compatibility has been described using a partitioning model based on the elastic strain caused by the accommodation of a misfitting ion ((Blundy & Wood, 1994; Blundy, Robinson, & Wood, 1998)) Pyroxene is a common mineral at pressure under lunar conditions and is produced in high quantity in the suite of experiments included in this study (24 wt.% - table 3.8, Chapter 3) The crucial aspect of the ‘bow-shaped’ REE trends witnessed in the BSM are that the HREE are required to be more compatible than the LREEs.

Garnet Harrison and Wood (1980) have suggested two possible mechanisms for the incorporation of REEs into pyrope garnet ($Mg_3Al_2Si_3O_{12}$).

- 1) A coupled exchange with the dodecahedral site, in which REE accommodation is coupled with an aluminium substitution.

- 2) A second dodecahedral substitution coupled with a vacancy. A large number of coordinating anions, as in the dodecahedral site in garnet, make the accommodation of a large ion more favourable, by Pauling’s rules of coordination (Pauling, 1929).

The potential importance of garnet as a potential HREE sink is considerable due to the large difference in compatibility of the Heavy and Light REEs, approximately three orders of magnitude (fig. 4.4). However, the pressure of the lunar core is 4.71 GPa (D. R. Williams, 2020), which is not high in the context of the stability field of garnet (fig. 4.5). A further condition that comes from the mare basalts is that

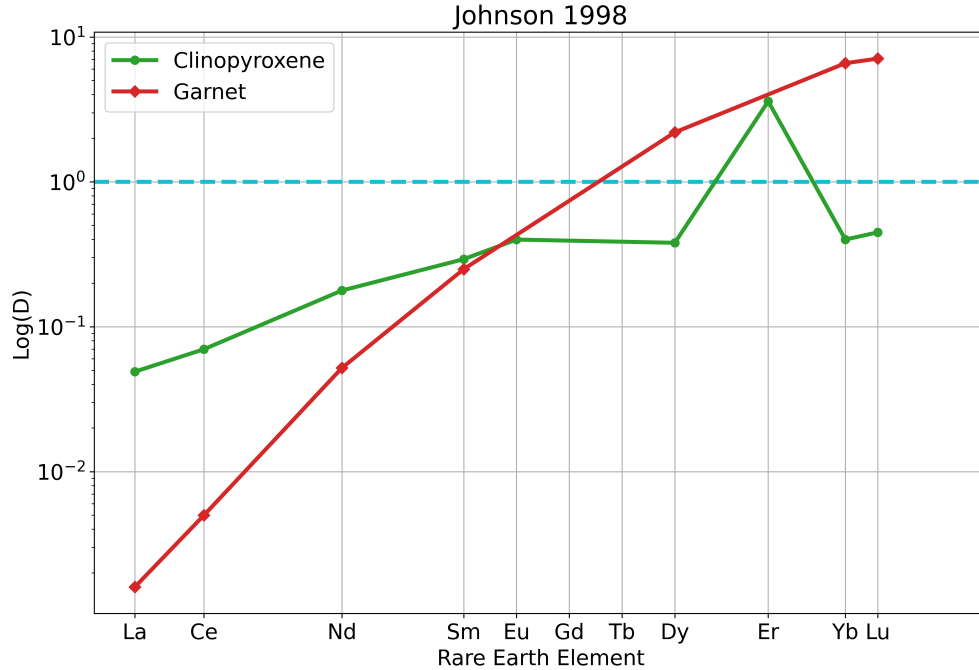


Figure 4.4: Experimentally determined partition coefficients (D) for REEs in garnet and clinopyroxene at 1300–1400 °C and 2–3 GPa taken from (Johnson, 1998). The very large range of garnet compatibility would strongly deplete the liquid in HREEs, as the partition coefficient is greater than 1.

the most Mg-rich rocks, those that crystallised first, must have done so before any HREEs have been removed, as the most Mg-rich mare basalts show the low and flat REE trends. Therefore, it is unlikely that garnet would be present at depth during the crystallisation of these early minerals.

Plagioclase Plagioclase is a tectosilicate, with a 3-dimensional structure of silicon tetrahedra forming the A and T sites. The A sites are larger and octahedrally coordinated, they are able to accommodate larger ions with lower charges; The T sites are tetrahedrally coordinated and contain smaller, higher charged ions. The REEs are typically found as 3+ ions in geological settings and must be accommodated in the A site due to their large size. Such accommodation requires coupled substitution in T-sites to balance charge.

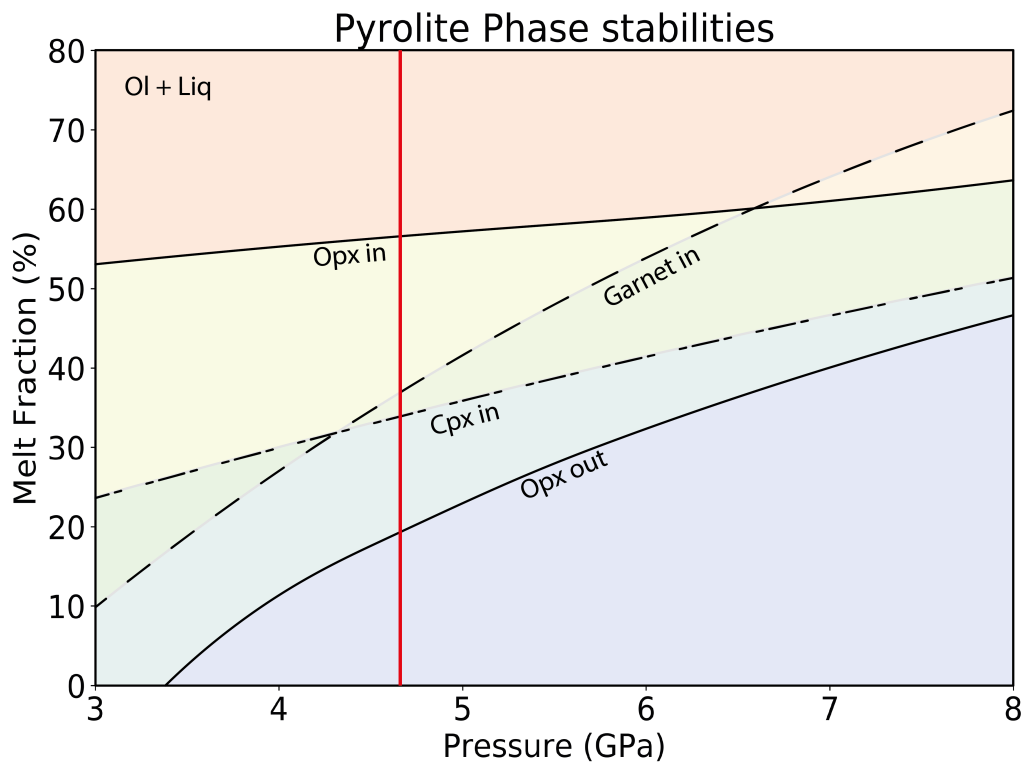


Figure 4.5: Melt fraction plotted as a function of pressure to demonstrate pressure dependent phase stability fields in a pyrolitic system. The pressure at the centre of the Moon (4.71 GPa) is represented by a red line. Figure modified from (Walter, 1998). At the pressure of the Moon's core garnet does not appear until 65% of crystallisation has occurred, at this point if the LMO was crystallising fractionally the pressure would have dropped by approximately half.

4.1 Experimental methods

To test the predictions made by the experimental series (Chapter 3) REE compatibility has been experimentally defined. The REEs chosen for this study are added to the experimental charge during mixing. After the correct weights of oxide have been added to the mix, the sample was ground under acetone until homogeneously and intimately mixed. After synthesis the sample is de-carbonated by heating in a 1 atmosphere furnace at 800 °C for at least 12 hours. After the sample is cooled and the sample is ground under ethanol again.

After the sample has been mixed for another 30 minutes correct quantities of the REEs are added, dissolved in molar nitric acid, as spec-pure ICP-MS standard solutions (Alfa Aesar). To prevent contamination of the REE standards and to ensure accurate doping of the sample a micro-pipette is used with a disposable tip. Once the REEs are added to the sample it is then ground and homogenised again under ethanol. Once homogeneous the sample is left to dry in a lamina flow fume hood covered in aluminium foil, to stop dust or other contamination. After the sample is dry it is pelletized, then held in a brushed alumina crucible and lowered into a vertical drop tube furnace and reduced to an fO_2 of IW+1 (See section 2.1.3) at >1000 °C, using the appropriate $\frac{CO}{CO_2}$ gas mix specified by French and Eugster (1965) and a total mas flow of 200 *ml/min*. At this temperature the nitric acid is removed in the gas flow and the pure REEs are left in the sample. At this point the experiment is carried as described in Chapter 3.

4.1.1 Doping and choice of REEs

The lanthanides all form 3+ ions in most geological systems, combined with the steady increase in atomic number the ionic radius of the lanthanides decreases steadily across the group. As ΔG (change in Gibbs free energy) of fusion, the main factor in determining partitioning, varies most strongly with the elastic strain of the

lattice, REE partitioning is predictable (Blundy & Wood, 1994). Therefore, not all the lanthanides are needed to capture the major trend of lanthanide contraction and the trend can be simply inferred. The most common error with Ar-torch ionisation is to form $M - Ar^+$ or $M - O^+$ polyatomic ions (May & Wiedmeyer, 1998), such as $^{143}Nd^{16}O^+$, which would have the same charge to mass ratio as Terbium, $^{159}Tb^+$. Ensuring that these mass interferences are minimised, or at least acknowledged and avoided, is key to quantifying REE partitioning. The REEs added have been chosen to reduce analytical error and capture the major trend of the lanthanide contraction (table 4.1).

Table 4.1: Rare Earth and Trace elements added

Element	Concentration (ppm)	Vol (μ l)	Mass (mg)	added	% total mass
Nb	1000	400	0.4		0.04
La	1000	400	0.4		0.04
Sc	1000	200	0.2		0.02
Nd	1000	200	0.2		0.02
Sm	1000	200	0.2		0.02
Hf	1000	200	0.2		0.02
Y	1000	160	0.16		0.016
Er	1000	160	0.16		0.016
Zr	1000	160	0.16		0.016
Yb	1000	120	0.12		0.012
Lu	1000	120	0.12		0.012
Th	1000	60	0.06		0.006
Total mg	na	na	2.38		0.238

4.1.2 Experimental conditions and program

This experimental series was run in parallel with the major element experimental series presented in Chapter 3. The experiments that match the criteria for success laid out in Chapter 3 have been taken for LAICPMS analysis. Experiments found near the top of the graph are from 1 atmosphere glassing experiments, which were used to check the accuracy of synthesis (fig. 4.6).

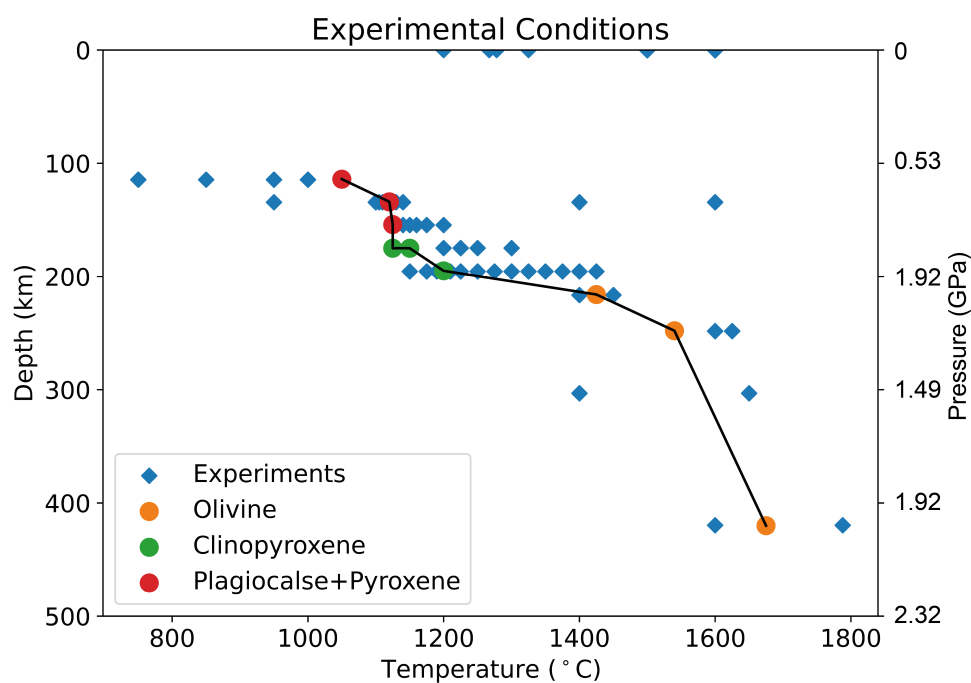


Figure 4.6: Pressure and temperature conditions tested during the initial experimental suite presented in Chapter 2. ‘Successful’ experiments are coloured for crystals present when melt proportion was correct. The irregular crystallisation path is because the drop in pressure and change in composition also effects the position of the liquidus and solidus. The points do not all have corresponding REE data as some charges did not produce crystals that can be analysed cleanly on LAICPMS.

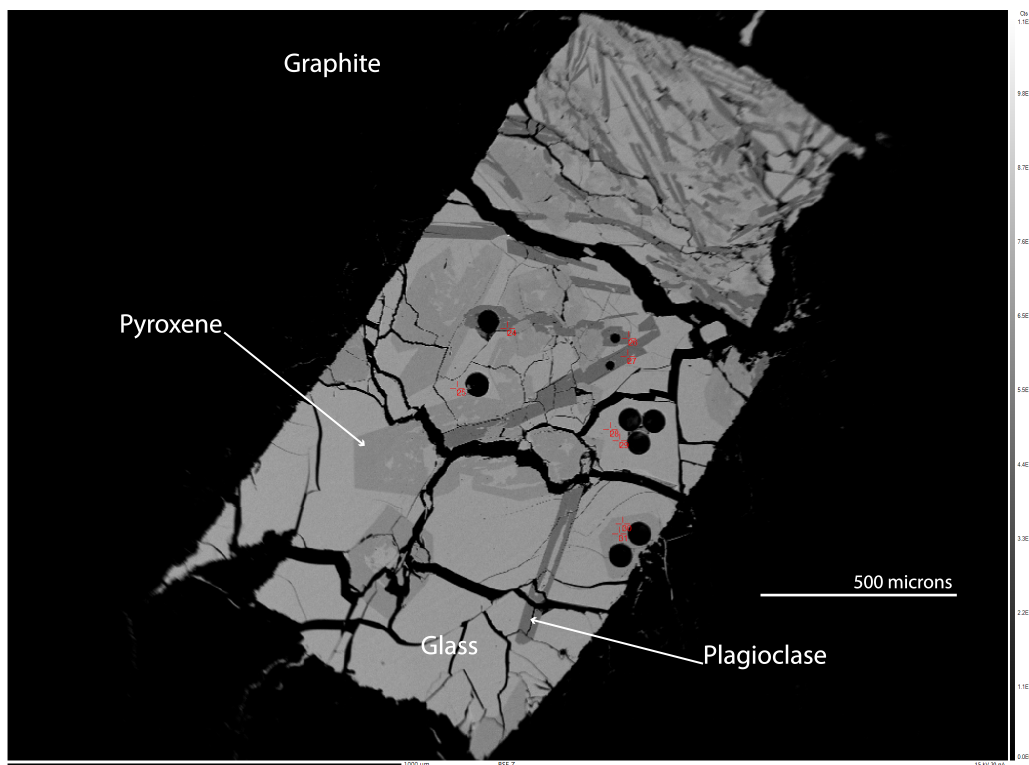


Figure 4.7: BSE image of experiment EB68. Each red cross represents an EPMA point taken, associated with laser ablation pits. The black background is the graphite inner capsule.

4.2 Analytical methods

4.2.1 Electron Probe Micro Analyser - EPMA

For each laser point taken a major element standard is required to benchmark the LAICPMS data. The laser pits are much larger than the EPMA points and may be contaminated with melt or other phases present below the surface of the sample, as the depth of each phase is not well known from the backscatter image.

4.2.2 LAICPMS

The basis of the REE partitioning aspect of this project relies on the ability to detect, at the ppm level, the concentration of REEs in distinct phases. For this reason, Laser-Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-

ICPMS) was chosen to provide the REE analysis of the phases (Gray, 1985; Jackson, Longerich, Dunning, & Fryer, 1992). An additional benefit of this chosen analysis is that it requires little additional sample preparation after EPMA analysis. The instrument used for analysis was a New Wave research UP213 laser coupled to a Perkin Elmer Nexion ICPMS, in the Earth Science department at the University of Oxford.

In order to control the depth of ablation, and to ensure that the beam does not become defocussed and thus spread, a constant fluence of 18–20 Jcm^{-2} was used across all samples, which excavates a hole approximately 10 μm deep in 40 seconds. Beam sizes of 10–20 $\varnothing \mu m$ and 50–100 $\varnothing \mu m$ were used for crystals and glasses, respectively. The frequency of the beam was set to 10 Hz and held constant for standard and unknown analysis.

Once vaporised samples were flushed with He to a NexION 400Q Inductively Coupled Plasma Mass Spectrometer. The He and sample was then passed to a radio frequency ionisation torch which ionises all matter with first ionisation enthalpies less than that of $Ar-Ar^+$. This plasma was then passed to a quadrupole mass spectrometer for counting.

Operation

1. Prior to analysis the LAICPMS was flushed with He in order to remove any contaminants from the system. The purging of contaminants was repeated three times with each iteration of the procedure taking approximately two minutes.
2. The He flow was then reduced to allow the plasma torch to ignite reliably. Once the torch was lit the He flow was increased and the instrument was left for 90 minutes to allow the torch and He flow to stabilise.
3. Now the machine is purged and ready to take accurate measurements, the

sample standards are measured. NIST 610 and GSE-1G glasses are used as samples standards (Jochum et al., 2005; Guillong, Hametner, Reusser, Wilson, & Günther, 2005).

4. Unknown analysis is now preformed, using BSE images taken by EPMA to compare to the microscope image provided to target the laser.
5. The standards are revisited and analysed every 45 minutes; this is to assess instrument drift and allows for interpolation to correct instrument drift.

Standards At the beginning of each sample run, and every 45 minutes during analysis, the sample standards were measured. Published standards, NIST 610 and GSE-1G (Guillong et al., 2005; Jochum et al., 2005), were provided by the USGS for use in this study. The compositions of these standards can be found in (Jochum et al., 2005; Guillong et al., 2005). Each reference back to the standard involved multiple measurements in order to ensure bad or contaminated spots could be identified and excluded. In addition, obtaining multiple analytical points of each standard enables the automatic correction of instrumental drift. Ca or Fe are used as the standardisation ions.

4.2.3 Analytical Partitioning Relationships

Blundy and Wood 1994 Fundamentally, Blundy and Wood (1994) link the ΔG of fusion to the energy of elastic deformation of the crystal lattice. An ion that is accommodated in a specific site deforms the lattice whether it is too small, too big, or aliovalent. These principals have been quantified to produce eq. (4.1). Some variables are given in reference tables, for example the original ionic radius (r_0) (Shannon, 1976). Other variables, such as the young's modulus (E_i) must be inferred for each cation site as they are not necessarily the same as the average crystal young's modulus.

Beattie 1994 Beattie (1994) takes a similar approach to Blundy and Wood (1994), likewise relating partitioning of cations to elastic strain, but focusses on olivine. The coupled substitutions of Al into a Si site, which is required for a charge balanced REE accommodation, is required to be measured explicitly. This contrasts with eq. (4.1), which does not need Al and Si partitioning to be measured directly, but taken relative the partitioning of iosvalent cations.

$$D_i(P, T, X) = D_0(P, T, X) \cdot \exp \frac{-4\pi E N_a \cdot (\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3)}{RT_k} \quad (4.1)$$

Equation 4.1: From (Blundy & Wood, 1994), describing the partitioning of ion of radius r_i based on the strain energy required to accommodate a misfit ion. D_i = Partition coefficient of ion of interest, D_0 = Partition, coefficient of compatible ion, E = Youngs Modulus of site of interest, N_a = Avogadro's Number, r_0 = Original ion radius, r_i = Ion of interest radius, R = Ideal gas constant, T_k = Temperature in kelvin

$$\ln(D_R^{Ol/L}) = \ln(D_{Mg}^{Ol/L}) - \ln\left(\frac{D_{Al}^{Ol/L}}{2D_{Si}^{Ol/L}} - \frac{\Delta C_p}{R} - \frac{6\pi N_A r_0^3}{RT_k} \cdot \phi^{Ol,Oct} \cdot K^{Ol,oct} \cdot (\Omega_R - \Omega_{Mg})\right) \quad (4.2)$$

$$\Omega = \varepsilon^2 \cdot \left\{1 + \frac{\varepsilon(1 + \sigma^{\alpha,site})}{3(1 - \sigma^{\alpha,site})}\right\} \quad (4.3)$$

$$\Sigma^{\alpha,site} = \frac{2(1 - 2\sigma^{\alpha,site})}{3(1 - \sigma^{\alpha,site})} \quad (4.4)$$

$$\varepsilon = \frac{r_M}{r_0} - 1 \quad (4.5)$$

Equation 4.2: From (Beattie, 1994), this equation describes the partitioning of a trivalent ion of size r into olivine. $D_R^{Ol/L}$ = The predicted partition coefficient, $R = 8.31$ = Universal gas constant, $\Delta C_p = 55 J mol^{-1} K^{-1}$ = difference in heat capacity of Al and Si tetrahedra in olivine and melt phases, T_k = Temperature in Kelvin, $N_A = 6.022 \cdot 10^{23}$ = Avogadro's number, $r_0 = 0.58 \text{\AA}$ = zero strain radius, r_M = Radius of the incident metal, $K = 180 \text{ GPa}$ = Bulk Modulus, $\sigma = 0.24-0.27$ = Poisson's ratio (0.25 chosen)

Curve fitting algorithm For the analysis of the partitioning relationships found in the REE compatible phases, my observations have been fitted to the compatibility curves described by eqs. (4.1) and (4.2). To repeatably fit the curve the *scipy.optimize.curve_fit* algorithm from the scientific python distribution was used. The algorithm modifies given variables inside the defined functions to optimise the fit using a 'Levenberg-Marquardt' algorithm, minimising the R-squared misfit. The fitted parameters are given in tables 4.2 and 4.3, for pyroxene and plagioclase respectively. The function outputs the optimal fitted parameters and a sigma error matrix for each fit parameter. The error matrix describes the sensitivity of fit and a standard deviation is then calculated from the sigma error matrix.

4.3 Results

Here I present the concentrations of REEs measured in different phases. All concentrations are measured by LA-ICP-MS. All raw data plotted can be found in table B.1 and in fig. 4.8. figs. 4.9, 4.11 and 4.13 plot data from fig. 4.8.

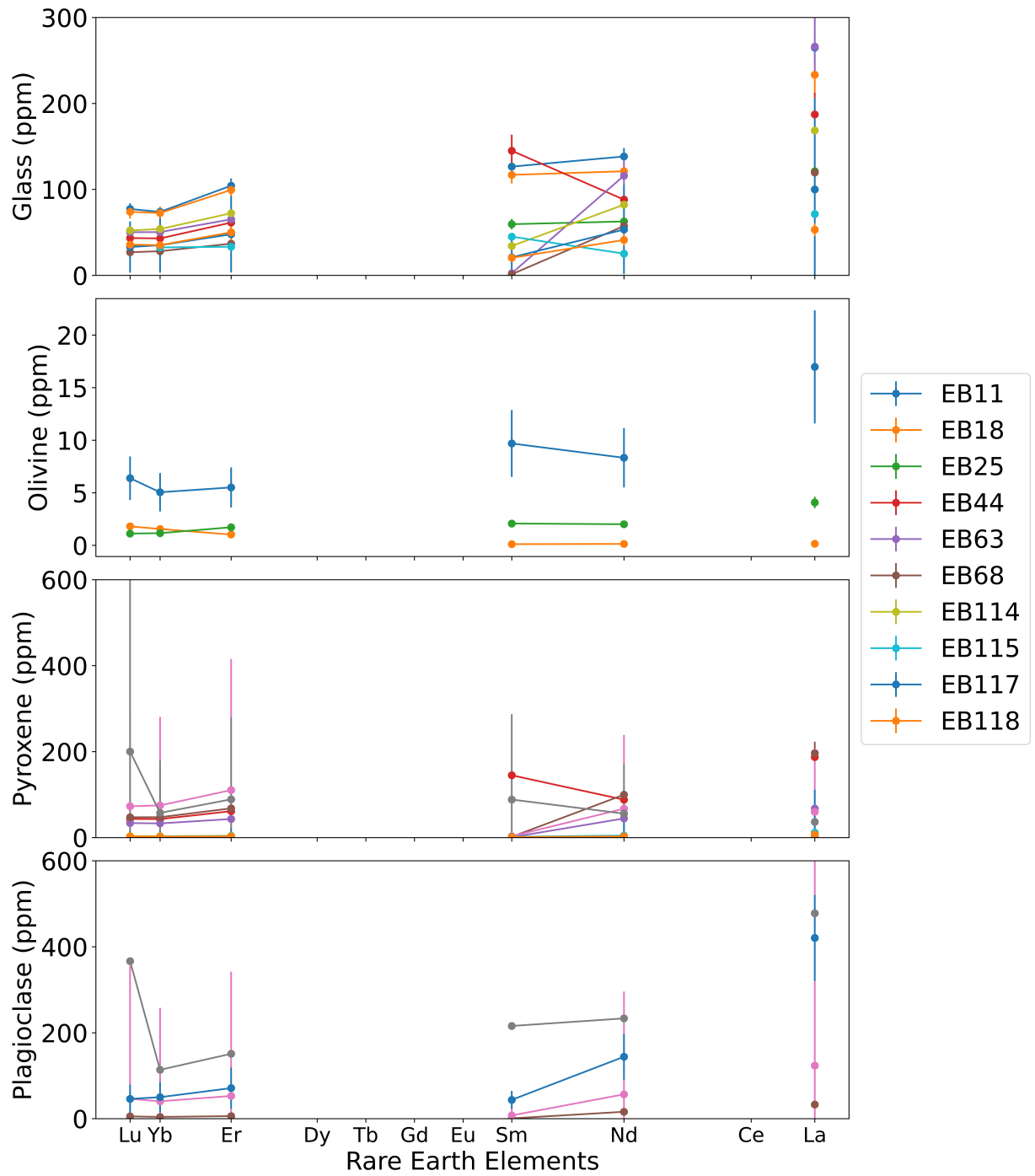


Figure 4.8: Average concentration of REEs in Glasses, Olivine, Pyroxene and Plagioclase, from all experiments in the series. Concentrations are plotted against the Rare Earth ionic radius. 'Missing' elements were not added to the experimental sample and so were not measured.

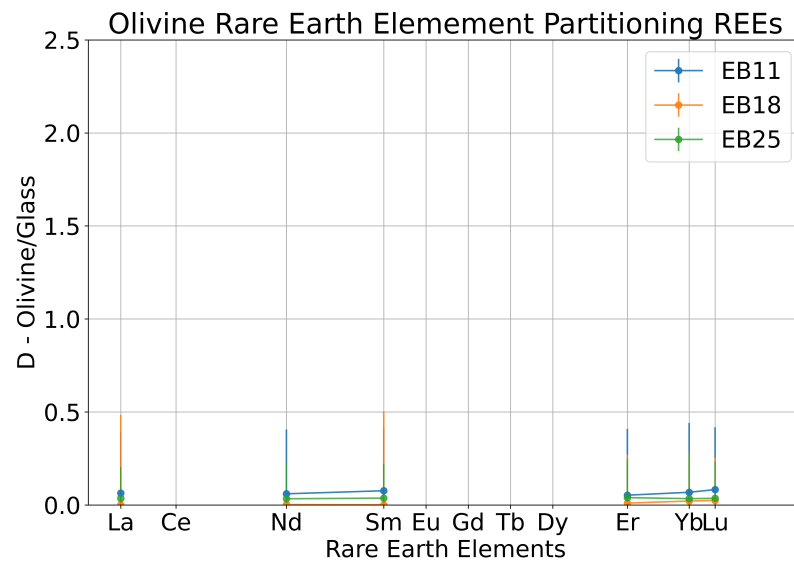


Figure 4.9: The average partition coefficients of REEs for olivine as a function of the REE ionic radius. Y-axis is unitless

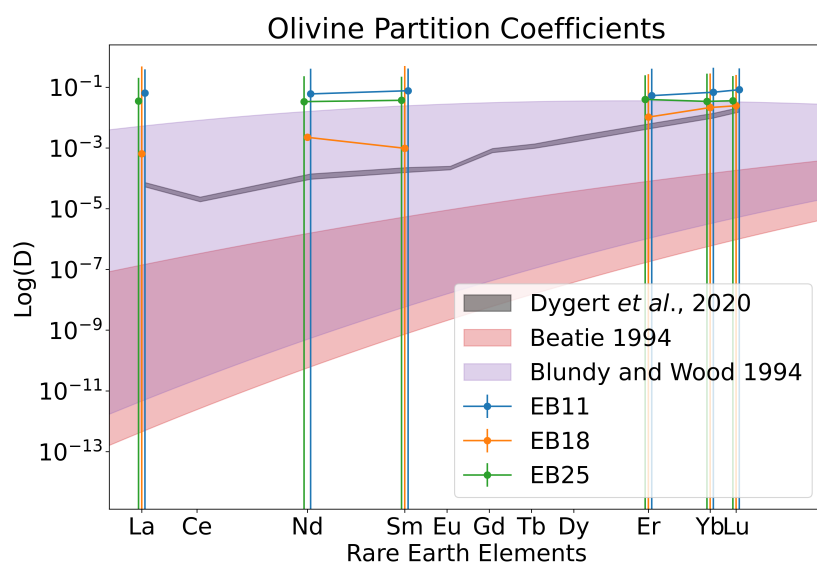


Figure 4.10: The average partition coefficients of REEs for olivine as a function of the REE ionic radius. Models by Beattie (1994) and Blundy and Wood (1994) have been plotted for comparison along with experimental data, at lower temperatures from N. Dygert et al. (2020). In order to plot the Beattie model partition coefficients for Si, Mg, and Al are required for the olivine. For these elements, median values from all the relevant experiments of this study were used.

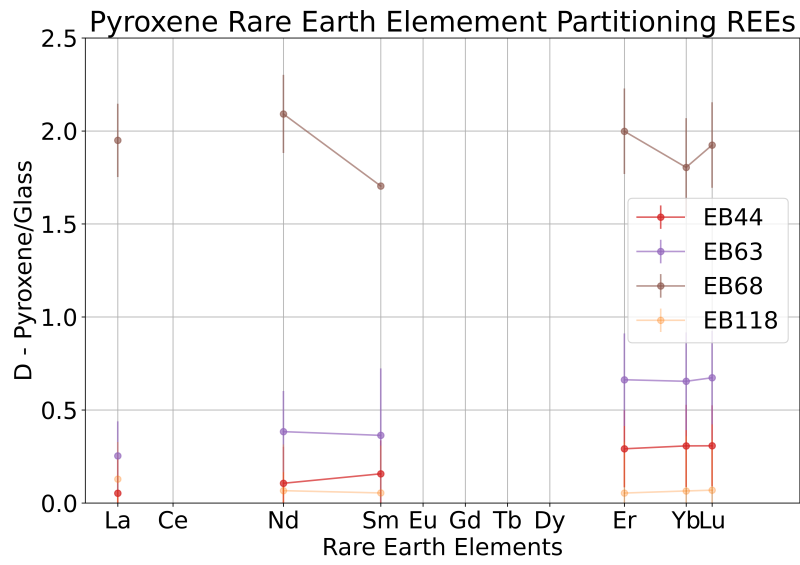


Figure 4.11: The average partition coefficients of REEs into pyroxenes as a function of the REE ionic radius. Smaller error bars here represent larger concentrations and crucially, larger crystal sizes which have allowed cleaner points.

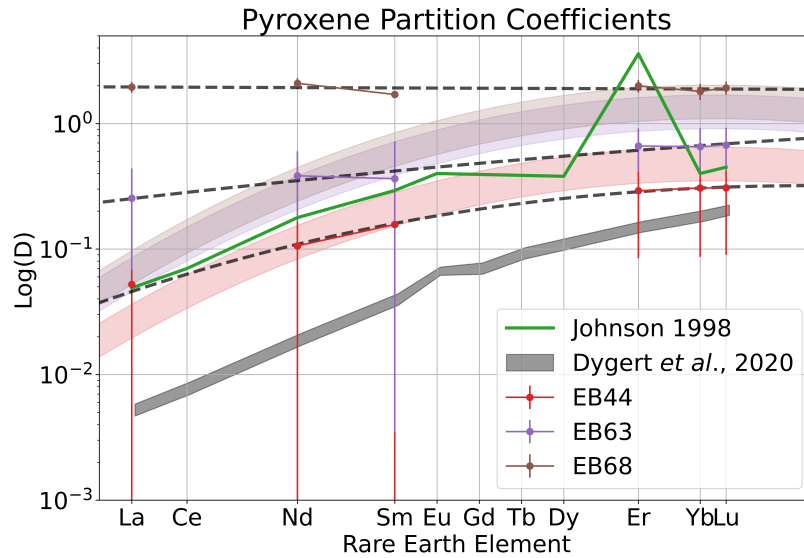


Figure 4.12: The average partition coefficients of REEs in pyroxene as a function of ionic radius. For comparison the experiments from Johnson (1998) are plotted as a green line. Shaded areas represent predicated partition coefficients from Blundy and Wood (1994). Dashed lines fit Equation 1, from Blundy and Wood (1994), with variables fit to best recreate the observed patterns. EB118 has been omitted as the fitted equation requires a negative young's modulus. Dygert data (N. Dygert et al., 2020) plots ~ 1 log unit below other data.

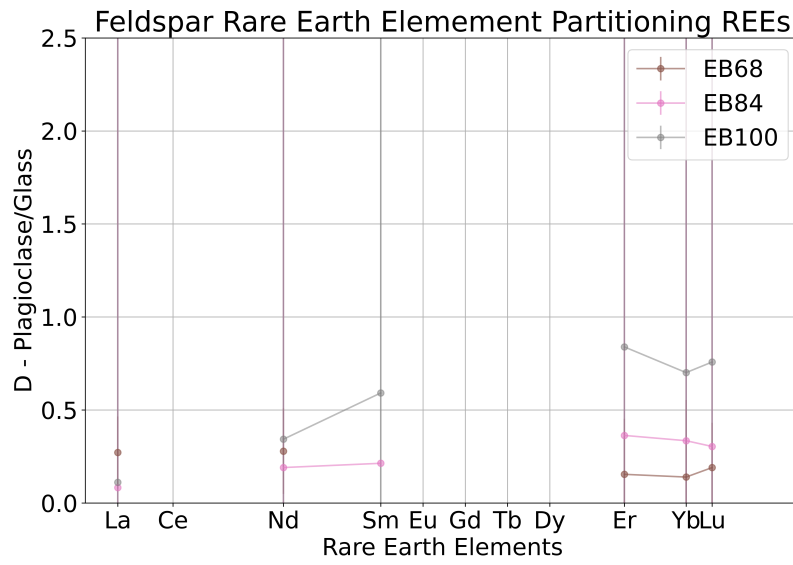


Figure 4.13: The average partition coefficients for REEs into plagioclase as a function of ionic radius. A small increase in compatibility as ionic radius decreases is indicated. Some plagioclase producing experiments are omitted as the crystals are not sufficiently large enough to gather clean points.

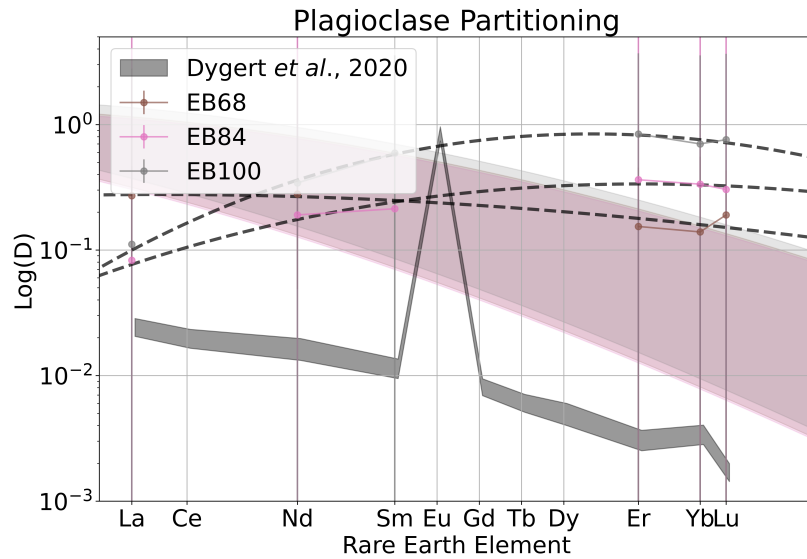


Figure 4.14: The average partition coefficients of REEs into plagioclase as a function of ionic radius. Shaded areas represent predicated partition coefficients from Blundy and Wood (1994). Dygert data from N. Dygert et al. (2020). Dashed lines fit the equation 4.2 by Blundy and Wood (1994) with variables fit to best recreate the observed patterns.

The partition relationships of REEs in olivine (figs. 4.9 and 4.10) align more with the Blundy and Wood (1994) model than that of Beattie (1994), as the Blundy and Wood (1994) predicts partitioning relative to isovalent cations. Qualitatively, both analytical expressions indicate that the higher-temperature experiments should result in REEs being more compatible. The very low concentrations of REEs found across the olivines in this study makes the associated error bars large as a proportion of the total concentration, consistent with a lack of 3+ sites.

The low partition coefficients (figs. 4.9 and 4.10) mean that the main effect of olivine crystallisation would be simply to enrich the melt in the whole suite of REEs.

The partitioning of REEs in pyroxene (figs. 4.11 and 4.12) is in good agreement with the modelled data of Blundy and Wood (1994); Blundy et al. (1998) and the experimentally found partitioning from Johnson (1998)(fig. 4.4). The data from EB68 seems to be anomalously high - all REEs partition coefficients are within error of each other. As the partition coefficients are all close to 1, the laser point likely ablated through the plagioclase crystal and sampled melt. The large variation shown in figs. 4.11 and 4.12, could be a combination of liquid contamination and the temperature and compositional control on the structure of the REE accommodating sites. Data from N. Dygert et al. (2020) is consistently below that predicted by my experiments, this is likely due to differences in temperature, with my experiments done at higher Temperatures. A further difference is in the melt composition, with my experiments done over a much wider range of melt compositions.

As seen in fig. 4.7, the plagioclase crystals are associated with pyroxene and are thin. The crystal size and distribution may explain why the data from EB68 has larger errorbars: as the laser ablated through the plagioclase and started sampling either melt or plagioclase.

The feldspar data is the sparsest, principally due to the size and distribution of the feldspars, which made it difficult to isolate and laser; the tendency of plagioclase

to form in association with, and interleaved between, clinopyroxene (fig. 4.7). This made finding large clean areas for laser spots very challenging. It is likely that the difficulty in analysis has resulted in the considerable error bars.

The errors plotted are those reported by GLITTER, they are based on propagation of combined errors from calibration and standard values. Poisson statistics are used to calculate the uncertainties on background and signal count rates. This uncertainty is combined with the uncertainty of the yield values when converting results for the calibration standards to their 'true' values, calculated by lineally interpolating the multiple standard measurements. these uncertainties are combined and reported for each data point.

By treating each point, even from the same phase, individually the maximum error bars are plotted.

Table 4.2: Fitted coefficients for REE partitioning data from pyroxenes. In these experiments T is held constant as it is an intensive parameter applied by the experiments.

	EB68		EB84		EB100		(Blundy & Wood, 1994)
Plagioclase	Coeff.	1 std.	Coeff.	1 std.	Coeff.	1 std.	
E (GPa)	59.4	73.4	165.89	67.6	293.43	59.1	190.3
R_0 (Å)	1.15	0.1	1	0.02	1.02	0.01	1.196
D_0	0.28	0.03	0.34	0.02	0.84	0.04	N/A

Table 4.3: Fitted coefficients for REE partitioning data from plagioclase. As in the pyroxene fit, T is held constant as it is a measured known.

	EB44		EB63		EB68		(Blundy et al., 1998)
Pyroxene	Coeff.	1 std.	Coeff.	1 std.	Coeff.	1 std.	
E (GPa)	127.96	21.58	14.19	49.21	0.07	34.08	262
R_0 (Å)	0.95	0.02	0.5	1.91	5.16	1900.04	0.98
D_0	0.32	0.01	1.58	5.09	5	3472.69	N/A

In general, the elasticity coefficients found from the REE set of experiments are similar but smaller than those in the literature (Blundy et al., 1998; Johnson, 1998). Any contamination of points would have the effect of making the crystal look more compatible and therefore make the site appear less specific. Low site-specificity is consistent with lower young's moduli. It is not possible to , with the curve fitting algorithm, weight the variables by the inverse of the error, so the fitted curves cast a harsh view of the experimentally found partitioning data. However, it is easy to see that the pattern of compatibility follows that predicted; and that the high-temperature pyroxene phase, for which the data are best, is much more amenable to HREEs than LREEs.

I have combined the information from all these partitioning relationships to track the composition of solid and melt phases throughout the lunar mantle fig. 4.15.

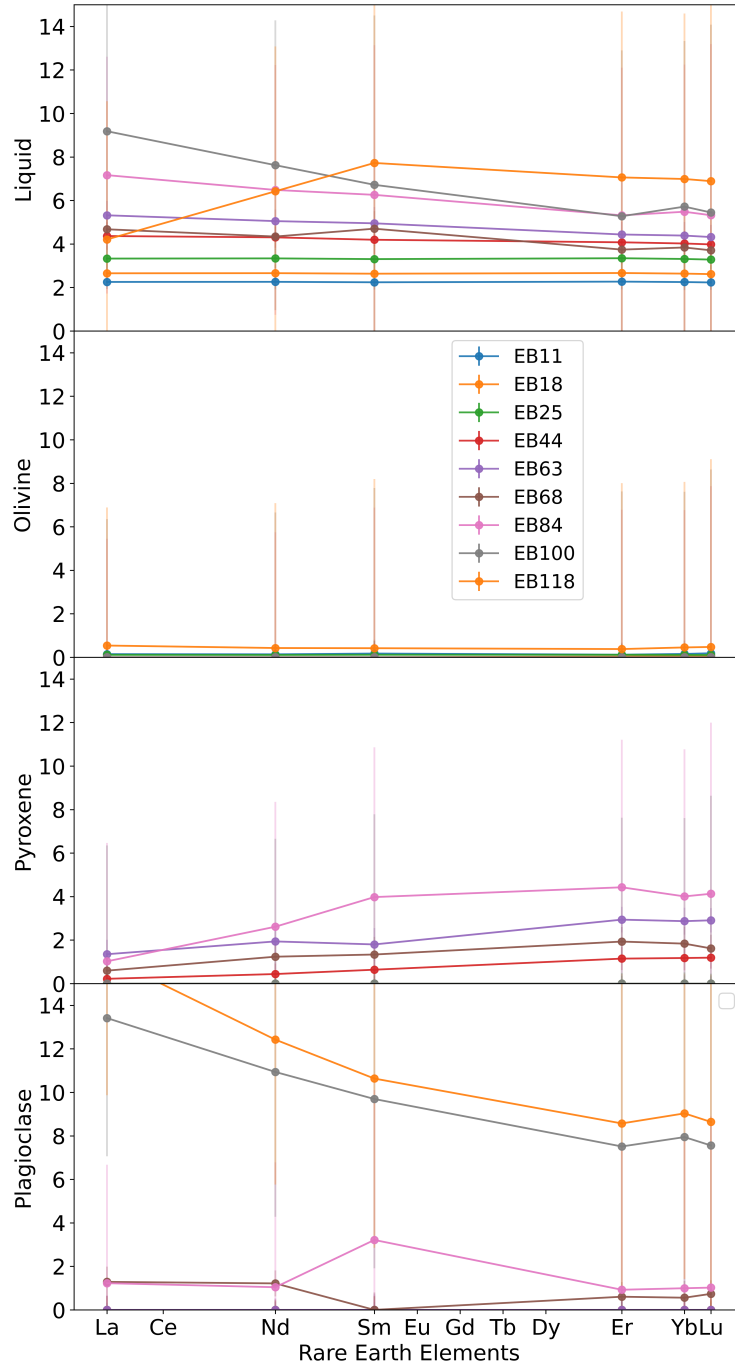


Figure 4.15: Chondrite normalised REE concentrations (unitless) in experimental phases. The concentration has been carried through, using the partition coefficients from each experiment to find how any REE becomes enriched through the crystallisation sequence. Pyrolytic starting composition was taken from McDonough and Sun (1995). Compounding of errors with the propagation of partitioning through the experimental sequence, has led to significant errors.

4.4 Discussion

4.4.1 HREE enriched phases

Garnet is known to have a strong preference for HREEs (Klein, Stosch, Seck, & Shimizu, 2000). For this reason, it has the potential to explain the significant depletion in HREEs observed across a range of mare basalts. Two implications of a garnet phase in the deep Moon are: 1) A deep Al-rich phase will reduce the Al available for the feldspathic crust, increasing the requirement for the Moon to be enriched in refractory enrichments. However, the inventory of lunar Al is split between plagioclase and pyroxene, so any Al required for garnet could be taken from pyroxene (Longhi, 1995). 2) A dense phase like garnet, 4300 kgm^{-3} (Robie & Bethke, 1962), is required to precipitate close to the bottom of the LMO due to its stability at pressure. A dense phase at the bottom of the LMO will act to lower the moment of inertia factor of the Moon, such a deep dense phase could be balanced by a shallow dense phase. However, a dense mass near the bottom of the LMO would be gravitationally stable. My mixing models (chapter 3) require the whole lunar cumulate stack to be involved in the overturning fig. 3.13. The experiments presented in this chapter demonstrate that a high-temperature clinopyroxene phase is able to preferentially take in HREEs, acting as a sink for the HREEs, allowing the bow-shaped REE patterns to arise. The amount of pyroxene produced is substantial, accounting for 24 wt. % of the final product of the crystallisation of the LMO table 3.8. The preference of clinopyroxene for the heaviest REEs is three times that of the lightest REEs.

The experimental series shows that the heavy REE sink, pyroxene, begins to crystallise after 60 wt. % crystallisation, less than predicted from the pHELTS model.

4.4.2 The role of trapped melt

In the scenario of a fractionally crystallising LMO, one defining precondition must be met: the presence of a viscous sublayer of crystals and melt, with a lower convection velocity than the prevailing LMO. A viscous sublayer is required to decrease the characteristic length scale of convection, lowering convective velocity below settling velocity.

The presence of trapped melt doesn't constrain the temperature or viscosity of the bulk LMO, as in the whole it does not have an effect on crystal settling (Tonks & Melosh, 1990). Previous studies have taken round values for the degree of trapped melt (e.g., 0, 5, 10 % , (Charlier et al., 2018)), however, the degree of trapped melt does not change the chemical evolution of the LMO. The influence of trapped melt is on the chemistry of the cumulate, effectively making the partitioning of all REEs closer to 1 by the amount of trapped melt. These pockets of melt, by definition, would be the liquidus phases. In the case of a low degree partial melt, where the degree of melt is less than the amount of trapped melt, the melt produced would be of the same composition as the LMO at the time.

The volume of mare basalts produced is expected to be small, as they represent a small fraction of the lunar crust, 0.1–0.5 vol. % (Head & Wilson 1992) . If the volumetric fraction of mare basalts is correct, the amount of melting required from the cumulate to produce the mare is also small on average, so the proportion of any trapped melt in the source of the mare basalts should be high. The effect of such trapped melt would be to produce a REE signature opposite of the minerals which crystallised from the LMO at that time. In short, a low degree melt, defined above, of a garnet-bearing rock would be enriched in the LREEs, if garnet was not melted.

4.4.3 fO_2 controls on partitioning

The REEs are stable in geological systems in the 3+ species in every case except Eu, which, thanks to a half-complete F shell, can form the Eu^{2+} ion ($[Xe]6s^04f^7$). The $Eu^{2+/3+}$ transition occurs just below the iron-wüstite buffer (Papike, Karner, & Shearer, 2005); this is within the possible range of oxygen fugacity's of the lunar magma ocean. The Eu-speciation event is geologically important because it controls Eu partitioning: Eu^{2+} is much more compatible in plagioclase compared to other REEs, including Eu^{3+} .

The clear Eu anomaly seen in the trends of the mare basalts indicates that at least some of the Eu is in a 2+ configuration, however, this state is stable for a range of fO_2 s around the IW transition. In addition, compositional effects such as increasing the Ca and Al content of pyroxene increase the compatibility of Eu^{3+} in pyroxene (Shearer et al., 2006). As Eu^{3+} behaves in a similar way to the other lanthanides, the *-ve* Eu anomaly will be most pronounced in pyroxenes that are poor in Ca and Al and produced under reducing conditions.

A second effect of fO_2 , more difficult to constrain, is Fe speciation's effect on phase stability. Fe is the only major element that has a variable oxidation state in a putative pyrolite LMO. Generally more Fe^{3+} will stabilise pyroxene over olivine; however, this effect is likely to be minor, because any plausible fO_2 has very small amounts of Fe^{3+} .

4.4.4 How does the REE containing phase impact the REE profile of mare basalts?

In most mare basalts, the REE dominant phase is apatite (Jolliff et al., 2006). In order to produce apatite, high concentrations of P and Ca are required. These elements are found in very low concentrations in the bulk Moon, but their high incompatibility concentrates them in the final liquids near the surface of the Moon,

enabling such crystals to form. Merrillite and other low-concentration REE containing minerals are common in KREEP lithologies. (McLeod & Krekeler, 2017).

In the deeper LMO, garnet, pyroxene, and plagioclase are capable of accommodating different quantities of REEs and are volumetrically significant enough to contain a meaningful quantity of REEs.

Garnet The strong preference for HREEs of garnet would deplete any resulting melt in HREEs, assuming garnet remained a solidus phase during melting. The density of garnet ($3600\text{--}4300\text{ kgm}^{-3}$) is more dense than the early Mg-silicate minerals like olivine and orthopyroxene ($\sim 3200\text{ kgm}^{-3}$) (Robie & Bethke, 1962). This density difference may isolate garnet-containing assemblages from adiabatic melting caused by lunar mantle overturn.

Pyroxene The most abundant of the HREE compatible phases, pyroxene is the first mineral to melt in the cumulate stack where it is present.

In order to generate the bow shaped REE pattern found in the mare basalts, some remelted cumulates must have a flat REE profile, with limited enrichment. Therefore, some of the available material for remelting must not have the HREE depleted signature. The affinity for HREEs shown by garnet, relative to the LREEs, is four orders of magnitude ($D_{La} = \sim 0.002$, $D_{Lu} = \sim 9$). For the steepest pyroxene produced in this study, the differential is about two orders of magnitude. The change in partitioning means that to produce the same HREE depletion, only a 100^{th} of the garnet produced is required.

A deep highly-HREE enriched layer could be melted to release the HREE enriched melts, but such melts would need to be precisely mixed with high-Mg and HREE depleted melts, to ‘cancel out’ the HREE signature, for example, in the case of the Apollo 11 Olivine normative mare basalts (fig. 4.1), which have relatively flat REE profiles. For this reason, I believe that the most likely store of HREEs in the

lunar mantle is pyroxene. For example, a flat REE profile is naturally produced, in the absence of Garnet, in the most Mg rich and K poor cumulate layers.

4.4.5 KREEP

The KREEP basalts are highly enriched in REEs (fig. 4.2), such enrichment would require that they represent the very final stages of crystallisation, after producing minerals which are not compatible with REEs, dominantly olivine. Experiment EB118, a late batch crystallisation experiment of composition Q (table 3.6), produces fayalite rich olivine (*Fo*35). This is consistent with the major element crystallisation trend of KREEP, measured by core to rim profiles in plagioclase and pyroxene.

An additional complication to the formation of KREEP from the last traces of the LMO are the low Fe contents. A possible solution are Fe rich silicate liquids, which are kept liquid due to high concentrations of incompatibles and are immiscible at low temperature. These late stage exsolved liquids allow more fractionation to further enrich the liquid in REEs (Hess et al., 1975). Unfortunately, the degree of fractionation required for the formation of these liquids was not within the scope of this set of experiments. The REE partitioning between these two immiscible fluids is unknown. Fundamentally, the liquid enrichment of REEs found in these experiments is not sufficient to explain the extraordinary enrichment seen in the KREEP basalts, fig. 4.17.

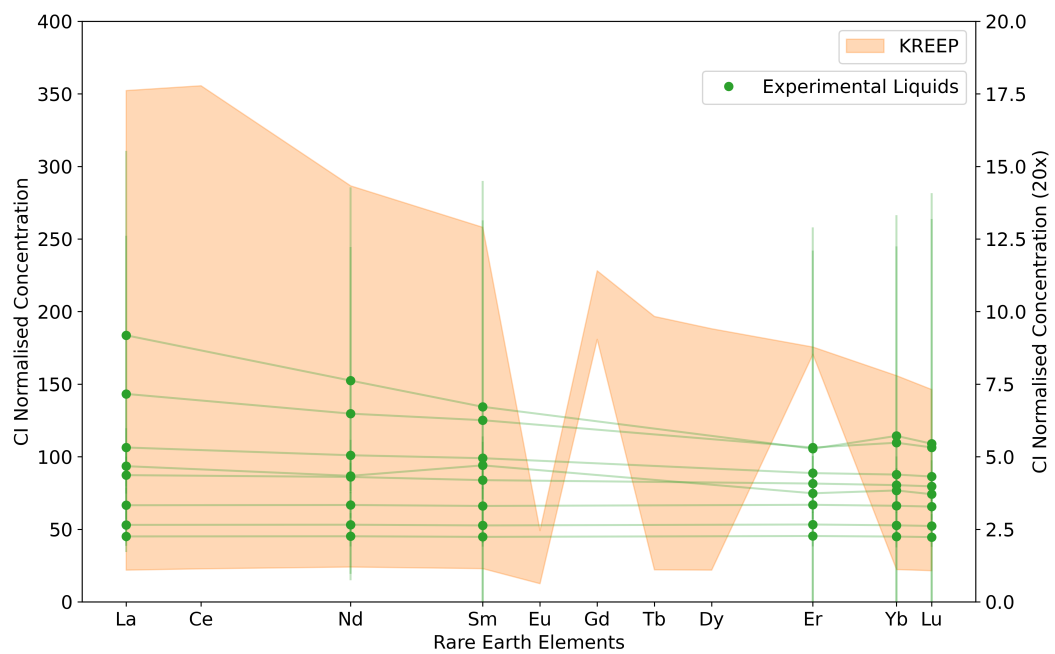


Figure 4.16: KREEP natural concentrations compared to experimentally produced liquids. The apparent shape around Er and Gd is due to a lack of data. The melts produced experimentally are enriched approximately 10 times after ~98% crystallisation. The enrichment on the KREEP, up to 350 times, requires at least 99.75 wt.% crystallisation.

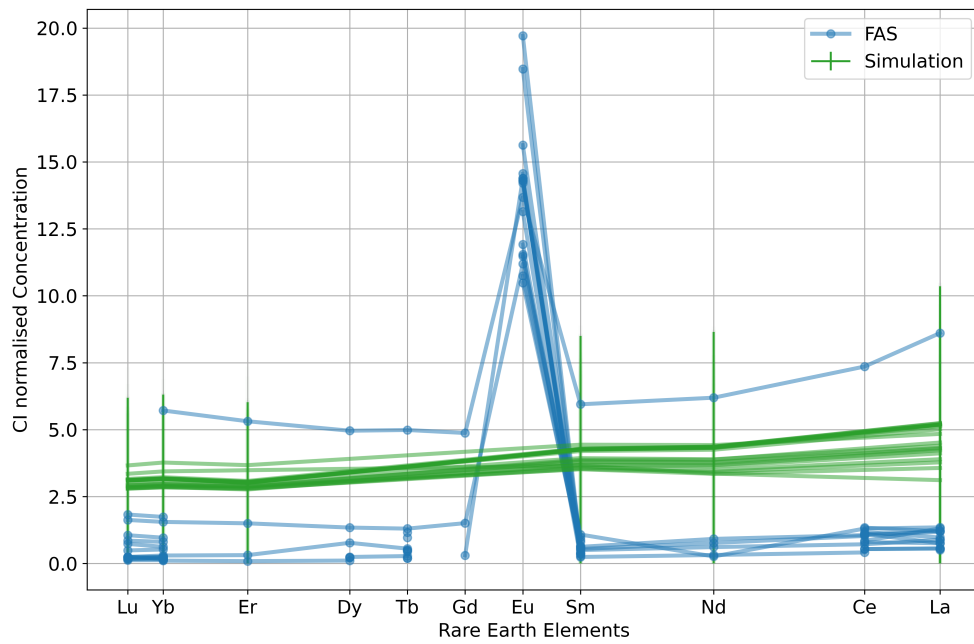


Figure 4.17: FAS simulation compared to the FAS data (Jolliff et al., 2006). Average REE profiles for all experimentally produced minerals as generated for fig. 4.15. The degree of enrichment is intermediate between the highest and lowest FAS profiles. The highest profile is from sample 67016,326; and is rich in melt and pyroxene according to the recombination models, Chapter 3.

4.4.6 Ferroan Anorthosite Suite

The REE pattern of the FAS is dominated by the Eu^{2+} anomaly, which indicates a reduced fO_2 (Shearer et al., 2006) around the IW buffer. Eu was not analysed on in this experimental series due to its fO_2 sensitivity and the analytical difficulties with Ar^+ and O^+ compounds (May & Wiedmeyer, 1998). The flat pattern of REE abundance, despite the LREE enrichment seen in the feldspar (fig. 4.13) is recreated by the mixing models, by balancing it with HREE enriched pyroxenes fig. 4.16 . This confirms the assertion of a dominance of crystals rather than accumulated melt. The higher concentration of REEs than the background could be due to the sampling bias of the Apollo missions. Most of the samples are from shallow rocks which may be closer to the earlier crystallised plagioclases, which could be older and sampling less enriched melt. Meteorites, which samples a wider range of locations on the Moon, show a greater diversity of REE concentrations (Russell, Joy, Jeffries, Consolmagno, & Kearsley, 2014).

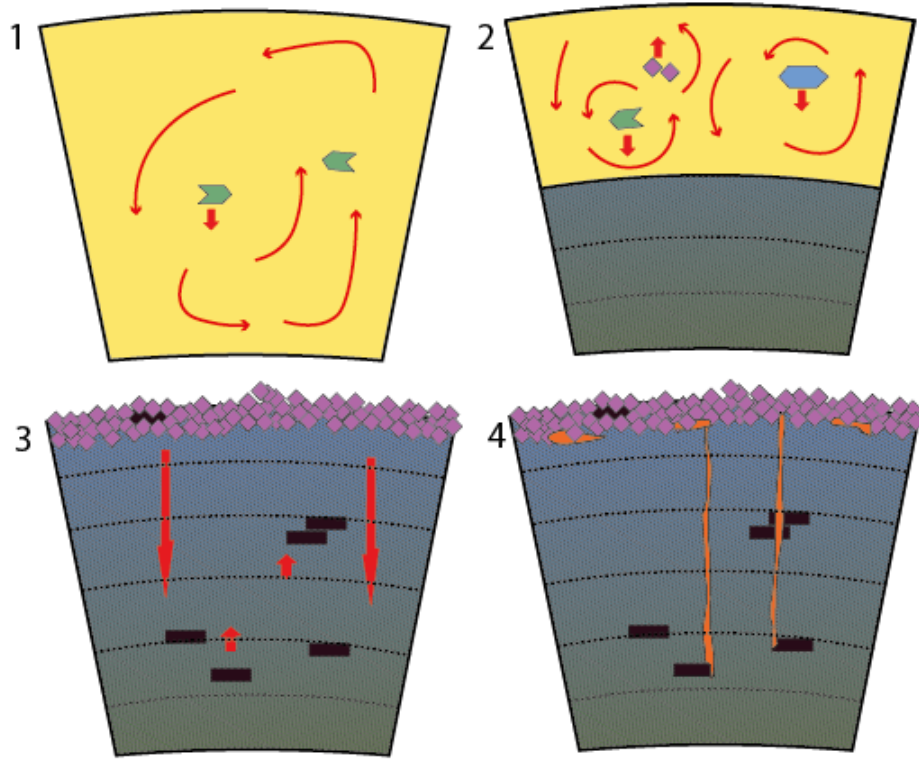
4.5 Conclusions

1. In order to recreate the mare basalts REEs profile, the HREE-compatible phase must crystallise after the early Mg-rich cumulates forms. Pyroxene satisfies this condition and crystallises alongside plagioclase, allowing the REE profiles to evolve with plagioclase precipitation.
2. The stability field of garnet in a pyrolytic bulk composition precludes it from forming under lunar conditions as a primary igneous mineral. Furthermore, the strength of garnets affinity for HREEs would make the whole LMO after garnet crystallisation depleted in HREEs. Any cumulates produced from a garnet-depleted cumulate stack would be highly enriched in LREEs. For these reasons, any garnet present in the Moon would be stabilised by lower temperatures, and its formation limited by kinetics of diffusion after LMO crystallisation. If crystal sizes are as large as suggested (8 cm, (Tonks & Melosh, 1990)), diffusion would be too slow to produce any.
3. The REE pattern of melts produced from cumulate lithologies is highly dependent on the degree of melting because much of the HREE signature is concentrated in phases like pyroxene and to a lesser extent plagioclase. Therefore, if the melt does not exhaust pyroxene the melt will be richer in HREEs. Any olivine melted will dilute the melt in HREEs.

5 Discussion and Conclusions

Here I assess my findings in the context of the total differentiation of a lunar magma ocean. I then suggest some avenues for future work.

Figure 5.1: The canonical model of lunar solidification and differentiation 1. A wholly liquid LMO cools to the liquidus, crystallising olivine with high Mg#s which are denser than the liquid. The crystals exit the convective cell at the bottom of the ocean. 2. After ~ 75 wt.% crystallisation, feldspar has begun to crystallise. Multiple liquidus phases and a smaller difference in buoyancy increase collisions and inhibit settling. Feldspar crystallisation densifies the liquid. 3. Late crystallised dense phases initiate long length-scale downwelling's, promoting Lunar Mantle Overturn. 4. Radioactive heating and the conversion of gravitational potential energy initiates melting. Melts are produced, ascend, differentiate, and some are extruded onto the surface of the Moon.



The received model for the crystallisation of the lunar magma ocean, fig. 5.1; this model has been developed since the LMO concept was first proposed by Wood, Dickey, Marvin, and Powell (1970). A wide range of possible LMO compositions have been suggested, table 1.3, and given the predictions made by my experiments, I discuss the implications of a pyrolytic LMO.

5.1 Physical State of the lunar interior

5.1.1 Moment of Inertia and Density

The normalized moment of inertia (MOI) of the Moon is, 0.3932 ± 0.0002 , just below that of a perfectly homogeneous planet (0.4 - Konopliv et al., 1998), indicating that the Moon has a small density gradient. However, the Moon’s MOI is very sensitive to the density of the shallowest parts of the Moon. For this reason, the late ilmenite layer, and the efficiency with which this has sunk into the Moon, reduces any understanding that can be gleaned from measurements of moment of inertia. In the case where the Moon was enriched in Fe, Ti or other refractory elements, the amount of late crystallising dense material would be increased, making the lunar mantle overturn dynamically more probable.

Mare basalts cannot be representative of the whole lunar mantle as they would transform to an eclogitic assemblage at depth, denser than the bulk Moon (Shearer et al., 2006); bulk lunar density is 3343.7 kgm^{-3} (Kuskov, 1997; Kuskov & Kronrod, 1998). In general, in order to conserve mass, a low density, less iron-rich bulk mantle is compatible with a larger or more iron-rich core. Using the *Perple_X* program and the *stx11* thermodynamic system (Connolly, 1990, 2005; Helffrich & Connolly, 2009; Stixrude & Lithgow-Bertelloni, 2011) and assuming a chemically homogeneous mantle, a drop in *FeO* content from 9.24 wt.% to 8.05 wt.% is consistent with a mass change of $2 \times 10^{20} \text{ kg}$. A constant radius, 250 km, Fe-FeS core could accommodate this change with a 45 wt.% increase in FeS content. While physical constraints on the composition and size of the core are poor, there is evidence for a partially liquid outer core, likely due to sulphur, arising from Lunar seismometers (Matsumoto et al., 2015; Wiczorek, 2009; J. G. Williams et al., 2001). In turn, the likely presence of a liquid outer lunar core suggests that a significant amount of the Moon’s inventory of lunar sulphur is present in the core.

5.2 Lunar asymmetry

The systematic difference between the near and far side of the Moon is visible in the thickness of the primary lunar crust, ~ 10 km thinner on the near side (Wieczorek et al., 2013). Therefore, it is possible that, unlike the Earth, the Moon’s mantle is not spherically symmetrical at all. Because of the position of the Apollo landing sites on the near side, seismic information may not have sampled a representative section of the lunar mantle.

Multiple mechanisms have been advanced to explain such asymmetry. Including, a large impactor which removed a significant amount of crust and tilted the axis of rotation. Any tilt would maximise mass around the equator, subsequent mare basalt extrusion could over correct and force the axis of rotation back. It is also possible that the heat radiated from the early Earth slowed crystallisation on the lunar nearside, delaying crystallisation on the near side would make the crystal trends more Fe rich. Earth’s thermal radiance might also have been responsible for a change in the convection cells on the Moon, concentrating the cool down-welling limb onto the far side of the Moon. This convective configuration would force any floating anorthosite crust to the lunar far side. (Parmentier, Zhong, & Zuber, 2002; Wasson & Warren, 1980).

Both of these close-Earth mechanisms are time limited because the Moon formed closer to Earth than it is now. After 100 ma the Moon will be more than half way to its present orbital radius, decreasing the effect of ‘Earth shine’ by 75%.

An additional mechanism proposed to introduce asymmetry occurs at the point of lunar mantle overturn, this mechanism is predicted by numerical models of the downwelling of dense ilmenite cumulates (Elkins Tanton et al., 2002, 2011). Thicker, dense layers, with stronger viscosity contrasts develop lower harmonic degree downwelling’s. Ilmenite and incompatible enriched liquids may naturally form a hemispheric scale downwelling, eq. (1.4).

The density contrast required for a mode one downwelling is not produced in the same way that Elkins Tanton et al. (2002); Li et al. (2019) find are required for any downwelling of Fe- Ti- rich material, i.e. the downwellings mechanisms which are numerically predicted are not mode one. In addition, the highlands, which did not take part in the lunar mantle overturn, show a compositional difference, of the anorthitic crust, between the near and far side of the Moon (Ohtake et al., 2012). Therefore, it is most likely that lunar asymmetry existed before any lunar mantle overturn. A simple modification to the spherically symmetrical models would be to tilt convective cells, as suggested by Ohtake et al. (2012), such that the downwelling limbs are concentrated on the lunar farside. Such tilting could be driven by 'Earth shine'; I believe this is the most likely explanation for the observations of lunar asymmetry.

The most conclusive way to test the timing of crustal growth on the near and farside of the Moon would measure Eu anomalies in mafic crystals found in anorthosite crystals in the farside with high Mg/Fe ratios. The farside's mafic crystals should have less pronounced *-ve* Eu anomaly profiles; if true the asymmetry must have started before any lunar mantle overturn.

5.3 Geochemistry

5.3.1 Primary Crust

The ‘primary crust’, onto which the mare basalts are extruded, forms directly from the floatation of buoyant feldspar during the crystallisation of the LMO (N. J. Dygert et al., 2017; Warren, 1990), evidenced by the complimentary REE trends. The efficiency of buoyant plagioclase separation from a multiphase, convecting, magma ocean is debated, (Martin & Nokes, 1989; Suckale & L.T. Elkins-Tanton, 2011; Suckale, Sethian, et al., 2012; Suckale, Elkins Tanton, & Sethian, 2012), but it is unlikely to be 100% efficient.

A review (Ryder, 1982) of mare petrogenetic models found that cumulates which formed contemporaneously with the feldspathic highlands require a Mg# of 50-70, in line with my experimentally found feldspars, which crystallise with cumulates with Mg# of 48-75 (tables 3.3 to 3.6). Feldspar crystals in the highlands are An_{70} to An_{98} (Vaniman & Papike, 1980), the feldspar generated in these experiments range between An_{81} to An_{91} .

The GRAIL survey mission estimates the thickness of the lunar crust to be between 34 and 43 km thick (Wieczorek et al., 2013) but the high porosity makes it difficult to estimate the purity of primary crust with precision. My experiments produce 7-8% feldspar by volume, using the GRAIL estimates of crustal thickness this maps to a LMO depth of 700-1400 km. Though this must be taken with caution as trapped melt and imperfect flotation of plagioclase decreases the fidelity of this calculation.

The mixing and recombination study performed for the FAS suggests that the mafic component of the FAS is best reproduced using crystal phases that were experimentally produced alongside feldspar. 80 % of the mafic crystals found in the FAS are similar to the crystal phases produced concurrently. The 20 % which are

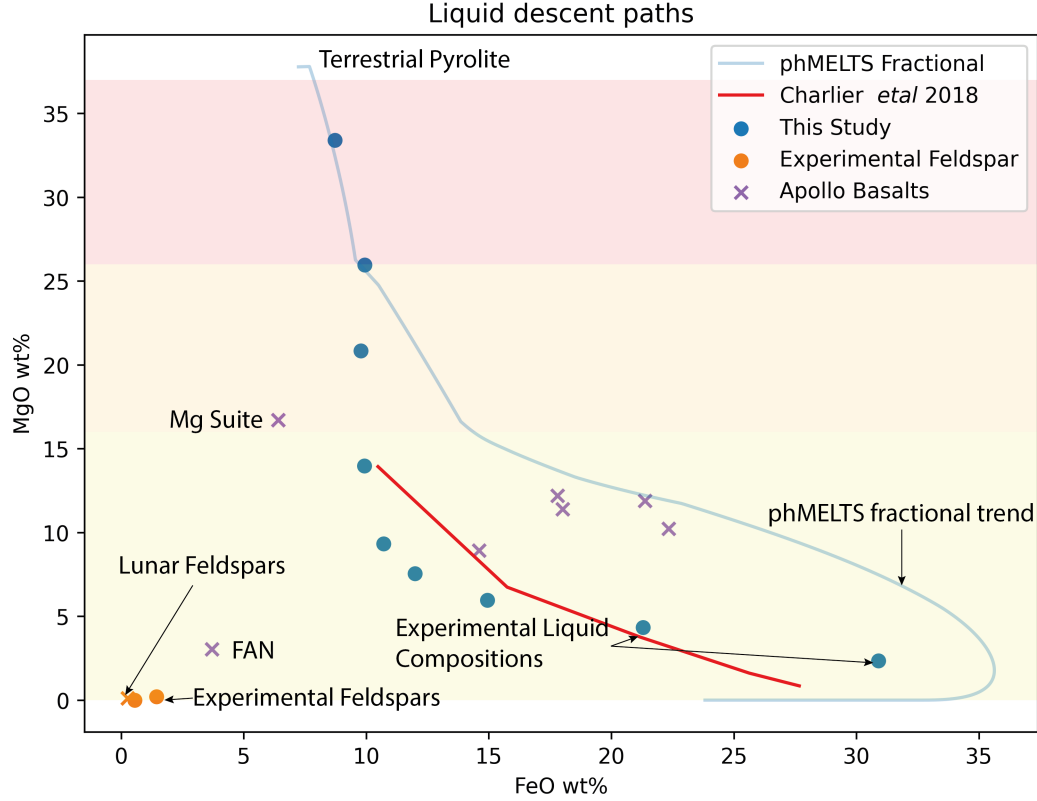


Figure 5.2: Evolution of fractional liquids in FeO - MgO space. Light blue line is liquid composition predicted by the phMELTS modelling program. phMELTS predicts large Fe enrichment early on, continuing to more than 35 wt.%. Solid red line is the evolution of the LPUM composition (Longhi, 1992), discretised and evolved experimentally by (Charlier et al., 2018). Blue dots are the evolving bulk compositions from this work. Lunar bulk rock data plotted as purple crosses with average lunar FAS feldspars plotted as an orange cross. Experimentally produced feldspars plotted as orange dots.

more similar to experimental liquid come from two groups of sample 67513, which have very large mafic contents. The recombination results indicate that inefficient plagioclase flotation/separation, rather than trapped melt, is the dominant source of mafic crystals in the ferroan anorthosite suite. The volume of plagioclase produced, combined with the inefficiencies of flotation suggests an LMO in excess of 1000 km deep, if plagioclase separation is as inefficient as predicted.

5.3.2 Mare Basalts

Mare basalts are chronologically separated from the primary crust, with liquid mare melts extruded billions of years after the formation of the primary crust. Secondary re-melting of cumulates, arising from both lunar mantle overturn and radiogenic heating, occurring at variable depths, makes direct comparison with simple petrogenetic models problematic. In general mare basalts require partial melting of 75-85 Mg# cumulates (Ryder, 1982), consistent with the experimentally generated cumulates which are 75-92 Mg#, before feldspar crystallisation, and the characteristic mare basalt ‘bow shaped’ REE patterns (fig. 4.1).

Light REEs are concentrated in the KREEP basalts, which are also enriched in other incompatible elements and represent the final stages of LMO crystallization (Warren & Wasson, 1979). My experiments also find that HREEs are compatible in an early clinopyroxene phase. Taken with the LREE-rich KREEP basalts, these formations can explain the observed ‘bow shaped’ REE patterns of the mare basalts. The REE characteristics of mare basalts are not uniform; the largest $-ve$ Eu anomalies are found in the high Ti mare basalts. This pattern is consistent with Ti enrichment which arose from hybridization of mare basalt melts with rutile or ilmenite saturated melts, after feldspar crystallization. The final liquids produced in my crystallisation sequence are highly enriched in LREEs (fig. 4.15). However, the level of enrichment is not as great as in the KREEP basalts.

A bulk silicate Moon with the same composition as the bulk silicate Earth is able to differentiate to produce the mare basalts. The remelting, that produces the mare basalts, requires the whole lunar mantle to be accessed.

5.4 Conclusions

5.4.1 Bulk lunar element composition

The hypothesis that I have tested in this thesis is: **Is it conceivable that silicate Earth and silicate Moon are identical in refractory element composition?** Through the major element set of experiments, chapter 3, I have experimentally fractionally crystallised a pyrolytic composition. The final liquid was significantly enriched in Fe (8-30 wt.% FeO) and Ti (0.2-3 wt.% TiO_2), a level of enrichment greater than the Fe and Ti concentration exhibited by the mare basalts. The timing of Fe enrichment in the lunar magma ocean occurs later than predicted in computational models. The timing of enrichment is important because it allows the high Mg melts to form at shallower depths than previously predicted. The steep depletion in Fe_{Tot} , which is required to produce a KREEP like composition, is not seen in my experiments but, this could be remedied by the crystallisation of FeTi oxides or Fe rich liquid immiscibility (Daly, 1914; Charlier et al., 2011; Charlier, Namur, & Grove, 2013).

Ultimately the pattern of element enrichment required for the petrogenesis of the mare basalts and the primary lunar crust is consistent with the fractionation of a bulk lunar magma ocean of pyrolite (Terrestrial) composition. There is therefore no requirement for the lunar magma ocean to be enriched, relative to Earth, in refractory elements such as Al or Ca. Hence, the silicate Moon could be entirely derived from material originating from the proto-Earth. This argues for a well mixed Earth-Moon system after impact, and would point to a highly energetic head-on collision.

5.4.2 Experimental versus modelling approach

Computational modelling programs do not accurately recreate the crystallisation of the LMO. This is unsurprising since the thermodynamic models employed are limited principally by the data used for calibration, which are dominantly terrestrial. In the case of a LMO of pyrolite bulk composition, the conditions of crystallisation are so dissimilar to those on Earth that the composition very quickly moves away from that of Earth's mantle.

5.4.3 Rare Earth Elements through the lunar mantle

Garnet is not a primary igneous mineral on the Moon (Walter, 1998), and hence could not sequester HREEs during LMO crystallisation. High temperature pyroxene, however, accommodates HREEs approximately seven times more than the LREEs. The high temperature clinopyroxene is also modally abundant and will sequester significant amounts of HREEs. Therefore, a melt which equilibrates with a clinopyroxene HREE sink will be depleted in HREEs. These experiments predict that the HREE concentration through the Moon will be correlated with the abundance of clinopyroxene, and both HREEs and LREEs will be strongly depleted in the deep lunar mantle, richest in Mg rich olivine.

5.4.4 Mare basalt source

The lunar mantle is well represented through the lunar mare basalt suite. Mixing models require that a significant proportion of the mare basalt melts were derived from the early crystallised Mg-rich silicates, while the late crystallising Fe- and Ti-rich cumulates are required to explain the large enrichment of Fe and Ti seen in the high Ti basalts. The degree of mixing and recombination of the cumulate stack of the LMO is necessarily high, to explain the spread of different zones from which melt is drawn from. This high degree of inferred mixing may at least partially explain

the moment of inertia factor of the Moon (0.3929- D. R. Williams, 2020), which is close to the value of a homogeneous planet.

5.4.5 Petrogenesis of the Ferroan Anorthite suite

The fit of the mafic component of the ferroan anorthite suite with crystal phases, produced alongside the experimental feldspars was good, indicating that the 'mafics' in the FAS dominantly represent trapped crystals. The amount of trapped melt in cumulate layers of the lunar magma ocean is not clear, however in the FAS it is small. The trapping of crystals in the FAS may have increased as crystallisation proceeds, evidenced by the measured increase in Fe with depth through the south pole Atkins-terrain. This observation gives credence to the idea that increasing crystal collisions decreases the efficiency of crystal sorting (Suckale, Sethian, et al., 2012; Suckale, Elkins Tanton, & Sethian, 2012). If true it is likely that the cumulate stack is both clear of significant melt and anomalous crystals.

The global composition of the lunar highlands is different on the near and far side of the Moon (Ohtake et al., 2012). In general, the spread of Mg#’s is higher, more primitive, on the far side of the Moon. If it is the case the first floated plagioclase crystals are found on the far side of the Moon it is likely the result of an asymmetry in convection, likely caused by tidal heating or Earth-shine.

5.5 Further questions for lunar science

1. How could uneven flotation crust of feldspar change the structure of convective cells?
2. What is the effect of multiple suspected crystals on the viscosity of the late lunar magma ocean, what convective length scales could be accommodated by multiple suspended crystal phases?
3. How would REEs and selectively volatile elements like Cu and Zn partition between late forming low temperature immiscible liquids?

A Chapter 3 - Data Tables

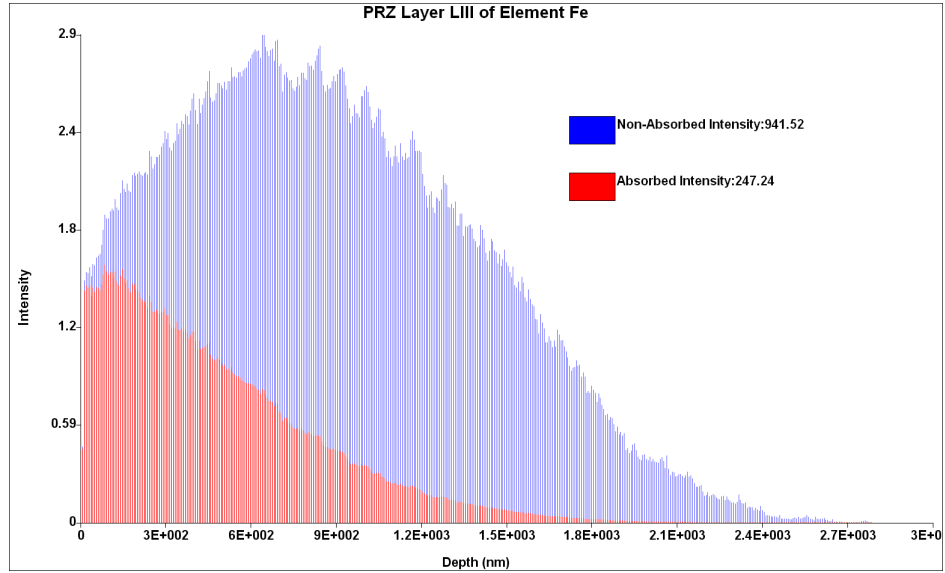


Figure A.1: L-line X-ray emissions from Fe in $FeMgSiO_2$ olivine as a function of depth.

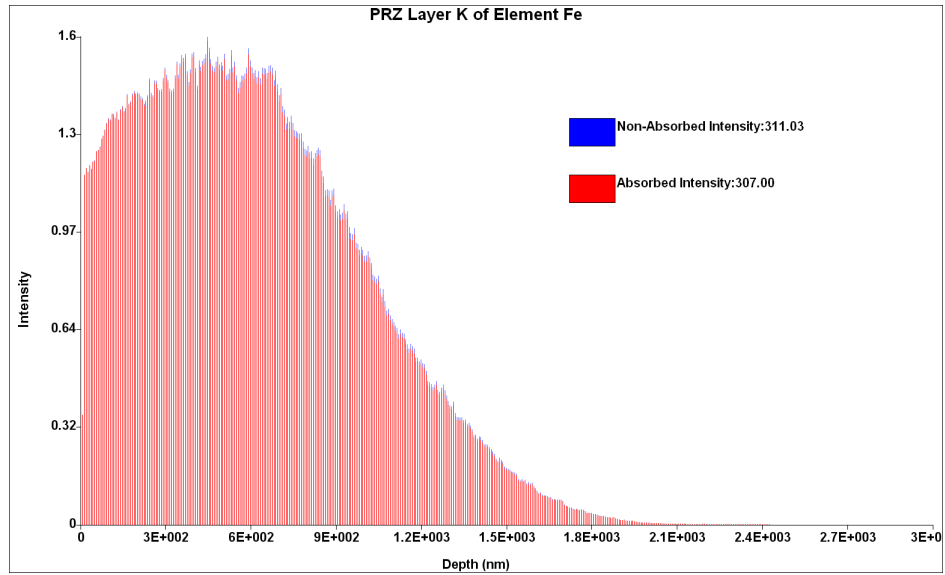


Figure A.2: K-line X-ray emission from Fe in $FeMgSiO_2$ olivine as a function of depth. Simulation produced by Casino2D electron simulation program, from a 10 000 electron, 15 kV, 1 μ m beam, with a 20 nm thick carbon coat. The K line has a significantly greater proportion of X-ray's emitted.

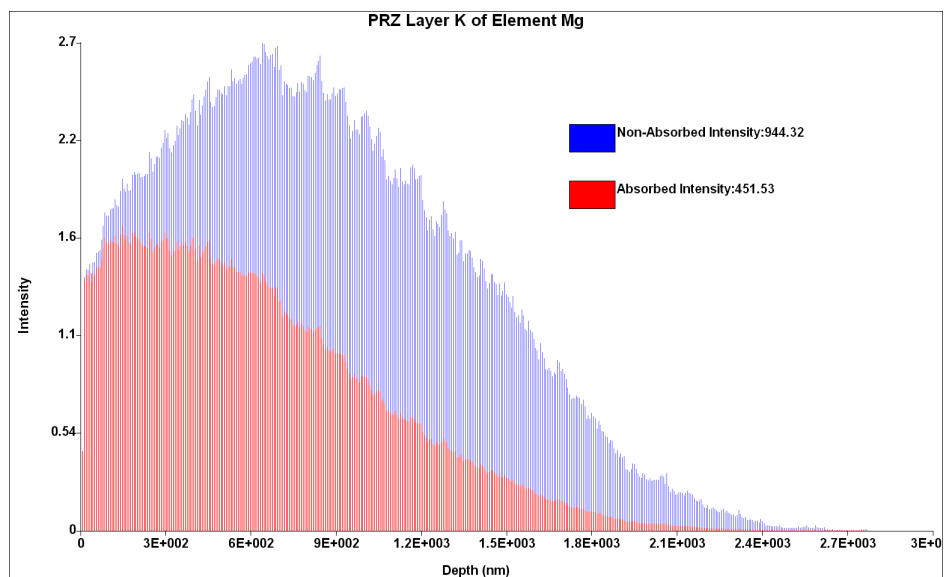


Figure A.3: K alpha X-ray emissions from Mg in $FeMgSiO_2$

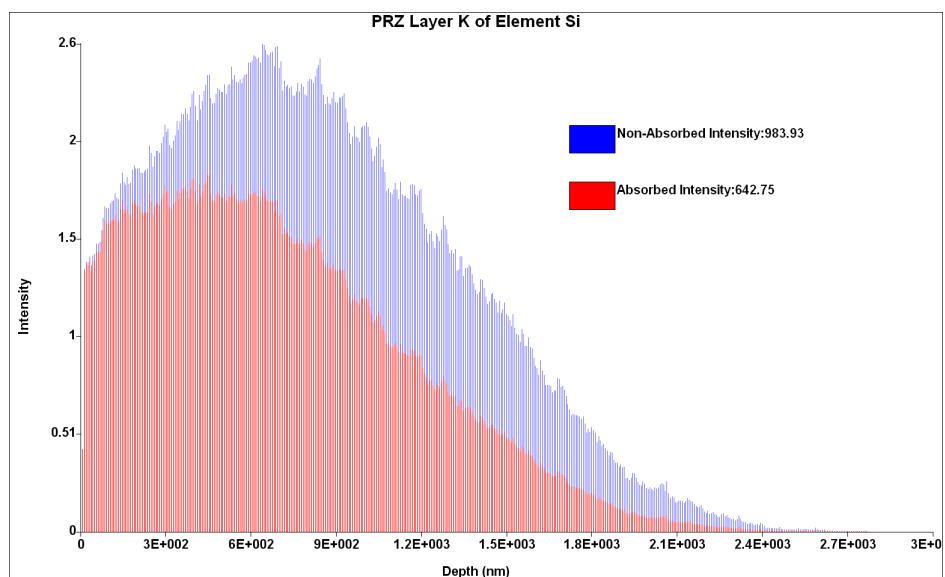


Figure A.4: K alpha X-ray emissions from Si in $FeMgSiO_2$. ‘Softer’ X-ray’s are preferentially absorbed and hence less able to be detected at the X-ray counters

Table A.1: Ferroan Anorthite suite target compositions.

Sample	Subgroup /sub- clast	Na_2O	MgO	Al_2O_3	SiO_2	CaO	FeO	Total
15415		0.4	0.3	35.1	43.9	20.1	0.2	100
60015a		0.4	0.5	35.3	44.3	19.2	0.3	100
60015b	,63-,64	0.4	0.3	35.4	44	19.6	0.3	100
60215	,30	0.4	0.1	35.5	44.5	19.3	0.2	100
65315	,32	0.3	0.3	35.2	44.7	19.3	0.3	100
61016	,184	0.4	0	34.9	45	19.6	0.1	100
60025	,45	0.4	0.2	34	45.1	19.7	0.5	100
67455	clast	0.4	1.3	32.4	45.1	18.2	2.6	100
74114	,5	0.6	0.5	33.7	44.6	19.6	0.9	100
67075	,11	0.3	3.1	30.9	44.9	16.9	3.9	100
62236a		0.2	3.6	30.3	44.5	17.7	3.7	100
62236b	,9	0.2	3.9	30.2	44	17.7	4.1	100
62237		0.2	5.2	29.9	42.3	16.5	5.9	100
15363		0.3	3.9	28.3	45.8	17	4.8	100
62236,43		0.2	6	27.7	44.1	15.8	6.2	100
64435c	CTA	0.3	8.3	26.6	44.4	15.2	5.2	100
67215c	,46	0.3	4.3	28.3	45.2	16.3	5.5	100
67016	,326/8	0.3	5.3	26.3	45.6	15.9	6.6	100
67513	,7097	0.2	6.7	20.1	47.8	14.4	10.8	100
67513	,7012	0.2	10.3	11.3	48.9	13.3	16	100

Table A.2: The optimal mixes of the components in Table 3.8 to produce the targets in table 3.6.

Sample ID#	Subgroup /subclast	Plagioclase	Melt	Olivine	Pyroxene	SSQM
15415		97	0	0	3	0.44
60015a		97	0	0	3	0.05
60015b	,63-,64	97	0	0	3	0.03
60215	,30	99	0	0	1	0.04
65315	,32	98	1	0	2	0.34
61016	,184	97	0	0	3	0.61
60025	,45	94	2	0	5	0.86
67455	clast	88	4	2	6	0.14
74114	,5	92	4	0	4	0.72
67075	,11	83	0	6	11	1.43
62236a		78	0	5	17	0.94
62236b	,9	77	0	6	17	1.25
62237		76	0	10	13	5.9
15363		70	7	5	18	0.84
62236,43		69	0	10	21	5.91
64435c	CTA	62	0	7	31	17.86
67215c	,46	74	0	9	18	1.54
67016	,326/8	67	0	10	24	1.91
67513	,7097	30	43	5	21	1.32
67513	,7012	6	33	8	53	1.19

Table A.3: FAS Mixing Components

	Plg	Albite	N-gl	O-gl	P-gl	Q-gl1	Q-gl3	N-cpx	O-cpx	P-cpx	Q-cpx	Q-ol1	Q-ol2	Q-ol3
<i>Na₂O</i>	0	11.8	0.7	0.7	0.6	1.1	0.2	0.2	0.2	0.2	0.2	0	0	0
<i>MgO</i>	0	0	6.1	4.4	2.4	2	4.3	12.8	12.5	8.1	3.9	13.5	15	15
<i>Al₂O₃</i>	36.6	19.4	16	13.3	10.2	16.1	12	12.7	8.7	11.6	12	0.1	0	0.1
<i>SiO₂</i>	43.2	68.7	49.2	46.5	43.9	46.4	44.4	46.8	48	45.5	43.2	33.1	32.9	33.9
CaO	20.2	0	12.8	13.3	10.8	11.8	18.6	19.9	17.4	18.9	17.6	0.7	0.8	0.8
<i>FeO</i>	0	0	15.2	21.8	32.1	22.5	20.5	7.6	13.2	15.8	23.1	52.6	51.3	50.2

Table A.4: Mare basalt target compositions

Oxide (wt%)	High K (11)	Low K (11)	Low K (17)	Pig. (12)	Pig. (15)	Ol (12)	Ol (15)	Il. (12)	High Al (14)	High Al (L16)	High Al (G5)	VHK (14)	VLT (17)	VLT (L24)
<i>SiO₂</i>	40.8	40.9	38.8	46.5	48.1	44.2	45	43.4	45.3	43.8	45.9	45.8	48.1	45.8
<i>TiO₂</i>	11.7	10.2	12.5	3.5	1.8	2.6	2.4	4.3	2.6	4.9	2.6	2.1	0.6	0.9
<i>Al₂O₃</i>	8.9	10.4	9	10.5	9.3	8	8.8	8.4	11.1	13.7	11.8	11.8	10.8	12.1
<i>Cr₂O₃</i>	0.4	0.3	0.5	0.5	0.5	0.6	0.7	0.5	0.5	0.3	0.5	0.6	0.6	0.3
<i>FeO</i>	19.2	18.8	18.6	19.8	20.1	21.2	22.4	21.4	17.8	19.4	17.5	16.6	18	21.3
<i>MnO</i>	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.9	0.3	0.3
<i>MgO</i>	7.5	7	9.1	7.6	8.9	14.3	10.2	11.9	12.2	7.1	10.3	12	11.4	7.3
	10.8	11.8	10.8	11.2	10.5	8.5	9.8	9.4	9.8	10.4	10.8	9.9	10.1	11.8
<i>CaO</i>														
<i>Na₂O</i>	0.5	0.4	0.4	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.1	0.2

Table A.5: The optimal coefficients for combining the components to accurately recreate the sampled mare basalts, coefficients are grouped by crystal phase

Mare group	Section	Ol	Pyx	Plg	FinLi	An	FeTi	SSQM
High K (11)	4.2.2	0.22	0	0.01	0.67	0	0.11	0.92
K (11)		0.19	0	0.03	0.68	0	0.1	0.03
Low K (17)	4.2.1	0.31	0	0.04	0.51	0	0.14	0.09
Pig. (12)		0.2	0	0.26	0.52	0	0.02	4.81
Pig. (15)		0.25	0	0.28	0.47	0	0	11.31
Ol (12)	4.2.5	0.42	0	0.07	0.49	0	0.02	0.15
Ol (15)		0.28	0	0.12	0.59	0	0.01	1.33
Il. (12)		0.34	0	0.05	0.58	0	0.04	0.13
High Al (14)		0.35	0	0.11	0.42	0.1	0.02	0.24
High Al (G5)	4.2.4	0.3	0	0.18	0.43	0.07	0.02	0.61
High Al (L16)		0.2	0.07	0	0.63	0.04	0.06	0.51
VHK (14)	4.2.3	0.36	0.01	0.28	0.23	0.1	0.01	0.14
VLT (17)	4.2.6	0.38	0	0.16	0.46	0	0	5.18
VLT (L24)		0.18	0	0.07	0.74	0	0	0.35

Table A.6: FAS components are mixed to produce the FAS samples. Plagioclase and Albite are stoichiometrically correct and converted to wt%. N,O,P,Q refer to the bulk composition of the Experiment (Table 4). Glass, gl; Pyroxene, cpx and olivine, ol refer to the phase used from each experiment.

	Plg	Albite	N-gl	O-gl	P-gl	Q-gl1	Q-gl3	N-cpx	O-cpx	P-cpx	Q-cpx	Q-ol1	Q-ol2	Q-ol3
<i>Na₂O</i>	0	11.8	0.7	0.7	0.6	1.1	0.2	0.2	0.2	0.2	0.2	0	0	0
<i>MgO</i>	0	0	6.1	4.4	2.4	2	4.3	12.8	12.5	8.1	3.9	13.5	15	15
<i>Al₂O₃</i>	36.6	19.4	16	13.3	10.2	16.1	12	12.7	8.7	11.6	12	0.1	0	0.1
<i>SiO₂</i>	43.2	68.7	49.2	46.5	43.9	46.4	44.4	46.8	48	45.5	43.2	33.1	32.9	33.9
CaO	20.2	0	12.8	13.3	10.8	11.8	18.6	19.9	17.4	18.9	17.6	0.7	0.8	0.8
<i>FeO</i>	0	0	15.2	21.8	32.1	22.5	20.5	7.6	13.2	15.8	23.1	52.6	51.3	50.2

Table A.7: Picritic glasses mixing components

Oxide	B5%	E5%	J5%	K5%	N5%	O5%	P5%	Q5%	R	S	T	Late An	Early An	Il.	Rutile
<i>SiO₂</i>	45.7	44.11	44.97	46.08	41.35	46.99	38.86	34.97	42.34	46.23	47.13	51.05	48.63	0	0.23
<i>TiO₂</i>	0.74	0	1.48	2.08	2.05	2.94	6.52	0	3.28	0.03	0.01	0.03	0.07	52.65	98.92
<i>Al₂O₃</i>	7.27	1.01	10.4	20.72	19.49	16.04	12.58	1.82	9.83	14.5	16.21	28.38	31.05	0	0.14
<i>Cr₂O₃</i>	0.11	0.91	0.18	0.05	0	0.1	0.11	1.4	0	0.11	0	0	0	0	0.16
<i>FeO</i>	8.91	20.45	10.72	8.06	14.54	16.41	25.11	50.51	30.9	20.1	22.21	3.03	1.45	47.35	0.55
<i>MnO</i>	0.13	0.21	3.01	3.42	3.08	2.38	3.89	0.2	0.34	0.23	0.25	0.05	0.02	0	0
<i>MgO</i>	23.31	31.13	14.52	6.1	6.12	3.32	2.31	5.62	2.35	1.97	1.75	0.19	0.2	0	0
CaO	12.47	2.18	14.52	13.35	12.38	11.23	10.41	5.47	10.41	15.98	11.34	14.65	16.29	0	0
<i>Na₂O</i>	1.36	0	0.21	0.14	0.99	0.59	0.2	0	0.55	0.86	1.11	2.61	2.29	0	0
	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Table A.8: Picritic optimal mixing coefficients, the same mixing components are used for the mare basalts and picritic glasses. (Longhi, 2006), determines a common source composition which, according to his model, represents the parental melt composition of the mare basalts. 1FF40 refers to the melt produced from the incremental adiabatic melting of the source starting at 4 GPa (40 Kbar) and 3 GPa (30 Kbar). FF refers to the fractional fusion of melt, where material once melted is removed from equilibrium with the remaining solids, the melt is then accumulated elsewhere.

	Ol	Py	Pl	FinLiq	An	FeTi	SSQM
FF401	0.54	0	0.06	0.39	0	0	0.01
FF301	0.5	0	0.06	0.39	0.03	0.01	0.2
Ap15G	0.48	0.01	0.03	0.45	0.02	0	0.26
Ap14 Group B	0.64	0.03	0.06	0.27	0	0	0.47
Red/Blk Glass	0.5	0.04	0.26	0.01	0	0.19	0.11

B Chapter 4 - Data Tables

Table B.1: REEs from LAICPMS

		Exp	La139	Nd146	Sm147	Sm152	Er167	Yb173	Lu175
B	Ol	EB11	16.98 (0.32)	8.33 (0.34)	5.96 (0.36)	9.69 (0.33)	5.51 (0.35)	5.05 (0.36)	6.39 (0.32)
	Gl		264.923 (0.074)	138.303 (0.071)	127.383 (0.072)	126.457 (0.071)	104.283 (0.08)	73.853 (0.084)	77.21 (0.086)
E	Ol	EB18	0.151 (0.475)	0.136 (0.17)	0.17 (0.221)	0.114 (0.495)	1.03 (0.24)	1.555 (0.239)	1.81 (0.206)
	Gl		233.305 (0.089)	121.063 (0.086)	116.743 (0.087)	116.89 (0.086)	99.423 (0.098)	72.538 (0.103)	73.875 (0.103)
F	Ol	EB25	4.08 (0.133)	2.01 (0.166)	2.06 (0.174)	2.075 (0.154)	1.72 (0.171)	1.16 (0.211)	1.12 (0.156)
	Gl		121.08 (0.1)	62.68 (0.1)	60.07 (0.11)	59.52 (0.1)	50 (0.12)	35.1 (0.13)	34.45 (0.12)
J	Cpx	EB44	9.41 (0.13)	8.97 (0.15)	21.71 (0.13)	22.04 (0.12)	17.27 (0.14)	12.56 (0.16)	12.98 (0.15)
	Gl		187.22 (0.14)	88.1 (0.13)	146.3 (0.13)	144.96 (0.13)	61.38 (0.15)	42.97 (0.16)	43.37 (0.16)
K	Cpx	EB63	67.55 (0.13)	44.47 (0.16)	na	0.87 (0.28)	43.18 (0.18)	32.92 (0.19)	33.81 (0.18)
	Gl		266.1 (0.13)	115.92 (0.15)	2.22 (0.31)	2.4 (0.23)	65.18 (0.18)	50.32 (0.19)	50.21 (0.18)
N	Cpx	EB68	196.5 (0.16)	99.7 (0.16)	1.91 (0.25)	1.79 (0.2)	67.97 (0.18)	47.35 (0.19)	47.33 (0.19)
	Pl		32.92 (0.11)	16.08 (0.17)	na	na	5.96 (0.24)	4.09 (0.37)	5.35 (0.14)
O	Gl		119.56 (0.11)	57.36 (0.14)	na	na	36.88 (0.14)	28.07 (0.19)	26.93 (0.13)
	Cpx		59.94 (2.43)	67.19 (2.54)	na	3.16 (3.01)	110.45 (2.74)	74.75 (2.74)	72.9 (2.89)
P	Pl	EB84	123.61 (3.84)	56.66 (4.09)	na	na	52.9 (5.1)	40.52 (5.07)	46.12 (6.22)
	Gl		722.28 (2.91)	352.55 (3.07)	12.77 (4.01)	14.78 (4.06)	304.09 (3.46)	223.19 (3.45)	239.86 (3.8)
Q	Cpx		36.45 (1.98)	55.75 (2.05)	86.07 (2.24)	88.48 (2.24)	88.95 (2.14)	57.36 (2.14)	200.24 (2.19)
	Pl	EB100	477.94 (1.88)	233.31 (1.94)	214.81 (2.08)	215.71 (2.09)	150.97 (2.01)	113.71 (2.01)	366.53 (2.04)
Q	Gl		327.19 (1.79)	162.61 (1.84)	148.21 (1.95)	149.54 (1.95)	106.02 (1.89)	81.84 (1.89)	264.22 (1.91)
	Ol		6.8 (0.14)	2.73 (0.18)	1.03 (0.27)	1.1 (0.2)	2.68 (0.2)	2.28 (0.22)	2.47 (0.19)
Q	Pl	EB118	204.41 (0.14)	79.73 (0.16)	28.95 (0.17)	28.03 (0.16)	60.78 (0.19)	45.44 (0.19)	44.87 (0.19)
	Gl		53.06 (0.14)	41.21 (0.17)	19.86 (0.17)	20.36 (0.16)	50.06 (0.19)	35.15 (0.2)	35.77 (0.19)

Table B.2: Trace Elements from LAICPMS

		Exp	Sc45	Y89	Zr90	Nb93	Hf178	Th232
B	Ol		15.23 (0.33)	9.18 (0.32)	6.78 (0.33)	15.92 (0.31)	7.89 (0.33)	24.68 (0.33)
	Gl	EB11	139.38 (0.04)	124.02 (0.059)	107.897 (0.058)	246.053 (0.055)	128.113 (0.088)	377.467 (0.112)
E	Ol		13.89 (0.18)	1.01 (0.203)	0.111 (0.56)	0.177 (0.357)	0.281 (0.395)	0.228 (0.619)
	Gl	EB18	116.86 (0.05)	146.245 (0.071)	101.895 (0.07)	222.938 (0.065)	113.61 (0.106)	345.655 (0.134)
F	Ol		2 (0.17)	1.88 (0.127)	1.56 (0.14)	4.12 (0.117)	2.43 (0.164)	6.38 (0.171)
	Gl	EB25	61.3 (0.06)	56.66 (0.08)	51.64 (0.08)	120.12 (0.08)	58.2 (0.13)	178.58 (0.16)
J	Cpx		64.29 (0.06)	19.36 (0.1)	6.84 (0.12)	6.57 (0.12)	11.25 (0.16)	10.98 (0.2)
	Gl	EB44	43.46 (0.05)	75.23 (0.1)	79.67 (0.1)	169.04 (0.09)	81.04 (0.16)	264.86 (0.21)
K	Cpx		70.84 (0.05)	60.92 (0.07)	36.78 (0.08)	56.37 (0.08)	52.63 (0.19)	101.74 (0.21)
	Gl	EB63	36.82 (0.07)	103.06 (0.07)	95.94 (0.07)	257.32 (0.08)	86.87 (0.19)	380.85 (0.2)
N	Cpx		62.55 (0.06)	85.76 (0.12)	75.69 (0.12)	156.24 (0.11)	90.22 (0.2)	300.43 (0.25)
	Pl	EB68	na	10.03 (0.11)	9.87 (0.13)	19.2 (0.11)	8.85 (0.17)	39.37 (0.1)
O	Gl		na	47.6 (0.1)	46.55 (0.11)	92.11 (0.1)	44.06 (0.13)	158.94 (0.11)
	Cpx		280.62 (2.64)	134.96 (2.65)	85.5 (2.67)	43.76 (2.51)	129.2 (2.66)	57 (2.19)
O	Pl		na	108.31 (4.74)	62.34 (4.74)	88.7 (4.09)	43.97 (4.69)	108.07 (3.08)
	Gl	EB84	166.24 (3.24)	552.38 (3.31)	366.9 (3.32)	729.16 (3.04)	327.47 (3.3)	913.96 (2.52)
P	Cpx		224.7 (2.1)	95.06 (2.09)	75.65 (2.1)	14.4 (2.02)	111.29 (2.09)	26.42 (1.85)
	Pl		58.18 (1.99)	181.63 (1.97)	201.56 (1.98)	494.22 (1.92)	179.72 (1.97)	668.51 (1.77)
P	Gl		66.33 (1.87)	132.43 (1.85)	135.6 (1.87)	320.43 (1.81)	119.66 (1.86)	426.63 (1.7)
	Ol		8.52 (0.07)	3.08 (0.09)	2.44 (0.1)	5.81 (0.09)	3.12 (0.21)	10.22 (0.22)
Q	Pl		46.45 (0.05)	72.85 (0.08)	63.29 (0.07)	186.88 (0.08)	77.27 (0.2)	293.57 (0.22)
	Gl	EB118	85.31 (0.05)	56.62 (0.08)	44.44 (0.08)	35.79 (0.08)	65.36 (0.21)	75.68 (0.22)

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