

**Chemical Composition, Thermodynamics, and Recycling: The Beginnings
of Predictive Behavioral Modeling for Ancient Copper-based Systems**



Benjamin J. Sabatini
Linacre College
University of Oxford

A thesis submitted for the degree of
Doctor of Philosophy
Michaelmas 2016

Chemical Composition, Thermodynamics, and Recycling: The Beginnings of Predictive Behavioral Modeling for Ancient Copper-Based Systems

Submitted for the degree of Doctor of Philosophy

Benjamin J. Sabatini, Linacre College, Michaelmas 2016

In their attempts to understand the unwritten past of human technology and progression, archaeologists have borrowed aspects of the natural sciences to answer big questions. In one such pursuit, fundamental aspects of the sciences have been employed towards the chemical compositional analysis of copper-based artifacts, often to simply classify which is bronze, brass, or pure copper, and to explain why they are significant in limited space and time. This thesis takes the variety of identified metal types and compositions from these analyses and builds the beginnings of an ambitious thermodynamic model based on the accepted premise of consistent and widespread recycling of ancient metals over time. Following the laws of thermodynamics, in systems at equilibrium, the model predicts the outcome of metal losses over the course of ancient pyrometallurgical processes from molten systems through both volatilization and oxidation using rigorous and established mathematics and theory. Elemental loss likelihoods are modeled for all binary copper-based metals, using activity coefficients, and ternary copper and zinc-based systems, with the excess Gibbs free energy, respectively. The calculations are performed using custom-written software designed to account for hundreds of thousands of compositional permutations after the method described by Redlich and Kister (1948). The results of these calculations are given as activity (binary) and isoactivity (ternary) contour lines. Quantified tables for the oxidation and volatilization of elements from a copper melt at 1200 °C and 1 *atm* are also given as rough indicators of element loss in ancient pyrometallurgical systems. A proof of concept of the models viability is also provided for binary Cu-M and ternary Cu-M-Zn (M = Ag, As, Au, Bi, Co, Fe, Ni, Pb, Sb, Sn, Zn), Cu-Sn-Pb, and Cu-Sb-As systems from the Late Bronze Age to post-medieval periods in Britain, which is based on several substantial artifact chemical datasets. For each ternary system, the interaction parameters used for higher-order calculations from the fitted behavior of each contributing binary systems are provided.

Comparison of the calculated models to available experimental system assessments, and to published archaeological chemical datasets, show that in both respects the proposed modeling of ancient copper-based metal losses works. And given the near ubiquity of ancient metal use around the world, the consistency in metal production and recycling technology, and the chemical analyses available, this preliminary model can be applied virtually anywhere the technology for smelting and recycling existed. In addition to loss modeling, this thesis has the additional offshoots of predicting ancient furnace conditions based on the calculated behavior of interacting metals, and of the controlling thermodynamic factors in the ancient calamine process.

Acknowledgements

I would like to thank my supervisor, Professor Mark Pollard, for his support and mentoring style that allowed me to pursue such an unusually themed thesis. Thanks also to Dr. Robert Thomas, who, when first we met, remarked with a very surprised look that my research aspirations were “very ambitious”. Without his help and counsel, I would not have the theoretical and mathematical understanding of thermodynamics that I have today. And, especially, thanks to my parents, Richard and Dale Sabatini, who have supported me throughout my educational ambitions, and without whom none of this would have been possible.

Contents

1. Introduction.....	1
1.1 The Foundation of this Research	8
1.2 Other Important Concepts.....	12
1.3 Mole Fractions and Calculations	12
1.4 Equilibrium in a Non-Equilibrated World	13
1.5 Thesis Design and Terminology	14
1.6 List of Mathematical Symbols.....	20
2. The Equilibrium Constant, Oxidation, and Activity	22
2.1 The Equilibrium Constant, Oxidation, and Activity	26
2.2 Activity and Vapor Pressure	30
2.3 Gibbs free energy of Formation and Oxidation	34
2.4 The Gibbs-Duhem Relationship for Binary Systems.....	40
2.5 Analytical Methods and Activity	44
2.6 Summary.....	45
3. Activity Diagrams for Binary Copper-Based Systems	46
3.1 Positive Deviation Binary Systems.....	47
3.1.1 Lead	47
3.1.2 Silver.....	50
3.1.3 Bismuth.....	52
3.1.4 Nickel.....	55
3.1.5 Cobalt and Iron	59
3.2 Negative Deviation Binary Systems	64
3.2.1 Antimony	64
3.2.2 Arsenic.....	67
3.2.3 Tin.....	72
3.2.4 Zinc.....	74
3.2.5 Gold	78
3.3 Summary.....	80
4. Volatilization in Binary Copper-Based Systems	82
4.1 Arsenic, Bismuth, and Antimony	84
4.1.1 Arsenic.....	84
4.1.2 Bismuth.....	86
4.1.3 Antimony	87
4.2 Zinc.....	88
4.3 Lead and Tin.....	89
4.4 Nickel, Cobalt, and Iron.....	90
4.5 Silver and Gold.....	91
4.6 An Order of Volatilization.....	92
4.7 Volatility Calculations in Binary Systems.....	92
4.7.1 Re-Ordered Volatilization.....	97
4.8 Summary of Element Volatility.....	98
5. Element Behavior and Ionic Melt Theory	100
5.1 Summary.....	106
6. Interpretation of Artifact Chemical Changes Using Oxidation and Volatilization.....	108
6.1 Binary Mixtures	110
6.2 Ternary Mixtures	113
6.3 Summary.....	120
7. Case Study Introduction: Ancient Brass, the Calamine Process, and Loss Modeling of Zinc and Other Metals from the Late Bronze Age to post-medieval periods in Britain.....	121
7.1 Ancient Manufacture of Brass and the Calamine Process	126

7.2 The Calamine Process and Loss Modeling of Zinc and other Metals from Liquid Copper	130
7.2.1 Considered Binary and Ternary Systems.....	134
7.2.2 Cu-As-Zn	136
7.2.3 Cu-Ag-Zn.....	142
7.2.4 Cu-Au-Zn.....	148
7.2.5 Cu-Bi-Zn.....	152
7.2.6 Cu-Co-Zn.....	157
7.2.7 Cu-Fe-Zn.....	161
7.2.8 Cu-Ni-Zn.....	165
7.2.9 Cu-Pb-Zn	170
7.2.10 Cu-Sb-Zn	174
7.2.11 Cu-Sn-Zn	177
7.2.12 Cu-Sn-Pb.....	182
7.2.13 Cu-Sb-As	187
7.3 Summary.....	191
8. Comparison of Artifact Chemical Data to the Thermodynamic Models.....	193
8.1 Visualizing and Discussing Recycling, Metal Flow, and Thermodynamic Changes	200
8.1.1 Thermodynamics	204
8.2 Summary.....	221
9. Conclusions.....	222
9.1 Overview.....	222
9.2 The Future of Archaeometallurgy.....	225
10. References.....	227
Appendix A.1: Volume and the Derivation of the Ideal Entropy of Mixing.....	241
Appendix A.2: Mixing, Mole Fractions, and the Partial Derivative.....	243
Appendix A.3: The Activity Coefficient and Independent Variables.....	244
Appendix A.4: Binary Zn-M Phase Diagrams.....	245
Appendix A.5: Custom Software.....	248
Appendix B.1: Site Names and Abbreviations.....	250
Appendix B.2: Site Dates	252
Appendix B.3: Combined Artifact Chemical Dataset.....	253

Figures

FIGURES 1A AND 1B: ELLINGHAM DIAGRAM	37
FIGURE 2: CU-Pb BINARY ACTIVITY	48
FIGURE 3: CU-Pb BINARY PHASE DIAGRAM	49
FIGURE 4: CU-Ag BINARY ACTIVITY.....	51
FIGURE 5: CU-Ag BINARY PHASE DIAGRAM.....	52
FIGURE 6: CU-Bi BINARY ACTIVITY	54
FIGURE 7: CU-Bi BINARY PHASE DIAGRAM	55
FIGURE 8: CU-Ni BINARY ACTIVITY	57
FIGURE 9: CU-Ni BINARY PHASE DIAGRAM.....	58
FIGURE 10: CU-Co BINARY ACTIVITY.....	59
FIGURE 11: CU-Co BINARY PHASE DIAGRAM.....	60
FIGURE 12: CU-Fe BINARY ACTIVITY	62
FIGURE 13: CU-Fe BINARY PHASE DIAGRAM.....	63
FIGURE 14: CU-Sb BINARY ACTIVITY	65
FIGURE 15: CU-Sb BINARY PHASE DIAGRAM	66
FIGURE 16: CU-As BINARY ACTIVITY	68
FIGURE 17: CU-As BINARY PHASE DIAGRAM	71
FIGURE 18: CU-Sn BINARY ACTIVITY	72
FIGURE 19: CU-Sn BINARY PHASE DIAGRAM	73
FIGURE 20: CU-Zn BINARY ACTIVITY.....	75
FIGURE 21: CU-Zn BINARY PHASE DIAGRAM	76
FIGURE 23: CU-Au BINARY PHASE DIAGRAM.....	80
FIGURE 24: CU-As-Zn ISOACTIVITY DIAGRAM CONSTRUCTION.....	135
FIGURE 25: Zn-As BINARY ACTIVITY	137
FIGURE 26: CU-As-Zn (ZINC ACTIVITY)	138
FIGURE 27: CU-As-Zn (ARSENIC ACTIVITY)	139
FIGURE 28: CU-As-Zn (COPPER ACTIVITY).....	140
FIGURE 29: Zn-Ag BINARY ACTIVITY.....	142
FIGURE 30: CU-Ag-Zn (ZINC ACTIVITY).....	143
FIGURE 31: CU-Ag-Zn (SILVER ACTIVITY)	144
FIGURE 32: CU-Ag-Zn (COPPER ACTIVITY)	146
FIGURE 33: Zn-Au BINARY ACTIVITY.....	148
FIGURE 34: CU-Au-Zn (ZINC ACTIVITY).....	149
FIGURE 35: CU-Au-Zn (GOLD ACTIVITY)	150
FIGURE 36: CU-Au-Zn (COPPER ACTIVITY)	151
FIGURE 37: Zn-Bi BINARY ACTIVITY	153
FIGURE 38: CU-Bi-Zn (ZINC ACTIVITY)	154
FIGURE 39: CU-Bi-Zn (BISMUTH ACTIVITY).....	155
FIGURE 40: CU-Bi-Zn (COPPER ACTIVITY).....	156
FIGURE 41: Zn-Co BINARY ACTIVITY.....	157
FIGURE 42: CU-Co-Zn (ZINC ACTIVITY).....	158
FIGURE 43: CU-Co-Zn (COBALT ACTIVITY).....	159
FIGURE 44: CU-Co-Zn (COPPER ACTIVITY)	160
FIGURE 45: Fe-Zn BINARY ACTIVITY.....	162
FIGURE 46: CU-Fe-Zn (ZINC ACTIVITY).....	163
FIGURE 47: CU-Fe-Zn (IRON ACTIVITY)	164
FIGURE 48: CU-Fe-Zn (COPPER ACTIVITY)	165
FIGURE 49: Ni-Zn BINARY ACTIVITY.....	166
FIGURE 50: CU-Ni-Zn (ZINC ACTIVITY).....	167
FIGURE 51: CU-Ni-Zn (NICKEL ACTIVITY)	168

FIGURE 52: CU-NI-ZN (COPPER ACTIVITY)	169
FIGURE 53: PB-ZN BINARY ACTIVITY	170
FIGURE 54: CU-PB-ZN (ZINC ACTIVITY)	171
FIGURE 55: CU-PB-ZN (LEAD ACTIVITY).....	172
FIGURE 56: CU-PB-ZN (COPPER ACTIVITY).....	173
FIGURE 57: SN-SB BINARY ACTIVITY.....	174
FIGURE 58: CU-SB-ZN (ZINC ACTIVITY)	175
FIGURE 59: CU-SB-ZN (ANTIMONY ACTIVITY).....	176
FIGURE 60: CU-SB-ZN (COPPER ACTIVITY)	177
FIGURE 61: ZN-SN BINARY ACTIVITY	179
FIGURE 62: CU-SN-ZN (ZINC ACTIVITY)	180
FIGURE 63: CU-SN-ZN (TIN ACTIVITY).....	181
FIGURE 64: CU-SN-ZN (COPPER ACTIVITY).....	182
FIGURE 65: PB-SN BINARY ACTIVITY	183
FIGURE 66: CU-SN-PB (LEAD ACTIVITY).....	184
FIGURE 67: CU-SN-PB (TIN ACTIVITY)	185
FIGURE 68: CU-SN-PB (COPPER ACTIVITY)	186
FIGURE 69: SB-AS BINARY ACTIVITY.....	187
FIGURE 70: CU-SB-AS (ARSENIC ACTIVITY)	188
FIGURE 71: CU-SB-AS (ANTIMONY ACTIVITY).....	189
FIGURE 72: CU-SB-AS (COPPER ACTIVITY)	190
FIGURE 73: TIME PERIOD AND ARTIFACT CHEMICAL COMPOSITION.....	200
FIGURE 74: LEAD AND TIN PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS	209
FIGURE 75: ZINC AND LEAD PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS.....	213
FIGURE 76: ZINC AND TIN PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS	217

Tables

TABLE 1: OXIDATION, EQUILIBRIUM CONSTANTS, AND THE GIBBS FREE ENERGY OF FORMATION	24
TABLE 2: CALCULATED VOLATILITY COEFFICIENTS	95
TABLE 3: PARTIAL VAPOR PRESSURE OF SPECIES	97
TABLE 4: ORDERED SUMMARY OF CALCULATED OXIDATION AND VOLATILIZATION	99
TABLE 5: ATOMIC AND IONIC RADII	102
TABLE 6: CU-AS-ZN BINARY PARAMETERS	142
TABLE 7: CU-AG-ZN BINARY PARAMETERS.....	147
TABLE 8: CU-AU-ZN BINARY PARAMETERS.....	152
TABLE 9: CU-BI-ZN BINARY PARAMETERS	156
TABLE 10: CU-CO-ZN BINARY PARAMETERS.....	161
TABLE 11: CU-FE-ZN BINARY PARAMETERS.....	165
TABLE 12: CU-NI-ZN BINARY PARAMETERS	169
TABLE 13: CU-PB-ZN BINARY PARAMETERS.....	173
TABLE 14: CU-SB-ZN BINARY PARAMETERS.....	177
TABLE 15: CU-SN-ZN BINARY PARAMETERS	182
TABLE 16: CU-SN-PB BINARY PARAMETERS.....	186
TABLE 17: CU-SB-AS BINARY PARAMETERS.....	190

1. Introduction

The connection drawn between chemical composition, thermodynamics, and recycling of copper alloy artifacts has the potential to open new avenues in, not only, the interpretation of ancient technology, but trade networks, migration patterns, and related aspects of civilizations. This threefold relationship to understanding ancient technology is extremely complex, yet combined and once fully understood offers a powerful means of interpretation that has seldom been mentioned by archaeologists or even archaeometallurgists. While it is common to encounter studies centered on metallographic and chemical composition analyses of metal artifacts, with some theoretical insight into the thermodynamics of ancient furnaces and operation, this thesis offers a completely new approach that is mathematically rigorous providing a framework not only for this thesis work, but for future archaeometallurgical research and interpretation. The applications of this research approach to archaeology are diverse, but for this thesis it is focused on demonstrating that copper artifact chemical compositions are predictable using thermodynamic mixing models with reasoning and results that are supported by reconstructed ancient melting experiments. The chemical compositional data of ancient copper alloys themselves are used only for confirmation that the models work. In order to leverage what thermodynamics can tell us about ancient metallurgy, and to create convincing thermodynamic models for ancient metal systems, it is necessary to describe the behavior of element interactions in combinations common in ancient metals. In modern metallurgical thermodynamics the combinations and compositions of ancient copper alloys are typically not described -as they are not used- thus they have been calculated from the basic thermodynamic systems data. These include, and without consideration for fluxes -although some can be used as such-; Fe, Co, Ni, Cu, Zn, As, Ag, Sn, Sb, Au, Pb, Bi, and of course O

and S. With the exception of sulfur and oxygen, these elements are usually reported in copper-based artifact chemical analyses and comprise the metals and metalloids of interest for this thesis.

Furthermore, problems inherent to the study of ancient metals of recycling, mixing, and consequent metal flow, and in interpreting technological and material culture through the chemical composition of artifacts, are undeniably unavoidable. No longer can it be ignored that metal was laborious to attain, highly valuable in the forms of scrap, ingots, etc., and so routinely recycled throughout history. At last recognizing the problem recycling has caused in accurately interpreting metal material culture, many scholars have used “recycling” and “modeling” as attractive buzzwords in their research, but none have provided insight into the question of how we, as archaeologists, anthropologists, historians, etc., can understand recycling and produce appropriate models without drawing spurious correlations from the chemical datasets themselves. The reasons behind the resultant chemical composition of copper-based artifacts is far too complex to be modeled with anything but a bottom-up thermodynamic approach, since the chemistries of iterations of recycled and mixed ancient metals changed dynamically and rarely resulted in compositions linearly progressive from the initial created alloy.

For solving the problem of compositional changes in alloys due to ancient recycling, the laws of thermodynamics provide the foundation and tools that can predict, qualitatively and quantitatively, the behavior of elements and occurrence of reactions in copper re-melting and recycling. This thesis is focused on re-melting and recycling, however the same approach can be applied to primary copper smelting. Using the well-studied and documented properties of activities, activity coefficients, and ionic behavioral theories in molten metal systems, the variety of elemental compositions and temporal changes in archaeological copper alloys can be logically explained. Furthermore, all of the systems produced in this thesis are adjustable

to the varied temperatures and conditions that might have occurred throughout the history of pyrometallurgy. Adjustments to the parameters that describe the systems are possible using well-defined thermodynamic relationships.

Much of the acquired data presented in this thesis were obtained empirically from modern refining and experimental techniques; that is, within the last one hundred years under controlled conditions. The conditions under which the data were reported are designed to show only the most basic properties of the alloys and their behaviors while molten. In the studies consulted there were no modern techniques employed to improve the efficiency of the process of melting, and were, just as in antiquity, simply fire refined. Under these basic conditions, that were present and persistent throughout the span of ancient metallurgy, reasonable approximations based on the conditions necessary for melting copper-based alloys are possible. Because modern laboratory experimental conditions are highly controlled, there are several differences between ancient and modern pyrometallurgy that must be addressed. Examples of these differences are in the temperature and atmosphere, which are calculable when one considers the similarities and differences in the sources of energy used (e.g. gas, charcoal, electric furnaces), the development and limitations of ancient furnace technology compared to modern, and the corpus of archaeometallurgical literature detailing ancient pyrometallurgy. For instance, the estimated temperatures attainable by ancient furnaces can be determined by analyzing slag remains that show characteristic phase formations. Using past studies on the furnace conditions in ancient metallurgical processes, the calculations in this thesis were made within the scope of ancient metallurgy using modern metallurgical experimental data.

The ability to apply modern thermodynamic data to ancient technology is logical as the metals, conditions, and procedures of processing, both in antiquity and modern times, are

not dissimilar. In each instance the laws of thermodynamics govern energy and balance, and in systems containing the same elements they are bound by fundamental rules and thus exhibit similarly predictable outcomes. With this knowledge in hand, and that of the pyrotechnological conditions under which ancient metallurgical practices were conducted, an assessment of the pyrometallurgical life histories, and concomitantly the cultures therein, of ancient copper-based objects can be made if one understands the mechanisms of change found in modern empirically defined equivalent systems.

The combined knowledge mentioned above can then be applied to interpreting ancient pyrometallurgical processes towards the elucidation of the history and prehistory of copper-based metal recycling. The methods employed are discussed in great detail over the course of the thesis. The task of interpreting and predicting the behavior of alloys systems is by no means simple, having posed a challenge to scholars of metallurgy, metallurgical thermodynamics, materials science, physical chemistry, and related disciplines for decades. Multiple methods of measuring and calculating the thermodynamic properties of alloys, and at varying temperatures in different phases, have been developed; however, now, much of the more difficult and tedious mathematics have been somewhat trivialized by the development of specialized software coupled with databases of thermodynamic data. Regardless of these recent computational advancements, however, this thesis builds upon a well-known method of system calculation for reasons of transparency and reproducibility, and because these software and databases do not typically include data relevant to ancient alloy chemical compositions. Modern computational software and databases are primarily designed to address modern-day materials production and research. Custom written software, therefore, much simpler in design and purpose, were created address ancient alloys with relevant data in order to accelerate the calculation of each system and construct diagrams using a stringent mathematical approach detailed later in this thesis. The calculations performed by these

software, but not the code itself, because of its nascency, are given in Appendix A.5. It is hoped that future development of this software may lead to its release in a free and open format.

The primary goal of this thesis is to provide a model framework for, and explain the analyzed chemical composition of, artifacts in combinations that are applicable to the composition of ancient copper alloy finds. It sets out to reason and quantify the temporal and processual mutability of the chemical composition of ancient copper-based artifacts through predictable patterns of change, including both increases and decreases, of elements that are the direct result of fire refining. With this knowledge one could then apply its principles to most -if not all- ancient cultures as the laws of thermodynamics do not change from one site to another or across continents. It should be noted that pyrotechnological knowledge and ability varied between regions and cultures, however, these differences can be accounted for by studying the metals, and the ancient furnace remains and related paraphernalia, without detracting from the meaning of the set of models produced in this thesis.

This thesis is unique in that it relies on methods and scientific interpretations that have not, to this author's knowledge, been explored for the purposes of archaeometallurgical studies. To this author the application of thermodynamics and modelling to ancient pyrometallurgy are now seemingly inseparable. The information presented in this work has the potential to solve many questions related to copper-based alloys and geographic and transitional irregularities that have baffled archaeologists and historians alike; who, hampered by only scattered pieces of information on the processes which control the loss and gain of elements during metals processing, have sought to logically and meaningfully explain the composition of metal artifacts (e.g. Caley, 1964; Dungworth, 1995).

One of the benefits of the approach taken by this thesis, too, is in the possible reverse engineer of ancient pyrometallurgical processes that could be used to determine the conditions, but not physical form, of ancient furnaces based on the chemical makeup of artifacts. Ancient furnaces are often not found intact; however, fragments are somewhat common. Reconstructed pyrometallurgical processes, based on fragments and in some instances whole furnaces, have been attempted; however, these have not considered thermodynamics in relation to observed artifact chemistries. The construction of ancient furnaces can be interpreted from archaeological finds, but without a manual or written record their operation cannot be determined without thermodynamics. Therefore, as a means to circumvent this lack of knowledge provided by archaeology alone, reasoning through thermodynamics, with comparisons to the actual chemical composition of artifacts, is used in its stead. This point is particularly important as it is necessary to ascertain the progression of chemical change that may have occurred in re-melted and recycled metal. In brief, it is possible to make good approximations of the conditions (e.g. temperature, atmosphere, and degree of control of the molten system) in ancient furnaces, and build models within the confines of the available artifact chemistry.

Developing working models for chemical changes in re-melted copper-based alloys requires their comparison to artifact chemical compositional datasets. The most obvious choice for datasets are those that are large and contiguous, although it may certainly be possible to find meaningful relationships and patterns in non-contiguous data through statistical analysis. It is then possible to identify the inflow and outflow of elements from the overall flow of metal in a region, when new technologies and methods of metals processing were introduced, and relate this information back to the accompanying archaeology based on the study of other material remains. In such a methodology the archaeology of a region is therefore vital, so like the chemical data itself, more is better. In this way one might identify

geographically significant trade routes, mark periods of expansion or disruption, and identify objects of foreign origin through thermodynamically explainable dissimilarities. In order for artifact chemical modeling to be effective, it should be used in conjunction with archaeological evidence whenever possible, but never relegated to simply a supportive role. If the model does not match the artifact chemistry, or the chemistry does not match the model, there is clearly a need for more investigation. The thermodynamic models created in this thesis are correct in their execution, having been compared to published examples whenever possible, but must be applied in light of archaeological context.

Determining the behavior of impurities commonly found within nearly pure copper and copper ores, and intentionally and unintentionally manufactured alloys produced through smelting and recycling, requires several interpretative approaches. None of the approaches can satisfactorily explain the observed chemical content of ancient copper-based alloys on their own. It is therefore not surprising that the application of thermodynamics to ancient metallurgy did not come sooner. The progression of elemental changes; that is, from ore to object end-of-life, or burial, requires multiple steps and its explanation must account for the high complexity and diversity of regional and temporal primary and secondary smelting processes and refining techniques. But with enough information, such as the maximum sustainable temperatures of ancient furnaces, ore sources and their approximate chemical makeup, and present chemical composition of artifacts, this is entirely possible. However, given the grand scale of explaining ancient pyrometallurgy, this work's focus is limited to the behavior of elements only after the bulk removal of sulfur from ores, and in cases with high percentages of copper metal. In the presence of sulfur, the behavior of alloying metals, often referred to as impurities when unwanted, have been found to be markedly different and must be explained separately (e.g. Choudary *et al.* 1977; Itagaki *et al.* 1979; Itagaki *et al.* 2005; Itagaki *et al.* 2006; Lynch 2009; Lynch and Zhong; 1997; Mendoza *et al.* 2001, 2002). The

presence of sulfur in re-melted metal artifacts is not completely disregarded by this thesis, however, its role in ancient pyrometallurgy should only be addressed by thermodynamic studies of primary smelting operations.

1.1 The Foundation of this Research

Since this thesis is based in thermodynamics, it is important to review the relevant laws that are integral to the methodological approach taken, which, as happens, have given rise to many applied scientific fields, now including what may be termed archaeometallurgical thermodynamics. The first law is the best recognized having the simple premise of the conservation of energy, as energy relates to heat and work. Under the first law energy can be transported, converted, but not created or destroyed.

The first law can be succinctly defined mathematically by the Equation $dU = dQ - dW$, where dU is the internal energy of the system, dQ the energy supplied as heat, and dW the work done by the system. In this equation the variables of heat and work depend on the path of energy transfer, and in a closed system $(Q - W)$ is equal to the internal energy. As written the differentials of Q and W are not in fact exact. The medium of transfer and path taken is especially important for this thesis that considers solids, liquids, and gases of metal components. Within a defined system for these media, where limitations are imposed such as temperature and pressure, the heat, provided by charcoal, is transferred into the system by interaction of the system with its surroundings. The system is the defined and restricted area of interest, and the surroundings is everything else. According to the first law if heat is supplied the energy will increase, and if the system does work to the surroundings, the energy will decrease.

In the second law there is a net degradation of energy, and explainable reversible and irreversible states where the energy for doing work is completely consumed. It can, unlike the

first law, predict whether a process will occur, and further shows that the transfer of heat to work is incomplete. The second law is important since once the energy is consumed a point is reached called the equilibrium state. Equilibrium states are useful in describing molten metal element behavior, and persist as long as no external energy is added from the surroundings.

The second law is furthermore related to entropy, S , and can be understood in a given system by the relationship $\Delta S = \frac{Q_r}{T}$, where T is temperature, and Q_r the total heat. Within a system that is reversible, for example ones designed for smelting, when the system does the maximum amount of work, pressure is greater than zero with increased volume, and the system has done more work for the same natural result. An example of a reversible system is vaporization. This basic definition of work is the explanation for some processes observed in metallurgical thermodynamics, which is succinctly shown by forms of the equation for entropy rather than by written explanation. If this equation is written with an equal sign $=$, it indicates that the reaction is reversible, and with an inequality, $\geq$, irreversibility. Under conditions of irreversibility the pressure in the system is not equal to zero when there is an increase in volume, and the system does less work with the same result. In terms of entropy for reversible processes, the total entropy change is zero where the gain in the system is equal to the loss in the surroundings. In an irreversible process there is a net gain in entropy and degradation of work.

Entropy not only describes the work done by a system, but may also show aspects of statistical thermodynamics that are important in discussions of mixing. Here in the postulate (Equation 1.0) for entropy of the system, Ω , from Equation 1.1, is the number of configurations the atoms in the system can be arranged, and k the Boltzmann constant. Accordingly, in a unary system the total possible arrangements of the same atom in a regular lattice of n sites results in an entropy of zero. It follows that in a binary mixture of molecules

of types 1 and 2 in quantities of n_1 and n_2 , the probability of atom distribution and entropy of the system can be described by Equation 1.2, substituting 1.1 into 1.0, and using Stirling's approximation for factorials where $(\ln n! = n \ln n - n)$. The two terms $\frac{n_n}{n_n + n_m}$ in Equation 1.2 are the mole fractions x_1 and x_2 , respectively, which, results in Equation 1.3 when Equation 1.2 is multiplied by $\frac{N}{(n_1 + n_2)}$ and accounting for the Boltzmann constant where $k = \frac{R}{N_A}$ (Gokcen, 1986, 62 – 63). When there are no intermolecular interactions, the atomic radii of the two species are the same, and disregarding their shape, Equation 1.3 expresses the ideal entropy of mixing in a binary solution. For more complex systems of three or more components the equation may be expanded with additional $x_n \ln x_n$ terms while adjusting for the total mole fractions.

$$S = k \ln \Omega \quad 1.0$$

$$\Omega = \frac{(n_1 + n_2)!}{n_1! n_2!} \quad 1.1$$

$$S_{n_1 + n_2} = -k \left[n_1 \ln \left(\frac{n_1}{n_1 + n_2} \right) + n_2 \ln \left(\frac{n_2}{n_1 + n_2} \right) \right] \quad 1.2$$

$$S = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad 1.3$$

Related to entropy is enthalpy, which is defined as $H = U + PV$ where H is enthalpy, P is pressure, V is volume, and the free energy of the system is controlled by two factors.¹ The first is that the reaction attempts to minimize energy, and second to maximize entropy. For the first, reactants are unstable and exchange energy to become more stable and have a minimum energy state. In the second, the system seeks a natural maximum disorder and

¹ The above defined ideal entropy of mixing may also be derived using volume. See Appendix A.1.

higher entropy. From the first and second laws, and equations, one can then derive the Gibbs free energy defined as $G \equiv H - TS$, and approximately at constant temperature $dG = dH - TdS$. Furthermore, since there are no intermolecular interactions the enthalpy, ΔH , is zero, and thus the free energy is only dependent upon temperature and entropy. The free energy has many possible applications in thermodynamics, such as, among others, determining the free energy of mixing (Equation 1.4), which contributes to the explanation of the behavior of molten metal systems neglecting all intermolecular interactions. Accordingly, the energy of mixing is always negative, lowest at equal mole fractions, and zero for pure substances.

$$\Delta G_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2) \quad 1.4$$

$$\Delta G_{excess} = \Delta G_{expt} - \Delta G_{ideal} \quad 1.5$$

In real systems, however, the free energy of mixing is almost certainly different. In addition to the limiting assumptions of Equation 1.4, mixing is also dependent on composition, and must instead be explained by the difference of the experimental and ideal free energy that together leads to what is known as the Gibbs excess free energy (Equation 1.5). In binary systems the excess energy is not needed to describe deviations from ideality, as the differences are shown clearly by the activity coefficient; however, it plays a direct role in predicting the outcome of higher order systems. In fact, calculations based on the excess energy have long been considered the best way of predicting thermodynamic properties (Redlich and Kister, 1948; Tomiska, 2009). From these properties and the fundamental approach of this thesis, one is required to completely rethink how archaeologists have understood ancient pyrometallurgy, and especially a cautionary reappraisal of previous literature on the subject is necessary.

1.2 Other Important Concepts

The following is a brief discussion of oxidation and why it is important to understanding pyrometallurgical processes. As the name implies, in metal refining/recycling oxidation typically involves oxygen and its coupling to a metal ion, atom, or molecule. However, this simple viewpoint of the reaction is misleading. In archaeometallurgy oxygen is often the only element considered, leading some to conclude that oxygen must be involved; however, what is actually occurring are simultaneous oxidation and reduction reactions, or redox, and the exchange of electrons between a donor and acceptor ion. In the case of the metal systems considered in this thesis, the metal is the donor and oxygen the acceptor. Under the limited condition of recycling, redox reactions between metals and oxygen are often enough to describe the oxidative behavior of elements in a system; however, of equal importance is the redox of sulfur and metal, especially in ancient metal artifacts that are not always devoid of sulfur. In either case the metal is the electron donor that assumes a positive charge, and the acceptors are oxygen and sulfur assuming negative charges. Since redox reactions only require the exchange of electrons, reactions can also occur between metals. In copper pyrometallurgy to understand a system's behavior, it is enough to consider reactions only between the non-metals of oxygen and sulfur, and metals. The likelihood and order of a host of element's oxidation is based on the Gibbs free energy of the system, and in a copper melt may result in the formation of sulfides and oxides.

1.3 Mole Fractions and Calculations

In metallurgical thermodynamics calculations of activity and related equilibria are performed using mole fractions. This thesis likewise uses mole fractions, which, if applied either backwards or forwards to archaeometallurgy, must be converted to the more commonly used weight percentages used by archaeologists and historians. Conversion from weight percent to mole fractions is performed as follows: with the number of moles n of each

component known, found simply, for example, by dividing the mass of the solution (g) by the atomic weight (g/mol) of solute for both solvent and solute, the mole fraction can be found according to Equation 1.6 for simple binary solutions. For more complex solutions additional terms in the denominator need only be added.

$$x_j = \frac{n_j}{n_i + n_j} \quad 1.6$$

To convert from mole fraction to weight percent one must multiply the atomic weight of the component by the mole fraction, and then simply divide by sum of the atomic weight of each component times their mole fraction times 100%.

1.4 Equilibrium in a Non-Equilibrated World

The premise of this thesis, the quantification and predictability of ancient pyrometallurgical practices, is built on equilibrium calculations, which, although successful in predicting the outcomes of controlled systems, require additional thought as to the complications added by non-equilibrium conditions; as if metallurgical thermodynamic modeling were not already complicated enough! Non-equilibrium conditions are varied and in ancient metals processing may have included, after Yazawa and Nakazawa (1998): formation of solid solutions, melts, or components instead of pure substances; slow reaction kinetics and delay of heat and mass transfer, especially at heterogeneous interfaces; incomplete phase separation; inhomogeneity in the furnace; back reactions; and overcharge. The purpose of this section is not to propose a solution to interpreting non-equilibrated circumstances, but to recognize that metallurgical thermodynamics is imperfect. Even at sufficiently high temperatures, enough to melt copper and smelt copper ores, non-equilibrium conditions can prevail due to the diffusion limitations of atoms across temperature or concentration gradients, the rate of phase transformations, and insufficient and irregular partial pressures. One must also consider the influence of grain size, impurities, and furnace

geometry. Furthermore, non-equilibrium states are often intermediaries between the start and finish of a process, and therefore the path taken may be irrelevant to the overall results. Should non-equilibrium conditions one day prove significant to the premise of this thesis through well-conceived archaeometallurgical experimentation of alloys, the above outlined influencing factors should be explored. Despite the above considerations, it should be understood that in practice non-equilibrium fractionation should be insignificant to the modeled thermodynamic behaviors of the systems in this thesis.

1.5 Thesis Design and Terminology

To begin, an overview of the behavior of key elements in liquid copper in terms of equilibrium constants is discussed followed by their activities at their individually available thermodynamically assessed concentrations. The definitions of these concepts, and those related, are provided in a clear and concise manner in chapter 2 assuming no in-depth knowledge on the part of the reader of thermodynamics, physics, or chemistry. Basic concepts and understanding of physics and chemistry are however necessary and will not be discussed. Also discussed in chapter 2 are the methods used to calculate binary activity values for elements combined with copper. These calculations provide a rough guide to element behavior through activity, but these values, given their limited applicability calculated in binary systems to complex archaeologically derived copper objects, should be used with caution. They are, nonetheless, good estimates for the complex systems that often occur during recycling and re-melting of metals.

These basic concepts and methods are followed in chapter 3 with the introduction and discussion of several activity values in binary systems over a range of temperatures from the most recently available published research. The data include both calculated and experimentally derived values, in addition to values calculated specifically for this thesis

under specified conditions, and explanations for unusual occurrences of activity behavior. Insight into the behavior of elements in copper are given throughout this thesis, since the interpretation of each system can only be performed with all available information in mind. By the end of chapter 3 all of the introduced concepts taken together only partially explain the meaning behind the element combinations and compositions of ancient copper-alloy objects. To further refine the interpretation of copper alloys, and to understand the various processes in molten metals, Chapter 4 gives a lengthy discussion on the volatilization of metals and metal oxides and how they accompany and are separate from oxidation. Activity on its own may be used to determine loss of elements through evaporation, however, the mechanisms behind element losses and gains are not straightforward and must be discussed in further detail. Calculations for the volatility of elements in molten copper are given in a similar format to activity data from Chapter 3 for each element and species of element relevant to their thermodynamic behavior in molten copper.

Chapter 5 introduces ionic melt theory, a concept that helps explain the interaction of elements according to each element's ionic radii and valencies, and their possible substitution for each other leading to behaviors of attraction and repulsion. These properties likely contribute or are directly responsible for the observed altered vapor pressures of elements when present in a bulk copper melt. In the slurry of molten metals this theory suggests that the bonding type between metals at high temperatures are best explained as ionic rather than, for instance, covalent or metallic bonding. This portion is important as it supports the thermodynamics discussed in previous chapters providing theory and substance for observed and predicted solute metal behaviors. The purpose behind including ionic melt theory and radii is given in section 1.1 of this chapter where the importance of statistical thermodynamics and element ordering is clear.

Following the fundamentals and integrated theories of element interaction and vapor pressure, Chapter 6 begins with a discussion of the issues involved in determining component behavior in increasing numerous molten metal combinations. Behavior of each component can only be determined by knowing how it interacts with another, so in order to understand the thermodynamics of a component it must be examined in at least a binary system. Elements alone cannot, from their own individual thermodynamic properties at a given temperature and pressure, be used to predict their behavior in mixtures. Following this short discussion of component interactions in binary and higher systems, derivations and calculations considering multiple metal solutes are given. A method for the calculation of ternary systems is provided, which clearly highlights the increasing complex mathematics required beyond that of simple binary solutions. The method presented provides for the prediction of higher order systems made from only the observed interactions of binary systems. Although the equations themselves are trivial, more parameters and the sheer number of necessary calculations needed to completely describe a system are daunting.

Chapter 7 provides a case study with thermodynamically evaluated binary and ternary systems using the methods outlined in Chapter 6 for the practical application of these predictive models towards the interpretation of ancient copper-based metals systems. In Chapter 8 the predictive outcomes of these models for the behavior of each component are then compared to an archaeological copper alloy chemical dataset from roughly the 1st millennium AD, Britain. Conclusions drawn in Chapter 8 are directly from the models, not from the dataset itself. In Chapter 7, summary explanations for these systems are given for components in terms of thermodynamic manufacturing restraints and chemical compositional recycling outcomes that would have occurred within the technological boundaries of ancient metallurgy. To show how one can apply knowledge of metallurgical thermodynamics to real archaeological problems, the recently compiled chemical dataset and accompanying

discussion from the First Millennium AD, Britain from Pollard *et al.*'s (2015)

“Characterising Copper-based Metals in Britain in the First Millennium AD: A preliminary quantification of metal flow and recycling” is examined. The paper by Pollard *et al.* discusses an idea for the loss modeling of zinc through the identification of chemical changes due to recycling that are observed in analyzed artifact chemical data following and expanding upon a method described in Bray and Pollard (2012). The data they refer to is a combination of elemental chemical datasets from Caple (1986), Blades (1995), Dungworth (1995), and Bayley and Butcher (2004), which together form a suitably large body of archaeologically relevant chemical data useful for a cursory, and thermodynamically meticulous, interpretation of ancient metal recycling and mixing trends. Larger datasets are beneficial as they reduce error caused by such obstacles as outliers and incomplete analyses.

In summary, the work by Pollard *et al.* (2015) applies an artificial cut-off to chemical data analyses to explain changes seen in metal circulation and recycling of copper alloys from the late Iron Age to the early Medieval period. And, by redefining metal groups by their composition more akin to ancient alloy percentages rather than modern, such as gunmetal, into a scheme of presence and absence of elements, and by using these new groups to examine key elements weighing in on their degree of distribution, they have shown how the elemental composition of artifacts may apply to more than provenance studies or supposed technological markers. This idea of redefinition is novel, and inspired the research done here in this thesis; however, their work is only cursorily mentioned as it is fundamentally a different approach, which is evident throughout this thesis.

This thesis uses the calculated thermodynamic behaviors of the following metal, metalloid, and non-metals combinations with copper in binary, and with copper and zinc in ternary, systems: O, S, Fe, Co, Ni, Zn, As, Ag, Sn, Sb, Au, Pb, and Bi to approach the

problem of ancient recycling and metal flow from the most basic level. Additional considered systems in this thesis include the Cu-Sn-Pb and Cu-Sb-As ternary systems, since these are prominent in archaeology and in the later examined datasets. Ultimately the purpose of Chapters 7 and 8 is to compare the expected outcomes of element behavior gains and losses to those seen in the archaeological analytical metal record, and make informed conclusions about the processes of recycling, mixing, reuse, and the manufacturing of ancient alloys.

Finally, a brief word on the terminology used in this thesis is necessary before proceeding further to avoid confusion when applying the information provided in this thesis to the jargon of archaeology and archaeometallurgy. This thesis is written from the perspective of the sciences involved and contains terminology that is based primarily in the discipline of metallurgical thermodynamics. It should therefore not be used in archaeological contexts without proper consideration for the differences of meaning that have evolved in either discipline. For example, the use of words and concepts such as “loss”, “remove”, and “fire refining” are common in metallurgical thermodynamics and refer to the likelihood of loss, as well as being suggestive of the kinetics, of so called impurity elements from desirably refined metals. Loss and removal of an element in this context does not imply that the element is completely purged from the system, rather that there is an initiation of the lessening of it that may eventually reach dilute amounts over an undefined timeframe during which the metals are molten. Fire refining is, as it implies, the practice of re-melting metals in order to purify them by removing impurities through a combination of oxidation and volatilization. Within the practice of recycling within the constraints of ancient furnace technology, with the same or similar temperatures and pressures, the act of re-melting and fire refining are the same. Furthermore, archaeometallurgical and archaeological jargon, just as those in the sciences is discipline dependent, must be reconsidered in relation to metallurgical thermodynamics. Many of the terms used in archaeology have been adopted

from other disciplines and taken on completely different or assumed summary definitions. One such case is that of reduction and oxidation, which in the contexts of this thesis are not as they are applied in typical archaeological discussions. Again, oxidation is not the loss of an element from copper. Oxidation only implies a simple exchange of electrons and by itself says nothing about compositional change. Similarly, reduction is not reserved for the act of primary smelting of copper ores. A second is the definition of an alloy, which is often defined in archaeology as a combination of a metal base with other elements. This definition is useful in describing an objects final form, but is insufficient in metallurgical thermodynamics. In metallurgical thermodynamics the definition of an alloy must be more flexible because one is describing the behavior of matter rather than a final product. An alloy in the contexts of this thesis, from the perspective of the science involved, is a metallic solid, in other words it is constituted by metallic bonds, or it is a liquid and consists of mostly ionic bonds (see Chapter 5). However, keeping both the archaeological and thermodynamic perspectives in mind while reading this thesis is imperative as both are discussed and one must be able to relate one to the other. Furthermore, the question of alloying intentionality in archaeology and controlled outcomes is one of distinct controversy in the field, especially, for example, in the case of copper-based alloys that contain arsenic. Intentionality is touched upon throughout this thesis, and especially in Chapter 7, 8 and 9 in terms of alloy manufacturing and recycling.

However, in this thesis the elements of concern are primarily tin, lead, and zinc, which were almost certainly intentionally combined with copper to form bronze, brass, and leaded bronze and brass. Other combinations of elements with copper have, however, also been modeled to provide a complete set of the possible alloys of brass and bronze. It is important to note that at low concentrations, and in trace amounts, the behavior of the solute(s) is not expected to deviate from the modeled trends in as much as its concentration is directly linked to behavior. Only through experiment can behavioral abnormalities be

identified and then remodeled by thermodynamics. Returning to the intentionality of brass and bronze –and in particular Sn, Pb, and Zn–, there is no question that these alloys and metals were recognized by craftsman and so objects were likely chosen for recycling based on their constituent elemental compositions. This is an important point that will be discussed in Chapters 8 and 9.

Regarding the definitions of an alloy, it is important to keep both of the above interpretations in mind when reading this thesis. This thesis however, as said above, is written from the perspective of the sciences involved rather than strictly archaeology or archaeometallurgy with consideration for metallic, and, too, ionic bonding, which is further detailed in Chapter 5. Therefore, when reading the information given in this thesis, it is important to adopt the language of thermodynamics, where the terms and ideas originated, rather than what they have become in other fields.

1.6 List of Mathematical Symbols

a	Activity
a_M	activity of metal component
a_{MO}	activity of metal oxide
A	Margules parameter
AM	atomic mass
B	interaction parameter B
C	interaction parameter C
D	interaction parameter D
E	energy on mixing
G	Gibbs energy
G^E	Gibbs excess free energy
G_B^E	excess free energy of component B
G_C^E	excess free energy of component C
G_D^E	excess free energy of component D
H	Enthalpy
H_{mix}	Enthalpy

k	Boltzmann constant $1.380 \cdot 10^{-23} \text{ J K}^{-1}$
K_a	activity equilibrium constant
n_n	moles of component n
MW	molecular weight
N_A	Avogadro's number 6.022×10^{23}
p_M	partial pressure of metal species
p_M°	partial pressure of metal species at its standard state
p	partial pressure
p°	partial pressure of pure substance at its standard state
Q_r	total heat
R	ideal gas constant $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
S	Entropy
T	temperature in K
V	Volume
x_n	mole fraction of component n
z	coordination number
γ	activity coefficient
γ_M°	activity coefficient of metal species M at infinite dilution
γ_{nB}	activity coefficient parameter B for n component
γ_{nC}	activity coefficient parameter C for n component
γ_{nD}	activity coefficient parameter D for n component
δ	partial derivative
ΔG	Gibbs energy
ΔG_{excess}	Gibbs excess energy of mixing
ΔG_{mix}	Gibbs energy of mixing
ΔG_{ideal}	Gibbs ideal energy
ΔG_{expt}	Gibbs experimental energy
ϵ	bond energy
μ	chemical potential
μ°	chemical potential at its standard state
μ^{ideal}	ideal chemical potential
μ^{mix}	chemical potential of mixing
Φ_i	volatility coefficient
Ψ	proportionality constant

Ω number of configurations

2. The Equilibrium Constant, Oxidation, and Activity

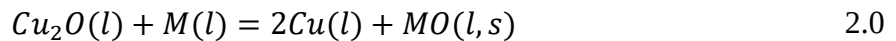
The recycling of copper-based alloys and the oxidation of its impurities can be understood by their equilibrium relationship (Equation 2.0), and products of the mole fraction concentrations of the reacting constituents (Equation 2.1), in a Cu-M melt where condensed and gaseous oxides are formed. Using these equations the values of the equilibrium constant K_a for each binary metal combination have been calculated at 1200 °C by Azakami and Yazawa (1976) with the accompanying Gibbs free energy of formation by this author (Table 1). These equations, and the resultant data from them given in Table 1, have been extensively measured, calculated, and reevaluated by scholars over the past several decades (e.g. Yazawa and Azakami (1969), Azakami and Yazawa (1976), Lu et al. (2012)). Leading up to and including the publication by Yazawa and Azakami (1969), constant improvements in analytical techniques have led to better representative data for binary copper-based alloys and the increased accuracy of these system's calculated component behaviors. In addition to the data compiled by Azakami and Yazawa (1976), select binary systems have been reevaluated and updated with newly determined activity coefficients for each component in infinitely dilute solutions at 1250 °C by Lu *et al.* (2012). Data from all three sources have been combined and are shown in Table 1. Comparably, the activity values from these sources, although calculated at slightly different temperatures, are similar, corroborating those calculated previously by Azakami and Yazawa. Their data have been used extensively throughout this thesis to produce all tables and diagrams. It should be noted that their results and methodological approaches, although directed towards the modernization and optimization of modern metal smelting and recycling, are fully applicable to the interpretation of ancient pyrometallurgical processes.

As pointed out by Yazawa and Azakami (1969), and as a general rule common to each study, increasingly larger values of K_a , from Au – Ca (Table 1), indicate the increased ease of the solute forming oxides at equilibrium. However, despite many of the components having K_a values less than Cu, the Cu will not be completely reduced regardless of the hierarchy given in Table 1 since the melt is saturated with oxygen and too little solute exists. In Equation 2.0, the activity and concentrations of the products in the numerator, and reactants in the denominator, at a given temperature, are expressed by Equation 2.1. Equation 2.1 represents the rate of a reaction in terms of the proportion of mole concentration of reactants at equilibrium. The activity is the result of the interaction of ions or molecules with other different ions and molecules, and is dependent on temperature, pressure, and composition. It is directly related to the activity coefficient in non-ideal solutions, and represents, numerically, the tendency of ions or molecules to escape a system. It is from the activity, the number that explains the interaction of components in a defined system, that one can model aspects of recycling and fire refining.

The equation for the constant K_a uses the measured activity, as denoted by the subscript a to provide a value that can roughly indicate the limit of element removal by oxidation and subsequent volatilization. This value can be converted to the Gibbs free energy of formation, and is listed alongside the equilibrium constant in Table 1 for each element in infinite dilution in a copper melt. In archaeometallurgical studies the Ellingham diagram has served a similar purpose as K_a by providing an easily read graphic representation of the Gibbs free energy of formation, unfortunately it has often been misconstrued since the diagram is only meant to be used to explain the oxidation of a single element in isolation with oxygen. In ancient alloys, in binary and multi-component systems, however, where the metal contained considerable amounts of impurities, the activity of each metal component in solution must be calculated to determine the stability of the solute and their ability to form

oxides. This is true for all solutes, except in the case of noble metals that do not form stable oxides in molten copper. The Ellingham diagram is nevertheless extremely useful, and is discussed in more detail throughout this thesis. For now, it is enough to say that the standard state energy lines of formation shown in the Ellingham diagram are subject to change, which rotate counterclockwise around $T = 0$ when the activity is not equal to 1.

Returning now to the equilibrium constant, it serves an additional purpose whereby $K_a \ll 1$ indicates that the system favors the reactants, and $K_a \gg 1$, the products. In the context of this thesis the products are the oxidized metals, and, as seen in Equation 2.1, indicate a shift to the right. It is with this fact in mind that a different approach to the interpretation of the chemistry of ancient artifacts was taken by leveraging first principles as they apply to ancient pyrometallurgy. Under the circumstances of oxygen saturation in a given molten system, in this case an ancient furnace, only Au and Ag have a lower equilibrium constant than copper (1). These values indicate that neither element would have been lost as a volatile oxide in an ancient furnace at any temperature, but this fact does not preclude their loss as pure species.



$$K_a = \frac{a_{Cu}^2 \cdot a_{MO}}{a_{Cu_2O} \cdot a_M} \quad 2.1$$

Table 1 ² : Oxidation, Equilibrium Constants, and the Gibbs free Energy of Formation					
Element	K_a 1200 °C	ΔG_f° 1200 °C	γ_M° 1200 °C	γ_M^* 1250 °C	p_M° (atm) 1200 °C
Au	$1.2 \cdot 10^{-7}$	195,158	0.14	0.135	$4.9 \cdot 10^{-7}$

² Partially reproduced from Azakami and Yazawa (1976) and Lu *et al.* (2012); *activity coefficient values at 1250 °C from Lu *et al.* (2012); **total vapor pressure of species (e.g. $p_{Sb} + p_{Sb_2} + p_{Sb_4}$)

Hg	$2.5 \cdot 10^{-5}$	129,772			$5.2 \cdot 10^2$
Ag	$3.5 \cdot 10^{-5}$	125,651	4.8	2.705	$2.2 \cdot 10^{-4}$
Pt	$5.2 \cdot 10^{-5}$	120,803	0.05	0.00317	$6.4 \cdot 10^{-13}$
Pd	$6.2 \cdot 10^{-4}$	90,450	0.06	0.0302	$8.5 \cdot 10^{-7}$
Se	$5.6 \cdot 10^{-4}$	91,696	0.002		69
Tl	$1.7 \cdot 10^{-3}$	78,997	8.9	0.594	$1.1 \cdot 10^{-1}$
Te**	$7.7 \cdot 10^{-2}$	31,399	0.033		3.9
Bi**	0.64	5465	2.7	2.566	$4.2 \cdot 10^{-2}$
Cu	1.0	0	1		$4.5 \cdot 10^{-6}$
Pb	3.8	-16,349	5.7	7.08	$1.9 \cdot 10^{-2}$
Ga	5.7	-21,314	0.04		$1.4 \cdot 10^{-4}$
Ni	25	-39,410	2.22	2.93	$2.8 \cdot 10^{-8}$
Cd	31	-42,054	0.73		32
Sb**	50	-47,908	0.013	0.0399	$7.9 \cdot 10^{-2}$
As**	50	-47,908	0.0005	0.0015	$5.0 \cdot 10^2$
Co	$1.4 \cdot 10^2$	-60,517	15.4	9.53	$3.2 \cdot 10^{-8}$
Ge	$3.2 \cdot 10^2$	-70,641	0.02		$4.2 \cdot 10^{-7}$
Sn	$4.4 \cdot 10^2$	-74,541	0.11	0.0741	$6.5 \cdot 10^{-6}$
In	$8.2 \cdot 10^2$	-82,165	0.32		$8.1 \cdot 10^{-4}$
Fe	$4.5 \cdot 10^3$	-103,016	19.5		$7.8 \cdot 10^{-8}$
Zn	$4.7 \cdot 10^4$	-131,747	0.11	0.149	10
Na	$1.1 \cdot 10^5$	-142,161			8.7
Cr	$5.2 \cdot 10^6$	-189,382	43	13.13	$3.2 \cdot 10^{-7}$
Mn	$3.5 \cdot 10^7$	-212,733	0.51	0.235	$9.3 \cdot 10^{-4}$
Si	$5.6 \cdot 10^8$	-246,687	0.006	0.00155	$1.0 \cdot 10^{-6}$
Ti	$5.8 \cdot 10^9$	-275,316		0.594	$6.3 \cdot 10^{-10}$
Al	$8.8 \cdot 10^{11}$	-336,818	0.0028	0.0019	$1.3 \cdot 10^{-5}$
Ba	$3.3 \cdot 10^{12}$	-353,005			$6.3 \cdot 10^{-2}$
Mg	$1.4 \cdot 10^{13}$	-370,703	0.044		2.1
Be	$5.4 \cdot 10^{13}$	-387,235			$9.5 \cdot 10^{-6}$
Ca	$4.3 \cdot 10^{14}$	-412,644	0.0005		$1.3 \cdot 10^{-1}$

2.1 The Equilibrium Constant, Oxidation, and Activity

Using the activity values for metals a_{MO} and a_M , which are the activities of each component as either an oxide or pure metal in the melt, Azakami and Yazawa (1976) calculated the equilibrium constant for each solute. The value of K_a , at a controlled temperature of 1200 °C and constant pressure, was then arranged in Table 1 for dilute solutions in ascending order. Those elements with large values of K_a are more easily oxidized, and may then be volatilized. However, no matter how large K_a becomes, trace amounts of these elements can still exist in processed copper as nonmetallic inclusions, in nonmetallic states, including oxides and sulfides, even after multiple re-melting processes (Yazawa and Azakami, 1969). The behavior of elements residing in the middle of Table 1, from Bi – In, and to a lesser extent the entire list, require further interpretation, since in practice their removal is not comprehensively explained by their activity to copper, oxygen, and the arranged order of their equilibrium constants. An in depth explanation of the behavior of these elements, as well as insight into their perpetuation through metallurgical processing, is provided in detail in subsequent chapters. Briefly explained here, however, not all oxides are volatile, but often may become so due to reduction. All oxides, as well as all pure elements, are also subject to mass transport restrictions (e.g. surface area, and oxide and other slag forming layers) at the liquid-gas interface. And finally, the interaction of components to both the melt and each other will alter their behavior and influence oxide formation and potential loss by volatilization. These points are important to consider in understanding the compositional changes that would have occurred in repeatedly melted ancient copper-based alloys.

In order to better understand Equation 2.1, and its relationship to Table 1, some modification to it is required, substituting in Equation 2.2 for activity and assuming that the

activity of copper is 1 (Equation 2.3). In Equation 2.1, the ratio $\frac{a_{Cu}^2}{a_{Cu_2O}}$ is assumed to be equal to unity for systems that are saturated with dissolved oxygen in the melt (Azakami and Yazawa, 1976). The assumption that the activity of copper is equal to 1, simplifies the later discussed systems by providing a common basis for all components where copper is the solvent. In Equation 2.2, the activity of the solvent a_M is determined empirically at infinite dilution and, the activity coefficient in a binary Cu-M melt can be defined by Equation 2.3 where a_M is the activity and x_M the mole fraction.

At infinite dilution activity is equal to its concentration, and the activity coefficient can therefore be easily determined for the pure component x_{MO} -that is the solute metal oxide- in a copper melt binary system. Understanding the role of the activity coefficient is important since its behavior, and most importantly the calculations and results given in Table 1, will remain constant. It is important to note, however, that at higher concentrations of solute, the activity coefficient is no longer constant and varies with composition.

$$a_M = \gamma_M^\circ x_M \quad 2.2$$

$$K_a = \frac{a_{MO}}{a_M} = \frac{\gamma_{MO}^\circ \cdot x_{MO}}{\gamma_M^\circ \cdot x_M} \quad 2.3$$

Equation 2.2 is well known in chemical metallurgy, and related disciplines, as Henry's Law, and holds true for dilute solutions. The usefulness of Henry's Law for binary systems is, however, limited to low concentrations of solute where it describes the behavior of a component devoid of other influencing factors. However, where Henry's Law is no longer valid due to increased component concentrations, Raoult's Law –discussed in the following section– can better represent the behavior of components in a system. Since Henry's Law is valid for low concentrations of

solutes, where the activity coefficient remains unchanged with respect to unlike ion and molecule interactions, it is typically shown graphically as a straight line with a positive slope.

The activity coefficient is essential to understanding the coexistence between solvent and solute(s) in a copper melt, and is a numeric representation of the bond intimacy between elements. The activity coefficient, and compositional variation accounted for by activity, are also inferred by the enthalpy of mixing H_{mix} as it relates to temperature, entropy ΔS_{mix} , and Gibbs free energy of mixing ΔG_{mix} (Equation 2.4). The entropy of mixing is negative when bonds between unlike atoms are favored, and positive for like-like ones.

$$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$$

Similarly, the activity indicates the degree to which one atom prefers the same or different atoms, and in rudimentary terms the higher its value the more likely an element will be volatilized from the melt. The activity of a component indicates how its behavior deviates from ideality, the properties of elements within simple and complex systems, and the formation of metallic networks. Furthermore, at ideality there is no enthalpy of mixing. Values for the activity coefficient of solutes γ_M° in a copper melt, focusing on those that are relevant to ancient metallurgy, are given at 1200 and 1250 °C in Table 1 and discussed individually in Chapter 3.

Building on the equilibrium constant and activity from Equations 2.2 and 2.3, the activity can also be understood through its relationship to the chemical potential of the system (Equation 2.5), which is also directly related to the Gibbs free energy of mixing where $\Delta\mu_M = \Delta G_M^{mix}$. Furthermore, since activity is a ratio of the measured pressure of a component at its standard state, the change in chemical potential may be rewritten as Equation 2.6. The

relationship of the activity to partial pressure is seen in the rightmost terms of both Equations 2.5 and 2.6. From these equations one can see that the chemical potential can be used to define the partial pressure of components. Further, from Equations 2.1 and 2.3, that the values for K_a are based on both the mole fraction concentrations of reactants, and calculated values of γ_M° for binary Cu-M alloys.

$$\mu_M - \mu_M^\circ = \Delta\mu_M = RT\ln \gamma_M + RT\ln x_M = RT\ln a_M \quad 2.5$$

$$RT\ln a_M = RT\ln \left(\frac{p}{p^\circ} \right) \quad 2.6$$

In addition to the interaction of copper with secondary components, the chemical potential of oxygen must also be considered. The reduction of metal from its oxide, and conversely oxidation, in metal recycling is extremely important since it contributes to the loss of components as pure species and/or oxides. The reduction reaction between metal atoms must have a lower activity than that for oxygen to proceed, and for the loss of impurities through their preferential oxidation it must be higher. Equation 2.7 can be used to calculate the oxygen potential where $\mu_{O_2}^\circ$ is zero in an ideal gas and $a_{O_2} = p_{O_2}$, resulting in Equation 2.8.

$$\mu_{O_2} = \mu_{O_2}^\circ + RT\ln a_{O_2} = \mu_{O_2}^\circ + RT\ln p_{O_2} \quad 2.7$$

$$\mu_{O_2} = RT\ln p_{O_2} \quad 2.8$$

Although oxygen within the melt, and that partially contributed from the furnace atmosphere, are important considerations in understanding the volatilization of components from a copper melt, it should be noted that neither, for the most part, are responsible for the commonly high concentrations of oxygen found in artifacts. Oxygen in artifacts is largely the result of the casting process where exposure to air, and moisture in molds, results in rapid oxidation just before the metal freezes.

2.2 Activity and Vapor Pressure

Activity coefficients and equilibrium constants in dilute solutions are shown in Table 1 for impurities in Cu-M systems that are commonly found in copper bearing ores. These data also apply to the recycling of copper-based alloys. For the purposes of consistency and simplification, this thesis discusses and calculates each of these systems at 1200 °C and 1 atmosphere (atm). This temperature was chosen because it is more than 100 °C above the liquidus of copper, reducing complications caused by phase changes and the possible higher liquidus' of the considered element components and combinations. In most cases, for this thesis, the considered systems are completely molten and thus the calculations are simplified, but instances of non-liquid phases do exist and are noted in each instance. Furthermore, the standard temperature of 1200 °C is also similar to that likely reached and sustained in ancient furnaces. Merkel (1983), in a reconstructed furnace design from Late Bronze Age Timna, however, noted a maximum of 1400 °C with a cooler center around 1300 °C. Nevertheless, the chosen standard temperature well represents the behavior of elements despite these reported temperature variations. For comparison, however, additional temperature variation data are included and discussed in order to exemplify the influence of temperature on activity, and to show how it alters element behavior and interpretation. The pressure in the considered binary systems in this thesis is 1 atm, which was likely little altered by any significant amount by ancient pyrometallurgists. Furthermore, when experimental data were unavailable at 1200 °C, or lacked multiple temperature variations, the data were extrapolated to several logical step-wise temperature increments using known thermodynamic relationships. These increments aid in demonstrating the change in element behavior interactions, and are especially important when one considers the likely lack of precise temperature control in ancient furnaces. All binary and ternary activity diagrams discussed in

later chapters were constructed using the below defined equations at the standardized temperature.

The behavioral loss of impurities during fire refining, according to Yazawa and Azakami (1969) in the above defined conditions, is best facilitated by small values of the activity coefficient of copper and oxygen, and large values of the activity coefficient of impurities and K_a . A smaller mole fraction of copper metal and oxygen is also helpful. The smaller the value of γ_M° , the higher the affinity of the components to the bulk copper melt. Conversely, unchanged concentrations of secondary components is facilitated by small values of K_a , large γ_{MO} or x_{MO} , or small γ_M° . The activity coefficient, when less than 1, shows what is known as negative deviation from the ideal behavior of Raoult's law, implying increased intimacy of bonds and thus stability between unlike species. Another explanation of this phenomenon is that when the vapor pressure of the component is lower than ideality, and attraction of unlike species is higher, its tendency to escape is lower than in its pure state. A component's vapor pressure and ability to escape is especially important in regard to the formation of volatile elemental species and oxides. The volatilization of elements from a binary copper melt are discussed in Chapter 4.

On the other hand, a value of γ_M greater than 1 indicates positive deviation and immiscibility, which implies increased volatility of a component and decreased affinity to unlike atoms in the solution. Solutions that exhibit positive deviation are also known as segregating systems, and may result in phase separations or compound formations and have positive values of the excess Gibbs energy of mixing. Similarly, negatively deviating systems, with negative excess Gibbs energy of mixing, indicate solution stability. The tendency for components to escape are therefore higher than in the pure state. Furthermore, since activity is a measure of pressure, where $a_M = \frac{p_M}{p_M^\circ}$ in an ideal solution, negative and

positive deviations indicate a change in evaporation rates. In summation, negative and positive deviations occur when above and below unity, respectively, and can be summarized as stronger or weaker binding intimacies, and negative and positive Gibbs energy of mixing, between unlike ions and molecules.

Raoult's law is indispensable in the study of ion interactions and describes how the vapor pressure in an ideal solution is dependent on the total chemical and mole fraction components. At unity the law states that the activity of the system is at equilibrium. In an ideal solution, where each of its component's act independently, Raoult's law is expressed by Equations 2.9 and 2.10 between two components.

$$p_M^\circ - \frac{p_M}{p_M^\circ} = x_M \quad 2.9$$

$$p_M = p_M^\circ \cdot x_M \quad 2.10$$

However, in non-ideal solutions the activity coefficient must be included to account for differences in the molecular sizes of atoms, and since $a_M \neq x_M$, Equation 2.10 is rewritten substituting in the activity for the mole fraction (Equation 2.11). Since Equation 2.11 is written in terms of vapor pressure, it is useful in determining the activity of non-volatile components. In relation to the chemical potential, a positive deviation behaves as if the solution contains a higher concentration than indicated by its mole fraction. Accordingly, an activity coefficient greater than 1 indicates increased chemical potential. Conversely, negative deviation with activity lower than 1, shows a chemical potential that is lower than its composition. Substituting Equation 2.2 into 2.11 for the activity, it is then possible to calculate the activity and activity coefficient for a component when their vapor pressures and mole fractions are known (Equation 2.12).

$$p_M = p_M^\circ a_M \quad 2.11$$

$$p_M = p_M^\circ \gamma_M x_M \quad 2.12$$

Finally, the activity of an element can be calculated for non-ideal solutions using the following; Equation 2.11 for monatomic, and for multiple species of a component M (e.g. As, Bi, and Sb), and Equation 2.13, which can be simplified to $a_{Mi} = \left(\frac{p_{Mn}}{p_{Mn}^\circ}\right)^{\frac{1}{n}}$ where p_M is the partial pressure of species M , and p_M° the standard state.

$$a_M = \left(\frac{P_{M_4}}{P_{M_4}^\circ}\right)^{\frac{1}{4}} = \left(\frac{P_{M_3}}{P_{M_3}^\circ}\right)^{\frac{1}{3}} = \left(\frac{P_{M_2}}{P_{M_2}^\circ}\right)^{\frac{1}{2}} = \left(\frac{P_M}{P_M^\circ}\right) \quad 2.13$$

For equal mole fractions of solute found in association with copper, and in molten copper Cu-M binary solutions and constant a_{MO} , Yazawa and Azakami (1969), using the relationship found in Equation 2.3, established the following order for the increasing tendency of impurities to oxidize in a predominantly copper melt binary system. For elements commonly found in ancient copper alloy objects, this list can be shortened to the following; Au, Ag, As, Sb, Cu, Bi, Pb, Sn, Ni, Co, Zn, Fe, Mn, Ca. In most cases the higher the value of K_a and the lower γ_{MO} , and the more stable its oxide form the more likely, for values greater than 1, that the reaction is irreversible and complete. Values much less than 1 would conversely indicate a reduction in reaction potential, and the possibility of reaction reversibility. In the above list it is important to note that under the defined conditions the mole fraction of each component, being dilute, plays the primary role in determining the equilibrium constant as interaction is strictly between the component and the bulk copper melt. In a binary system there is no solute-solute interaction to consider. The value of a_{MO} , being set to unity, is done in order to describe the system from the baseline primary component, copper.

$$K_a \gamma_M^\circ = \frac{a_{MO}}{x_M} \quad 2.14$$

From the above list of oxidization tendencies, one notices that the order of oxidation does not necessarily follow the values of K_a nor γ_M° as listed in Table 1. The reason for each element's inconsistency from the expected order is explained in greater detail in the following Chapters 3 and 4. Briefly, however, Equation 2.14 considers the activity coefficient, and for a larger $K_a \cdot \gamma_M^\circ$ and constant a_{MO} the order of oxidation listed above is valid. The equation describes, ideally, the formation of oxides in the melt, but does not indicate their respective volatility. In this instance, although it can change with composition while other conditions remain constant, both oxide stability and bond affinity are relevant and necessary in calculating the interaction and loss of several coexisting elements from a copper melt.

Lastly, one should consider the effects of slag skimming that can reduce the value of N_{MO} in Equation 2.2. For instance, flux silica can be used to remove lead, and the addition of soda ash Na_2CO_3 or lime $CaCO_3$ will remove As, Sb, Sn, and Pb and decrease the value of γ_{MO} (Azakami and Yazawa, 1976). These factors are important to consider in relation to modern metal refining, but whether ancient metalsmiths used similar techniques, perhaps inadvertently, is unknown. The effects of slags on volatility, however, is not discussed here as they are more appropriate for primary smelting than recycling.

2.3 Gibbs free energy of Formation and Oxidation

In a multicomponent melt the interaction of elements with one another, including oxygen and sulfur, can be extremely complex, which can dramatically alter the outcome of refining processes. To explain these influences as they relate to the chemical composition of artifacts, archaeometallurgists have often referred to the oxide formation approximations given by the Ellingham diagram. This diagram has several forms and provides a simplistic

view of the standard free energy versus temperature for the interaction of elements with one mole of oxygen. However, according to the above defined factors that influence the interaction of elements with one another, one can see that the Ellingham diagram has limitation applications. The diagram can only account for the formation of pure metal oxides in their standard states, and is therefore inappropriate for ancient metals. It provides a rough guide to the order and energies of oxidation, and thus is only rudimentarily related to changes due to recycling in artifact chemistry. The values of ΔG_f° provided in Table 1 have been calculated based on the activity of each binary system using Equation 2.15, resulting in a noticeable difference from the standard state of components given in the Ellingham diagram. Adjustments to the Gibbs free energy, with these binary interactions in mind under non-standard states, are made with the aid of the activity quotient, the last term, in Equation 2.16 where the species of the products are A and B, and reactants M and N, at given stoichiometric moles a, b, m, n.

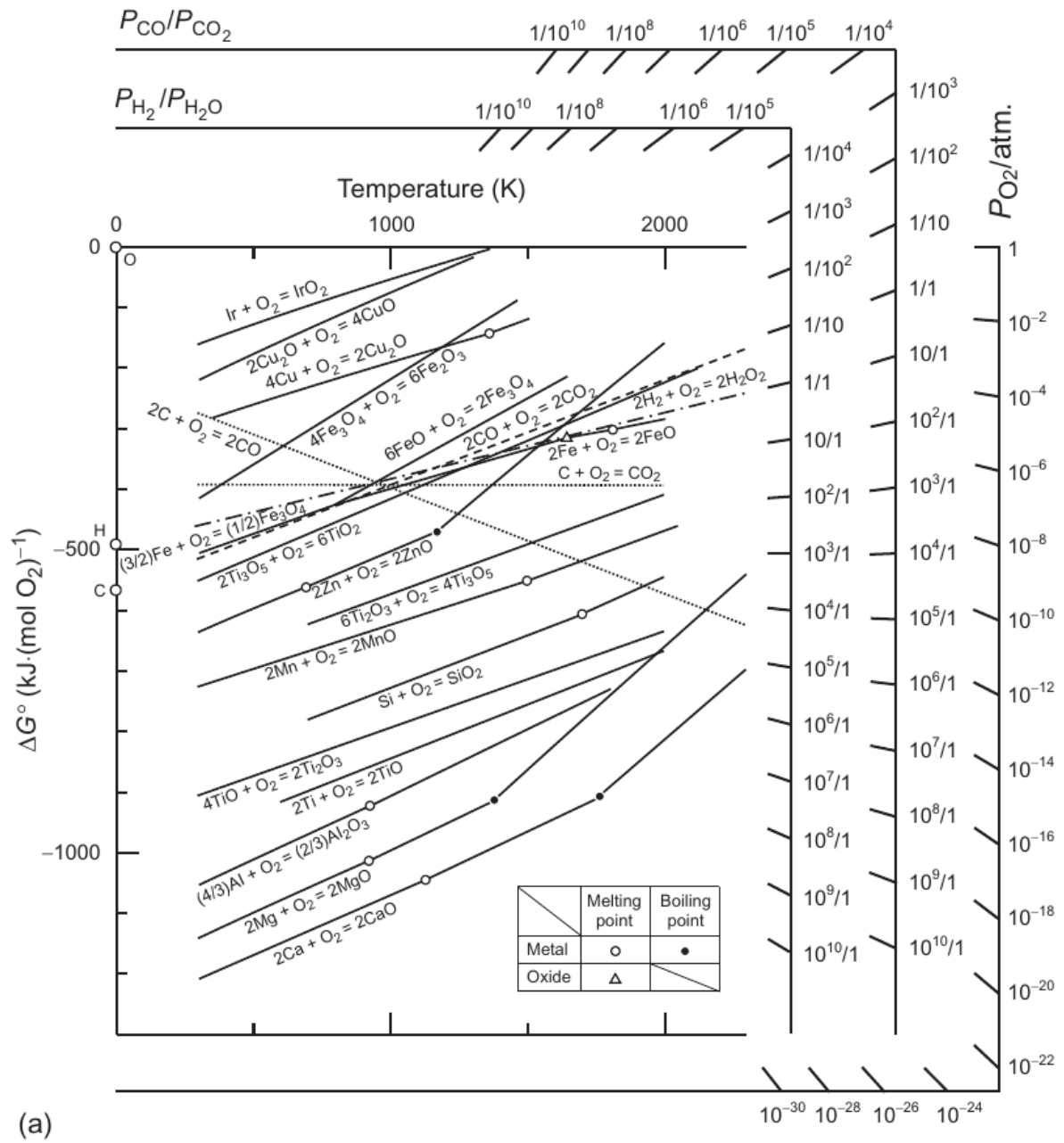
$$\Delta G = \Delta G_f^\circ + RT \ln(a_{MO}) \quad 2.15$$

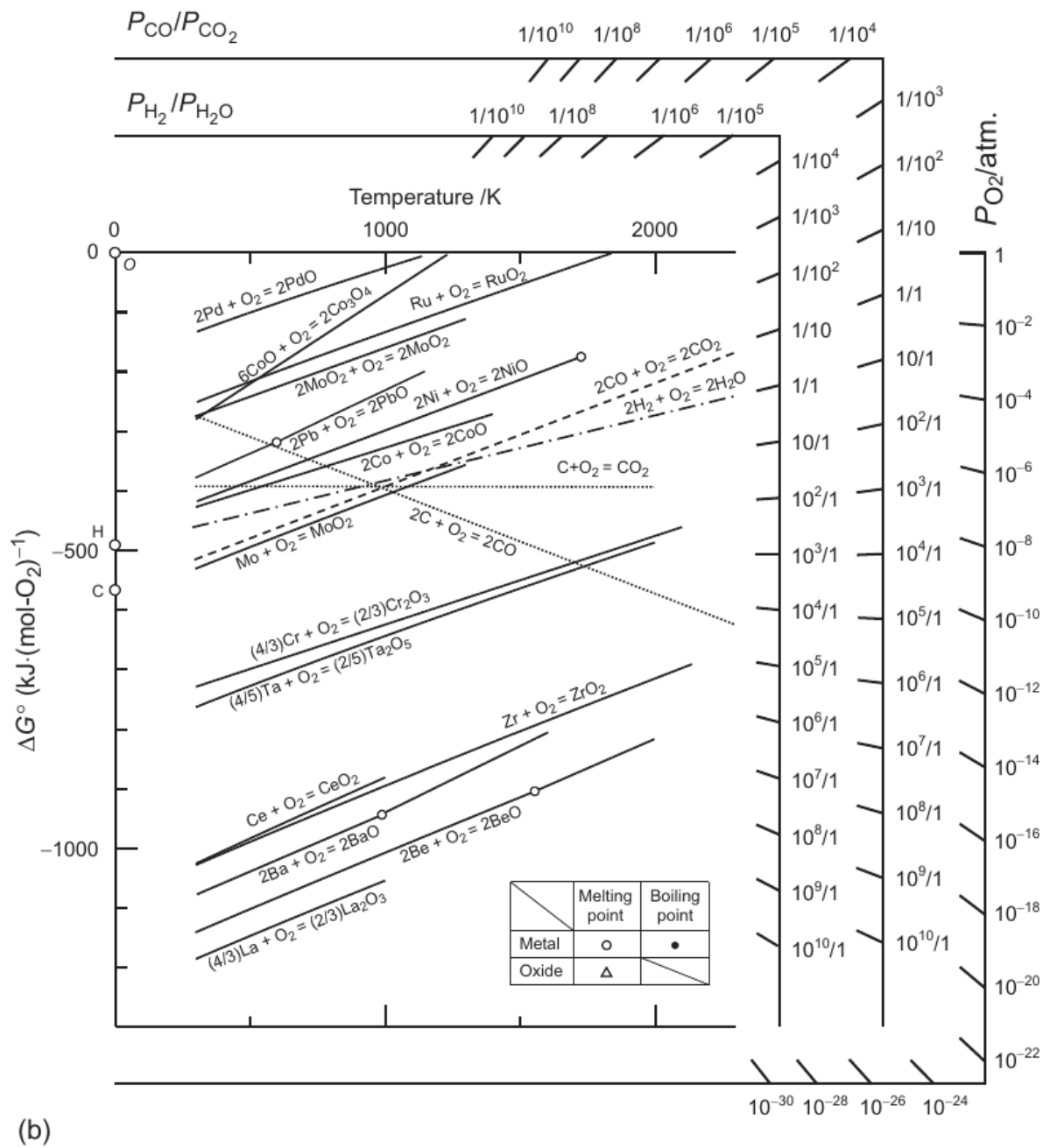
$$\Delta G = \Delta G_f^\circ + RT \ln \left(\frac{a_M^m a_N^n}{a_A^a a_B^b} \right) \quad 2.16$$

$$\Delta G_f^\circ = \Delta H^\circ - T \Delta S^\circ \quad 2.17$$

As can be seen in Figures 1a and 1b, the slope of the line at standard state conditions increases when the entropy ΔS° decreases (Equation 2.17). The more negative the entropy change, in this exothermic reaction, the steeper the slope, which is equal to $-(-\Delta G^\circ)$. Entropy change is negative because the gas volume decreases when the oxygen is used. The sudden changes in slope occur at points such as sublimation, melting, and boiling of the oxide, and are all allotropic transformations. The change in Gibbs free energy, where ΔH° is the change in enthalpy, and ΔS° , entropy, may also be used to predict the direction of a

reaction (e.g. Equation 2.0). If $\Delta G < 0$ the reaction proceeds to the right, if > 0 to the left, and if equal to 0 the reaction is at equilibrium and neither side of the equation will change.





FIGURES 1A AND 1B: ELLINGHAM DIAGRAM (SOURCE: SEETHARAMAN ET AL., 2014, 508-9)

Temperature influences the activity coefficients, vapor pressures, and, consequently, the equilibrium constant, K . The relationship between temperature at equilibrium, combining the ratio from Equation 2.3, can be expressed according to the Van't Hoff isotherm (Equation 2.18). At constant temperature, the Gibbs free energy of formation can be rewritten as Equation 2.18, and K calculated by rearranging its terms (Equation 2.19). What one should note from

these two equations is the dependence of the equilibrium constant on temperature, which is why several temperatures are compared in the activity diagrams in Chapter 3. Another important factor to consider is that oxidation, according to the findings by Takeda *et al.* (1983), decreases in exothermic reactions with increasing temperatures; the implications being that some elements are less likely to oxidize at higher temperatures, especially those approaching unity.

$$\Delta G^{\circ} = -RT \ln K \quad 2.18$$

$$K = e^{\frac{-\Delta G^{\circ}}{RT}} \quad 2.19$$

The separation of each line of oxide formation (Equation 2.20) in the Ellingham diagram is in fact a measure of energy whereby the oxides below are favored over the ones above. This is also true for the reduction caused by the negative slope of carbon and hydrogen (e.g. Equation 2.21). The bond type formed by metals to oxygen are generally strongly ionic compared to the weak attractive forces between unlike metal ions and molecules. In theory this means that those elements with more negative ΔG° (i.e. those below) can reduce the oxides of those above. In addition, metals themselves may be used as reducing agents, and in ancient pyrometallurgy may have included calcium and magnesium oxides. Disregarding activity, the stability of the oxides can be used to roughly predict the order of oxidation of components in a copper melt. The degree to which these predictions are correct, however, is dictated by the composition and the combined interaction of all components.



Oxidation takes place at both the surface and within the melt, and seems to occur at particular thresholds for individual elements and their species. Shibata *et al.* (1999) reported on the rate of element loss by oxidation of zinc, tin, and lead, and found that the loss of lead was delayed until the removal of both zinc and tin from copper. The ordered loss of these elements follows both the Ellingham diagram as well as the values of K from Table 1, and noticeably both zinc and tin have more negative free energy than lead. It was further shown that only when the oxygen concentration in the copper melt reached a critical point did the oxidation of lead begin, even after the loss of other metals. Component metals, having an oxidative range dependent on temperature, suggests that the zinc and tin acted as deoxidizers, removing enough oxygen as volatile molecules to delay the loss of oxidized lead.

Until now the role of oxygen and its partial pressure has only been addressed tangentially to the interpretation of molten copper and component metals. The following is a discussion of how the Ellingham diagram relates to the partial pressure of oxygen and the volatility of oxides. The free energy of a component is a function of its temperature, the gas constant, oxygen partial pressure, and concentration. Using Equation 2.22, the value of K_p , similar to Equation 2.19, is substituted using the relationship at equilibrium for pure metal and oxide at unity (Equation 2.23). This simple equilibrium equation for pure metals is governed by the value of p_{O_2} , which is called the dissociation pressure. Since the activity is unity, the equilibrium is simply equal to the limit of the stability of the oxide at the given oxygen partial pressure. The Gibbs free energy of formation may therefore be expressed in terms of the equilibrium constant (Equation 2.23), and for this reason the value of K_p directly indicates oxide stability at a given temperature. The stability of the oxide at a given temperature and Gibbs free energy of formation can be determined by drawing a line from the origin to the nomographic scale on the rightmost side of Figures 1a and 1b. If the oxygen partial pressure is greater than the equilibrium constant at the crossing the metal will oxidize,

and if lesser it will be reduced. The stability of these oxides are especially important to consider in relation to their volatilization, and are discussed in Chapter 4. One must be aware that not all oxides are volatile, and that their loss from a copper melt may require additional processes and conditions.

$$K_p = \frac{1}{p_{O_2}} \quad 2.22$$

$$\Delta G^\circ = RT \ln p_{O_2} \quad 2.23$$

The formation of oxides at 1200 °C in a copper melt, from the combination of either condensed liquid or solid phases and dissolved oxygen gas, can be read directly from the Ellingham diagram. The phases formed, however, may differ depending on the metal reactants. For instance, manganese oxidizes according to the reaction $2Mn(solid) + O_2(gas) = 2MnO(solid)$, resulting in a solid oxide. Zinc, on the other hand, reacts with oxygen $2Zn(liquid) + O_2(gas) = 2ZnO(gas)$ to form a gas oxide. Noticeably, not all data for the formation of oxides with the components discussed in this thesis are given in Figures 1a and 1b. These missing data are often not included, or not available, in commonly produced representations of the Ellingham diagram. These missing data are, however, discussed in Chapter 4 in relation to the available empirical evidence for the volatility of each oxide compound.

2.4 The Gibbs-Duhem Relationship for Binary Systems

To determine the activity of each component, Azakami and Yazawa (1976) used three methods to measure the partial pressure of the metal vapor in each Cu-M binary systems. The choice of using multiple methods circumvented technical issues in measuring very low and high vapor pressures of some elements, and apparatus that caused conflict by forming species unrelated to the analyses. Having chosen suitable techniques, as described in the previous

sections, the activity was then calculated using the relationship of the vapor pressure of the pure components, the components in the melt, and their respective compositions. The data they collected agreed well with previous studies, however, determining the activity of low concentrations of arsenic proved to be especially difficult due to the lack of a fixed integration constant. Later research methodologies remedied this issue and are discussed below along with additional reevaluations of the activity of each binary Cu-M systems.

For Cu-Pb, Cu-Bi, Cu-Sb, and Cu-Zn the transportation method was used, and the pressure of component M was calculated using Equations 2.2 and 2.6. To attain the simultaneous activity of copper in these binary systems, the activity of component M was used to calculate the activity of copper with the Gibbs-Duhem integration (Equation 2.24). The relationship in Equation 2.24 is necessary for binary systems where the measurement of a component is unreliable, but also serves as a dependable means to quickly obtain activity data for both components.

$$\ln a_{M_2} = - \int_1^{x_{M_2}} \frac{x_{M_1}}{x_{M_2}} d \ln a_{M_1} \quad 2.24$$

In a similar fashion, using a variant of Equation 2.24, it is possible to replace the activity on both sides with the activity coefficient, which can then be used to calculate the activity using Equation 2.2 for values of the secondary component. This was the method utilized by Azakami and Yazawa (1976) to calculate the activity of copper since it does not result in infinite values as a_{M_1} approaches zero. To prevent values at the opposite extreme, at negative infinity, as a_{M_1} approaches one, on the other hand, this author applied Darken's alpha function 2.25, which gives finite results nearing both zero and one. The Gibbs-Duhem integration can be altered to accommodate the alpha function by replacing the activity coefficient, and the product of the alpha function and mole fractions on the right side of the

equation. Equation 2.26, being more accurate and precise, was applied to all binary systems studied in this thesis.

$$\alpha_i = \frac{\ln \gamma_i}{(1 - x_i)^2} \quad 2.25$$

$$\ln \gamma_1 = -\alpha_2 x_{M_1} x_{M_2} - \int_1^{x_{M_2}} \alpha_2 dx_1 \quad 2.26$$

The graphic representation of activity, based on Equations 2.24 – 2.26, in binary systems is plotted in mole fractions against ideality, and is temperature dependent. Lines are drawn from either corner of an activity diagram, where $N_M = 0$ and $N_{Cu} = 0$, to the opposite adjoining corners. A straight line crosshatched between each corner indicates the ideal behavior of the system, and the lever rule is applied to reading the diagram. These diagrams are shown and discussed in the following Chapters.

Due to the lower vapor pressures of silver and tin, Azakami and Yazawa (1976) measured them using the Knudsen effusion method. For pure silver and tin, and their alloys with copper, Equation 2.27 was used where G_M is the effused quantity of M over unit time, M_M is the molecular weight of component M , and k the correction factor known as the Clausing factor. The Clausing factor is determined by the radius and length of the effusion hole by which pressure in the system is measured. The accommodation coefficient, α (not to be confused with the alpha function), is the fraction of colliding molecules through the hole, and A and B are the area of the hole and effective vaporization area, respectively. Once the vapor pressure is determined the activity can then be calculated using the values of G_M and G_M° , replacing p_M and p_M° in Equation 2.11.

$$p_M = \frac{G_M}{kA} \sqrt{\frac{2\pi RT}{M_M}} \left(1 + \frac{kA}{\alpha B}\right) \quad 2.27$$

For arsenic, however, Azakami and Yazawa (1976), using the E.M.F method, were unable to measure arsenic in low concentrations. This shortcoming was later rectified by the application of a double Knudsen cell and quadrupole mass spectrometer by Hino and Toguri (1986) at 1150 °C. Here, the vapor pressure of arsenic was measured by the ratio between known and unknown arsenic vapor intensities of the relatively stable species As₂(g) using Equation 2.28. For Cu-As, the vapor pressure measured by mass spectrometry is calculated using ion intensity. Hino and Toguri calculated the activity of arsenic below ten percent at three intervals, which were then combined with data from previous studies (Azakami and Yazawa, 1969; Azakami and Yazawa, 1976; Jones and Philipp, 1979; Jeffes *et al.*, 1984; Hino, 1985; 1995). What is clear from these studies is that pinpointing the activity of arsenic at infinite dilution is extremely difficult, and is reflected in the different value of the activity coefficient in each study. However, what has been established, despite a difference of several orders of magnitude between each study, is the extreme affinity of arsenic for copper at low concentrations (Pei, 1993; Chen *et al.*, 2010). With these differences in mind, it is worth nothing that Azakami and Yazawa (1969) did not account for As₃ that dissociates from As₄, an important consideration when one is measuring the overall pressure within a system. They had unfortunately not included the trimer equilibrium pressure in their calculations. Nevertheless, the equilibrium constant, which has been mentioned to reveal oxidative order, remains unchanged in its position in Table 1 since the trimer comprises a very small portion of the total vapor pressure of arsenic at temperatures above 1000 °C.

$$\log a_{As(unknown)} = \frac{1}{2} \ln \left[\frac{I_{As_2(unknown)}^+}{I_{As_2(known)}^+} \right] + \log a_{As(known)} \quad 2.28$$

2.5 Analytical Methods and Activity

In their study that measured activity using the Transportation Method, E.M.F (electromotive force), and Knudsen effusion cells, Yazawa and Azakami (1969), and Azakami and Yazawa (1976), compiled a complete list of elements and corresponding plotted activity data for impurities commonly found within copper. Electromotive force and Knudsen effusion are methods applied to the study of the partial vapor pressure of elements in high temperature solutions. Often one method is more suitable to detect a particular element than another for reasons such as the inability to accurately measure a component with very high or low partial pressure. The methodologies used to study the vapor pressure of metals were not conducted for this thesis, rather, data from these highly specialized studies were gathered from various databases and scientific journals and compared. Consequently, these methods will only be briefly described.

A Knudsen cell measures the component effusion, the partial vapor pressures, through an isothermal vessel (a crucible with a small opening). At equilibrium the vapor pressure of the escaping molecules can be calculated to determine activity. With the E.M.F method, an electrolytic cell is set up, under reversible conditions at constant temperature, that is designed to measure potential differences and thus the Gibbs free energy. The Gibbs free energy is then used to calculate activity. Lastly, the transportation method uses an inert gas that is passed over the molten metal until saturation of the metal vapor in the inert gas is at equilibrium. As the vapor migrates to a cooler part of the furnace, where it condenses, and by weighing the metal before and after the experiment, and knowing the flow rate of the inert gas, one can calculate the activity.

2.6 Summary

This chapter has outlined the knowledge necessary to understand the relationship between metallurgical thermodynamics and theory, and binary molten metal systems. It introduces, and explains the mathematical dependence of, the Gibbs free energy of formation, enthalpy of mixing, equilibrium constant, activity coefficient, and activity as they relate to temperature, pressure, and oxidative tendencies and behavior of copper binary molten systems. It furthermore details the measure of activity as it relates to the vapor pressure of a component in a binary system, showing that the composition causes dynamic changes in the behavior of each element. Together these concepts provide the foundation for the science and methods used to produce the models introduced later in this thesis. Later chapters provide and discuss the activity for each component as they relate to known alloys from antiquity by building upon the information and definitions from Chapters 1 and 2. The concepts discussed in this chapter are necessary to fully understand later ones.

3. Activity Diagrams for Binary Copper-Based Systems

Using the mathematical relationships described in Chapter 2, the affinities of each element for copper are calculated for binary activity diagrams, and shown with corresponding binary phase diagrams in the following sections. The activity diagrams, in agreement with the phase diagrams, are shown at compositions between 0 and 1 mole fractions for Cu-M systems that commonly appear in archaeological records and object analyses. Phases often correspond to the behavior of components in a system, and binary phase diagrams are shown for this reason; however, the diagrams are merely rough guides to behavior, not structure. The discussed systems include -in the order they are introduced-; Pb, Ag, Bi, Ni, Co, Fe, Sb, As, Sn, Zn, Au. From their activity, and supported by multiple intermetallic phases in their equilibrium phase diagrams, it is clear that several stable phases of Cu-As, Cu-Sn, and Cu-Sb exist, indicating their strong affinity for copper. Conversely, the phase diagrams for Cu-Ag and Cu-Pb show immiscibility, and too show repulsion in their respective activity diagrams. The former behaviors indicate difficulty in separating arsenic, tin, and antimony from copper due to their low activity coefficients in the metallic phase; and in the latter, the high activity coefficients and inability of lead to alloy with copper. The behavior of lead in the Cu-Pb binary is likely due to the formation of molecular lead that is thought to exist in high reducing environments, which coincides with an increase in its activity coefficient (Požega et al., 2010). In the activity diagrams below, each plot was created using a combination of published activity data and the thermodynamic relationships described in Chapter 2. Published tabulated activity data, or those garnered from diagrams, were plotted using the loess regression analysis function from the R-base statistical software package. This function allowed for the interpolation of data and curve fitting.

3.1 Positive Deviation Binary Systems

3.1.1 Lead

Important to note for the Cu-Pb system is that lead exists as unalloyed and segregated suspended globules in metallic copper having very low solubility in low concentrations, which is primarily due to the vast difference between the atomic radii and melting point of copper and lead. The segregation of lead in copper is of course important in the study of ancient metallurgy as leaded copper and bronzes are common. Lead is furthermore thought to have been added to copper to both lower its liquidus and increase fluidity during casting and pouring (e.g. Northover, 1988; Ottaway and Roberts, 2008), although it was likely added only to increase castability. The presence of lead is important for the interpretation of ancient recycling and re-melting practices as its addition was at first intentional in early aged leaded copper, and as such must be recognized as possibly being added at any point in the life history of the copper metal. Its composition may therefore fluctuate either positively or negatively due to additions of lead to increase castability, or due to mixing and refining losses, respectively. Copper scrap/objects known to contain lead may have also been mixed with copper resulting in low percentages of lead.

Important for the interpretation of recycling and re-melting of this commonly found archaeological metal, experiments designed to identify the activities of lead and copper show highly positive activity of lead approaching ideality with higher temperatures. High positive deviation indicates that an element prefers itself as a nearest neighbor repelling the unlike atoms of copper. Repulsion of this type aids in the components loss through its volatilization as pure lead, and in oxidative losses, being more available for oxidation at the liquid-gas interface. As the first activity diagram shown in this thesis, the Cu-Pb system serves as an example of positive

deviation from Raoult's law, suggesting the more likely loss of lead from the melt. It should be noted, however, that in every molten system discussed in this chapter the activity provides only a partial explanation of component behavior that is further elaborated upon in later chapters.

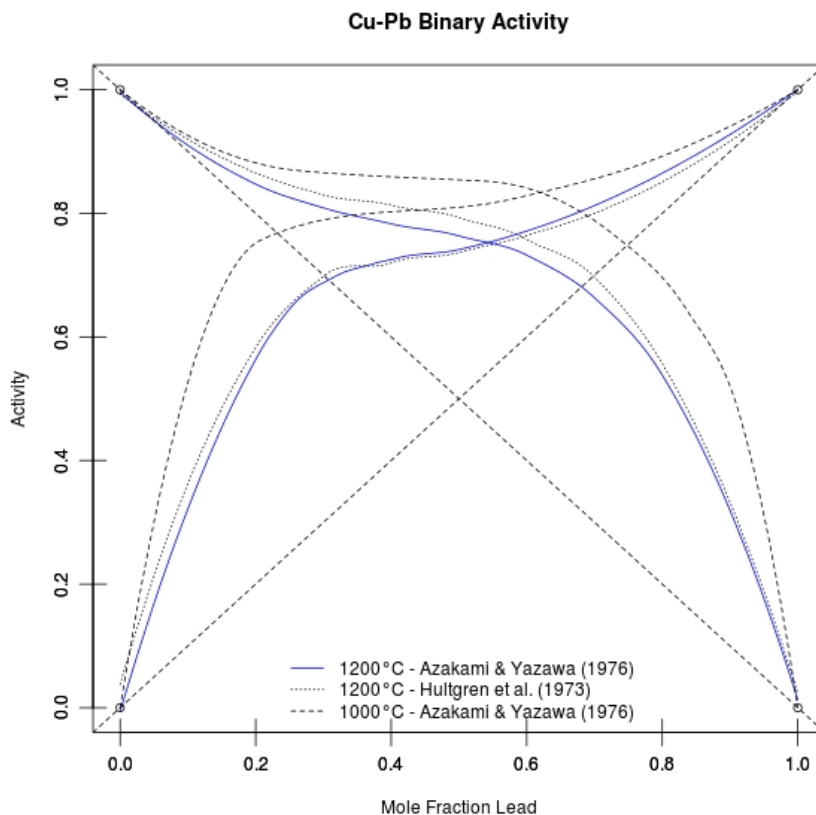


FIGURE 2: CU-PB BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Activity values from Azakami and Yazawa (1976) (Fig. 2) show that copper and lead are highly immiscible, and only approach ideality nearing high mole fraction N_M lead or copper. Similarly, compared to the Cu-Pb phase diagram (Fig. 3), which is mostly immiscible, at temperatures equivalent to those represented by the activity diagram only a liquid phase exists confirming the uniformity of their activity curves with increasing and decreasing mole fractions. In some systems the formation of phases can result in dramatic changes in component activity, however, for Cu-Pb no intermetallic compounds exist at the standardized temperature. Activity

measurements by Azakami and Yazawa (1976) at 1200 and 1000 °C indicate that at lower temperatures the activity of the Cu-Pb binary system increases, which in turn results in greater immiscibility and more segregation. The data are supported by Hultgren *et al.* (1973) and Choudary *et al.* (1977) in their study of the Cu-Pb-S ternary and Cu-Pb binary systems at 1200 °C. Under ancient furnace conditions the behavior of the binary would behave as observed by Merkel in reconstructed mid-12th century BCE furnaces from Timna (Merkel, 1983; 1990), and summarized by Pernicka (1999; 2004), in that lead would be lost while the copper left unchanged.

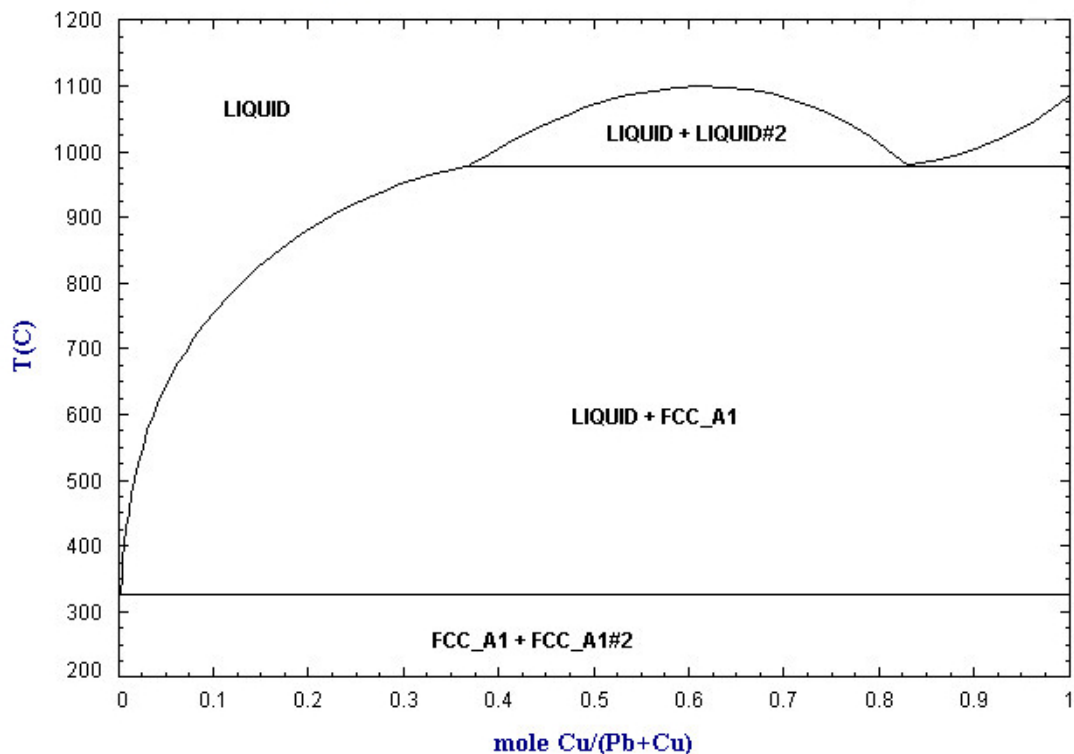


FIGURE 3: CU-PB BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://www.crtc.polymtl.ca/fact/))

3.1.2 Silver

Low percentages of silver are commonly found in copper artifacts having been unintentionally transferred from copper ores (Gale *et al.*, 1985), mixing and recycling of debased silver coinage (Caley, 1964), and additions of lead not refined by cupellation. They become enriched in the copper metal after smelting and can sometimes reach upwards of 1 wt% (Tylecote, 1970; Pernicka, 1999; 2004). Enrichment has been demonstrated by Merkel (1983) where an apparent gain in silver was observed after smelting and a single re-melt due to some losses of copper. Silver, unlike lead that improves castability, does not alter copper's working properties, however, the color of silver was desirable and achieved by means of adding arsenic in a process known as silvering (Eaton and McKerrell, 1979; Eaton, 1980; Lechtman, 1996).

Silver is, however, similar to lead thermodynamically in that it also shows high positive deviation approaching ideality with higher temperatures (Fig. 4), which has been confirmed by single and double Knudsen cell mass spectrometry at temperatures of 1100 °C, 1200 °C, and 1250 °C (Zakeri *et al.* 1998). Furthermore, this system's activity calculated by Azakami and Yazawa (1976), from data provided by Hultgren *et al.* (1973) at 1150 °C to 1000 °C –as well as Hultgren's data itself-, agrees with the trend of increasing positive deviation at lower temperatures. In comparison to its phase diagram, re-assessed by Witusiewicz *et al.* (2004), it shows noticeably high immiscibility at low temperatures, but, again like lead, only the liquid phase exists at the standardized temperature (Fig. 5).

At decreasing temperatures, the activity of silver becomes considerably more positively offset suggesting that it can be lost through volatilization. Conversely, because silver can only form stable oxides at temperatures well below the melting point of copper, and despite the repulsive force between copper and silver atoms at the standardized temperature, silver loss is

prevented through oxidation. Since silver has unstable oxides at high temperatures only its volatility as a pure metal gas is important to consider for loss modeling in ancient metallurgy. However, under increased oxygen potential can silver form oxides at copper melting temperatures, which, as noted by Pickles (1998), can be accomplished with the addition of forced oxygen injection.

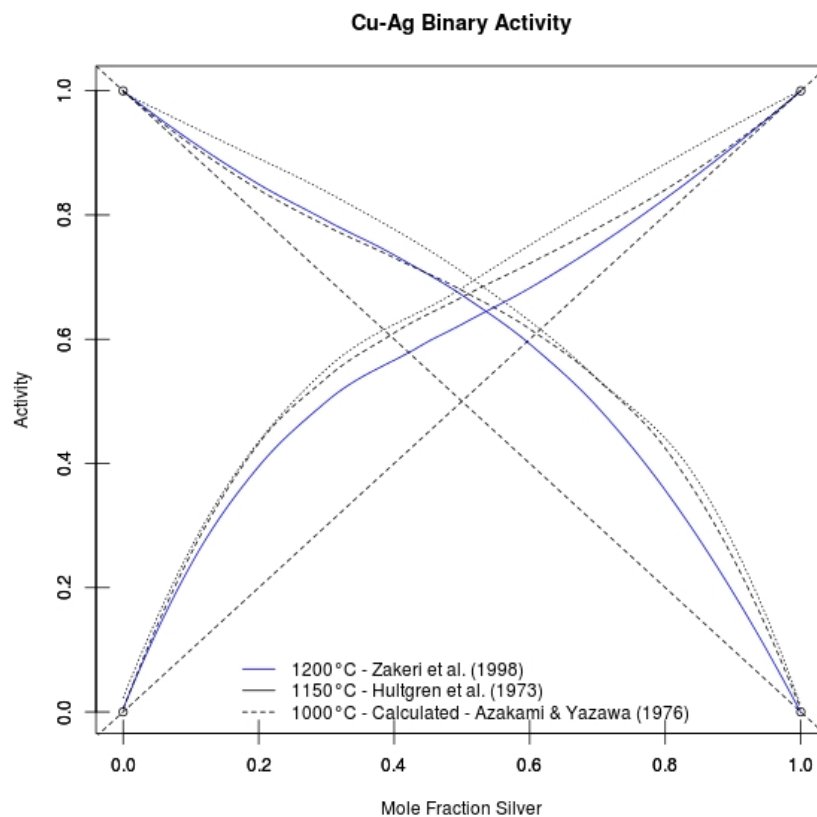


FIGURE 4: CU-AG BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

The inability of silver to oxidize at high temperatures, as suggested above, does not preclude silver loss during ancient pyrometallurgical processes. Experimental results by Merkel (1983; 1990) demonstrated no appreciable difference in silver concentration change between smelting and re-melting under oxidizing conditions at copper melting temperatures, yet

calculations, which are discussed further in chapter 4, indicate that the volatilization of silver, it having higher vapor pressure than copper according to its activity in low compositions, is indeed possible. Therefore, the activity, in agreement with Merkel (1983) who has shown a slight loss of silver from copper after being fire refined of approximately 130 ppm (from 860 to 730 ppm) measured using ICP-AES (Inductively Coupled Plasma – Optical Emission Spectrometry), is valid as shown in the activity diagram, and noted by the positive deviation of silver in the Cu-Ag activity binary diagram.

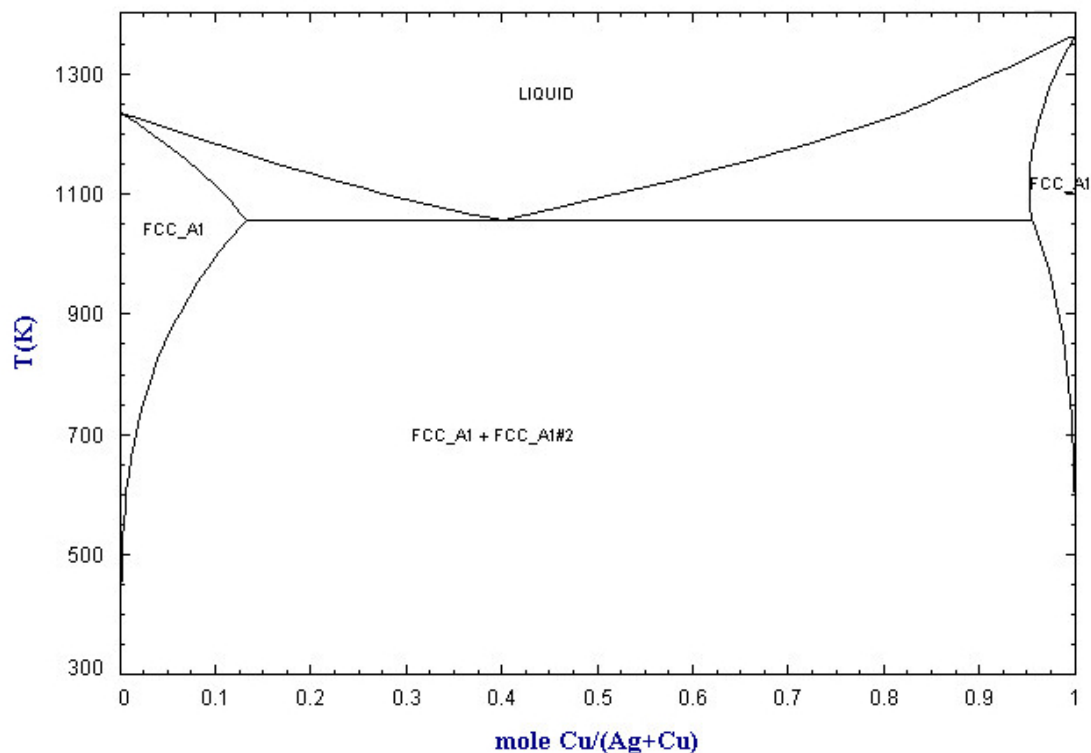


FIGURE 5: CU-AG BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://www.crtc.polymtl.ca/fact/))

3.1.3 Bismuth

Arsenic, bismuth, and antimony form polyatomic vapor species that require additional interpretation using their combined pressures, p_M , of their individual elemental partial pressures

by Equation 3.0 where P is equal to $p_{Sb} + p_{Sb_2} + p_{Sb_4} + p_g$. Equation 3.0 only accounts for the formation of elemental component species. Their oxides can be added similarly, but not in the same equation.

$$p_M = \frac{p_{Sb} + 2p_{Sb_2} + 4p_{Sb_4}}{p_{Sb} + 2p_{Sb_2} + 4p_{Sb_4} + p_g} P = \frac{p_{Sb} + 2K_{p_{Sb_2}} p_{Sb}^2 + 4K_{p_{Sb_4}} p_{Sb}^4}{p_{Sb} + 2K_{p_{Sb_2}} p_{Sb}^2 + K_{p_{Sb_4}} p_{Sb}^4 + p_g} P$$

$$K_{p_{Sb_2}} = p_{Sb_2} / p_{Sb}^2$$

$$K_{p_{Sb_4}} = p_{Sb_4} / p_{Sb}^4 \quad 3.0$$

As is seen in Figure 6 bismuth shows positive deviation nearing ideality with higher temperatures and in higher mole fractions, but in lower fractions it shows greater positive deviation indicating immiscibility with copper, as is echoed by the large miscibility gap in the Cu-Bi phase diagram (Fig. 7). Experimental activity data by Azakami and Yazawa (1976) at 1000 °C, 1100 °C, and 1200 °C, shows its tendency toward ideality with higher temperatures. Comparatively, activity data gathered by Itoh and Azakami (1984) for low mole fractions of bismuth at 1100 °C using Knudsen effusion and Electrobalance are much less positive at the same temperature, yet are instructive in that they confirm the system's positive deviation. At mole fractions below 0.1, however, the electrobalance method has a greater margin of error due to the high vapor pressure of copper at higher concentrations. Experiments by Teppo *et al.* (1990) provide the most recent data for this system, which agrees well with all prior research with the exception of Itoh and Azakami (1984).

Consensus among scholars as to the precise activity of this system varies, however the activity coefficient in the dilute solution conforms well between several studies (Nagamori *et al.*,

1975; Azakami and Yazawa, 1976; Sabri and Geiger, 1981). Regardless of these slight differences, at high mole fractions of bismuth the activity tends towards ideality and conforms well to the Cu-Bi phase diagram. The phase diagram is noticeably similar to Cu-Pb, as are their positive activity and activity coefficients.

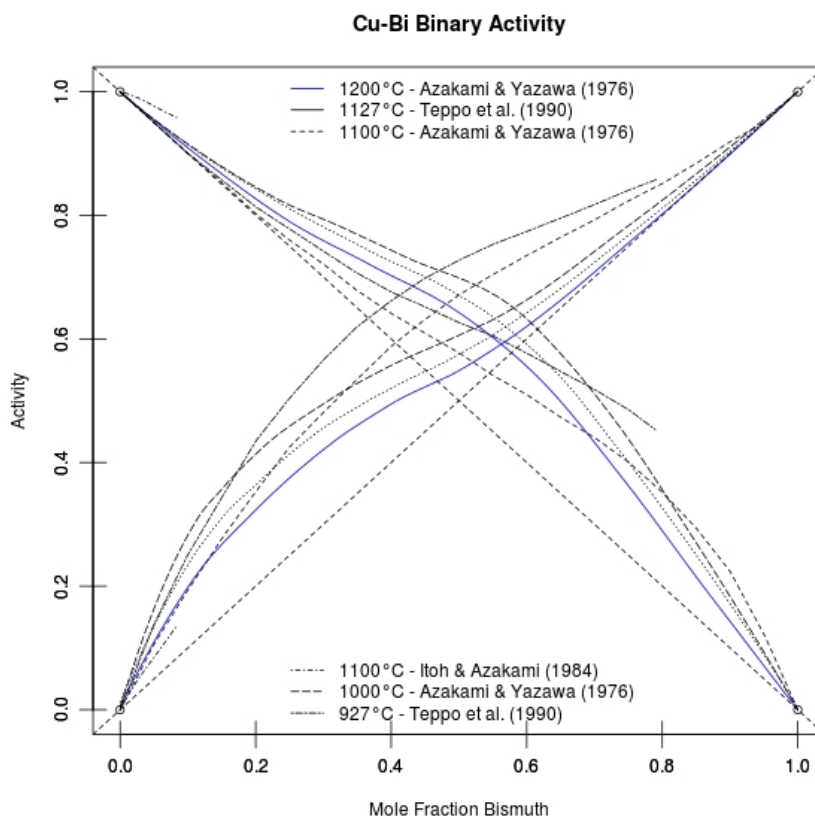


FIGURE 6: CU-BI BINARY ACTIVITY

Bismuth is rarely considered in archaeometallurgical studies having been neglected in past smelting and melting experiments (e.g. Merkel, 1983; 1990; Wayman and Duke, 1999), and only briefly discussed by a select few scholars interested in its application towards provenance studies (e.g. Pernicka, 1986; 1999; 2004). For provenance studies trace amounts of bismuth may

aid in identifying compositionally unique ore bodies and eliminating possible sources, much like cobalt.

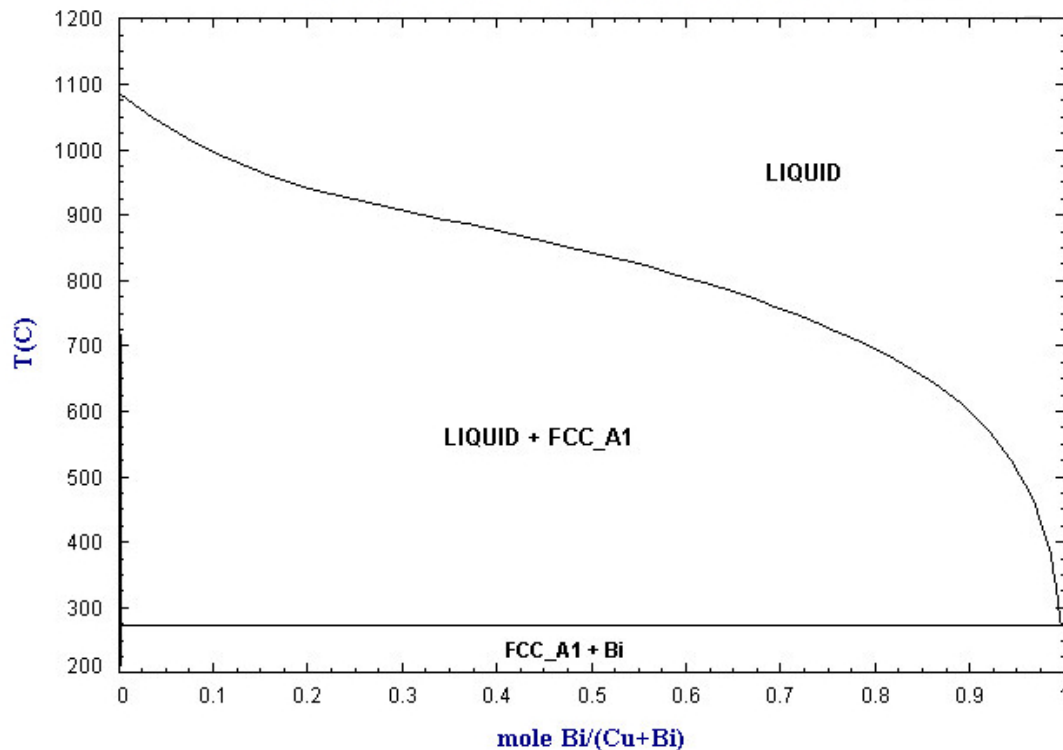


FIGURE 7: CU-BI BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

3.1.4 Nickel

The activity of the Cu-Ni binary system (Fig. 8) was measured by Oishi *et al.* (2003) at 700 °C and 1000 °C using E.M.F and copper-Beta-Alumina showing positive deviation for nickel agreeing with the high activity coefficient of nickel for copper at low mole fractions. Their method measured the activity of copper, and that for nickel was calculated using the Gibbs-Duhem integration, with results mirroring that of nickel activity measured using E.M.F by Rapp and Maak (1962). The activity values of copper from the prior study at 1000 °C were extrapolated by this author, beginning with this and later binary systems, to the standardized

temperature of 1200 °C using the following relationship for regular solutions (Equation 3.1).

This extrapolation is, further, reasonable for non-regular solution approximations over relatively small temperature differences such as those utilized in this thesis.

$$\begin{aligned} RT \ln \gamma_M &= RT' \ln \gamma'_M \\ \ln \gamma'_M &= \left(\frac{T}{T'} \right) \ln \gamma_M = \ln(\gamma_M)^{(T/T')} \\ \gamma'_M &= (\gamma_M)^{(T/T')} \end{aligned} \tag{3.1}$$

Activity estimations using Equation 3.1 have proven accurate, however, it is clear that when used over large temperature changes it becomes increasingly unreliable. For this reason, the measured activity closest to the standardized temperature was used, be it higher or lower than 1200 °C. Moreover, measurements by Kulkarni *et al.* (1973) of nickel in the binary Cu-Ni system at 1400 °C identified a tendency toward ideality with increasing temperature (Fujita *et al.* 1997).

Unusual to the Cu-Ni system, and important to understanding its behavior, is its isomorphic character allowing for unlimited solubility of nickel within copper, which makes possible the direct substitution of atoms in solid solution. Thermodynamic evaluations of the Cu-Ni solid solution, however, have identified a miscibility gap at temperatures below approximately 377°C (Mey, 1992). Regardless of this characteristic, that might suggest similar thermodynamic behavior when molten, they activities are nevertheless slightly positive to one another due to phase state at the standardized temperature, which leads to the repulsion of nickel in low mole fractions. The positive deviation of nickel from ideality is a contributing factor to its loss seen in the smelting and melting experiments conducted by Merkel (1983), however, it must

be considered with the formation of oxides, which is discussed in the following chapter. In comparison the Cu-Ni phase diagram (Fig. 9), which passes through all three phase regions of liquid, liquid and solid, and solid solutions at 1200 °C, shows no apparent change in the corresponding activity diagram at the same temperature. The activity trend is also maintained across the liquid alloy and solid FCC (face centered cubic) solution phase change at temperatures as low as 700 °C. The reason for its continuity is partially due to the fact that copper and nickel are completely miscible, and show the same activity trend both above the liquidus and below the solidus, as is evidenced in measured activities by Turchanin *et al.* (2007).

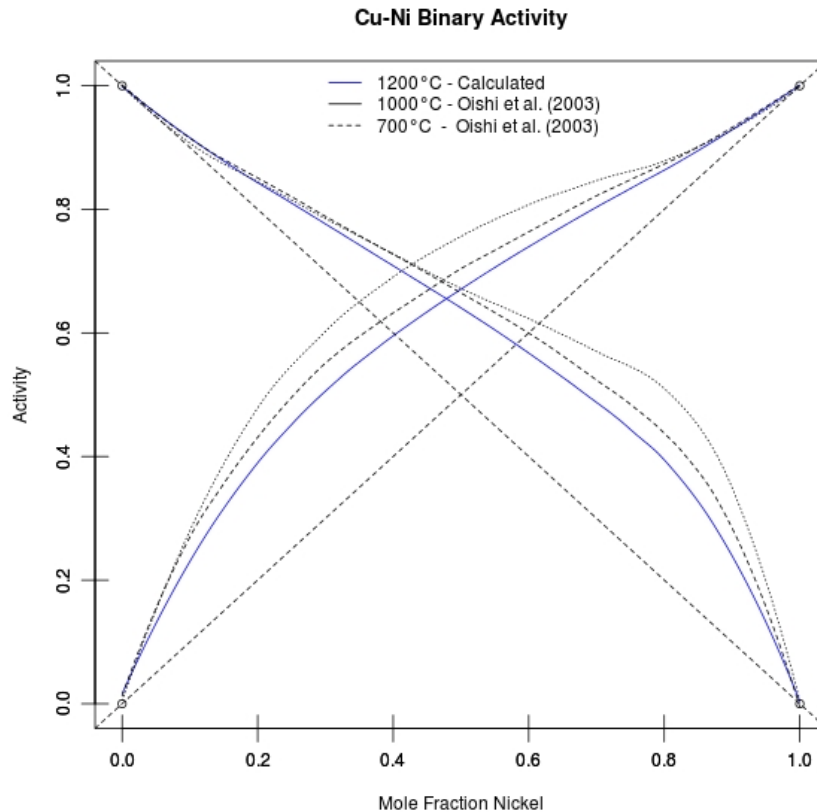


FIGURE 8: CU-NI BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Furthermore, evidence of nickel's positive deviation has been confirmed by experimental archaeometallurgy by Zwicker (Pernicka, 1999; 2004), whose melting of a Cu-Ni alloy under charcoal in a reducing environment shown a progressive decrease in nickel content after successive oxidizing steps of pouring and exposure to a gentle airflow. This observed behavior was the result of nickel's high activity coefficient and ability to form stable nickel oxides, having more negative Gibbs free energy of formation; all despite its relatively low vapor pressure compared to copper that would suggest minimal loss in a melt. For clarity sake, the loss of nickel in this case was due to the formation of oxides and their loss through pouring rather than as vapor in the air.

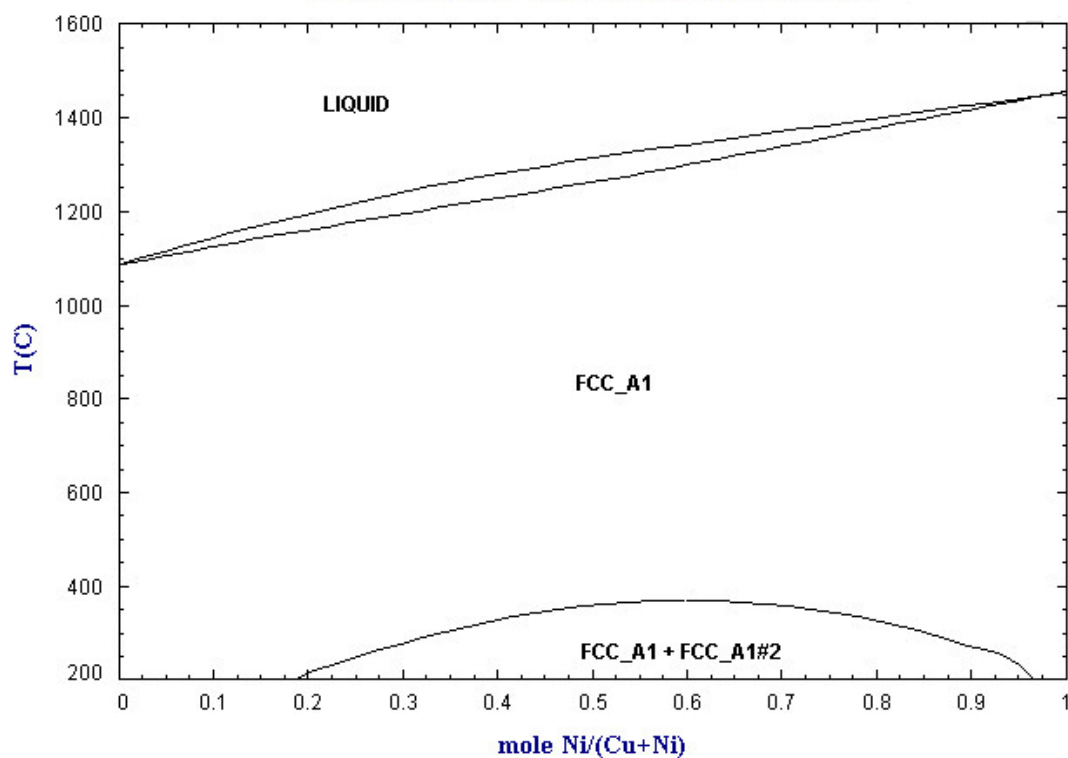


FIGURE 9: CU-NI BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://www.crtc.polymtl.ca/fact/))

3.1.5 Cobalt and Iron

The activity data for cobalt in the Cu-Co binary (Fig. 10) was measured by Oishi *et al.* (1981), by E.M.F, and Timberg *et al.* (1981), by Knudsen effusion and mass spectrometry at low mole fraction. The former was measured at 1250 °C, 1350 °C and 1623°C, and the latter at 1550 °C; temperatures of which show extreme positive deviation that trend toward ideality as they increase. Extrapolated activity values from those reported by Oishi *et al.* (1981) from 1250 °C to 1200 °C deviate more positively, as expected, having a cross section through the Cu-Co phase diagram (Fig. 11) with a wide miscibility gap. The calculated values agree well with Kubišta and

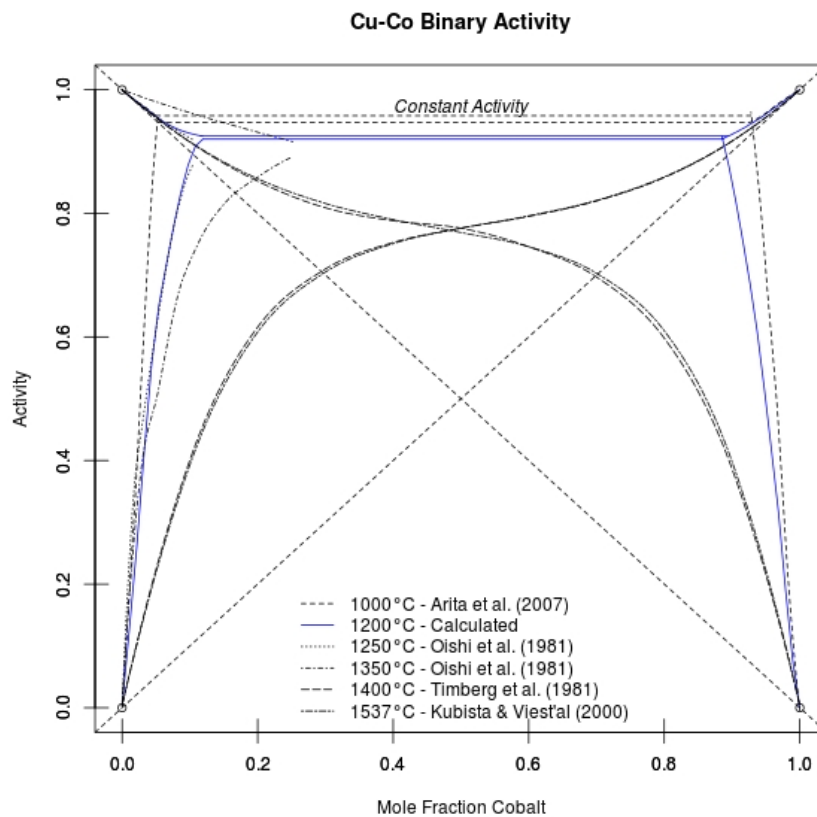


FIGURE 10: CU-CO BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Viešťál (2000) and with partial activity data published by Taskinen (1982) for cobalt and Arita *et al.* (1984) for copper at the standardized temperature in the binary system. These are further comparable to less precise measurements by Hultgren *et al.* (1973) at 1027°C. Compilations of phase equilibria and the thermodynamics of the Cu-Co binary, and calculation of its activities at 1000 °C by Turchanin and Agraval (2007), further support the data.

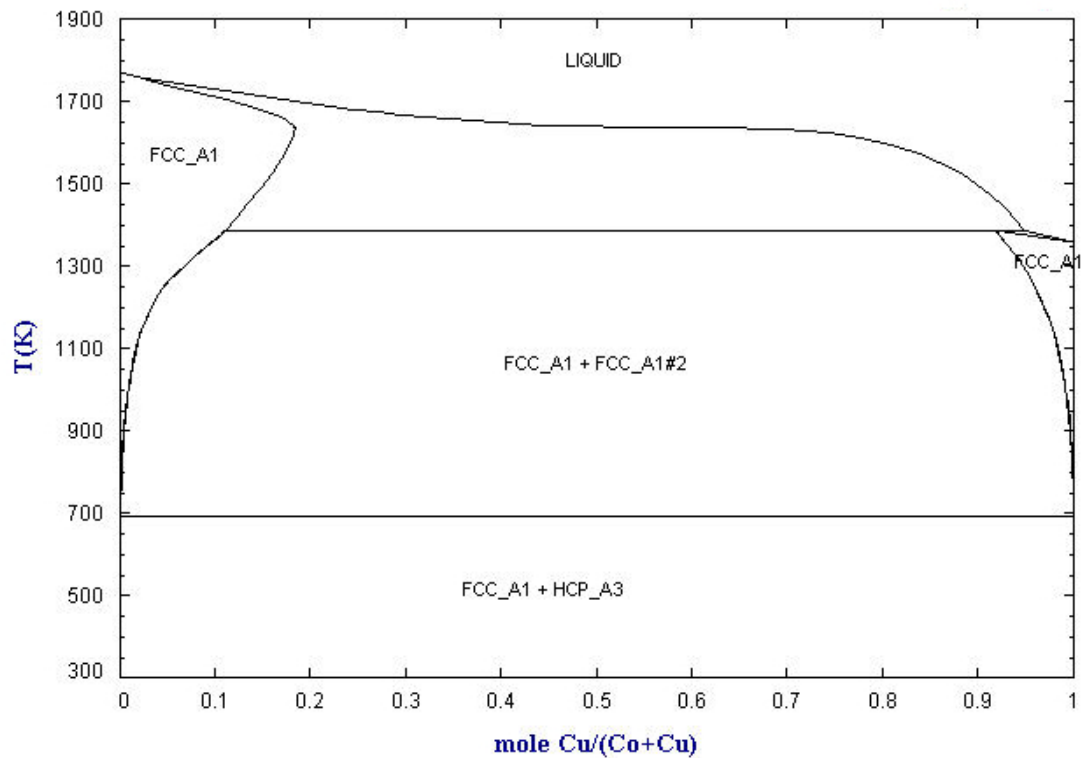


FIGURE 11: CU-CO BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

Similarly, activity data reported by Park and Gaskell (1989) for the Cu-Fe binary at 1300 °C, at low copper mole fractions and extrapolated to 1200 °C, similarly show extreme positive deviation. Activity values calculated by this author agree well with those reported by Turchanin and Agraval (2001), Park and Gaskell (1989), Arita *et al.* (1981), and Gachon *et al.* (1980) forming a continuously rising activity trend at temperatures beginning at 1018°C (Fig. 12).

From Figures 10 and 12 it is clear that both cobalt and iron behave similarly at low mole fractions in a copper melt (Kulkarni, 1973; Timberg *et al.*, 1981). For both cobalt and iron the activity models also show constant activity values that remain throughout most of the system's concentration. These values are the result of supersaturation of each solute in relation to its solvent, and, before correction, appear as a sinusoidal curve beginning at the maximum value of each system's components activity and ending at unity. Within this curve, with cobalt and iron on the left of each respective diagram and copper on the right, the negative slope of the decreasing activity value, where the derivative of $\frac{\partial a_B}{\partial x_B}$ is negative but $\left(\frac{\partial P}{\partial V}\right)_T$ must be positive, has no physical significance and is thus a range of constant activity between the two phases. Constant activity of the components is shown as a horizontal line drawn from the point of supersaturation, or weight percentages where the miscibility gap roughly begins in both phase diagrams (Figs. 11, 13), to the opposite side where it continues positively towards unity. Extrapolated activity values above this line are thermodynamically irrelevant. Furthermore, both cobalt and iron show extreme deviation due to their passing through respective FCC solid solution phases.

Smelting and re-melting experiments conducted by Merkel (1983) demonstrate the above discussed positive deviation, and strong mutual repulsion of iron and copper, in which he noted a reduction in iron after re-melting. Also apparent was the loss of cobalt; and, especially iron and cobalt, by oxidation when the molten metal was stirred using a wooden stick and subjected to a blast of air (Pernicka, 1999; 2004). In this experiment both the iron and cobalt were lost through oxidation and slag tapping, contrary to the description that suggests that the air was solely responsible. In both circumstances oxygen was introduced, especially if the wooden stick was green wood, allowing for the formation of each respective element's oxides having highly

negative Gibbs free energy of formation. At the same time stirring loosened these oxides both mechanically and with efflorescence of hydrogen gas, which then float to the top of the melt and are removed by skimming or adherence to the melting vessel.

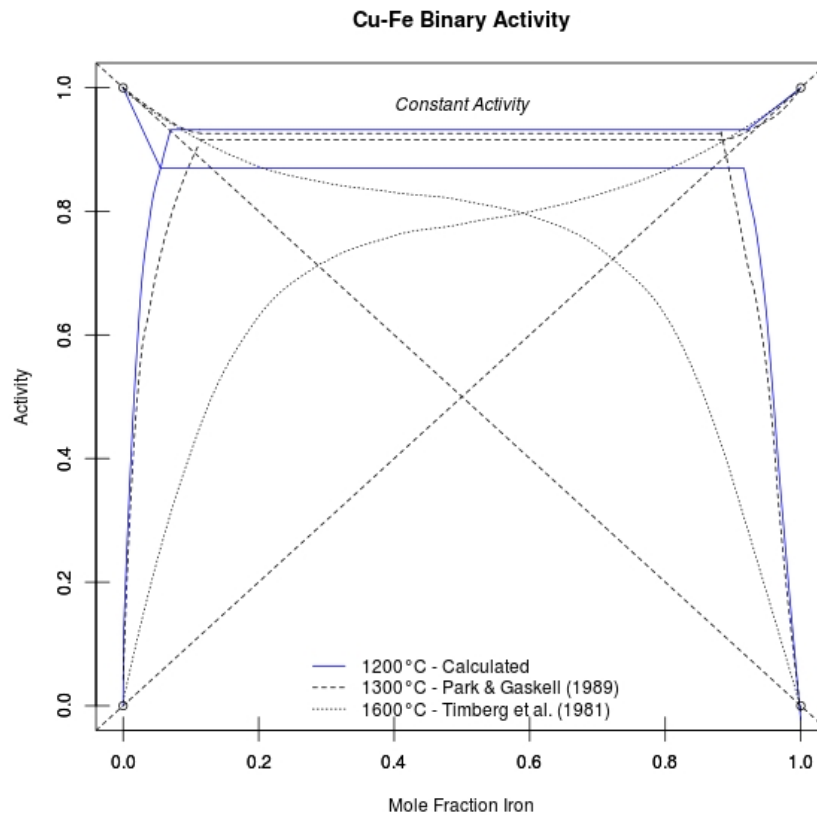


FIGURE 12: CU-FE BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Experiments by Merkel in furnaces based on archaeological furnace remains reached temperatures as high as 1400 °C, at which point the solubility of iron in molten copper is greatly increased. Its solubility is, according to Merkel (1983), approximately 2.8% at 1100 °C, 6% at 1200 °C, 10% at 1300 °C, 20% at 1400 °C, and sharply rises to 70% at 1450 °C. This trend agrees with the activity of iron in copper melts as can be seen by the decreased deviation of iron towards unity at higher temperatures allowing for greater solubility. These estimates assume a

simplified binary system of copper and iron, however, if sulfur, for example, were present the solubility of iron in copper drastically increases becoming 20% at 1200 °C with 2% sulfur, and 40% at 1300 °C with 3% (Craddock and Meeks, 1987). However, through metallurgical processing, such as re-melting and recycling, sulfur content is quickly lost to negligible amounts as it is generally lost earlier forming volatile molecular species with most impurities found in copper ores.

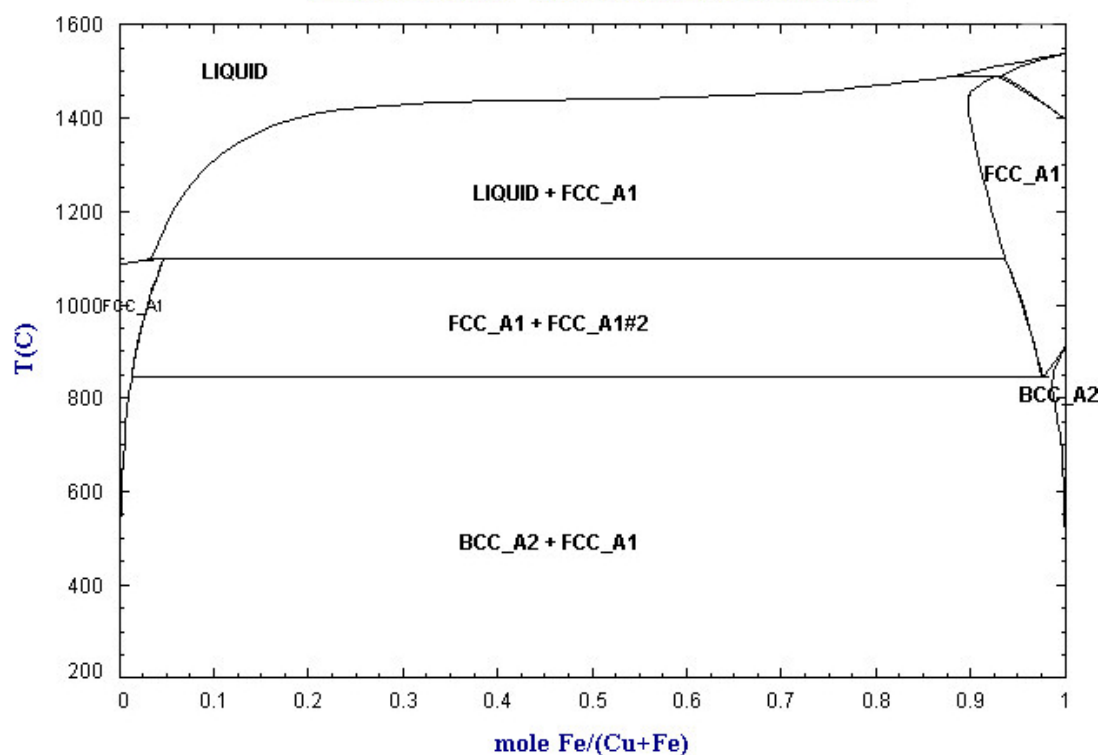


FIGURE 13: CU-FE BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

Then, with negligible sulfur content, it is possible to relate the solubility of the iron component to equilibrium, of which is influenced by temperature. As discussed above the activities of the components decreases as temperature is increased. And as the activity coefficient approaches unity, the maximum saturation of the solute increases.

Archaeologically cobalt is often disregarded in metals studies, except in cases of determining authenticity of ancient metal works (e.g. Oddy, 2004), and in provenance studies and native copper identification (e.g. Pernicka, 1999; 2004). Iron minerals, on the other hand, may have been intentionally added to copper to promote slagging (Craddock and Meeks, 1987), and its presence may have led to the eventual production of iron. The explanation for the transition from a copper to an iron system may best be explained by the thermodynamics of distribution and interaction of copper and iron.

3.2 Negative Deviation Binary Systems

3.2.1 Antimony

Copper-antimony activity, dependent on p_M from Equation 3.0, shows extreme negative deviation from ideality in low antimony concentrations, a markedly different behavior than the above discussed group. Antimony activity is shown in Figure 14 and indicates there is an increased likelihood in the formation of Cu-Sb phases, which is echoed in the system's phase diagram (Fig. 15). With the negative deviation of antimony also comes an activity coefficient value lower than 1, which is several orders of magnitude smaller than any of the previously discussed binary systems. Antimony, furthermore, shows a reversed tendency compared to previous systems away from ideality with increasing temperatures in low mole fractions. This reversal is important since it indicates less loss of antimony through volatilization from copper at copper smelting and melting temperatures. Activity measurements by Hultgren (1973) and Večer *et al.* (1957) agree with the activity trend of antimony, and further shows that at lower temperatures its activity increases across the majority of the system, except in low concentrations where it remains significantly low. The activity behavior in this system is further supported by later studies by Itoh and Azakami (1984), Kang *et al.* (1991), and Manasijević *et al.* (2009),

confirming the results of Azakami and Yazawa (1976), but showing slightly greater negative deviation at low mole fractions of antimony at the same temperatures.

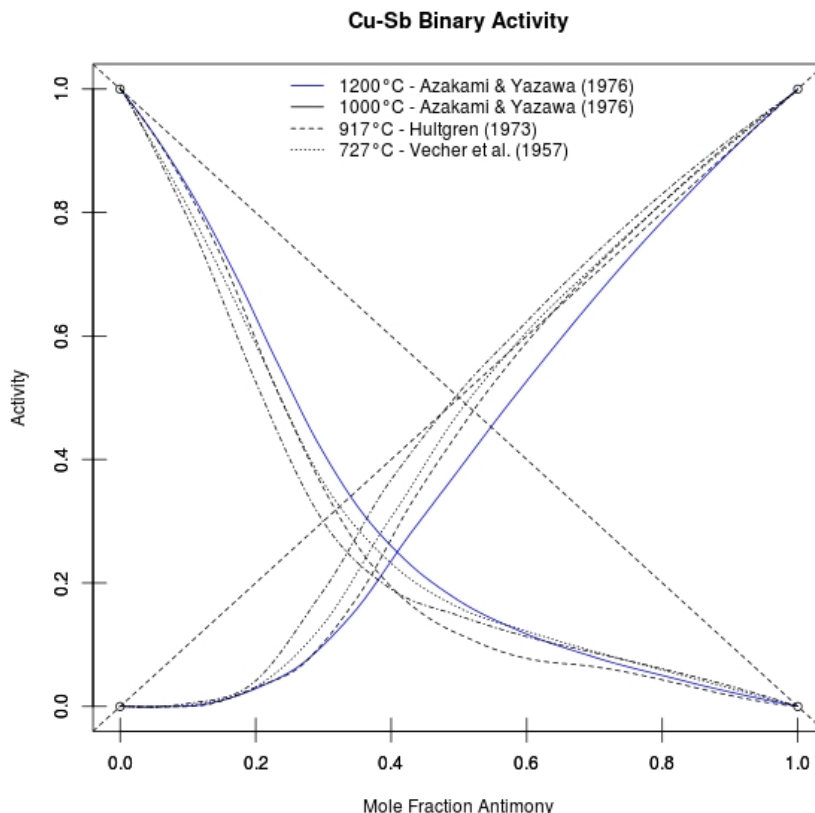


FIGURE 14: CU-SB BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

When the data are compared to archaeometallurgical studies it is apparent that the Cu-Sb activity behavior corresponds to the experimental results by Pollard *et al.* (1990b), which were conducted between 600 °C and 1100 °C under reduction using charges of mixed malachite and antimony trioxide. In their experiments the antimony levels remained relatively constant reflecting the extremely low activity of antimony in low concentrations. The likely reason for its persistence over the entire range of temperatures is the dissociation of its volatile trioxide due to the reducing effects of the added charcoal, which left only the possibility of its loss by

volatilization. In similar experiments the results given by Merkel (1983; 1990) show the strong attraction between copper and antimony with an increase in antimony after smelting, due to the preferential loss of other elements, and a slight decrease after fire refining. In addition, prior results by McKerrel and Tylecote (1972) for working of antimonial copper, in agreement with their findings, have shown significant losses of antimony could only be caused by oxidative conditions. Altogether these past three archaeometallurgical experiments confirm the results of the activity of antimony showing that it is slowly lost through volatilization, and is accelerated through oxidative evaporation.

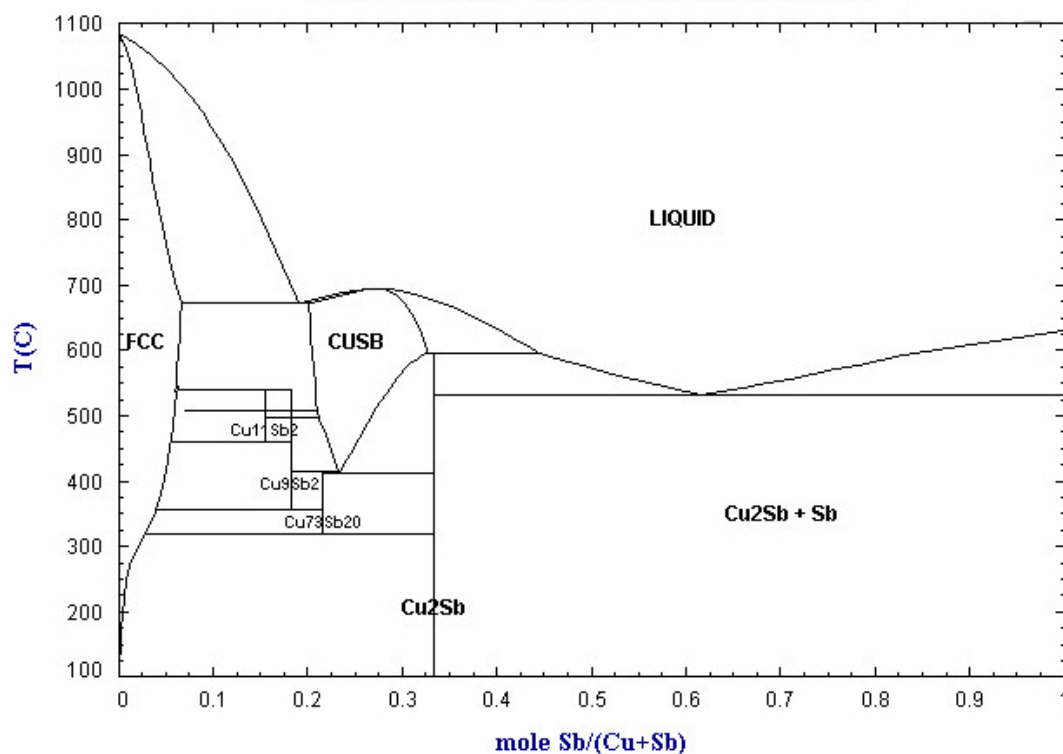


FIGURE 15: CU-SB BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

3.2.2 Arsenic

Similar to antimony, arsenic shows highly negative deviation from ideality (Fig. 16) in high copper concentrations indicating a tendency to form Cu-As compounds having an extremely low arsenic activity coefficient in dilute solutions (Azakami and Hino, 1986; Wypartowicz, 1995). Further, the collective data obtained by several authors, and by various analytical methods, for the activity of both copper and arsenic, is in good agreement with the arsenic activity calculated and shown by Azakami and Yazawa (1976) at 1200 °C. For these studies the arsenic component was calculated using the Gibbs-Duhem integration at arsenic mole fractions below 0.4 and copper over 0.6 (Hino and Toguri, 1986; Hino, 1985, 1995; Hino and Toguri, 1986). The varying results shown illustrate the difficulty in determining the activity, and activity coefficient mentioned previously, of arsenic having overlapping values despite a difference of 200 °C from the lowest to highest measured vapor pressure. Wyparowicz (1995) most recently measured both components directly using E.M.F and the isopiestic methods, for copper and arsenic, respectively, showing stronger agreement with activity values calculated from the Cu-As phase diagram (Fig. 17). However, according to Pei (1993), who presents the most recent and unified assessment of the Cu-As system, the activity coefficient in dilute solutions can be best represented using the relationship in Equation 3.2 and substituting for the desired temperature. The results of this simple calculation for activity of arsenic at 1200 °C is 0.005, which is one order of magnitude larger than reported by Azakami and Yazawa (1976), but still indicative of its extreme affinity for copper.

$$RT\ln\gamma_{As}^{\circ} = -62,229J/mol \quad 3.2$$

For archaeometallurgy what is clear from the data is that arsenic would be extremely difficult to remove in a semi-closed system under reducing conditions. This is in contrast, in

terms of loss through volatilization, to those conditions set up by Merkel (1983; 1990) where a loss in arsenic was observed in an oxidizing atmosphere and open system.

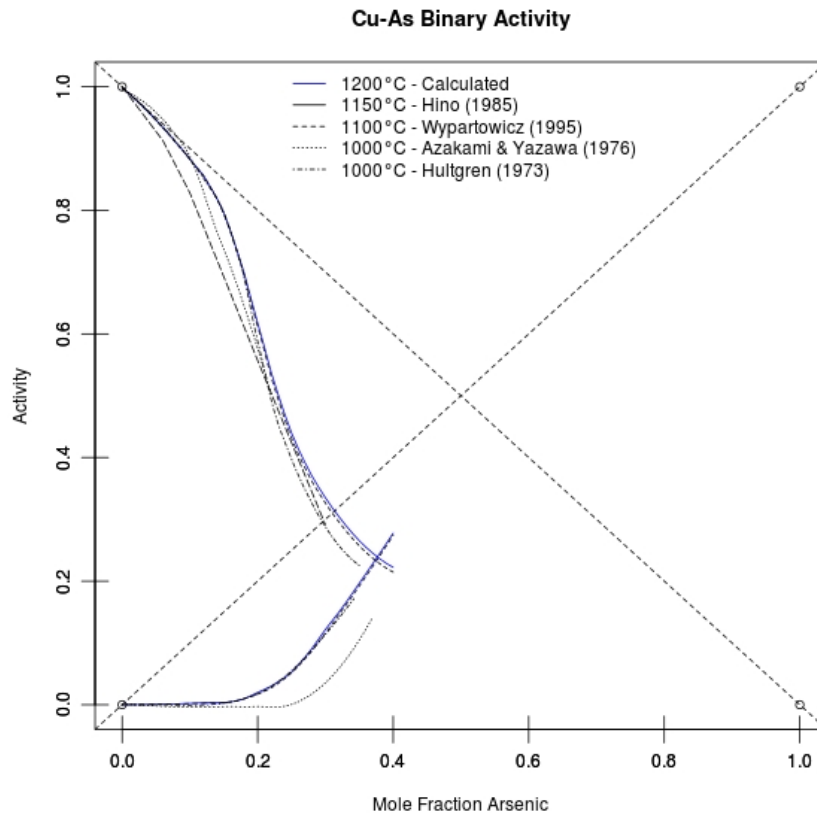


FIGURE 16: CU-AS BINARY ACTIVITY

Archaeometallurgical smelting and re-melting studies, by Pollard *et al.* (1990a, 1990b) and McKerrel and Tylecote (1972), demonstrate these findings and confirm that at temperatures of 1000 °C and above loss of arsenic can be minimal, and that arsenic does indeed have a high affinity for copper resulting in its negligible loss under reducing conditions. In experiments specifically designed to measure the vapor pressure of arsenic, where copper makes up the vast majority of the system, the activity of arsenic decreases and dissociates into simpler gas species with decreased arsenic mass percentages. It has been shown that under these conditions, for

arsenic below ten mass percent in the Cu-As binary, the vapor pressure of all added vapor species of arsenic is far less than that of pure arsenic (Pagador and Hino, 1996). However, above ten percent arsenic there is a transition where the As_2 species alone has nearly equal vapor pressure to copper and that of copper is surpassed only by the total of the arsenic species of As , As_3 , and As_4 . This phenomenon has no doubt contributed to high percentages of arsenic in copper artifacts up to and equal to ten mass percent arsenic. However, under these circumstances the existence of artifacts with greater than ten percent arsenic is improbable, but not impossible, which is a point clarified in Chapter 4. In such a system at lower temperatures the loss of arsenic is akin to roasting in the presence of sulfur, at temperatures of approximately 700 °C, and occurs when the activity of copper is itself low. Roasting is an important step in the processing of copper bearing ores, but is only briefly mentioned here as the thermodynamics of roasting is in itself a separate and complicated process. Contrary to the behavior of arsenic in a reducing environment, under oxidizing conditions, and in a relatively open system, the loss of arsenic would be measurably significant by any pyrometallurgical processing such as re-melting/recycling and hot working, as has been noted by McKerrell and Tylecote (1972).

Arsenical copper is a common and significant alloying combination in ancient metallurgy that warrants a more encompassing explanation as to the relationship of the arsenic and copper activity coefficients. The activity coefficient of arsenic is dependent on copper percentages and can decrease exponentially beginning at seventy percent copper for those impurities like arsenic and others that can volatilize as polymetallic species. At the same time the activity of copper exponentially increases forming stable compounds with impurities that have strong affinities for copper, again arsenic and antimony (Itagaki and Yazawa, 1983). The experiments conducted by Itagaki and Yazawa measured the vapor species of arsenic, antimony, and bismuth with copper

percentages of up to 80% at 0.1 atm SO_2 . Arsenic oxide $\text{As}_2(\text{g})$ shown linear progression regardless of copper percentage, however, the trend of AsO suggests it would surpass other gas species nearing ninety percent copper and above. The decreasing activity coefficient of arsenic and increasing copper activity heavily reduces volatilization, which results in high percentages of arsenic in refined blister grade copper (Yazawa *et al.* 2000). Furthermore, arsenic's decreased activity coefficient in copper for smelting and fire refining, for both arsenic and antimony, means that they concentrate in the copper rich phase rather than being lost to the slag (Itagaki *et al.*, 2006). These combined findings demonstrate the importance of arsenic oxide formation, in agreement with McKerrell and Tylecote that may occur during the smelting of sulfidic ores and the use of forced air into ancient furnaces. Their experiment relates well to the re-melting and recycling of ancient copper-based objects being designed within the same copper percentage range common to artifacts, and clearly illustrates the importance of losses through pure molecular gas species and oxidized arsenic.

From this evidence, and the activity and phase diagrams, it is clear that the removal of arsenic and antimony from molten copper is especially difficult given their extreme negative deviation, and, in addition, exemplified by the multitude of possible stable intermetallic phases shown in their respective phase diagrams (Figs. 15, 17). On a separate note more relevant for smelting, comparison of ternary Cu-S-M (M = As, Sb) to binary Cu-M systems have shown that, while still difficult, in the presence of sulfur either component is more likely to be lost. Results by Hino and Toguri (1987) show that the magnitude of arsenic activity in a binary dilute solution, to the ternary with sulfur, deviates more negatively making its loss from copper more likely during matte smelting and slagging. Further, in relation to possible phase formations, the low value of the arsenic equilibrium constant from Table 1 indicates the reversibility of the

oxidation reaction; meaning that as temperatures decrease within the system, assuming it is closed and escape of arsenic vapor is prohibited as pure vapor species or oxides, both can be reabsorbed into the copper as the system cools and freezes at equilibrium at decreasing temperatures.

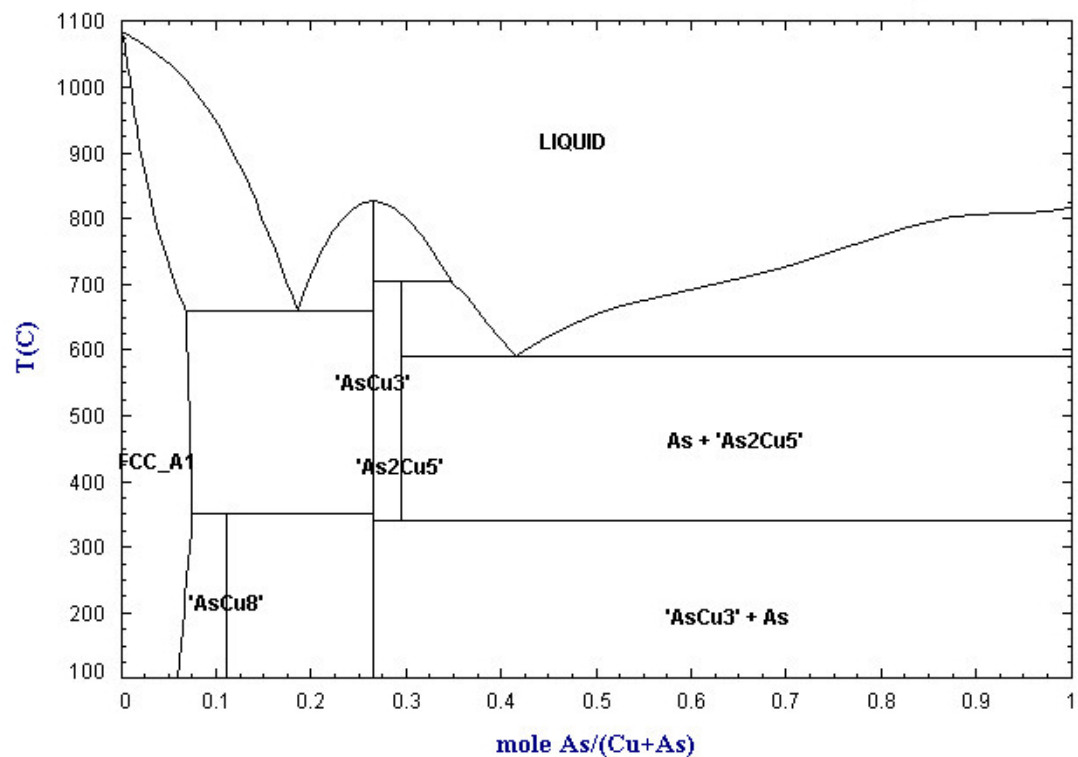


FIGURE 17: CU-AS BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://www.crtc.polymtl.ca/fact/))

3.2.3 Tin

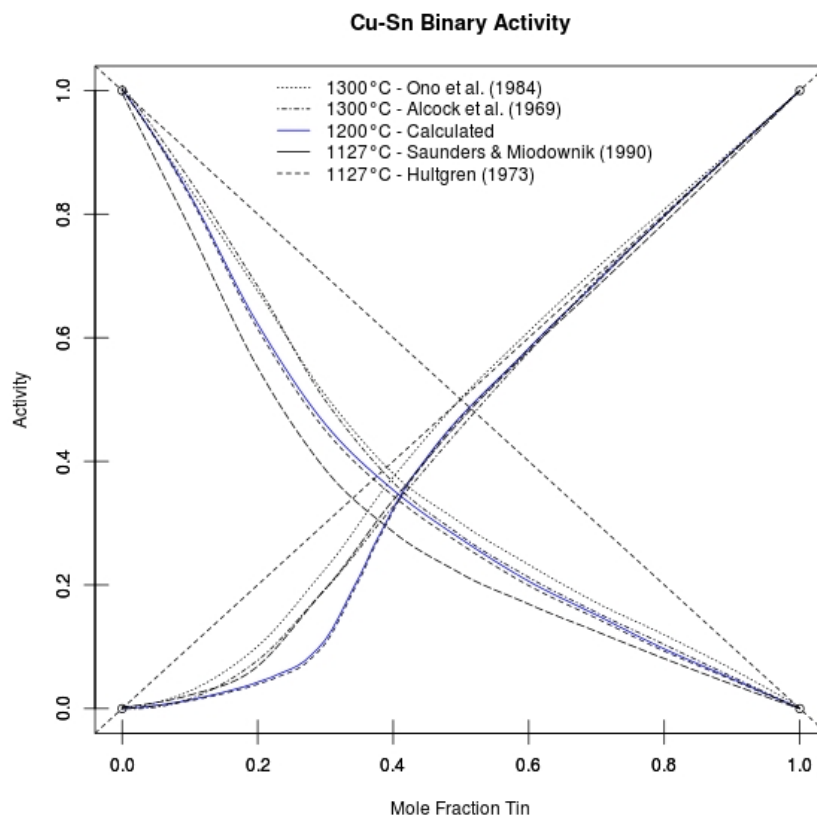


FIGURE 18: CU-SN BINARY ACTIVITY

The presence of tin in tin-bronze artifacts is especially important to archaeologists and archaeometallurgists alike, and the activity diagram of the binary Cu-Sn system partially explains its survival through metallurgical processes in low compositions. Figure 18 shows tin activity in molten copper, which shows highly negative deviation in low concentrations trending towards ideality with higher temperatures beyond 0.5 mole fractions. Unique to this system, tin approaches ideality at higher mole fractions, and is slightly positive at concentrations of approximately 0.9. In equal concentrations Ono *et al.* (1984), using Knudsen effusion and quadrupole mass spectrometry, recorded ideality at 1300 °C at high mole fraction concentrations,

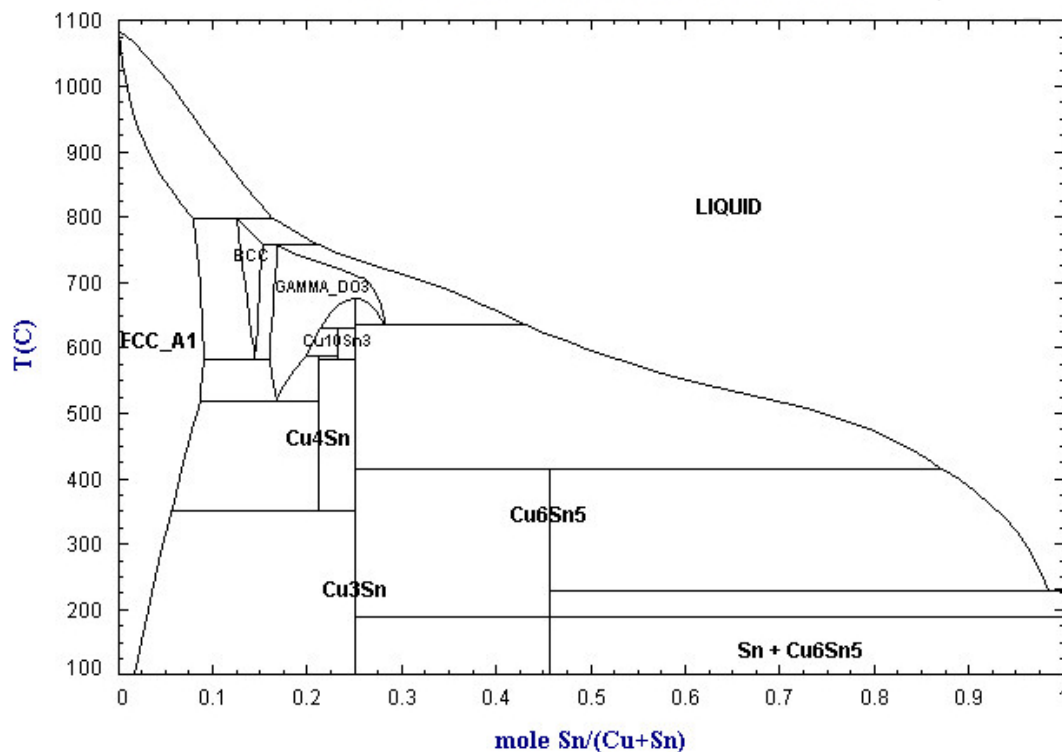


FIGURE 19: CU-SN BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

in addition to slightly less overall negative deviation than earlier studies. Of concern, however, and shown for contrast, is a contradiction to the expected trend in higher concentrations presented by the earlier work of Alcock *et al.* (1969) at 1300 °C where deviation was negative at higher mole fractions and more negative at lower. Saunders and Miodownik (1990), based on the above mentioned works, have suggested the activities show even further negative deviation confirming the negative trend in low tin concentrations for slightly higher mole fractions of tin. This latest empirically derived set of activity values has been used to extrapolate the standard temperature, as it is the most recent critical assessment of the system. The trend is further supported by values given by Hultgren (1973) and Kang *et al.* (1991) at 1127°C that agree with those of Azakami and Yazawa (1976) at 1130 °C and optimization calculations by Li *et al.*

(2009). Comparison of the tin activity to the Cu-Sn phase diagram (Fig 19) does little to explain its odd behavior showing that it resides entirely in the liquid state at copper melting temperatures.

3.2.4 Zinc

Measured at 1200 °C using the transportation method the activity of zinc shows negative deviation in copper despite (Fig. 20) having high vapor pressure, and behaving as a regular solution up to 0.6 mole fraction (Yazawa and Azakami, 1969; Azakami and Yazawa, 1976). Beyond this point, in zinc-rich regions of the binary, error prone measurements have instead been replaced by estimated activity between 0.6 and 1 mole fraction. In the measured region the activity coefficient of zinc can be calculated using Equation 3.3 assuming regular solution behavior in dilute concentrations from 850 to 1200 °C. The equation for the slope of the activity agrees with that of Sugino and Hagiwara (1986) in solutions containing less than 0.1 mole fraction zinc.

$$RT\ln\gamma_{Zn} = -6400N_{Cu}^2 \pm 90 \quad 3.3$$

Linear approximations by Bourgarit and Bauchau (2010), based on activity measurements by Baker (1970) at 1150 °C using the boiling point method, of zinc activity between 0.294 and 0.492 mole fractions are shown in red in Figure 20. The data were used by Bourgarit and Bouchau to determine the maximum zinc uptake by copper in their experiments demonstrating the possible ancient manufacture of high zinc brasses using the calamine process along the β phase seen in the Cu-Zn phase diagram (Fig. 21).

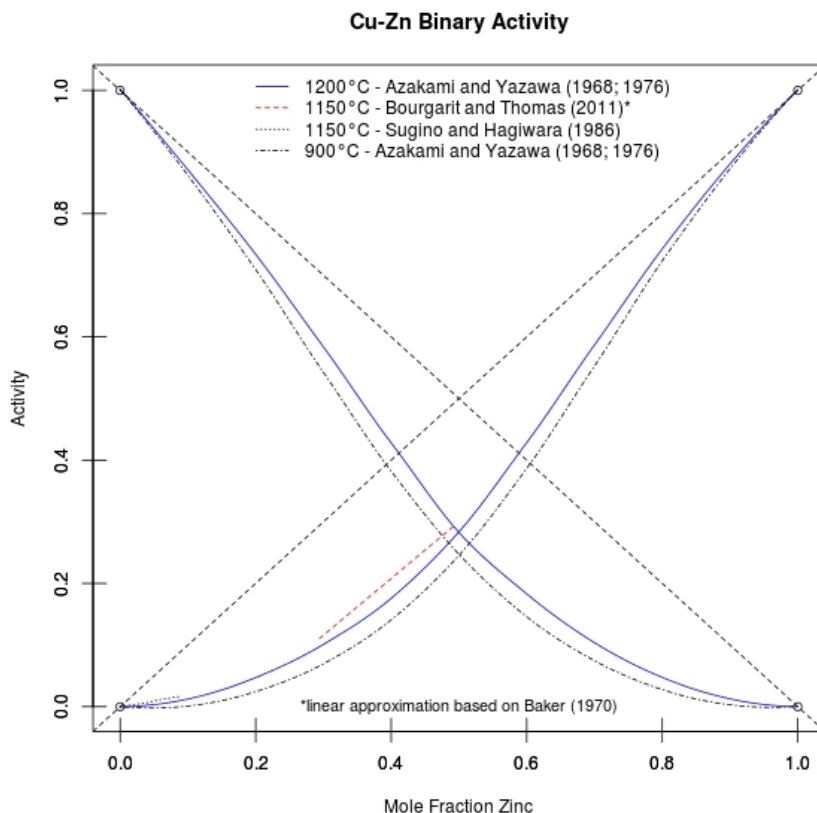


FIGURE 20: CU-ZN BINARY ACTIVITY

The importance of zinc to archaeologists and archaeometallurgists alike has historically been in its earliest introduction in the manufacture of brass, an alloy of copper and variable amounts of zinc that imparts a range of properties including color and workability. The manufacture of brass is thought to have had required specialized knowledge and technology due to the high volatility of zinc and its rapid loss at copper melting temperatures (Zwicker *et al.*, 1985; Bayley, 1984; Rehren, 1999), so its appearance in the archaeological record, if intentionally created, may indicate a marked advancement in pyrometallurgical ability. The loss of zinc despite its negative activity, since it has such a high standard vapor pressure, according to Table 1, as well as by oxidation shown by the Equilibrium constant and Gibbs free energy of formation, is clear, and has been confirmed by simple brass melting experiments conducted by

Dungworth (1995) in an electric furnace. Unfortunately, the furnace conditions, other than temperature, were unknown; however, zinc loss from liquid copper is assured by either elemental or oxidized volatilization.

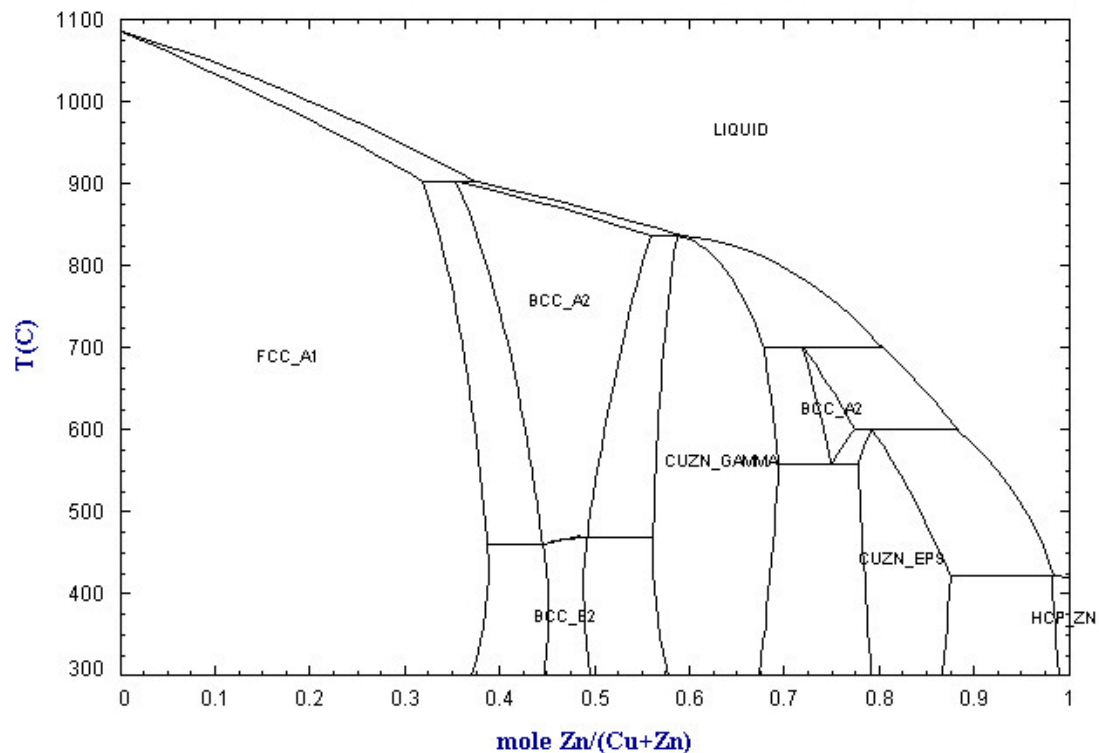


FIGURE 21: CU-ZN BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

The question of when brass objects were purposely created, the technology to do so developed, and to what geographic extent they had spread is difficult to determine and will not be pursued here; however, recent research seems to suggest that zinc was slowly introduced, at least in the Ancient Near East, as early as the 3rd millennium BCE as an intentional alloying element in relatively low zinc brasses and in combination with arsenic, tin, and lead (e.g. Thornton *et al.*, 2002; Thornton & Ehlers, 2003). It has been suggested by Bayley (1998) that these early examples of brass were not created using the calamine process, and that the existence

and significance of zinc as an alloying element was already known. The significance of these early examples of brass being in their introduction well before the 1st millennium CE and before the historical accounts of the calamine process found in Medieval Europe (Smith and Gnudi, 1942, 70-76; Craddock 1978; Hook and Craddock, 1996). The existence of zinc metal in the 3rd millennium BCE, however, is highly unlikely due to difficulties in containing the loss of highly volatile Zn (g) during typical ancient ore processing procedures. Instead, the existence of brass before the introduction of the cementation process was probably the result of the smelting of zinc rich ores as mentioned by Bayley and first suggested by Halleux (1973).

Caution must be taken, however, in the interpretation of zinc-rich artifacts that also contain high tin and/or lead above a few percent because of the negative effect these two metals have on the absorption of zinc gas by liquid copper during the cementation process. If either alloy were used for creating brasses instead of pure copper, it would have been far more difficult to achieve high percentage zinc brasses. Where combinations of zinc with copper and lead, copper and tin, or copper, lead, and tin exist, there are likely due to mixing and recycling of brass and bronze, but not of cementation. Later modeling of ternary molten metal combinations and explanation of the ancient brass manufacturing process will elucidate the issues involved with zinc gas absorption by liquid copper in complex systems. Nevertheless, lead, in a few percent in brass artifacts -from the zinc ore itself- is not uncommon (Craddock, 2009, 148). Additionally, it is probable that there might be high amounts of tin and lead in ancient brass alloys from use of recycled copper scrap metal in the cementation process (Dungworth, 1997), but their presence may also indicate they are modern having been made using alloys such as gunmetal.

3.2.5 Gold

Lastly, and one of the oldest historically studied binaries (Fig. 23), the activity of gold is shown in Figure 22 at 1200 °C based on activity data from Edwards and Downing (1956) who measured both components at 1277°C by Knudsen effusion. In the diagram both gold and copper show highly negative deviation that trends towards ideality with higher temperatures. There is slight variation in the activity values given by Edwards and Downing compared to Azakami and Yazawa (1976), in their calculations of low concentrations of copper, yet both otherwise show strong agreement with one another across the entire composition. Further, there is strong correlation of the activity data given by Edwards and Downing, which has been used to recalculate the activity at the standardized temperature, with the most recent assessment of the system by Sundman *et al.* (1998).

In accordance with its vapor pressure, value given in Table 1, gold is the lowest of all the considered copper binary systems. Coupled with the fact that its equilibrium constant is very low and it forms unstable oxides at high temperatures, the presence of gold in ancient copper-based artifacts as an unintentional addition is very likely. In fact, in such cases the copper, rather than the gold, would be readily lost through oxidation and volatilization with an apparent increase in weight percent of gold (Tylecote, 1970). Based on these combined data it is clear that copper and gold are strongly attractive to one another, alloy well together, and, indicative of gold's low vapor pressure and negative deviation, expected to long persist in artifacts after any number of recycling campaigns. Gold is further completely miscible in copper at all compositions. On a related note in relation to ancient brasses, a decrease in the activity of zinc has been observed with the addition of small amounts of gold to the Cu-Zn binary system (Sugino and Hagiwara, 1986).

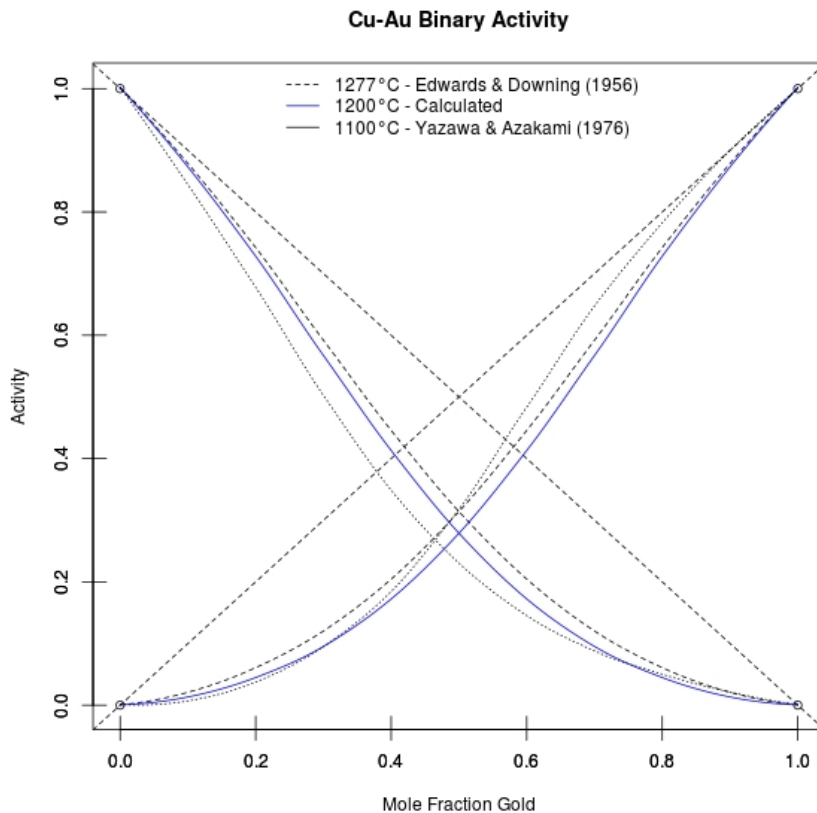


FIGURE 22: CU-SB BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Gold typically exists in copper-based artifacts in only trace amounts having been passed down from copper ores through smelting and refining processes with few examples of deliberate alloying, except, for example, during the British Middle Bronze Age (Tylecote, 1970) and Central Andes Middle Horizon (Lechtman, 1996). Archaeologically, gold is typically used, as first suggested by Tylecote *et al.*, (1977), for provenance studies concomitantly with lead isotopes to eliminate possible ore body sources (e.g. Gale *et al.*, 1985; Begemann, 2001; Pernicka, 1999; 2004).

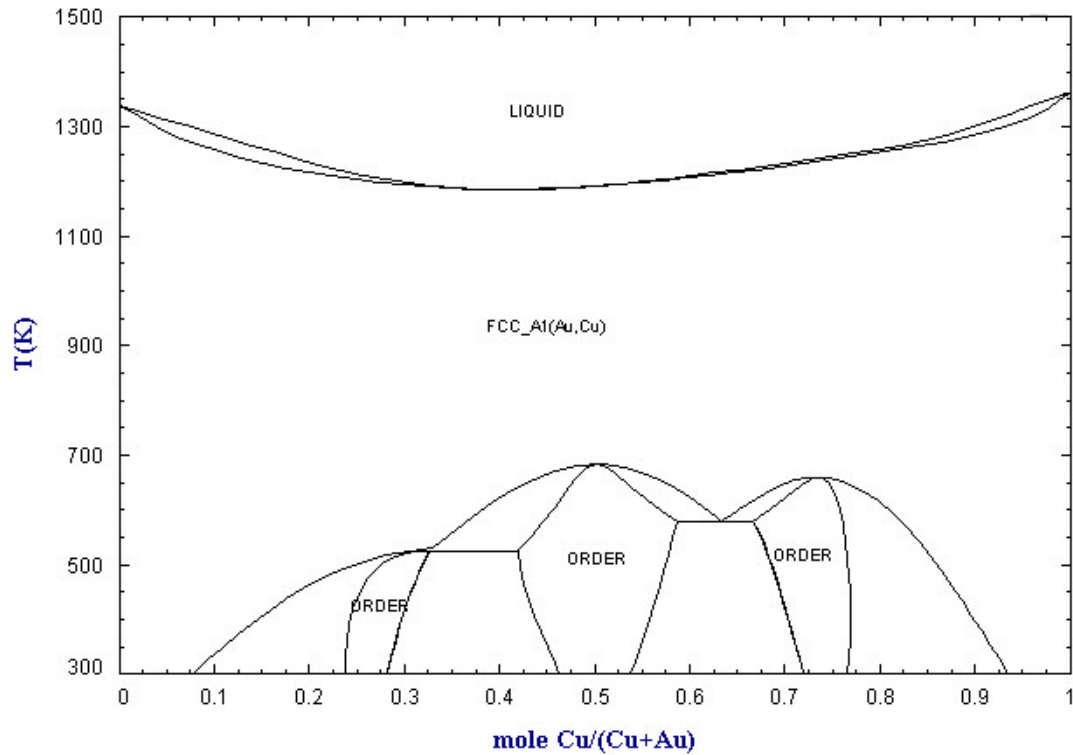


FIGURE 22: CU-AU BINARY PHASE DIAGRAM (SOURCE: [HTTP://WWW.CRTC.POLYMTL.CA/FACT/](http://WWW.CRTC.POLYMTL.CA/FACT/))

3.3 Summary

The above described behavioral tendencies of elements found in ancient copper, as purposely alloyed materials, unintentional additions, or remnants of ore source impurities, presents the mechanisms by which they would behave in binary systems according to their activity. The information is presented under conditions which ancient pyrometallurgy would likely have been performed with no alteration to atmospheric pressure, and were evaluated with data devoid of modern pyrometallurgical practices. The measurement of binary activities offers a humble beginning to the arduous task of explaining complex molten metal interactions, while exposing the basic thermodynamic data, such as partial vapor pressures, for further interpretation

of these systems. In no way should oxidation alone be viewed as the cure-all explanation to questions of the elemental change of ancient copper due to recycling efforts.

What is clear from the above plotted data, and in particular Table 1, is that it is possible to predict the oxidative loss tendencies of copper-based molten systems based on binary equilibrium constants, and that the chemical composition of some objects can be used to identify recycling efforts by ancient metalsmiths. There is uncertainty, however, due to the undoubted shift in the equilibrium constant in more complex systems of three or more components. Yet from the binary data, for instance, it is probable that iron will oxidize before arsenic according to the difference in their equilibrium constants and related Gibbs free energy, which may be evidenced by temporal trends of successive ancient recycling campaigns of the same metal that show iron loss followed by arsenic. The information presented in this chapter may seem to infer exactly this trend, however, care must be taken as the process of oxidation is not necessarily indicative of element loss. Concomitantly with the above partial explanation of element behavior, one must also consider the volatility of these metals at copper melting temperatures, which can be calculated using the relationship activity has to partial pressure. Chapter 4 introduces such methods and calculations to determine the volatility of elements and oxides that would have been common in ancient copper recycling. A secondary marker, the volatility coefficient, is introduced and used in conjunction with activity and partial vapor pressures to help visualize the order of element volatility. Like the previous chapter, information and discussions follow require one understands prior theory.

4. Volatilization in Binary Copper-Based Systems

As Tylecote (1980) rightly pointed out when discussing the smelting of sulfidic ores, temperatures that far exceed the vapor pressures of many of the impurities found in copper partially contribute to their loss. He was alluding to the assumed volatility of non-oxidized impurity elements in primary copper smelting without explicit explanation. Volatilization is an important factor to consider in tandem with oxidation due to conditions present during any process from primary smelting to refining, which would have influenced the rate of elemental loss. Vaporization of impurities, as well as the bulk copper melt itself, are the means by which changes in recycled metal would have occurred in relation to the binary activity systems discussed in Chapter 3. Important to keep in mind, is that even in a reducing atmosphere oxidation occurs within the liquid melt, as well as at the liquid-gas interface, with any free oxygen ions. Oxidation, however, does not necessarily imply loss of an element's oxide from the system. Only in combination with sufficient partial pressure can a pure metal species or oxide be lost as a gas. Those elements that volatilize at low pressure should be preferentially removed, however their removal is simultaneously determined by factors such as surface free energy, the activity and activity coefficients, bonding dynamics, and slag accumulation. In modern refining oxygen is ordinarily removed with deoxidizing agents that have more negative Gibbs free energy than the bulk melt. These agents are either themselves volatile or dross forming. This is an extra refining step likely not taken by ancient metallurgists, but illustrates two relatable means of impurity loss in ancient pyrometallurgy.

In reducing conditions when the melt elements have reached equilibrium with oxygen, oxidation at the liquid-gas interface is prevented resulting in an interface clear of oxides or slags.

A known characteristic of copper melts, this holds true unless, for example, fluxes are added. At this point volatilization, assuming no oxygen is present, is the predominant mechanism of elemental loss assuming the element itself is volatile. Within the melt, however, oxides that have formed and are at equilibrium may also be volatile and significantly contribute to overall losses. In general elements that are volatile will form volatile oxides. This point is important in relation to the volatility of elements discussed in Chapter 2, and may significantly increase the rate of elemental losses as oxides.

As mentioned previously, the activity is the direct result of partial vapor pressure measurements of each component and reflects their degree of volatility. The binary activity diagrams presented above are synonymous to the vapor pressure of each element at the same mole fraction. In the activity diagrams, the vapor pressure of each component is equal to its vapor pressure in its standard state at the same temperature. Changes in vapor pressure are calculable based on these diagrams, with the vapor pressure of components in a copper melt being dependent on the activity and mole fraction. According to Equation 4.0, at constant temperature and pressure where p_M° is the pressure of the pure metal, the vapor pressure of the component can be calculated.

$$p_M = p_M^\circ a_M = p_M^\circ \gamma_i^\circ N_M \quad 4.0$$

From this equation it is clear that metals such as zinc will volatilize easily while others, such as arsenic, are lost more slowly because of their low values of γ_M° or a_M despite their high values of p_M° at low concentrations. Volatilization of elemental arsenic, therefore, will occur contrary to previous reports by McKerrel and Tylecote (1972) discussed in Chapter 3. How much an element volatilizes is dependent on the mole fraction of a component and its activity, and is a

matter of kinetics. The volatilization of lead in a binary system, on the other hand, should be less difficult due to its high activity coefficient and thus lower binding affinity to the copper melt.

4.1 Arsenic, Bismuth, and Antimony

Of important note are elements that can form polymetallic species (e.g. As, Bi, Sb) that would be volatilized less because of their low activity coefficients (Lynch, 1980), which, if all other factors are constant, is a direct result of the high affinity to copper in high concentrations of copper. In relation to the uncertainty and variability of temperature in ancient furnaces, however, the loss of these elements, which might be initially thought to volatilize across a range of temperatures, is in fact negligible. For example, in a copper melt the volatilization of arsenic increases -as monatomic As, polymerized As_2 , As_3 , As_4 or polymerized AsO and $AsFeO_4$ concomitantly with increased oxygen partial pressure, meaning that the affinity of arsenic for copper is stronger at lower temperatures with low oxygen partial pressure. This implies little loss of arsenic at low temperatures that would have slowly increased in ancient furnaces until the liquefaction of the metal. This behavior is comparable for antimony, and to a lesser extent, bismuth.

4.1.1 Arsenic

In a reducing atmosphere and closed system, and despite its high vapor pressure, arsenic is difficult to remove through volatilization. Although its vapor pressure is comparatively very high, its low activity coefficient prevents its rapid loss in simple fire refining processing. In addition to the metallic species mentioned, at copper melting temperatures, and in the presence of oxygen, arsenic trioxide As_2O_3 , tetroxide As_2O_4 , and pentoxide As_2O_5 gas forms as a result of the dissociation of saturated tetratomic arsenic $As_4(g)$ from the melt to the dimer $As_2(g)$. The tetratomic arsenic forms at temperatures approaching 700 °C, along with all pure arsenic species

and molecules, and both the tetroxide and pentoxide are volatile.³ Arsenic trioxide forms according to Equation 4.1 and was thought to be a significant means of arsenic loss in ancient pyrometallurgy (McKerrell and Tylecote, 1972), however it is negligible at copper smelting and melting temperatures.

Tetratomic arsenic also dissociates to form AsO(g), and AsS(g) in the presence of sulfur and oxygen, but it is the pure dimer gas species that predominates at temperatures above 1000 °C when neither is present (Itagaki and Yazawa 1983; Pei, 1993; Yazawa *et al.* 2000; Sohn *et al.*, 2004). In particular, AsS(g) is important in primary smelting and roasting where it contributes the most to arsenic losses (Chaubal and Nagamori, 1983), and AsO(g) at copper melting temperatures (Roine, 1987). Arsenic oxide was undoubtedly the most significant contributor to the volatilization of arsenic in ancient re-melting and recycling processes in accordance with modern thermodynamic modeling of arsenic removal criteria (Yazawa, 1974; Nagamori and Chaubal, 1982; Chaubal and Nagamori, 1988; Padilla *et al.*, 1997; Plascencia, 2003).

Archaeometallurgically, it is clear from the volatility coefficients calculated in Table 2 for arsenic, and matching activity and unchanging levels of arsenic in experimental results by Wayman and Duke (1999) in a closed system, that only in an oxidizing atmosphere and open system can arsenic be noticeably lost through re-melting and recycling. Despite the supposed reducing effects of the charcoal fuel used in antiquity, with the use of forced air channeled through tuyères to drive furnace temperatures higher, incomplete reduction by carbon

³ Arsenic trioxide forms in the presence of oxygen in a Cu melt, except in the presence of iron where it forms Iron (III) Arsenate (FeAsO₄), which is non-volatile.

undoubtedly resulted in the oxidation of metals and metalloids in the system.⁴ In addition to the dissolved oxygen in the melt, as discussed in Chapter 2, the combination of several sources of oxygen at increased potential would have allowed for the formation of several types of arsenic oxide compounds.



4.1.2 Bismuth

Elemental bismuth gas predominates in the Cu-Bi binary system with comparatively little of the diatomic species, Bi₂, at copper melting temperatures (Nagamori and Chaubal, 1982; Sohn *et al.*, 2004). The partial pressure of bismuth, as is true with other elements with multiple gas phase compounds, is simply the summation of their species (Lynch, 1980; Pei, 1993). As mentioned in Chapter 4.1, at temperatures above the melting point of copper the formation of trioxides of bismuth becomes possible at lower oxygen potential (Plascencia and Utigard, 2003), which form oxides according to Equation 4.1. Bismuth is, however, highly unlikely to form oxides because of its positive free energy of formation (Table 1), having very low measured and calculated vapor pressure (Ohno, 1976). Accordingly, bismuth is lost readily as pure elemental gas at the liquid-gas interface as reflected by its extremely high volatility coefficient calculated below in Table 2. Further increases in its loss rate can occur by actively stirring the melt (Ohno, 1976).

⁴ Wayman and Duke conducted their melting experiments of native copper under a defined set of “standard conditions” whereby the metal was slowly heated in an electric furnace until it reached a temperature of 1120°C in a covered crucible, and then removed from the heat, still covered, and allowed to slowly cool. Under their experimental conditions the only possible means of arsenic loss, and any other component, was through volatilization and oxidation within the confines of the covered crucible, which in the case of arsenic probably allowed for its reabsorption into the copper as temperatures decreased.

Meanwhile for bismuth, Bi(g) linearly predominates, and, similar to antimony an increase in BiO(g) occurs in accordance with increased copper concentration (Itagaki and Yazawa 1983; Sohn *et al.*, 2004). Bismuth oxide, however, does not cause significant bismuth losses through evaporation. Only the monomer and sulfide BiS have vapor pressures high enough to facilitate significant evaporative loss. Of the three elements in ancient metallurgy capable of forming polymetallic species, bismuth is the only one that shows positive deviation and has vapor pressure near that of copper. It is more easily lost through volatilization in low grade copper where sulfur is present, much like arsenic and antimony; however, it becomes difficult at high copper metal concentrations (Nagamori and Chaubal, 1982; Steinhauser *et al.*, 1984).

4.1.3 Antimony

In a copper melt the species of antimony gas that predominate are Sb₂ and Sb, and in the presence of sulfur, with diminishing results and below the two other species trend wise beyond >80% copper, SbS (Chaubal and Nagamori, 1983). For oxides, the concentration of antimony oxide gas SbO is higher with increasing copper concentrations where it becomes the most significant means of antimony loss in the absence of sulfur (Sohn *et al.*, 2004; Pinakin and Nagamori, 1983). Vapor species measurements of blister grade and refined final stage copper shows that loss of antimony as an oxide SbO predominates (Nagamori and Chaubal, 1982; Chaubal and Nagamori, 1988). Accordingly, the volatility coefficients of both pure gas species shown in Table 2 indicate, like those values for arsenic, the extremely slow loss of antimony by volatilization of the pure element, leaving only consideration for its oxide. Therefore, because of the very low activity of antimony, for losses to have occurred in ancient furnaces there must have also been sufficient oxygen and an open environment.

The activity coefficient of antimony similarly decreases in increasingly purer copper, which results in a decrease in its volatilization with all other parameters constant. According to the Cu-Sb phase diagram it can form several stable phases, similar to Cu-As, even at high temperatures, which further leads to a reduction in its volatility. When comparing the two systems and determining which component will volatilize more readily, one notices that the activity coefficient of antimony is always greater than arsenic. Both are volatile at copper melting temperatures, so one might expect the loss of antimony to be slightly greater than arsenic in equal proportions; however, under reducing conditions, although both are volatile, arsenic more readily volatilizes due to its extremely high vapor pressure compared to antimony and the bulk copper melt. These properties of arsenic and antimony, in regards to volatilization and disregarding oxidation and the volatilization of oxides, holds true in reducing conditions of both the oxides of arsenic and antimony. Therefore, one would expect arsenic and antimony to be gradually lost through simple fire refining. Furthermore, in oxidizing conditions where both elements are present, arsenic should theoretically reduce antimony, and its oxide preferentially lost as shown in the above oxidative loss list. This subtle difference in state, however, is only didactic since both would be lost regardless of metallic species or oxides formed.

4.2 Zinc

The vapor pressure of zinc in its standard state (Table 1) is one of the highest of the elements considered in this thesis. Its volatilization is assured from an open system as Zn(g) , and in the presence of oxygen -since it has high affinity for oxygen-, ZnO(g) . Between the compound and pure zinc, the oxide is by far predominant with a vapor pressure roughly ten times that of the pure component (Kyllo and Richards, 1998; Azakami and Yazawa, 1976). In melting experiments by Wayman and Duke (1999), zinc was found to remain stable due to the closed

system design of their experiments, reminiscent of the technology used for brass manufacture in the calamine process; however, zinc is known to be lost significantly in open system simulated ancient furnaces (Merkel, 1983; Pernicka, 1999; 2004).

4.3 Lead and Tin

For lead, with increasing copper percentages more Pb(g) volatilizes, which is evidenced by its sharply increasing positive activity (Chapter 3.1.1). Lead shows highly positive deviation and has a vapor pressure much higher than that of copper. Further, with increased oxygen partial pressure, and given its negative Gibbs free energy, it oxidizes as PbO(g) before copper but with a lower vapor pressure than its monomer (Nagamori and Chaubal, 1982; Coursol and Stubina, 2005). Volatile species of lead also include PbS, which, when in the presence of sulfur in low grade copper, is by far the most prevalent. Under the alternating conditions of reduction and oxidation in ancient furnaces, lead should therefore be steadily lost as the pure gas monomer, as observed by Merkel (1983), and partially as its oxide.

Tin, unlike other binary systems discussed in this thesis, shows negative deviation at low concentrations, but nears ideality after approximately 0.5 mole fractions. In low concentrations it has slightly higher vapor pressure than the bulk copper melt, and has more negative Gibbs free energy of formation. Tin will therefore not be lost by any significant amount due to elemental volatilization, according to its activity and volatility coefficients (Tables 1, 2). However, it is readily lost by the formation of SnO after being reduced by carbon from nonvolatile SnO₂. Tin dioxide, like cobalt and iron, are commonly found in significant proportions in ancient copper slags (e.g. Charles, 1967; Wayman, 1989; Valério et al, 2013).

4.4 Nickel, Cobalt, and Iron

The volatility of the elements nickel, cobalt, and iron are considerably different compared to those components previously described. Unlike other metals commonly found in ancient artifacts, they have much lower vapor pressure in their standard states and compared to copper in binary Cu-M melts, requiring their removal, or loss, by different means. Starting with nickel, it shows positive deviation which is comparable to cobalt and iron in that it is indicative of immiscibility with copper. Each typically forms oxides that float on the surface of the melt and are non-volatile.

Nickel's volatilization as atoms or oxides is therefore very unlikely, however evaporation is possible as a sulfide NiS, which has higher vapor pressure but is nonetheless relatively low compared to copper (Nagamori and Chaubal, 1982). It is possible for nickel to form oxides as NiO at copper melting temperatures given an oxidizing atmosphere, however, these remain in the melt indefinitely if not removed in the dross. Merkel (1983) notes that in low percentages of nickel are retained in a copper melt and not distributed to the slag. In very low concentrations, in parts-per million, the loss of nickel through fire refining is negligible. Further, in a Cu-Ni binary melt the volatility of copper is too close to that of nickel, in low concentrations, which contributes to the illusion of nickel enrichment at the expense of other impurities. Nickel additionally has a relatively small Gibbs free energy of formation and would be reduced by a host of other impurities. Its reduction would further increase its likely perseverance through ancient copper recycling processes. For example, both arsenic and antimony would reduce its oxide, acting as deoxidizers and removing oxygen from the system, themselves forming volatile oxides. Similarly, cobalt and iron have highly positive deviation and readily form non-volatile oxides, only being lost by slag skimming and their adherence to crucibles.

Iron, with its high melting point and low vapor pressure, may act as a reducing agent whereby it forms stable oxides or spieess preferentially before arsenic, as well as a host of other impurities. It does not evaporate from copper, instead forming non-volatile oxides. Iron, and other slagging agents, can collect on the melt surface creating a semi-permeable layer preventing or limiting mass transfer of volatile elements into the gas phase. Silicon and cobalt are other slag forming impurities that create such layers, which together introduce rate limiting physical barriers that vary according to layer thickness and permeability.

4.5 Silver and Gold

The most noble of the ancient metals, gold and silver are easily reduced to metal at high temperatures and do not evaporate as oxides. Both silver and gold form unstable oxides as shown by the Ellingham Diagram (Fig. 1) and the recalculated free energy in Table 1, where their oxides spontaneously decompose at the decomposition temperature, T_D . However, evaporation of silver monomers $Ag(g)$ can occur in significant amounts (Azakami and Yazawa 1976). It is important to keep in mind that the activity vapor pressure of silver is proportional to the vapor pressure of copper, and both deviate positively. Therefore, at 1200 °C very slow loss of silver should be expected since the vapor pressure of silver is less than 10 Pascal ($9.869 \cdot 10^{-5}$ atm) (Ohno, 1976; Zakeri, *et al.* 1998). Given the low vapor pressure of silver and reasonably high volatility coefficient (Table 2), only active stirring can significantly increase its loss rate (Ohno, 1976), which for ancient recycling and re-melting probably rarely occurred except though periodic poling and casting. However, if sulfur is present the formation of silver sulfide Ag_2S ($AgS_{0.5}$) is possible, which, having a substantially lower vapor pressure than copper and showing negative deviation versus copper (Nagamori and Chaubal, 1998; Zakeri *et al.*, 1998), should have resulted in no loss of silver.

For gold, its activity is dissimilar to silver despite both metals often being categorically associated with one another since they are noble. The vapor pressure of gold is lower than copper and it forms unstable oxides (Nagamori and Chaubal, 1982), which not only results in the presence and perseverance of gold through recycling and re-melting in copper artifacts, but might lead to the loss of copper through oxidation at the melt surface. The extremely negative calculated volatility coefficient of gold (Table 2) further confirms its stability and highlights the fact that gold is not lost by either volatilization or oxidation.

4.6 An Order of Volatilization

Returning to Table 1, the order of elemental volatilization from low to high according to p_M at infinite dilution -from Equation 4.0- is; Ni, Au, Co, Sn, Fe, Cu, Sb, Ag, Pb, Bi, As, Zn (Azakami and Yazawa 1976). At low concentrations these elements have low vapor pressures and their loss through volatilization is low, however, at higher concentrations evaporation can lead to significant losses. The order here has no bearing on oxidation since oxygen is assumed absent from the system. The order of volatilization, given by Azakami and Yazawa, is based on the activity and partial vapor pressures of each element in copper and is therefore only a rough guide to their volatility. One needs additional parameters including the molecular weights of the components and the vapor pressure of copper in order to sort them more reliably.

4.7 Volatility Calculations in Binary Systems

Vapor pressure increases with temperature leading to increased volatilization. For volatile elements their concentration in the gas phase can be calculated using mass transfer, which enumerates the potential for transference from the liquid to gas phase. This aspect is important as most component elements are in fact lost by volatilization as pure elements or volatile oxides, rather than by the process of oxidation (Yazawa and Azakami, 1969). In dilute solutions,

impurity elements remain in the copper melt in trace amounts, and do so regardless of the stability and volatility of their oxides (Zakeri *et al.* 1998). Oxide formation and their presence in copper is also partially due to the fact that the partial pressures of some oxides can be lower than their pure atomic species (Sohn *et al.* 2004).

Olette (1961), to improve the efficiency of impurity removal using vacuum refining, introduced the volatility coefficient Φ_i for monatomic evaporation (Equation 4.2). In the following Equations, i is the volatile element that should separate from the copper, denoted by the subscript c . M_c and M_i are the molecular weights, and P_c° and P_i° are the vapor pressures of the element and copper (Olette, 1961). The subscript j is used to denote modifications to Olette's equation by Harris (1984) where individual vapor species are entered, and Ψ_i the proportionality constant relating composition to vapor pressure. Although the following equations were designed to determine the feasibility of vacuum refining, they provide a baseline for the evaporation of components similar to Raoult's law. From the below two equations, it is clear volatility is governed by the vapor pressure of individual species, molecular weight, and the activity coefficient at varying mole fractions. Further, according to Equation 4.2, high activity coefficients should increase the proportionality constant, which is large when the volatility coefficient is large.

$$\Phi_i = \frac{\gamma_i P_i^\circ}{P_c^\circ} \left(\frac{M_c}{M_i} \right)^{\frac{1}{2}} = \frac{\Psi_i}{P_c^\circ} \left(\frac{M_i}{M_c} \right)^{\frac{1}{2}} \geq 1 \quad 4.2$$

$$\Phi_{ij} = \left(\frac{M_c}{M_{ij}} \right)^{\frac{1}{2}} \frac{(\gamma_i)^j \cdot N_i^{(j-1)} \cdot P_{ij}^\circ}{P_c^\circ} \quad 4.3$$

For values greater than 1 evaporation and vacuum of an element is possible, and when greater than 20, vacuum refining becomes a worthwhile method of impurity removal (Li and Harris, 1991). When these values are large, they will also more likely be lost by simple volatilization. The evaporation rate of elements below 1, is of course, very slow, but still occurs.

Harris (1984) later modified Equation 4.2 to express the volatility of polyatomic species, which is relevant for arsenic, antimony, and bismuth (Equation 4.3). The resultant volatility coefficient must be greater than $\frac{1}{j}$, although, again, evaporation will occur slowly at lower values. As a general rule the larger the volatility coefficient, the greater the rate of volatilization and separation from the melt, but only to the point where evaporation is less than that of the bulk, and the increasing temperatures no longer increase the volatility coefficient of the solute (Li and Harris, 1991). In the case of a bulk copper melt where no impeding surface films are formed, in either oxidizing or reducing atmospheres, the rate of mass transfer is primarily controlled by evaporation.

In a copper melt mass transfer of volatile elements occurs in the following three steps; the element in the melt is transferred to the liquid-gas boundary interface, the atoms of the element are evaporated, followed by the transport of the atoms into the gas phase. A partial list of the volatility coefficients of elements in a bulk copper compiled by Li and Harris (1991) at 1183°C is shown in Table 2. Activity coefficients from Table 1, provided by Azakami and Yazawa (1976) and Sohn *et al.* (2004) at 1200 °C, were used to calculate additional volatility coefficients and the standardized temperature. Notably, the activity coefficients can vary depending on the calculation or experimental method used to attain them, but remains relatively small or large across different methodologies. The activity coefficient and relative vapor pressures, that is the

Table 2⁵: Calculated Volatility Coefficients

Element	Φ_i 1183°C	γ_M° 1183°C	Φ_i 1200 °C	$\gamma_M^{\circ*}$ 1200 °C
Au	$3.13 \cdot 10^{-3}$	0.14	$8.65 \cdot 10^{-3}$	0.14
Hg	$9.36 \cdot 10^7$	0.1		
Ag	148	3.27	180	4.8
Pt	$1.11 \cdot 10^{-8}$	0.0483	$4.05 \cdot 10^{-9}$	0.05
Pd	$1.8 \cdot 10^{-3}$	0.0581		0.06
Se	$3.12 \cdot 10^{-10}$	$1.86 \cdot 10^{-3}$		
Tl	$1.7 \cdot 10^5$	8.78		
Bi	$9.33 \cdot 10^3$	2.27	$7.11 \cdot 10^{3***}$	2.7
Bi₂			421 ^{***}	2.7
Cu				
Pb	$1.65 \cdot 10^4$	5.46	$1.33 \cdot 10^4$	5.7
Ga	1.12	0.0325	1.18	0.04
Ni	0.0168	2.24	0.0143	2.22
Cd	$3.64 \cdot 10^6$	0.526	$3.9 \cdot 10^6$	0.73
Sb			15.23 ^{***}	0.013
Sb₂	3.25	0.0133	4.57 ^{***}	0.013
As			0.093 ^{***}	$5.0 \cdot 10^{-4}$
As₂			7.35 ^{***}	$5.0 \cdot 10^{-4}$
As₄	0.053	0.011	0.77 ^{***}	$5.0 \cdot 10^{-4}$
Co	0.215	21.3	0.11	15.4
Ge	$8.11 \cdot 10^{-4}$	$8.52 \cdot 10^{-3}$	$1.74 \cdot 10^{-3}$	0.02
Sn	0.0105	$8.38 \cdot 10^{-3}$	0.11	0.11
In	69.9	39.4	42	0.32
Fe	0.502	20.2	0.36	19.5
Zn	$4.18 \cdot 10^5$	0.142	$2.4 \cdot 10^5$	0.11
Na	$4.67 \cdot 10^6$	1 ^{**}		
Cr	1.72	12.3	3.38	43
Mn	125	0.5	113	0.51
Si	$5.12 \cdot 10^{-3}$	1.75	$2.0 \cdot 10^{-3}$	0.006
Ti	$9.99 \cdot 10^{-5}$	0.371		
Al	0.0149	3.27	0.124	$2.8 \cdot 10^{-3}$

Ba	81.4	0.0264		
Mg	$9.49 \cdot 10^4$	0.0941	$3.32 \cdot 10^4$	0.044
Be	7.03	1**		
Ca	22.1	$4.65 \cdot 10^{-4}$	18.18	$5.0 \cdot 10^{-4}$

relationship of the bulk copper melt to its components in these binary systems, is in fact the same for several elements despite the temperature disparity. The calculated volatility coefficients are furthermore often within the same order of magnitude, showing the correlation of these calculations using either data source.

Seen immediately from the values provided by Li and Harris (1991), the volatility coefficient of bismuth and lead are far greater than arsenic, antimony, and nickel. For nickel ϕ_i is very small due to its low vapor pressure, while for arsenic it is due to its low activity coefficient. Equations 4.2 and 4.3, and these results, show that numerous properties and behaviors of elements must be considered for proper interpretation of even simple binary systems. In the discussion on activity in Chapter 3, for example, the high positive deviation of nickel may suggest an equally high volatility coefficient; however, it is limited here by its higher melting point. Increasing the temperature of the Cu-Ni binary will effectively lower nickel activity, but it is bound by the limitations mentioned above. Other instances include the noticeably larger ϕ_i for antimony than arsenic, which are due to the smaller value of P_i° of antimony for copper than arsenic.

⁵ Partially reproduced from Azakami and Yazawa (1976); Li and Harris (1991); *(Azakami and Yazawa (1976)); **unity assumed when no activity data exists; ***calculation based on vapor pressure of individual atomic species from Sohn *et al.* (2004)

4.7.1 Re-Ordered Volatilization

For the purposes of explaining element loss according to the volatility coefficient, it is useful to separate the metals used in antiquity into two groups of high and low volatility with volatility coefficients above one and below, respectively. In increasing order, the volatility coefficients are as follows according to Li and Harris (1991); Au, Sn, Ni, As₄, Co, Fe, Sb₂, Ag, Bi, Pb, Zn. The order is reasonable for all elements except arsenic, which Li and Harris (1991) calculated based on the vapor pressure of As₄. Polyatomic As₄ is, however, negligible at temperatures above 1000 °C as it dissociates into As₂. Antimony, on the other hand, is better represented with Sb₂, but also requires Sb, the predominate species, as both are important at copper melting temperatures. Bismuth also forms multiple species, namely Bi₂ and Bi, with the monomer being predominate. All three elements have been reevaluated, as well as the entire list, based on the individual elements species vapor pressures according to the activity values given in Table 1, and partial vapor pressures from Table 3 at 1200 °C. Elements in Table 2 and 3 listed in bold are those that are predominate. They are reordered as follows; Au, Ni, As, (Sn, Co), Fe, As₄, Sb₂, **As₂**, **Sb**, Ag, Bi₂, **Bi**, Pb, Zn with the group division lying from Au to As₄ for Group 1, and Sb₂ to Zn for Group 2. Immediately evident is that by recalculating the individual species of arsenic, its volatility coefficient has moved from Group 1 to Group 2. The groups are otherwise similarly ordered compared to those laid out by Li and Harris (1991).

Table 3⁶: Partial Vapor Pressure of Species

As	0.0091	Sb	0.0073	Bi	0.0215
As₂	0.1016	Sb ₂	0.0031	Bi ₂	0.0018
As₄	0.0151				

⁶ Sohn *et al.* (2004) for partial vapor pressure in matte

4.8 Summary of Element Volatility

Group 1 components consists of elements and their species with volatility coefficients less than 1. These are very unlikely to be lost through fire refining, nevertheless, cobalt, iron, and tin may be lost by other means such as oxidation and skimming. Cobalt and tin are coupled together sharing the same position and having nearly equal volatility coefficients, and likely have the same proportional rate of loss by evaporation. The inclusion of the monomer and tetramer of arsenic in Group 1, are counter to the assumed high vapor pressure of arsenic, and in fact make up only a small proportion of the total arsenic vapor present over a copper melt. In most modern industrial copper refining practices, the removal of either species is ignored. Their impact on the total loss of arsenic is considered negligible (Nagamori and Chaubal, 1982; Chaubal and Nagamori, 1988; Pei, 1993).

Group 2 contains As_2 , as well as both species of antimony and bismuth. All of the elements and species' elements listed in this group are highly volatile compared to Group 1. Their loss in a reducing or oxidizing environment is assured as either pure elements or oxides. Further, at low mole fraction concentrations the calculated volatility coefficients should remain constant in accordance with Henry's law as they are calculated in dilute solutions. Since there is no change in the activity coefficient, except at higher mole fractions according to the above activity diagrams, the volatility coefficient remains unchanged.

In reasonably refined copper where no component is in extreme excess compared to another, in order change the slope of the activity –which is different for each component and makes such a list merely a reference guide– the following summary of the loss of elements from a copper melt should have prevailed in ancient pyrometallurgy (Table 4). The summary is valid

if one assumes no 3-body+ interactions in ternary or higher systems, and gives a good first estimate of element loss.

Important to keep in mind is that during the recycling of metal, the buildup of oxygen in objects caused by rapid oxidation during casting of prior object generations, or simply oxidized scrap metal, would lead to initial high losses of elements as volatile oxides. Oxidation would then be followed by the deposition of an oxide film, which if removed or disturbed, would lead to increased volatility. The information provided in this chapter is key to understanding the loss and enrichment of elements in ancient refining/recycling. The following chapter, Chapter 5, goes further and explains one probable influence in the behavior of the elements in a copper melt according to ionic melt theory.

Table 4: Ordered Summary of Calculated Oxidation and Volatilization

<u>Oxidation</u>															
Least	Au	Ag	As	Sb	Bi	Pb	Sn	Ni	Co	Zn	Fe	Greatest			
<u>Volatilization</u>															
Least	Au	Ni	As	(Sn, Co)	Fe	As ₄	Sb ₂	As ₂	Sb	Ag	Bi ₂	Bi	Pb	Zn	Greatest

5. Element Behavior and Ionic Melt Theory

The two previous chapters explain the behavior of elements in molten copper according to oxidation and volatilization, but these give an incomplete picture and require a more comprehensive interpretation using ionic melt theory, if only to provide a visual representation of element behavior for the reader. For high grade modern mattes and converting, this theory, as opposed to a mixture of covalent and ionic bonding, has been successful in explaining the behavioral outcome of impurities mixed into molten copper. This theory supports the premise of this thesis that activity can be used to understand and predict the recycling of copper-based objects, but it should be noted that it is only one of many such theories. The atomic scale models of liquids are much less accurate than those for crystalline solids, but do offer insight into the behavior of molten metal system.

Very little is known of the actual structure of elements in a copper melt. Ionic melt theory postulates that in a copper melt the components behave according to ionic, rather than molecular/metallic bonding (Roine and Jalkanen, 1985; Larouche, 2001). In this system exists short-range networks of ionically bonded ions, and the possible substitution of one ion for another is based on individual atom valencies and sizes. Micro-groupings of metal-rich, and sulfur and oxygen-rich, regions also exist and their behavior to one another, and to the rest of the melt, are based on their affinities to the copper bulk and to themselves, which may result in them acting independently and deviating positively (Roine and Jalkanen, 1985). In relation to the enthalpy of mixing, the affinities of the metal- and sulfur and oxygen-rich regions can be explained by the bonding favorability of components discussed in Chapter 2. In refined copper, the kind that would contain insufficient amounts of O and or S ions to bond with every Cu or other metal cations, this theory seems lacking as there is no charge balance. In such cases it is

likely that metallic bonding is predominate, nevertheless ionic melt theory provides a better basis for the positive and negative deviation of components than other interpretative approaches. Ions of compatible sizes and smaller, that could perhaps group together to fill vacant positions of larger ones, would cause negative deviation, while those too large, positive.

In a copper ionic melt single and coupled substitution maintains electrical neutrality between anions and cations according to their nearest neighbors. Table 5 shows the valence charges and sizes for coordination six, which represents the number of neighbors for an ion that can contribute to charge neutralization. In substitution, one ion is exchanged for another of similar size and charge, and can occur for either the cation or anion. In coupled substitution, which is the more likely mechanism in a copper melt given the variety of elements, electrical neutrality is maintained through simple addition. If, for instance, an a^{3+} ion substitutes for a b^{2+} in a $2b^{2+}$ molecule there must be a simultaneous substitution of the other b^{2+} with a c^+ ion.

Furthermore, there are instances when a higher charged cation replaces two or more cations leaving a void where the second ion would have resided. In these situations, known as omissions, electrical neutrality is maintained but a void exists that can result in visible defects, such as color change once the lattice is frozen. This type of substitution is similar to coupled substitution, but with a non-existent naught ion.

The values for the atomic and ionic radii in Table 5 show the size differences and substitution possibilities for positively and negatively charged elements found in copper melts. In a network of large S^{2-} anions with small Cu^+ and Fe^+ cations between the anions, either the sulfur will be replaced by a similarly large sized atom or molecule, or the copper and iron by a similarly small atom. This is the case for matte smelting where both copper and iron have high

affinity for sulfur and exist as Cu_2S and FeS . For iron the oxidative states of Fe^{2+} and Fe^{3+} are most common with Fe^{3+} being the most stable, but due to size restrictions only the Fe^{2+} ion is considered.

In the absence of sulfur during copper refining, however, As and Sb are thought to exist in a molecular state, and as such should take the place of the larger S^{2-} ions. This theory helps to explain the low affinity of As and Sb, and high for Cu, for sulfur in converting and high grade matte smelting; since the comparatively large sizes of As and Sb cannot replace the smaller Cu^+ and Fe^{2+} cations. Furthermore, it is possible for As and Sb to exist in a metallic form within the ionic melt due to their low affinity for sulfur under high sulfur pressure.

Table 5: Atomic and Ionic Radii

Element	Atomic Radii	Ionic Radii							
		1-	2-	3-	1+	2+	3+	4+	5+
O	0.066		0.140						
S	0.104		0.184					0.037	
Fe	0.124					0.078	0.065	0.073	
Co	0.125					0.075	0.061	0.053	
Ni	0.125					0.069	0.060		
Cu	0.128				0.077	0.073	0.054	0.048	
Zn	0.133					0.074			
As	0.125					0.058			
Ag	0.144				0.115	0.094	0.075		
Sn	0.141							0.069	
Sb	0.136						0.076		0.060
Au	0.144				0.137		0.085		0.057
Hg	0.160				0.199	0.102			
Pb	0.175					0.119		0.078	
Bi	0.155						0.103		0.076

Bismuth and Pb, on the other hand, may take separate metallic forms due to their low affinities for copper and iron (Roine and Jalkanen 1985). It is also possible for the substitution of lead as stable Pb^{2+} ions for Fe^{2+} and Cu^+ that are bonded to S^{2-} despite the larger size of Pb. Lead being capable of forming Pb^{2+} and Pb^{4+} with the former being stable. The temporary substitution of larger ions for smaller ones is possible due to the short range order of ionic melts, which does not remain after freezing. Bismuth, furthermore, existing as Bi or Bi^{3+} ions, may substitute for sulfur, especially under oxidizing conditions because of the similar size of molecular bismuth and sulfur. The substitution of bismuth may occur temporarily and only with two additional neighboring sulfur or oxygen atoms to maintain charge balance. If nickel or cobalt is present they exist as Ni^+ and Co^{2+} ions -the Co^{3+} state of cobalt being unstable- and behave much like copper directly substituting for copper ions. Both ionic and atomic radii of nickel are similar in size.

During copper smelting and converting there is thought to exist areas of metal and sulfur micro groupings that dynamically exchange ions based on their random distribution and the affinity of one ion for another (Roine and Jalkanen 1985). In essence this means that any combination of ions will have low stability and are subjected to constant reformation. Meanwhile, the metallic constituents will dissolve into established groupings based on their affinities, or behave independent of the bulk melt.

For copper melts devoid of sulfur, and if one assumes the melt is saturated with oxygen, atoms form theoretical ionically charge balanced bonds according to their respective equilibrium constants as listed in Table 1. In modern refining great effort is expended to remove oxygen to improve such properties as the heat and electrical conductivity, however, it undoubtedly remained in ancient copper in large quantities not having been purified beyond the means of fire refining. In the stead of S^{2-} , therefore, O^{2-} would be responsible for the ionic bonding tendencies

in terms of charge balance, and with virtually no limitations despite the smaller O^{2-} radius size. The possibility of larger ions replacing smaller ones was already mentioned for Pb^{2+} ions, and here also applies for oxygen. This replacement, however, is also short-lived ultimately resulting in segregation and metallic lead.

In general, of the elements considered in a copper melt showing negative Gibbs free energy from lead to calcium in Table 1, and that form nonvolatile or have low volatility oxides, would likely remain in the melt as oxides due to the slow mass transfer of oxygen and oxides in copper. The rate of mass transfer restricted by strong ionic tendencies is evidenced by the practice of poling with green wood, which, among other changes, introduces agitation and hydrogen gas efflorescence aiding in the migration of oxygen to the surface of the melt. Elements listed above copper found in ancient copper objects from gold to bismuth behave independently of oxygen affinity, and substitute as atoms or temporary ions in the same manner as bismuth does and sulfur only under oxidizing conditions.

The behavior of tin and its oxides are comparatively unusual to all of the other elements considered. It exhibits both positive and negative activity deviations from unity warranting further explanation. Tin forms Sn^{2+} and Sn^{4+} oxidizing as the stable Sn^{4+} state with O^{2-} to form SnO_2 , which requires two oxygen atoms for every one of tin. Further, tin and tin dioxide form a tetragonal crystal structure when solid, and while molten, as the solute within copper, likely exists as such in short range order, which is incompatible with the cubic structure of copper and copper oxide. This incompatible structure is likely the reason why the activity of tin approaches ideality as more tin ions are present leading to its eventual positive deviation in mole fractions beyond 0.5. Upon freezing, however, it is possible for tin atoms to form metallic bonds with

copper due to the relatively close sizes of their atomic radii. The small size of the Sn^{4+} ion in the melt should replace Cu^{2+} leaving a vacant position maintaining charge balance.

In modern copper smelting ore undergoes continuous converting where, what was achieved in multiple heating and cooling steps in antiquity, is now a single process. Regardless of process, however, once these steps reach approximately 77 percent copper and metallic copper appears after freezing, a change is made from ionic to metallic bonds which then integrate themselves into the bulk copper metallic matrix (Larouche, 2001, 26). If high copper content ores were smelted in antiquity a high percentage copper matte may have been quickly achieved. At this point the radii of each component becomes especially important, since it will partially determine whether they can form long order stable metallic bonds with copper. If they are of the same crystal structure or otherwise compatible like tin, they may fit within the FCC lattice of copper, but will otherwise be rejected beginning with those elements that are still liquid, as is the case with lead. In comparison to the activity coefficients of impurities in matte, those in copper are much less, except for Pb. When metallic bonds begin to form a sharp increase in γ_{Pb} occurs indicating matrix incompatibility and the formation instead of unalloyed molecular lead (Kim and Sohn, 1998; Nagamori and Chaubal, 1982).

Once metallic copper forms the loss of elements becomes more difficult due to the increased stability of metallic bonds as opposed to ionic. Of note, however, is the high value of the nickel activity coefficient, which allows for the metal's survival through copper melting processes. Its activity coefficient is related to its size similarity to Cu and ability to form stable molecules and easily fit within, and become trapped in, the FCC lattice structure shared by both metals at ambient temperature. Other elements that alloy well with copper in this way include tin, arsenic, antimony, zinc, silver, and gold. In the case of silver, that also forms an FCC lattice,

and despite its positive activity coefficient, if present it is capable of forming metallic bonds and integrating into the copper matrix.

According to the above valencies and ion charges, the breakdown and reformation of metals by melting and nucleation follow set rules and processes. During re-melting and recycling a metal lattice is broken into smaller ranges of order, which is evidenced by decreased coordination and increased volume in the melt. When solid again a metal's long-ranged order is reestablished, and for elements to become integrated into this order they must satisfy the Hume-Rothery rules that state the following: there must ideally be less than ~15% difference in atomic radii; the same crystal structure; similar electronegativity, and; the same valence (Gokcen, 1986, 53 – 54). The first rule dictates that the closer the alloying metal is to the 15% limit, the less the metal can be dissolved into the solvent. However, even if the two metals are within the 15% limit, differences in their electronegativity ultimately determines solid solubility. Based on these rules it is clear why bismuth and lead do not alloy well with copper, why it is possible to manufacture high zinc brasses, and why nickel and copper are completely soluble.

5.1 Summary

The above chapter provides one possible explanation, amongst many, for the observed behavior of elements in molten metal binary systems according to the size of ions and their possible substitution for other ions in a copper melt. Substitution depends on the sizes and valencies of atoms and molecules. Once solid these ions then follow the Hume-Rothery rules. Ionic melt theory is useful in understanding the behavior of the molten systems discussed previously in this thesis, and especially in the following chapters where additional elements of varying size and charge are present. The information in this chapter is integrated into the ternary systems descriptions in Chapter 7, which provides an extra level of background and transparency

into the calculated behavior of each element. Derivations for binary and ternary systems are given in Chapter 6.

6. Interpretation of Artifact Chemical Changes Using Oxidation and Volatilization

The above summary, tables, diagrams, and written explanations provide good preliminary approximation predictions of individual element behavior in molten copper through the application of their thermodynamic properties in binary systems under standardized boundary conditions. What is clear is that the key to understanding the behavior of copper-based molten mixtures, is in their thermodynamic properties and interactive behaviors. However, just as each binary copper-based system is only understood in relation to each component to one another, in more complex systems, where one considers three or more elements, it is necessary to account for the interaction of each element in their respective binary pairs. For every ternary system consisting of elements *a*, *b*, and *c*, for example, one must calculate the interaction of element *a* for *b*, *a* for *c*, *b* for *a*, *b* for *c*, *c* for *a*, and *c* for *b* at a given temperature and pressure. Each of these basic calculations require several steps as outlined in previous chapters. Once these basic interactions are understood by calculating behavior over the entire range of the composition, it is then possible to calculate the approximate activity behavior of each individual component at specified compositions in each elements respective ternary.

However, given the binary Cu-M interactions, and in the absence of additional systems data and in-depth mathematical evaluations, it is possible to follow the ordered behaviors of element loss by oxidation and volatilization shown in Tables 1 and 2, although caution should be taken as these data are approximations of simple binary systems. Building on the binary thermodynamic data to predict the behavioral outcome of complex systems is done through calculable relationships of combined pairs of binary systems, giving good approximations of component behavior; however, additional evaluations should be sought through experiment if possible. Often the measured behavior of elements in complex systems deviate somewhat from

those found through calculation, which then requires that their mathematical descriptions be adjusted with additional interaction parameters.

The activity calculations for each element in the ternary requires the calculated binary activities, and related data such as mole fractions and activity coefficients, to be considered simultaneously where the sum of the components mole fractions are equal to 1. Isoactivity contour line approximation calculations can be then performed using several choices of related polynomial equations, of which this thesis utilizes the method described by Redlich and Kister (1948). This polynomial, like the basic calculations above, requires several steps that are discussed in detail in the equations in the following sections 6.1 and 6.2. In total the steps necessary to completely evaluate the activity of each component in the ternary and higher order systems from the binary interactions, excluding intermediary steps, is nine, or $n! + n$ where n is the number of components. Based on this simple permutation equation, if one then wishes to calculate quaternary or higher order systems it is clear that the number of calculations dramatically increases, as would their length as more steps and parameters would be necessary. For this reason, the scope of this thesis is limited to ternary systems with the possible addition of quaternary and higher systems in the future. The following discussions and derivations, beginning with binary systems, moving on to ternary, in the following sections of this chapter describe the method used in this thesis.⁷

⁷ Derivations provided by Dr. Robert Thomas, department of Physical & Theoretical Chemistry, University of Oxford.

6.1 Binary Mixtures

Equations 2.3, 2.4, and 2.5 give the simplest explanation of activity without the underlying derivations of the activity coefficient and mole fraction. Unfortunately, these are insufficient for understanding and calculating of ternary and higher systems since they do not account for interactions of multiple components. They are therefore systematically derived here for ternary systems.

Recalling the free energy of mixing from Equation 1.4 for mole fractions of two components and the chemical potential, the chemical potential of mixing (Equation 6.0) for i and j is given as the sum of the standard state of mixing and partial derivative of the free energy of mixing. However, differentiation with Equation 1.4 gives false results since it is defined according to dependent mole fractions rather than the total amount of molecules represented by n_1 and n_2 . Substitution of x_1 and x_2 by these terms and multiplication by Equation 1.4 gives 6.1, which are now represented as independent variables as well as independent of the total number of molecules. Differentiation keeping n_2 constant can now take place, giving Equation 6.2, where one can now see the relationship between the chemical potential of mixing and the Gibbs free energy of mixing. More importantly, these relationships play an important role in the calculation of the partial vapor pressure of individual components. Similar to the discussion of the free energy of mixing, it is possible to expand on these equations with additional terms in higher order systems.

$$\mu_i^{mix} = \mu_i^o + \left(\frac{\delta \Delta G_{mix}}{\partial n_i} \right)_{n_j} \quad 6.0$$

$$\Delta G_{mix} = RT \left(n_1 \ln \left(\frac{n_1}{n_1 + n_2} \right) + n_2 \ln \left(\frac{n_2}{n_1 + n_2} \right) \right) \quad 6.1$$

$$\mu_1^{mix} = RT \left(\ln \left(\frac{n_1}{n_1 + n_2} \right) + \frac{n_2}{n_1 + n_2} - \frac{n_2}{n_1 + n_2} \right) = RT \ln x_1 \quad 6.2$$

For the activity coefficient of ternary systems, the simplest model is that for quadratic mixtures, also known as regular solutions, for non-ideal behavior (Rowlinson, 1969, 122 – 123). Under this model the entropy of mixing is assumed to be ideal, but the enthalpy of mixing, unlike in the binary, is not zero. The activity coefficient, as discussed in detail in earlier chapters, represents the interaction of molecules, but as introduced does not explain the contribution of each binary in a ternary system. For this to be possible, we must define interaction parameters given the interaction of molecules in each binary. In a random mixture of type 1 and 2 molecules with average coordination number z , there is total contact of type 21 of zn_2 molecules when there are n_2 molecules of 2 in the mixture, and x_1zn_2 contacts with molecules of 1. For pure type molecules of 1 and 2, the contacts would have been 11 and 22, but in the mixture of 12 the change in bonding energy, ϵ , of component 2, and 1 is given by Equations 6.3 and 6.4. The total energy change, E , on mixing is then given by Equation 6.5, where the interactions are halved to prevent counting them twice, the mole fractions are written as the total number of molecules of 1 and 2, n_n , and $\frac{z(2\epsilon_{12}\epsilon_{11}-\epsilon_{22})}{2}$ is replaced by B . One can arrive at the interaction parameters C and D similarly for each binary combination.

$$x_1zn_2(\epsilon_{21} - \epsilon_{22}) \quad 6.3$$

$$x_2zn_1(\epsilon_{21} - \epsilon_{11}) \quad 6.4$$

$$E = \frac{1}{2} \frac{zn_1n_2}{n_1 + n_2} (2\epsilon_{21} - \epsilon_{11} - \epsilon_{22}) = B \frac{n_1n_2}{n_1 + n_2} \quad 6.5$$

Rearranging Equation 2.4, and if one assumes the enthalpy of mixing is the same as the energy of mixing, the energy becomes part of the excess free energy of mixing where $E = G^E$ in the regular solution model. The activity coefficient is then defined by the chemical potential, μ^E , in Equation 6.7, and each component's activity coefficient in the binary can be found by differentiating Equation 6.5 against G^E in 6.8. For a first approximation of the excess Gibbs energy in a binary mixture of components 1 and 2, Equation 6.9, dependent on temperature, is applied. Of note is that the excess free energy is commonly written in terms of mole fractions, and, this again, must be converted as above to represent the total molecules in the system in order to be properly derived.⁸

$$\mu_i = \mu^\circ + RT \ln x_i + RT \ln \gamma_i = \mu^{ideal} + RT \ln \gamma_i \quad 6.6$$

$$RT \ln \gamma_i = \mu^E = \left(\frac{\delta G^E}{\delta n_i} \right)_{n_j} \quad 6.7$$

$$RT \ln \gamma_1 = \left(\frac{\partial G^E}{\partial n_1} \right)_{T,P,n_2} = B \left(\frac{n_2}{n_1 + n_2} - \frac{n_1n_2}{n_1 + n_2} \right) = Bx_2^2 \quad 6.8$$

$$G^E = Bx_1x_2 \quad 6.9$$

⁸ See Appendix A.2 for a comprehensive derivation of mixing with respect to x_1 rather than n_1 . This derivation is necessary for standard models of ternary system calculations.

6.2 Ternary Mixtures

Based on the derivation of mixing with respect to x_1 from Appendix A.2, ternary mixtures, after Equation 6.10 for binary mixtures changed from (T, P, x_1, N_A) to $(T, P, x_1, x_2, 1)$, adds an additional term for x_2 . When this equation is applied to the free energy of mixing 1.4 without substitution of the x_2 variable, it agrees with Equation 6.2, which, as a first step, shows a necessary and logical connection to later ternary calculations.

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = (1 - x_1) \left(\frac{\partial G}{\partial x_1}\right) - x_2 \left(\frac{\partial G}{\partial x_2}\right) + G_m \quad 6.10$$

$$\frac{1}{RT} \left(\frac{\partial G}{\partial n_1}\right)_{n_2} = (1 - x_1)(\ln x_1 + 1) - x_2(\ln x_2 + 1) + x_1 \ln x_1 + x_2 \ln x_2 = \ln x_1 \quad 6.11$$

For the ternary, similarly to the topmost equation from Appendix A.2, Equation 6.12 is adjusted holding dn_1 and dn_3 constant and dividing by δn_2 , which results in Equation 6.13 with an additional term on the right side. Following Appendix A.2, with similar substitutions for the mole fractions but with n_1, n_2 , and n_3 following 6.14 and 6.15, Equation 6.13 becomes 6.16. For a ternary mixture Equation 6.16 is correct, but as written with only x_1 and x_2 requires a substitution for x_3 in terms of the first two mole fractions. Inclusion of x_3 , as done in 6.20, gives Equation 6.17, which is also given by Redlich and Kister (1948).

$$\begin{aligned} \left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n_1, n_3} dn_2 + \left(\frac{\partial G}{\partial n_3}\right)_{n_1, n_2} dn_3 \\ = \left(\frac{\partial G}{\partial x_1}\right)_{N_A, x_2} dx_1 + \left(\frac{\partial G}{\partial x_2}\right)_{N_A, x_1} dx_2 + \left(\frac{\partial G}{\partial N_A}\right)_{x_1, x_2} dN_A \end{aligned} \quad 6.12$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3} = \left(\frac{\partial G}{\partial x_1}\right)_{N_A, x_2} \left(\frac{\partial x_1}{\partial n_1}\right)_{n_2, n_3} + \left(\frac{\partial G}{\partial x_2}\right)_{N_A, x_1} \left(\frac{\partial x_2}{\partial n_1}\right)_{n_2, n_3} + \left(\frac{\partial G}{\partial N_A}\right)_{x_1, x_2} \left(\frac{\partial N}{\partial x_1}\right)_{n_2, n_3} \quad 6.13$$

$$\left(\frac{\partial x_1}{\partial n_1}\right)_{n_1, n_3} = \frac{1}{n_1 + n_2 + n_3} - \frac{n_1}{(n_1 + n_2 + n_3)^2} = \frac{(1 - x_1)}{N_A} \quad 6.14$$

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2, n_3} = -\frac{n_2}{(n_1 + n_2 + n_3)^2} = -\frac{x_2}{N_A} \quad 6.15$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3} = \frac{(1 - x_1)}{N_A} \left(\frac{\partial G}{\partial x_1}\right)_{N_A, x_2} - \frac{x_2}{N_A} \left(\frac{\partial G}{\partial x_2}\right)_{N_A, x_1} + G_m \quad 6.16$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2, n_3} = (1 - x_1) \left(\frac{\partial G}{\partial x_1}\right)_{x_2, x_3} - x_2 \left(\frac{\partial G}{\partial x_2}\right)_{x_1, x_3} - x_3 \left(\frac{\partial G}{\partial x_3}\right)_{x_1, x_2} + G_m \quad 6.17$$

According to Redlich and Kister (1948), to correct for deviations from the first approximations given by Equation 6.9, the Gibbs excess energy can be represented as a series expansion, which, explainable first in the binary using Equation 6.18 where $x_1 x_2$ and $(x_1 - x_2)$ ensures the correct limits and sign of the expression, respectively. Important to note is that the sign is reversed on the odd-order term C when the components are interchanged, and that this change introduces a limit, reducing the asymmetry in the components that arises when they are switched (O'Connell and Haile, 2005, 212). Before attempting the ternary activity coefficient calculations, it is helpful to first express a limited case for the B quadratic index where $C = D = 0$ (Eq. 6.19), after A.3.3, for the binary where as pure components $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ (O'Connell and Haile, 2005, 213). Limiting the system to the three binary combinations and single interaction parameter, the excess free energy is given as 6.20, and the activity coefficients using Equation 6.17 for just the B parameter for component 1B is given by Equation 6.21. For 2B and 3B, according to Porter (1920), it is then possible to cycle the components to find their activity

coefficients, since it does not matter which component is designated 1, 2, or 3, thus giving Equations 6.22 and 6.23. These three formulae for the activity coefficient are implied but not given by Redlich and Kister despite their importance for ternary calculations. Their validity here is confirmed by both Porter and Equation 6.24, which is the result of the subtraction of 6.21 and 6.22. It is further proven by the introduction of three components to the binary derivation of the excess energy after Equation 6.5, and since $E = G^E$ the partial derivation of Equation 6.25 results in an identical equation for the activity coefficient of 1B 6.26 as given by 6.21.

Before progressing further, a note on the excess Gibbs energy given by Equation 6.20 is necessary to explain the apparent lack of a ternary interaction parameter. Although this thesis calculates ternary systems, it does not include 3-body interactions since they, as explained for multi-body interactions in ternary systems and above, are implicitly embedded in each binary parameter. The advantage of the approach employed here is that multi-component systems can be calculated using only the binary interactions, although with some loss in accuracy (O'Connell and Haile, 2005, 216).

$$G_B^E = x_1 x_2 (B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots) \quad 6.18$$

$$RT \ln \gamma_{1B} = (1 - x_1)Bx_2 - Bx_2x_1 + Bx_1x_2 = Bx_2^2 \quad 6.19$$

$$G_B^E = x_1 x_2 B_{12} + x_2 x_3 B_{23} + x_3 x_1 B_{31} \quad 6.20$$

$$RT \ln \gamma_{1B} = (1 - x_1)(x_2 B_{12} + x_3 B_{31}) - x_2(x_1 B_{12} + x_3 B_{23}) - x_3(x_2 B_{23} + x_1 B_{31}) \quad 6.21$$

$$\begin{aligned} + G^E &= x_2 B_{12} + x_3 B_{31} - x_1 x_2 B_{12} - x_2 x_3 B_{23} - x_3 x_1 B_{31} \\ &= x_2(1 - x_1)B_{12} - x_2 x_3 B_{23} + x_3(1 - x_1)B_{31} \end{aligned}$$

$$RT \ln \gamma_{2B} = x_3^2 B_{23} + x_3 x_1 (B_{23} - B_{31} + B_{12}) + x_1^2 B_{12} \quad 6.22$$

$$RT \ln \gamma_{3B} = x_1^2 B_{31} + x_1 x_2 (B_{31} - B_{12} + B_{23}) + x_2^2 B_{23} \quad 6.23$$

$$RT \ln \left(\frac{\gamma_2}{\gamma_1} \right) = (x_1 - x_2) B_{12} + x_3 (B_{23} - B_{31}) \quad 6.24$$

$$G_B^E = \frac{n_1 n_2 B_{12}}{n_1 + n_2 + n_3} + \frac{n_2 n_3 B_{23}}{n_1 + n_2 + n_3} + \frac{n_3 n_1 B_{31}}{n_1 + n_2 + n_3} \quad 6.25$$

$$\begin{aligned} \left(\frac{\partial G^B}{\partial n_1} \right) &= \frac{B_{12}(n_2^2 + n_2 n_3)}{(n_1 + n_2 + n_3)^2} - \frac{n_2 n_3 B_{23}}{(n_1 + n_2 + n_3)^2} + \frac{B_{31}(n_3^2 + n_2 n_3)}{(n_1 + n_2 + n_3)^2} \\ &= (x_2^2 + x_2 x_3) B_{12} - x_2 x_3 B_{23} + (x_3^2 + x_2 x_3) B_{31} \\ &= x_2 (1 - x_1) B_{12} - x_2 x_3 B_{23} + x_3 (1 - x_1) B_{31} \\ &= x_2 B_{12} + x_2 x_3 (B_{12} - B_{23} + B_{31}) + x_3^2 B_{31} \end{aligned} \quad 6.26$$

The B parameter outlined above is but one part of the process of determining the activity of a single component in a ternary system. With the addition of the cubic C and quartic D parameters they can collectively give a best-fit activity coefficient value for non-regular solutions. The activity coefficient, or simply the behavior, of the component in question according to the three parameters in a binary mixture is discussed by Redlich and Kister (1948) and categorized as ideal, regular, Margules, and methanol/hydrocarbon. In the ideal situation $\ln \left(\frac{\gamma_1}{\gamma_2} \right) = 0$ following Raoult's law thus requiring no parameter, but for a regular solution, $B \neq 0$ and $\ln \left(\frac{\gamma_1}{\gamma_2} \right)$, after 6.24, is a linear function of x_1 that must pass through zero at $x_1 = 0.5$ (Rowlinson, 1969, 115 – 122). In the third categorization, the Margules regime is followed where $B \neq 0$, $C \neq 0$ and $D = 0$, and both B and C are determined from fixed points plotted by $\ln \left(\frac{\gamma_1}{\gamma_2} \right) - x_1$. The Margules regime is capable of describing binary mixtures that exhibit both

positive and negative deviation but fail where the activity coefficient is greater than unity and passes through extrema (O'Connell and Haile, 2005, 213 – 216). Finally, in the case of methanol/hydrocarbons, $B \neq 0$, $C = 0$, and $D \neq 0$, and the coefficients can be found similarly to the third. These conditions for non-electrolyte behavior give the foundations for each of the three parameters, but these, of course, require more explanation, as well as adaptation, for ternary systems.

These parameters may be further explained by the following: A regular solution model is obeyed when each component is at equal volume, but when they are not and $C \neq 0$, C is represented by 6.27. For the Margules equation, it is often written as 6.28 and is convertible to the so-called Redlich-Kister parameters by substituting A_{21} with $B + C$ and A_{22} with $B - C$. Evaluating the Gibbs excess energy for the C and D parameters for binaries is then done separately using Equations 6.29 and 6.30, and the activity coefficients of each parameter using 6.31 and 6.32 by applying 6.10. In both Equations 6.31 and 6.32 the indices are reversed, as opposed to the B parameter, as, in addition, is the sign of the C parameter as discussed by Rowlinson (1969, 122) and Barker (1953).

$$C = \frac{-B(V_1 - V_2)}{V_1 + V_2} \quad 6.27$$

$$Q = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \quad 6.28$$

$$G_C^E = x_1 x_2 (x_1 - x_2) C \quad 6.29$$

$$G_D^E = x_1 x_2 (x_1 - x_2)^2 D \quad 6.30$$

$$RT \ln \gamma_{1C} = (2x_1 x_2 (1 - x_1 + x_2) - x_2^2) C = x_2^2 (3 - 4x_2) C \quad 6.31$$

$$RT \ln \gamma_{1D} = (x_1 - x_2)(3x_1x_2(1 - x_1 + x_2) - x_2^2)D = x_2^2(5 - 16x_2 + 12x_2^2)D \quad 6.32$$

In the ternary mixture the C and D excess energies are expressed by Equations 6.33 and 6.34, and the activity coefficient for the C parameter for component 1 by 6.35 and simplified to 6.36. Components 2 and 3 are similarly expressed by the simplified Equations 6.37 and 6.38. The D parameter is found using the same method and is shown in Equation 6.39, and simplified as 6.40, 6.41, and 6.42 for each component. The resultant activity coefficients are finally added and then multiplied by the value of the mole fraction, x_n , originally supplied to solve for the activity coefficient of the desired component. These equations, specifically 6.20, 6.33, 6.34, are the means by which the isoactivity lines have been calculated in this thesis. In order to achieve high visual resolution in the diagrams, and accuracy in the results, they have been repeated thousands of times over for each component.

$$G_C^E = x_1x_2(x_1 - x_2)C_{12} + x_2x_3(x_2 - x_3)C_{23} + x_3x_1(x_3 - x_1)C_{31} \quad 6.33$$

$$G_D^E = x_1x_2(x_1 - x_2)^2D_{12} + x_2x_3(x_2 - x_3)^2D_{23} + x_3x_1(x_3 - x_1)^2D_{31} \quad 6.34$$

$$RT \ln \gamma_{1C} = (1 - x_1)((2x_1x_2 - x_2^2)C_{12} + (x_3^2 - 2x_1x_3)C_{31}) \quad 6.35$$

$$\begin{aligned} & - x_2((x_1^2 - 2x_1x_2)C_{12} + (2x_2x_3 - x_3^2)C_{23}) \\ & - x_3((x_2^2 - 2x_2x_3)C_{23} + (2x_1x_3 - x_1^2)C_{31}) + x_1x_2(x_1 - x_2)C_{12} \\ & + x_2x_3(x_2 - x_3)C_{23} + x_3x_1(x_3 - x_1)C_{31} \end{aligned}$$

$$\begin{aligned} RT \ln \gamma_{1C} = & (2x_1x_2(1 - x_1 + x_2) - x_2^2)C_{12} + 2x_2x_3(x_3 - x_2)C_{23} \\ & - (2x_3x_1(1 - x_1 + x_3) - x_3^2)C_{31} \end{aligned} \quad 6.36$$

$$RT \ln \gamma_{2C} = (2x_2x_3(1 - x_2 + x_3) - x_3^2)C_{23} + 2x_3x_1(x_1 - x_3)C_{31} \\ - (2x_1x_2(1 - x_2 + x_1) - x_1^2)C_{12} \quad 6.37$$

$$RT \ln \gamma_{3C} = (2x_3x_1(1 - x_3 + x_1) - x_1^2)C_{31} + 2x_1x_2(x_2 - x_1)C_{12} \\ - (2x_2x_3(1 - x_3 + x_2) - x_2^2)C_{23} \quad 6.38$$

$$RT \ln \gamma_{1D} = (1 - x_1)(x_2(x_1 - x_2)^2 + 2x_1x_2(x_1 - x_2))D_{12} \\ + (x_3(x_3 - x_1)^2 - 2x_3x_1(x_3 - x_1))D_{31} \\ - x_2(x_1(x_1 - x_2)^2 - 2x_1x_2(x_1 - x_2))D_{12} \\ + (x_3(x_2 - x_3)^2 + 2x_2x_3(x_2 - x_3))D_{23} \\ - x_3(x_2(x_2 - x_3)^2 - 2x_2x_3(x_2 - x_3))D_{23} \\ + (x_1(x_3 - x_1)^2 + 2x_1x_3(x_3 - x_1))D_{31} + x_1x_2(x_1 - x_2)^2D_{12} \\ + x_2x_3(x_2 - x_3)^2D_{23} + x_3x_1(x_3 - x_1)^2D_{31} \quad 6.39$$

$$RT \ln \gamma_{1D} = (x_1 - x_2)(3x_1x_2(1 - x_1 + x_2) - x_2^2)D_{12} \\ + (x_2 - x_3)(3x_2^2x_3 - 3x_2x_3^2)D_{23} \\ + (x_1 - x_3)(3x_1x_3(1 - x_1 + x_3) - x_3^2)D_{31} \quad 6.40$$

$$RT \ln \gamma_{2D} = (x_2 - x_3)(3x_2x_3(1 - x_2 + x_3) - x_3^2)D_{23} \\ + (x_3 - x_1)(3x_3^2x_1 - 3x_3x_1^2)D_{31} \\ + (x_2 - x_1)(3x_2x_1(1 - x_2 + x_1) - x_1^2)D_{12} \quad 6.41$$

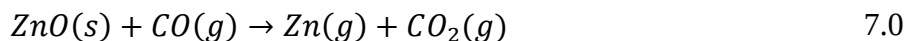
$$RT \ln \gamma_{3D} = (x_3 - x_1)(3x_3x_1(1 - x_3 + x_1) - x_1^2)D_{31} \\ + (x_1 - x_2)(3x_1^2x_2 - 3x_1x_2^2)D_{12} \\ + (x_2 - x_3)(3x_3x_2(1 - x_3 + x_2) - x_2^2)D_{23} \quad 6.42$$

6.3 Summary

This chapter describes a statistical theory for the interaction of molecules, or atoms, as they are understood in the simplest terms of a binary system before expanding upon and applying this knowledge to ternary systems. The derivations of both binary and ternary systems, ultimately resulting in the activity coefficient of three parameters that are inextricably bound to the Gibbs-Duhem relationship, explain how the ternary diagrams in Chapter 7 were built. The combined activity coefficients provide the means that the lines of isoactivity are drawn in ternary diagrams, which, as described above, was first described by Redlich and Kister (1948). The construction of the ternary diagrams and the interpretation of their results is discussed in detail in Chapter 7 and include a brief case study for brass, and other alloys, from the Late Bronze Age to post-Medieval periods in CE Britain.

7. Case Study Introduction: Ancient Brass, the Calamine Process, and Loss Modeling of Zinc and Other Metals from the Late Bronze Age to post-medieval periods in Britain

The calamine process (cementation) and the loss modeling of zinc, and of other metals commonly alloyed with copper in antiquity, are intimately intertwined. The cementation process proceeds across the solid-gas and liquid-gas interfaces with the absorption of Zn by Cu through the attraction of the unlike atoms of zinc and copper. Similarly, the loss of zinc occurs at the same liquid-gas interface by the evaporation of Zn(g), but under different system conditions. In cementation, in order for these two metals to alloy, at a time when the smelting of zinc through distillation was unknown, zinc ore ZnS (sphalerite) or ZnCO₃ (smithsonite) is combined in a covered crucible with copper and charcoal, or an alloy of copper, at copper melting temperatures to facilitate the direct reduction of the oxide (Equations 7.0, 7.1) and absorption of zinc gas into the molten metal. For this process to be successful the atoms of copper and zinc must obviously satisfy the Hume-Rothery rules discussed in Chapter 5, but also, given the high vapor pressure of zinc, be contained within a system devised to counteract its loss through evaporation. In the absence of such a system, the evaporation of zinc occurs rapidly despite the copper-zinc attractive force due to the high volatility of zinc; their attraction is enough to slow its loss but not eliminate it. If zinc were nonvolatile, its absorption into copper would be a simple matter of time rather than expedience. For zinc, therefore, when one discusses its loss modeling from copper, ostensibly one is also talking about the calamine process.



More specifically, cementation is possible because of the interatomic attraction of the two metals, which is directly influenced by their electronegativity and the atomic volume of zinc (Gerling and Predel, 1980). However, increasing the volume of zinc gas is incidental as the rate controlling factor of diffusion is the mass transfer of zinc across the liquid gas interface, which is limited by the viscosity and thickness of surface layers. As such in pure copper it is possible to achieve more zinc absorption simply by increasing the surface area of the copper in both the solid and liquid phases, as described for Cu(s) in many historical recipes with broken copper (Zacharias, 1989; Newbury et al., 2005), but more important to know is the baseline mechanism controlling both cementation and loss. The activity of the components is that mechanism, which provides both a measure of the vapor pressure of zinc above the molten metal for loss modeling and gives an indication of the attractive force of zinc to copper for understanding cementation. This thesis has already discussed activity in great detail, showing that zinc has one of the highest partial vapor pressures and volatility coefficients in a copper melt, second only to arsenic, compared to all other considered ancient metals. For this reason, with this knowledge combined with the derived equations from Chapter 6, this thesis, as it discusses the intricacies of activity and oxidation, is ideally positioned to explain the thermodynamic behaviors of brass recycling, initial creation, and the influence of other ancient metals in both loss modeling of recycled copper-based artifacts, as well as ancient brass production in binary and ternary systems.

It is clear from such works as Zwicker *et al.* (1985), Newbury *et al.* (2005), Ullwer (2008), Bourgarit and Bauchau (2010), and Bourgarit and Thomas (2011) that basic thermodynamics can be used to successfully solve archaeometallurgical questions and elucidate some ancient pyrometallurgical practices. In respect to ancient brass production, it has been shown by Bourgarit and Bauchau (2010) that high zinc brasses, above approximately 30 wt%,

were possible in antiquity using the calamine process despite earlier opinions otherwise (Werner, 1970). Their findings demand that archaeologists and historians rethink how high zinc brass relates to the progression of technological ability and that they change the dismissive opinion of discoveries of high zinc brass; however, several aspects of brass still need to be explored before any definitive answers may be declared.

The production of high zinc brass is certainly thermodynamically possible using the calamine process; however, it is unknown how prevalent it had become in the ancient world. The question remains whether high zinc brasses were commonly made through some established process and recipe, such as with Roman brooches (Dungworth, 1995, 10) and arsenical copper (Eaton and McKerrell, 1976), or the result of unusual happenstance. Bourgarit' and Bauchau's experiments are yet to be sufficiently proven by archaeological evidence, although high zinc unprovenanced brasses do exist (e.g., Caple, 2006, 41). Further complications to the questions of extent and frequency of brass manufacturing arise in regards to the false identification of brasses in the archaeological record (e.g., Stewart and Stewart, 1950), and the unintentional creation of brass from zinc-rich copper ores (Craddock, 1978; Dungworth, 1995; Bayley, 1998). To the second point, while the properties of zinc containing copper objects such as color were recognized, being made from nondescriptly named "mountain copper" ores (Craddock, 1978), ancient metal smiths did not necessarily have the means to reproduce brass from anything but these ores.

Regardless of the obstacles of archaeological uncertainty, questionable alloy identification, and possible unintentional ancient alloying outcomes, the application of thermodynamics has made significant inroads and progressed rapidly in archaeometallurgy. Recent exchanges of basic thermodynamic concepts in the study of ancient brass, specifically,

have vastly improved our understanding of ancient metallurgy as a whole. And having studied metallurgical thermodynamics in great detail, this author is of the opinion that there are clearly more in-depth analyses and concepts that can be applied to provide better evidence and interpretation ancient metallurgical processes.

Like archaeology, metallurgical thermodynamics is constantly maturing and becoming more sophisticated and accurate. Archaeometallurgical thermodynamics should therefore be no different. The progressively accurate understanding of ancient metal systems are improved upon with each new generation of analytical technique, introduced collection of data, and reworked and established theory. Similarly, the work of Bourgarit and Bauchau (2010), Ullwer (2008), and alike, who have contributed towards answering the enigma of high zinc ancient brass, can be vastly improved. As Bourgarit and Bauchau (2010) note in their concluding remarks, “...our experimental simulations were based on simplified model systems” and that given “...the assumed complexity of original working conditions (purity of compounds, scale effects, and so on)” future studies necessitate more experimentation and increased model complexity. The following sections in this chapter are designed to address both points, and an additional third one directly related to the chemical composition of copper-based artifacts, first, by including more detailed information on and interpretation of the calamine process, and second, by covering more complex scenarios of ancient metal systems that include combinations in ternary solutions. Additionally, because of the relationship of cementation and activity, for loss modeling, the confirmation is provided that recycling models of ancient metals works with a brief comparison to the data and results presented in Pollard *et al.* (2015) “*Characterising Copper-based Metals in Britain in the First Millennium AD: A preliminary quantification of metal flow and recycling*”. This thesis has already discussed the basics of the Cu-Zn system behavior in Chapters 3 and 4;

this is built upon and expanded here to include recent archaeometallurgical scholarship on the manufacture of brass and more rigorous thermodynamic explanation. For the second point, this thesis considers ternary Cu-Zn-M systems using data from the binary activity systems introduced in Chapter 3 in conjunction with a second set of Zn-M (M = Pb, Ag, Bi, Ni, Co, Fe, Sb, As, Sn, Au) binary activity systems data, which, when combined according to the derived equations and concepts in Chapter 6, provide valuable activity data for all components in their respective ternaries. These copper-zinc alloys are also considered in conjunction with the Cu-Sb-As and Cu-Sn-Pb systems in order to cover those discussed by Pollard *et al.* (2015). In total 12 sets of 3 (36) diagrams for just the Cu-Zn-M systems have been created from a total 23 binaries, of which the sets of Zn-M, Sb-As, and Sn-Pb are given later in this chapter with brief introductions. Finally, the results of the ternary activity calculations that are presented graphically in the prepared diagrams are compared to the results of Pollard *et al.* (2015). These diagrams are also compared to published experimental and alternatively calculated assessments of the same ternary systems when available.

One can see, based on the sheer number of calculations on the collected activity data, that the evaluation of a single ternary system, comprised of three binary activity diagrams, is daunting. For this reason, this thesis is limited to the interpretation of binary Cu-M and Cu-M-Zn ternary systems; however, an extension of the Redlich-Kister method to more complex multi-component solutions is relatively simple once one has mastered the concepts and mathematics needed to determine activity in ternary systems. It is the hope of this author that future research pursuits may include the modeling of higher-order systems to include all the variation of elements found in ancient smelting and recycling, including oxygen and sulfur.

7.1 Ancient Manufacture of Brass and the Calamine Process

The origins and manufacture of brass, briefly mentioned in Chapter 3, are unquestionably historically and archaeologically important, but perhaps more interesting technologically, and directly related to this thesis, is the assumed difficulty inherent to its manufacture, especially of high zinc brasses above the coined “magic limit” of approximately 28 to 32 wt% zinc (Werner, 1970; Zwicker et al, 1985; Welter, 2003; Newbury, 2005; Ullwer, 2008; Bourgarit and Bauchau, 2010). The assumption this limit carries is that objects containing higher zinc percentages are thought to have been made after the 16th century, when zinc distillation came into practice, or from imported Chinese distilled zinc into Europe, or that they are modern forgeries and thus often discounted as insignificant to ancient archaeological and technological interpretation (e.g., Caley, 1964, 104 – 115). Even artifacts below the limit have been considered suspect, with those approaching it treated with increasing distrust (e.g., Oddy, 2004; Craddock, 2009). The question of the authenticity of high zinc brass artifacts is not unwarranted as several have been thoroughly examined and found to be forgeries (Craddock, 1980; 2009), however recent thermodynamic calculations and controlled experimentation in reconstructed ancient furnaces have confirmed previous suggestions that the production of brass in excess of 32 wt% zinc using the calamine process was indeed possible (e.g., Zwicker *et al.*, 1985; Krapp and Mann, 1992; Ullwer, 2008; Welter, 2003; Bourgarit and Bauchau, 2010; Bourgarit and Thomas, 2011). Yet, some scholars remain unconvinced that the magic limit should be abandoned having accepted the science but contending that high zinc brasses were the exception rather than the rule (Newbury *et al.*, 2005). Indeed, the uptake of Zn(g) is not simply determined/limited by thermodynamics and is influenced additionally by the exposed copper surface area, crucible design, and charge and

charge packing, which are discussed below in conjunction with controlled cementation experiments.

In their experiments Bourgarit and Bauchau (2010) have demonstrated, in a covered crucible and reconstructed ancient calamine process under highly controlled conditions, that it is possible to create brass above 50 wt% zinc at 950 °C, having easily reached 40 wt%. At this composition the liquid solution has reached the β -phase that descends to β' on cooling, changing over from disordered bcc, having equal probability of zinc and copper at each lattice point, to ordered with either copper or zinc at the lattice cube corners. The magic limit corresponds with the transition between the α and $\alpha + \beta$ phases. Accompanying their results, they have calculated a predictive model based on activity data from Baker (1970) measured at 1150 °C. They have approximated, with Equation 7.3, a linear relationship between activity and the mole fraction of zinc at compositions between 30 and 50 wt%, likely reasoning that the activity values given by Barker are roughly linear up to 0.5 mole fractions.

$$a_{Zn} = 0.92 \cdot x_{Zn} - 0.16 \quad 7.3$$

At first glance their calculations are well reasoned according to known thermodynamic relationships, but they lack consideration for non-linear behavior and temperature difference, which could dramatically change their model results. Their linear zinc activity approximation based on Baker (1970) is comparable to Sugino and Hagiwara (1986) and agrees well with that of Azakami and Yazawa (1969; 1976), at mole fractions below 0.1; however, it does not take into account the effects of temperature on activity. As Figure 20 shows, the activity of zinc decreases at lower temperatures nearing the liquidus, which leads to increased affinity of zinc for copper. This makes sense, of course, since lower temperatures correspond with decreased zinc

volatility. In their experiments Bourgarit and Bauchau covered multiple temperatures ranging from 900 °C to 1100 °C in 50 ° intervals, but no mention of activity extrapolation was given -the implications being that there would be higher possible zinc absorption, less loss through evaporation, and the same composition percentages could be reached with less zinc oxide charge. Adjustments to the activity suggest that creating high zinc brass was a less arduous task than originally believed. Further, their approximation ends at a point in the complete activity diagram where zinc absorption would be slowed, shown by the increased slope of the zinc activity in the Cu-Zn binary, above 0.5 mole fractions, where it is no longer parallel to Raoult's law as higher concentrations of zinc are reached.

Based on previous descriptions of the activity and related thermodynamic properties from Chapter 2, to achieve the most effective zinc uptake, three conditions should be met: larger concentrations of zinc charge (x_{Zn}), smaller activity coefficient (γ_{Zn}), and a smaller equilibrium constant (K). To achieve effective uptake conditions, which are complicated by the fact that zinc absorption is best facilitated by staying just above the liquidus, as noted by Bayley (1998), one must keep in mind that the liquidus of the alloy decreases as zinc is absorbed (Figure 21), the activity coefficient changes with composition (3.19) and the equilibrium constant with it.

Central to Bourgarit and Bauchau's results, they note the sensitivity of the Zn:Cu charge ratio on final zinc percentage with the highest zinc uptake occurring where Zn:Cu = 3. However, zinc absorption is controlled not by the amount of zinc oxide charge but by temperature, the copper surface area, and the available Zn(g) volume. The zinc oxide charge and Zn(g) volume are related, but are not the same and must be understood separately. In their experiments more zinc oxide did not directly lead to higher percentage zinc absorption, rather it provided for adequate Zn(g) replenishment for the prolonged calamine process resulting in more uptake over

time where considerable amounts were lost through evaporation. Regardless of the initial ratio, the majority of absorption according to their experiments occurred within the first few hours, after which it slowed dramatically. The rate of absorption likely slowed because of the decreased availability of surface copper atoms for pairing, which are necessary in the calamine process allowing for Zn(g) deposition. It is likely, then, that zinc absorption is controlled by zinc atom dissemination and pairing of unlike atoms within the liquid itself in extended calamine processes, which requires large amount of Zn(g) in the system to perpetuate. It is therefore not surprising that at constant temperature and decreasing Zn(g) volume, zinc metal percentages begin to decrease much later in their experiments where atom pairing was at its maxima, or near maxima for cementation, and zinc oxide reduction was decreasing. When the Zn(g) volume decreases volatilization overwhelms absorption and equilibrium between the gas and liquid metal is reached, and continues to rebalance over time with more zinc evaporation. This phenomenon is the same as demonstrated in cementation experiments by Haedecke (1973), which are widely cited in support of the magic limit, showing that zinc absorption in the calamine process is at most approximately 31 wt%, and in repeated experiment replacing copper with brass in excess of this maxima, the alloy was found to lose zinc rather than gain. Haedecke noted that the brass returned to zinc levels comparable to those attained by cementation using copper, which he rightly reasoned must be the systems equilibrium state.

In addition, temperature plays an important role in zinc uptake (Werner, 1970; Haedecke, 1973), and is a controlling factor in its absorption rate during the calamine process as Bourgarit and Bauchau's results have shown. Accordingly, the reduction of zinc oxide is far more rapid and initial zinc absorption quicker as temperatures increase, however, equilibrium is also more quickly reached and zinc losses through evaporation are more substantial. This leads to

diminishing zinc percentages in the brass over time at constant temperature and with decreasing zinc oxide conversion. The vapor pressure of zinc within the system, in the closed calamine process, after equilibrium has been established is dependent on its activity coefficient in copper, which decreases in lower temperatures and at lower concentrations. As temperatures increase, and with increasing zinc metal percentages, reducing zinc losses through evaporation becomes increasingly more difficult as its activity increases nearing ideality. The rising activity coefficient in high zinc brass can be controlled by decreasing the system's temperature, but not below approximately 950 °C, at which point zinc oxide is reduced (Figure 1a). Since excessive Zn(g) is necessary to maintain zinc absorption, the calamine process is therefore limited by the reduction temperature of ZnO rather than the liquidus of copper or its alloys.

Furthermore, since there was no means to accurately measure and control the temperature in an ancient furnace, and to know whether adequate zinc oxide and charcoal reserves remained, it is likely that ancient metallurgists would have stopped the process as soon as the Cu-Zn alloy liquefied (Pollard and Heron, 2008, 196ff). The liquefaction of brass was simply the best indication that the process was successful, although trial and error of different recipes may have eventually yielded high zinc brasses. It is therefore the opinion of this author, in agreement with Newbury *et al.* (2005), that given the black box design of the calamine process that the production of high zinc ancient brass would have been unintentional. As Bourgarit and Bauchau have shown, it is certainly possible to create high zinc brass through cementation, but their results should not be viewed as having been commonplace.

7.2 The Calamine Process and Loss Modeling of Zinc and other Metals from Liquid Copper

The activity of zinc in the Cu-Zn binary was shown in Chapter 3 to deviate negatively versus copper indicating the strong attractive force between the two unlike atoms, made possible

by their strong electronegativity and closely sized atomic radii. Concomitant to this attraction, the volatility of zinc, apparent by both its activity and calculated volatility coefficient, is high, indicating rapid loss of zinc given an open system through both evaporation of elemental zinc and its oxide. The obstacle, then, in the success of the calamine process is in the ability to overcome losses of zinc through volatilization, which was done by adding excessive zinc oxide charge with charcoal, creating a reducing atmosphere, and containing the reaction within a specially designed closed system crucible (e.g., Bayley, 1984; Rehren, 1999). These crucibles were specially designed to limit evaporation with covers, and, since they were essentially sealed systems that required rapid heat transfer from outside sources and limited reaction time, there were thinly walled (Rehren, 1999).

According to Caley (1964, 99), echoed by Bayley (1998) and Dungworth (1995), each time a brass coin was melted down it lost up to 10% of its total zinc through volatilization, which implies that without a steady influx of zinc ores and reprocessing to replenish the effects of recycling, objects would eventually contain little to no zinc. Coins were not the only re-melted metal, nor was zinc the only element lost or changed, as noted by Dungworth (1995, 130 - 133). The loss of other elements due to recycling was typical, especially after the end of Roman occupation in Britain around 388 CE. Based on 1,212 objects, Dungworth observed zinc decreasing, and tin and lead increasing, between the 1st and 4th century CE, and suggested a rough model for these changes based on Caley's 10% loss prediction. His model was a simple exponential decay function that he attributed to the re-melting and annealing of brasses. The function is designed to lessen zinc every ten years, resulting in a smooth curve; however, as he notes, it does not match the analyzed data (Dungworth, 1997). One of the most glaring problems in his model is the assumption that zinc losses are constant despite composition changes and the

presence of other elements. Another issue, alluded to by Caley (1964, 99-100) and brought up explicitly by Pollard *et al.* (2015), is that apparent zinc losses over time might have been caused, not entirely by evaporation during re-melting, but by mixing of different metal types, which would also decrease zinc percentages by dilution. Mixing is certainly a possibility; however, Fleming (2012) states that the mixing of different alloy types during the Roman period would have been unusual. Controlled recycling and mixing of only brasses with brasses might have occurred in the Roman period, however, rising tin and lead percentages after the end of Roman control was likely caused by the increasingly indiscriminate mixing of brass, bronze, and gunmetals. As the mixing and re-melting of objects, and debasement of coinage, occurred, the more homogeneous, with losses through re-melting kept in mind, would the entire metal corpus from 1st millennium Britain become. One has to keep in mind that precious metal (e.g., gold, silver) coins were likely at first debased and made again into coins, and did not immediately join the general metal flow until they were thoroughly devoid of precious metals. Copper coinage, on the other hand, could enter the metal flow at any time, perhaps, if their value as a material was greater than what they were given as coins. Dungworth (1995) suggests later metals were entirely composed of scrap, an interpretation also shared by Fleming (2012) of random recycling of copper-alloys after the Roman period in the 5th and 6th centuries. After the Roman period he further suggests that debased silver coins were mixed with other object types since both gold and silver are present in several objects at later dates. In summation, a reasonable assessment of the rate of zinc loss is possible, but unfortunately not by the means so far attempted by Caley and Dungworth. It has also been suggested that low gold content in some objects may be the result of the recycling and mixing of gilded copper (Fleming, 2012).

In agreement with Fleming, Dungworth (1997) notes that little analytical work has been done on copper-based artifacts between the end of Roman occupation and the High Middle Ages, and suggests the mixing of of gunmetal, leaded gunmetal, and some bronzes (e.g., Blades, 1995). By the late Saxon and Viking period brass is, with zinc now presumably scarce, recycled regularly (e.g. Caple, 1986). Dungworth also suggests that brass was always mixed with bronze to make gunmetal, and that lead was added as pure metal or leaded bronze to make leaded gunmetal. Furthermore, he suggests that these alloys were purposely created, not for technical reasons such as workability and strength, but because of economics, social interactions, and symbolism. For example, the mixing of brass and bronze (Bayley, 1998; Dungworth, 1995) suggests they were combined to attain a desired color rather than improve their physical properties, perhaps imparting a gold-like appearance. These mixed or “blended” alloys were commonly used for brooches, coinage, and military fittings (Dungwoth, 1997), most likely because brass is more likely to be free of gas porosity when cast, and may therefore fall outside the normal recycling flow.

It should be noted, however, that the interpretation of later period Anglo-Saxon data is hampered by the limited number of analyses performed on copper alloys and the survival of material from all periods. The composition of objects in accordance with desirable properties such as workability is furthermore a consideration, but one that assumes too precise control over the manufacturing of all alloys in connection to modern standards, especially under circumstances of compositional changes caused by re-melting and mixing of relatively pure metal, alloys, and unintended and unknown amounts of impurities (e.g. silver content in debased silver coinage). While some objects may have had preconceived compositions, it is unlikely that these compositions were accurately attained.

7.2.1 Considered Binary and Ternary Systems

The systems considered in this thesis are limited to all discussed Cu-M binaries from Chapter 3, the Cu-Sn-Pb ternary, Cu-M-Zn ternaries, and with brief mention the Cu-Sn-Zn-M quaternary (M = Ag, As, Au, Bi, Co, Fe, Pb, Ni, Sb, (Sn), (Zn)). In addition, data and diagrams for the Zn-M binaries are added in this chapter allowing for the calculation of each ternary system. The evaluation of the data in these combined systems in relation to ancient copper-based artifacts, as discussed in Chapter 6, requires multiple calculations and resultant interpretations for each system demanding a great deal of time. The systems discussed here are therefore limited to three components; however, some inferences can be made for quaternary systems based on the behavior of particularly volatile or nonvolatile metals such as zinc and iron, respectively. These ternary activity diagrams are relevant for the behavior of the metals they describe, and they may generally be useful in more complex multi-component systems; however, they should not be used to evaluate losses in quaternary or higher systems without careful consideration. For example, arsenic and antimony are similar in behavior in their respective binary Cu-M systems, but they do not at all behave similarly in the Cu-M-Zn ternary. The different impact these two metals have on zinc will become clear in the following subsections, which are preceded by an explanation of how ternary isoactivity diagrams are arranged and read.

Thermodynamic calculations for each ternary system based on the Gibbs excess free energy were performed as outlined in Chapter 6. These are based on three contributing binary systems, and must be arranged in a particular order in ternary diagrams. There are no standardized representations of ternary isoactivity diagrams; however, all diagrams in this thesis are arranged clockwise from the bottom right (Cu). Fortuitously, using this arrangement the issues of sign reversal discussed in Chapter 6 for odd parameters are avoided since the cubic

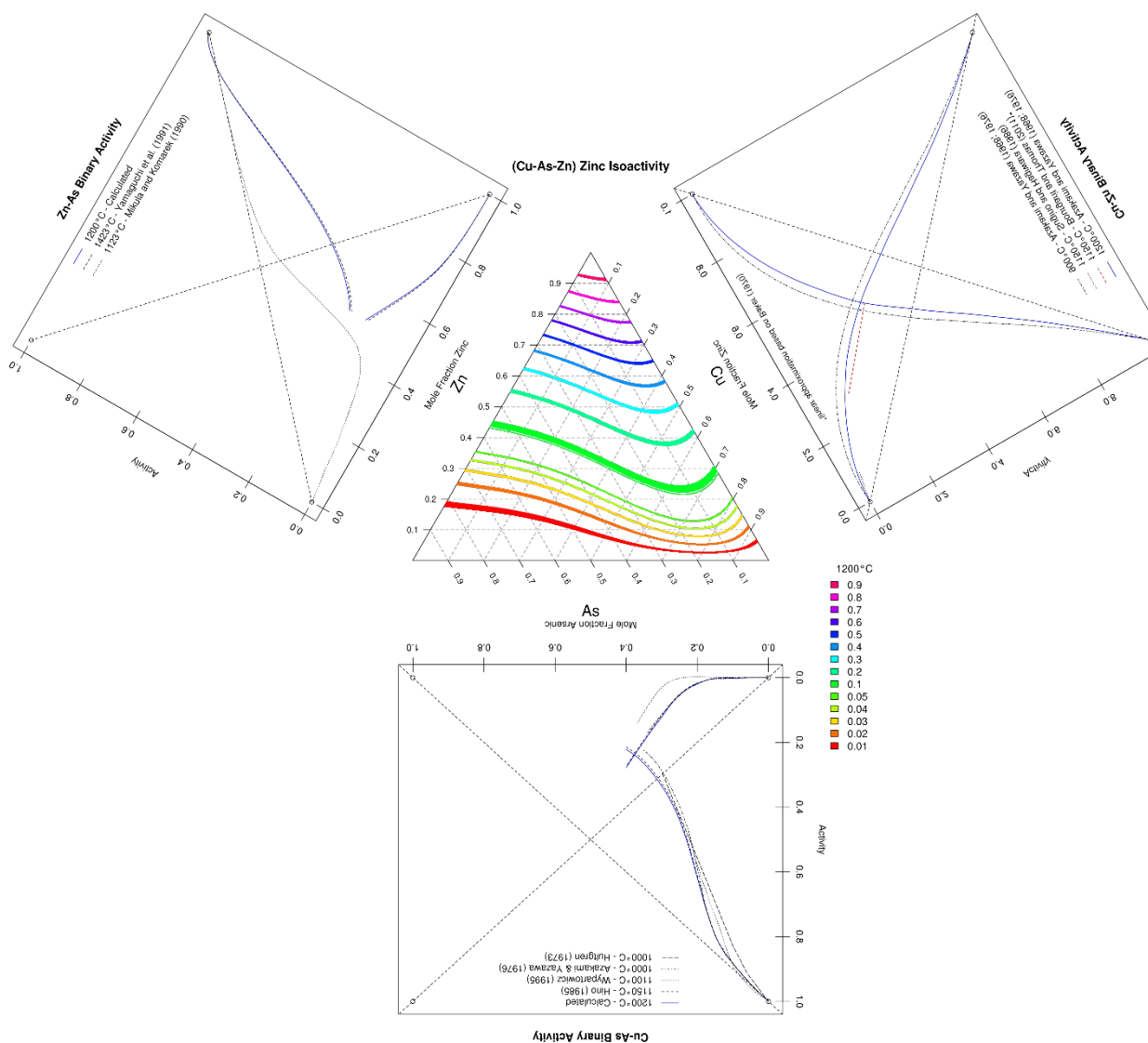


FIGURE 23: CU-AS-ZN ISOACTIVITY DIAGRAM CONSTRUCTION

term of the Cu-Zn binary activity diagram, which always resides on the right side of these ternary diagrams, is zero. Based on this clockwise arrangement, each binary diagram is positioned around the ternary at each corner where the component is at its highest concentration, much like a ternary phase diagram. Figure 24 shows how this has been done for each ternary in this thesis with the Cu-As-Zn system as an example. For the Cu-As-Zn ternary system, the contributing binary activity diagrams are arranged, as they are drawn along each respective x-

axis in each binary activity diagram included from Chapter 3 and the Zn-M systems provided in the proceeding subsection, with the reversal of the Cu-Zn binary (right side), rotation of the Cu-As (bottom), and unchanged orientation of the Zn-As (left side). The inverted view of the Cu-Zn system, including the text, and upside down Cu-As system are intentional and meant to show how the data is interpreted along each edge of the triangle. The arrangement of the binaries is similar to how one would create a ternary phase diagram and has the advantage of clearly showing the extent of the binary activity data, where it ends, and where interpolation of the activity begins. Most of the activity data used in this thesis falls within the compositional ranges of ancient artifacts, that is, within the regions of high copper and low alloying element concentrations. However, at times interpolation of the activity data of each component was necessary to complete the isoactivity diagrams.

7.2.2 Cu-As-Zn

The Cu-As-Zn ternary system is of particular importance due to the commonality of arsenic bearing brasses, as well as the ubiquity of ancient arsenical bronzes around the world in, for example, the eastern Mediterranean, the Caucasus, and the Americas (e.g., Lechtman, 1996; Hauptman, 2007; Koryakova and Epimakhov, 2007). Arsenical brass, as it may be called, is possibly the result of the use of arsenical copper and bronzes, rather than pure copper, in the cementation process. More likely however, and supported by the ternary behavioral models discussed below, is that Cu-As-Zn alloys are the result of the mixing of As-Cu and Cu-Zn binaries. The presence of arsenic in the calamine process has an adverse effect on the absorption of zinc and increases its evaporative loss. Calculations of these changes to the binary Cu-Zn system are shown graphically below along with interpretations and explanations of the decreased likelihood of zinc cementation and the evaporative and oxidative loss of all three components.

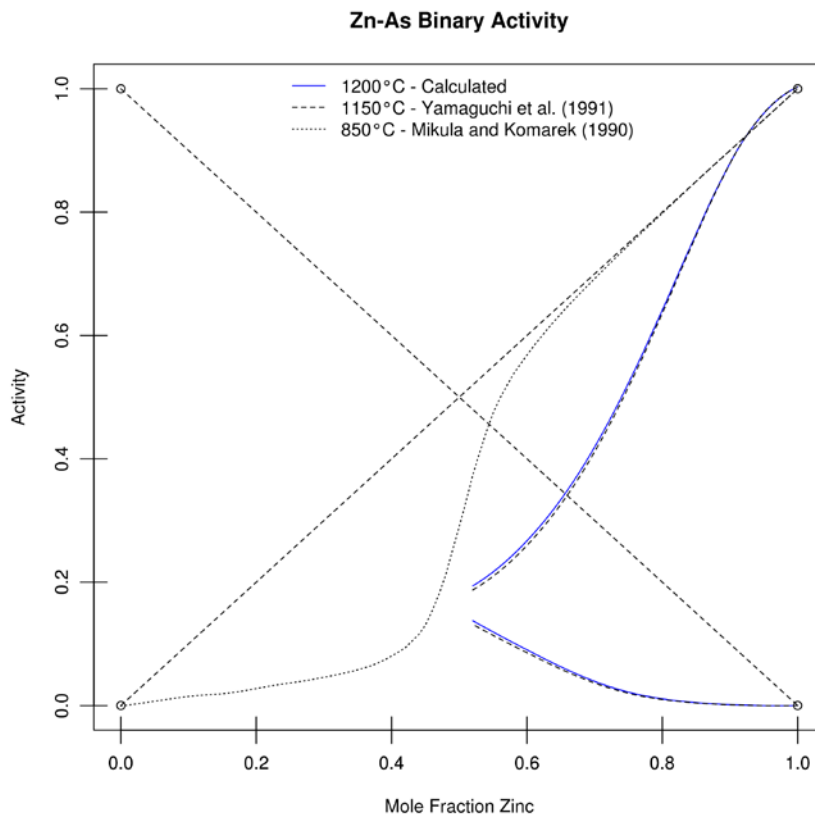


FIGURE 24: ZN-AS BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

Calculations of the isoactivity contour lines for each component were made using binary activity data from Yamaguchi *et al.* (1991) measured at 1150 °C using drop calorimetry for the Zn-As system, in addition to the two already discussed Cu-As and Cu-Zn systems from Chapter 3⁹. Data for the Zn-As system were extrapolated to 1200 °C using Equation 3.1 and plotted in Figure 25. The data are only given for high zinc and low arsenic concentration; however, due to the fact that the method described in Chapter 6 obeys the Gibbs-Duhem relationship, the fitted parameters shown in Table 6 provide considerably good estimations of regions lacking data. Of

⁹ See Appendix A.4 for the corresponding binary phase diagrams of M-Zn systems discussed in this chapter

note, Yamaguchi *et al.* described difficulty in measuring the zinc activity at approximately 0.43 mole fractions, suggesting chemical short-range ordering was contributing to the low activity of zinc with the formation of As_2Zn_3 or As_3Zn_4 . The formation of these molecules indicates the strong affinity of zinc for arsenic in high arsenic concentrations, confirming the interpolated values of the Zn-As system beyond the given data. For comparison and further confirmation, activity data from Mikula and Komarek (1990), which extends for the entire range of the system

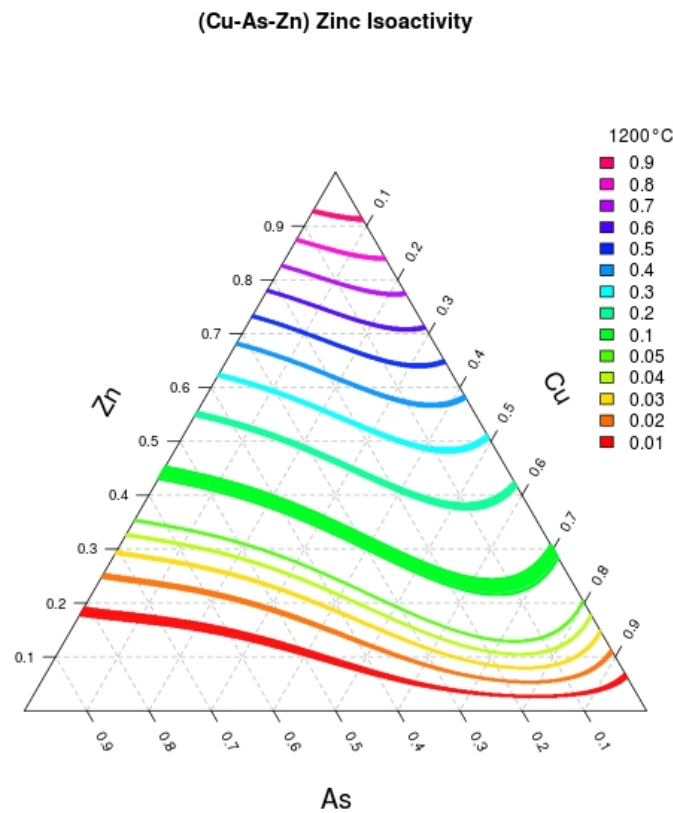


FIGURE 25: CU-AS-ZN (ZINC ACTIVITY)

for zinc, is also shown. The data are complete across the entire concentration and could have been used in conjunction with the Gibbs-Duhem equation to calculate the arsenic activity across the entire system for both components; however, between 45 and 85 at% zinc the alloys were measured in an undercooled state.

Meanwhile, the activity of arsenic, according to Figure 27, shows steadily increasing deviation in the presence of added zinc to the Cu-As binary system, but since the change is small, arsenic remains strongly attracted to the melt throughout and its loss therefore remains relatively low compared to the Cu-As binary system. Furthermore, in the closed system conditions of the calamine process its loss would be negligible as shown by Wayman and Duke (1999) due to reabsorption; its affinity for copper, after Figure 16, in fact having a much stronger affinity than zinc for copper.

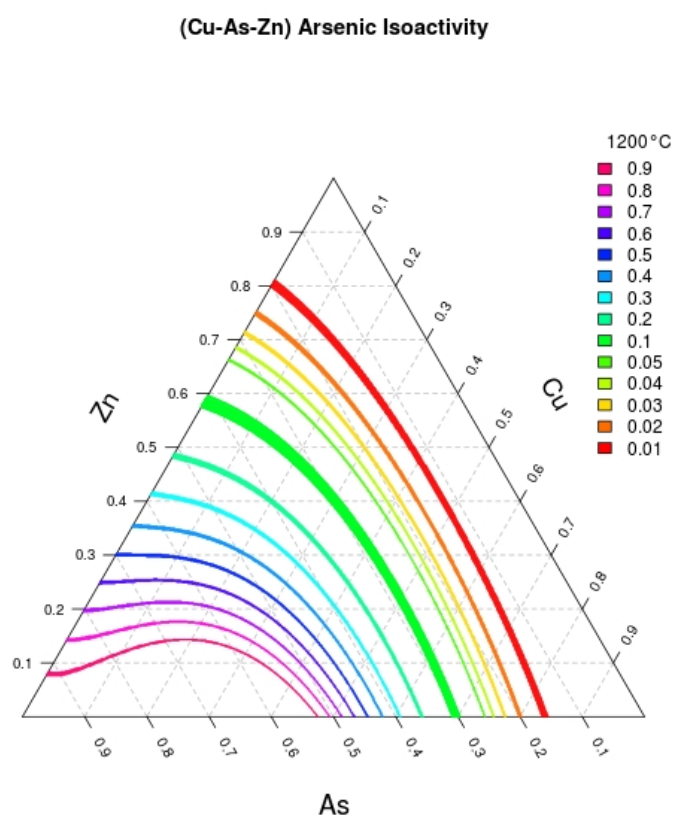


FIGURE 26: CU-AS-ZN (ARSENIC ACTIVITY)

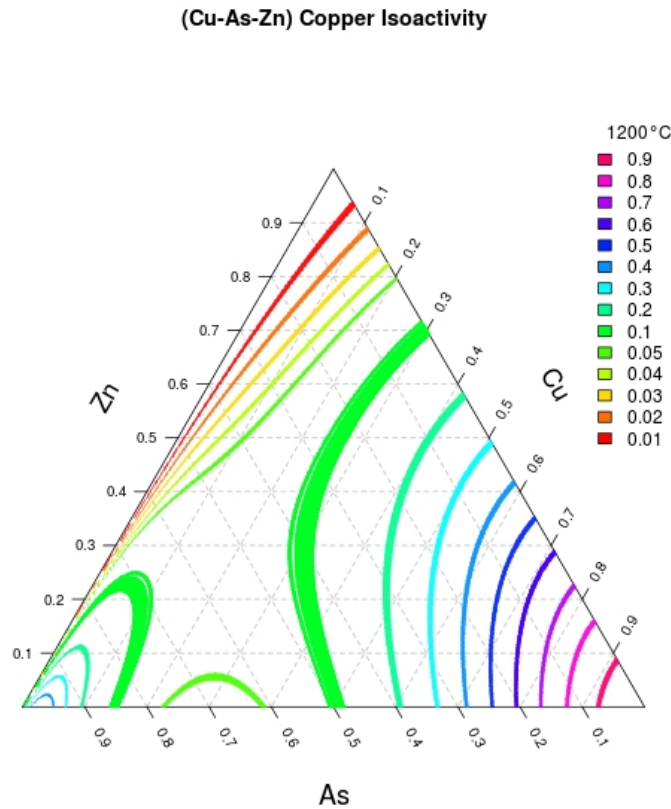


FIGURE 27: CU-AS-ZN (COPPER ACTIVITY)

Figure 28 shows the isoactivity lines for copper decreases and increases with added arsenic and zinc, respectively; which is unsurprising in the region of interest given the greater attractive force between copper and arsenic than copper and zinc. Nevertheless, the vapor pressure of copper (Table 1) is extremely low, so its activity change has negligible impact on its loss or gain during the calamine process or recycling. Of concern in Figure 28, the copper isoactivity lines are somewhat erratic in the high arsenic and low zinc region. The activity of copper, at compositions lacking empirical data and unlike the confirmed activity over the entire Zn-As system, is based on the best possible fit of the available binary activity data between 0.6 and 1 mole fractions copper in the Cu-As binary system (Fig. 16). Such a fit provides extremely precise representative parameters in this range and better results in the region of interest, but

beyond which is then subject to extreme error. For the purposes of this thesis, within the range of interest, these errors do not affect the systems interpretation in relation to ancient metallurgy.

In respect to recycling and re-melting of ancient alloys in open system furnaces described in the chapters above, the calculated isoactivity diagrams show that for a Cu-As-Zn alloy, and for loss modeling of these components, one should expect slightly less loss of zinc compared to the binary Cu-Zn system due to its reduced volatility. Zinc is lost as pure Zn vapor rather than as an oxide. Arsenic loss, on the other hand, would increase but be comparable to the Cu-As binary system, being lost predominantly as the As_2 species in a reducing environment (Table 3), and copper would remain unchanged. However, these diagrams only visually represent losses of each component by evaporation and do not directly show oxidative losses as either volatile or non-volatile oxides. It is expected that zinc losses, whether as an oxide or pure element, are assured since as both pure element and oxide is extremely volatile. Even if zinc were not oxidized during recycling, at copper melting temperatures it would no less be lost through evaporation, although at a much slower rate. Similarly, arsenic loss by volatilization is assured in the binary Cu-As system as either the pure element or oxide, but the vapor pressure of AsO is vastly greater, as discussed in Chapter 4, contributing to the majority of its loss (Roine, 1987). On the contrary in the ternary Cu-As-Zn system the reducing effects of zinc would prevent some arsenic oxide formation resulting in an overall decrease in the loss likelihood of arsenic as long as zinc is present. Zinc has the lowest Gibbs free energy of formation of the metals used in antiquity (Table 1), so if it were present in an ancient metals system, the consideration of the loss mechanism of other components would be based on the volatilization of pure species rather than oxides. Furthermore, the altered value of the Gibbs free energy of formation, incorporating the activity of each component, according to Equation 2.12, does not change the reducing effect of

zinc on arsenic or copper.

Table 6: Cu-As-Zn Binary Parameters

Parameter	Cu-As	As-Zn	Zn-Cu
B	-2.48	-4.5	-2.2
C	-4.2	-0.44	0
D	2.26	0	0.1

7.2.3 Cu-Ag-Zn

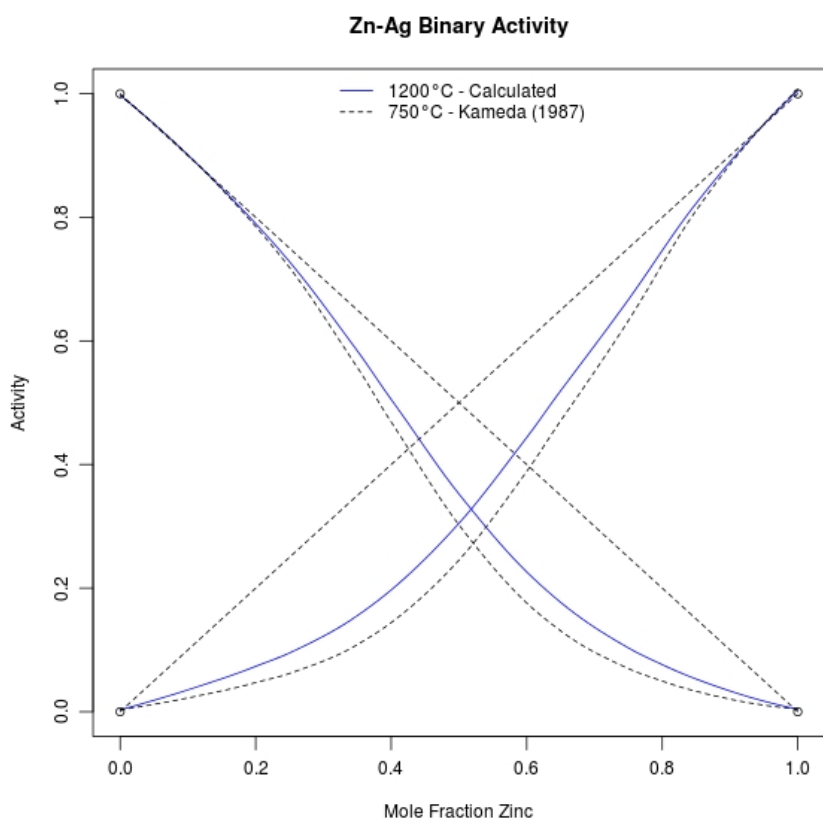


FIGURE 28: ZN-AG BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

The presence of silver in Roman brass, beyond what is considered trace amounts, is noted by Caley (1964), which he has suggested was the result of the mixing of debased coinage into the common flow of recyclable metals. In addition to coins, another contributing source of silver in

ancient brass is the use of silver rich copper scrap in the calamine process, which, if subjected to enough refining and recycling, can eventually become enriched accounting for percentages well above trace amounts (Tylecote, 1970). Silver enrichment in copper has been discussed in detail in Chapter 3.

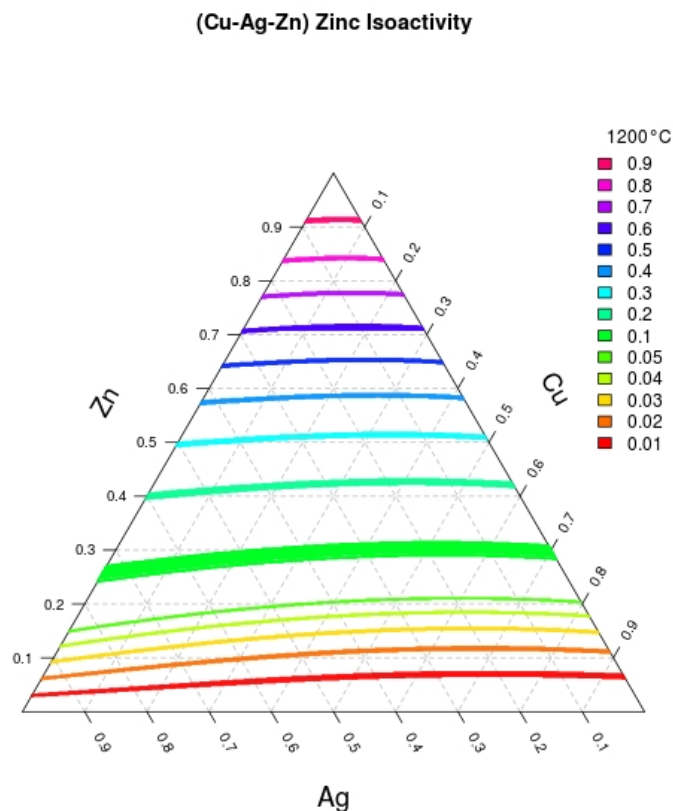


FIGURE 29: CU-AG-ZN (ZINC ACTIVITY)

The Cu-Ag-Zn system isoactivity was calculated using the above discussed Cu-Zn and Cu-Ag systems in addition to Zn-Ag activity data measured by Kameda (1987) using E.M.F at 750 °C between 0.27 to 0.85 mole fractions zinc (Fig. 29). The parameters for each binary are given in Table 7. The data were interpolated by Kameda (1987) for the remainder of the system

and extrapolated by this author to 1200 °C. The data was then arranged, as described in the above ternary system example, along the left side of the isoactivity diagram.

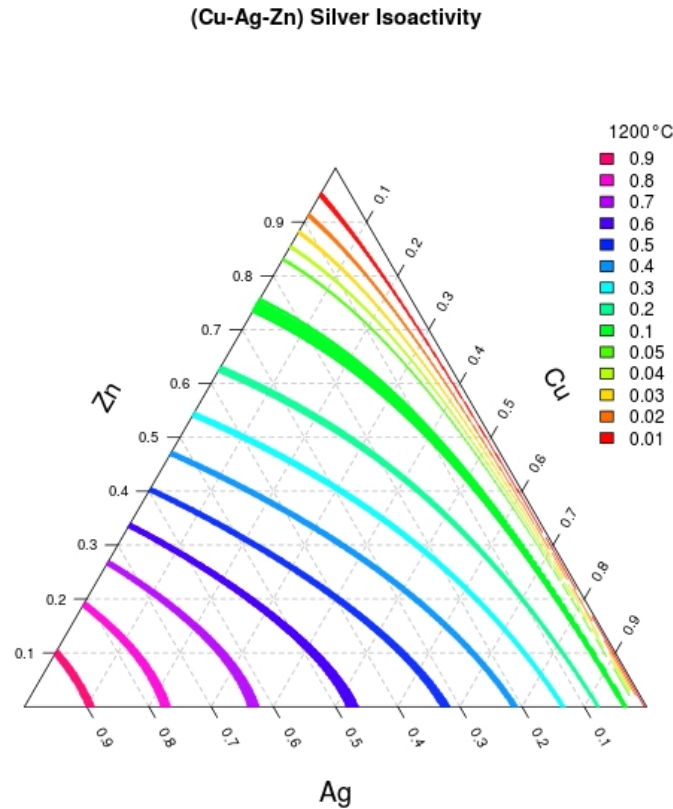


FIGURE 30: CU-AG-ZN (SILVER ACTIVITY)

According to the binary activity data, zinc shows strong negative deviation, having strong affinity for silver approaching ideality with increasing temperature. This affinity is confirmed by the multiple stable phases shown in the Zn-Ag phase diagram (Appendix A.4), however, notable is that the attractive force of zinc for silver compared to zinc for copper is not significantly different in high copper concentrations. Figure 30 shows the calculated isoactivity lines for zinc in the Cu-Ag-Zn ternary and highlights the similarity of the Cu-Zn and Cu-Ag binary systems showing little change in the activity in the region of interest. The activity of zinc is nearly

parallel to the mole fraction of zinc, so that adding additional silver at the expense of copper, while keeping the zinc concentration constant, has negligible influence on zinc deviation.

In both the Zn-Ag and Cu-Zn binaries, as well as the ternary, the negative deviation of zinc, in its respective solvent(s), obeys the Hume-Rothery rules discussed in Chapter 5 resulting in strong affinity of zinc for the ternary melt. Comparison of the calculated activity to experimental data by Surapunt *et al.* (1994: 1995), using the isothermal isopiestic method at 802°C, confirms in trend to those data calculated here, but are noticeably higher due to the temperature difference. Therefore, when silver rich copper scrap was used in antiquity in the calamine process, the success of zinc absorption compared to pure copper would be unchanged.

In the region of interest, the activity of silver (Fig. 31) shows a steady decrease indicating stronger affinity for the Cu-Zn binary system as zinc content increases. The vapor pressure of silver, which is already very low as discussed in Chapter 4 and shown in Table 1, is decreased further by the addition of zinc to the Cu-Ag binary. Therefore, in this ternary system, due to the low partial pressure of silver and instability of its oxide, one should expect silver enrichment at the expense of zinc, should this ternary brass be recycled.

For copper, its activity increases as silver is added to the Cu-Zn binary, however, given the low concentrations of silver in most ancient copper-based metals, and low vapor pressure of copper, it would not result in copper losses through re-melting (Fig. 32). There is, however, the unexpected behavior of silver in the Cu-Ag binary, which is common to the ternary Cu-Ag-Zn system that must be addressed. The positive deviation of silver, although it has low vapor pressure, is indicative of repulsive forces suggesting increased vapor pressure and higher likelihood of loss through volatilization (See Chapters 3 and 4). Yet it has been confirmed

through re-melting experiments and often repeated that silver is enriched under ancient pyrometallurgical conditions (e.g Tylecote, 1970; Pernicka, 1999; 2004), and that it should survive pyrometallurgical processes (Bray & Pollard, 2012). So why does silver show positive deviation, an indication of its increased vaporization, at all given the experimental results of silver enrichment and its presence in ancient copper-based objects? The answer likely lies in the difference in surface tension of copper and silver at high temperatures. In the binary Cu-Ag

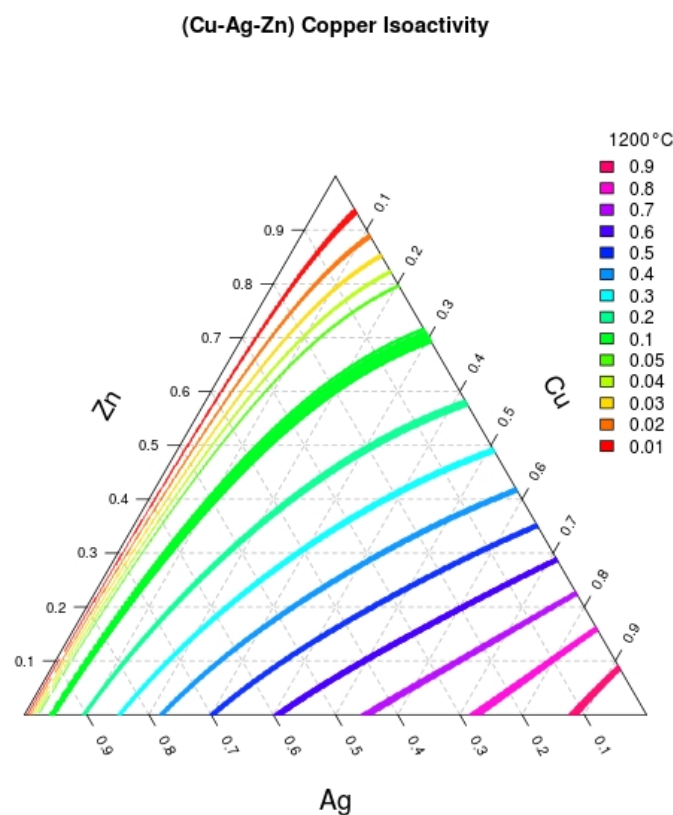


FIGURE 31: CU-AG-ZN (COPPER ACTIVITY)

system the surface tension of silver is drastically less than copper resulting in the formation of a thin layer, atoms thick, of liquid silver that lies above the molten copper despite the known densities of each metal (Lu and Jiang, 2005). This suggests loss of silver by volatilization at the

surface of the melt, which corresponds to the high activity values of silver given in Chapter 3 from controlled laboratory experiments. However, the presence of silver in ancient artifacts is well known contradicting the experimental activity results. There is, however, an explanation given in Chapter 4 for the Cu-Ag binary system related to the low vapor pressure of silver, which is insufficient given by the results of the calculations of this ternary system requiring a more complex explanation. The surface tension of silver is drastically low compared to copper, but even then that of zinc is far lower. The results of these differences being that zinc forms on the surface of the melt and is preferentially volatilized in the Cu-Ag-Zn system preventing or limiting arsenic volatilization, which can ultimately result in a depleted “silver only” type copper (Bray & Pollard, 2012), but that after the sacrificial zinc metal has been removed the loss of silver would commence at a very slow rate. Because of the extremely low vapor pressure of silver one would not notice any loss through simple ancient pyrometallurgical refining processes.

Comparison of all the calculated isoactivity lines and trends at 1200 °C for zinc, silver, and copper to those measured by Surapunt *et al.* show strong agreement in the liquid phase. In terms of losses through oxidation of these metals; copper is negligible, silver is unaltered because of its formation of unstable oxides, but zinc is extremely high being governed by its Gibbs free energy of formation, taking into account the high vapor pressure of zinc and its oxide measured by Kyllö and Richards (1998).

Table 7: Cu-Ag-Zn Binary Parameters

Parameter	Cu-Ag	Ag-Zn	Zn-Cu
B	1	-1.66	-2.2
C	0.16	0.32	0
D	0	0.26	0.1

7.2.4 Cu-Au-Zn

For the Cu-Au-Zn system this thesis uses the binary Zn-Au activity data measured by Gerling and Predel (1980) using the E.M.F method at 900 °C, extrapolated it to 1200 °C across the entire system (Fig. 33), and the Cu-Au and Cu-Zn binaries described in Chapter 3. These activity data indicate extreme affinity and the strong pairing of unlike atoms. The Zn-Au phase diagram similarly shows multiple stable phases (Appendix A.4) supporting the activity data. Interaction parameters for each binary system used to calculate the ternary system are given in Table 8.

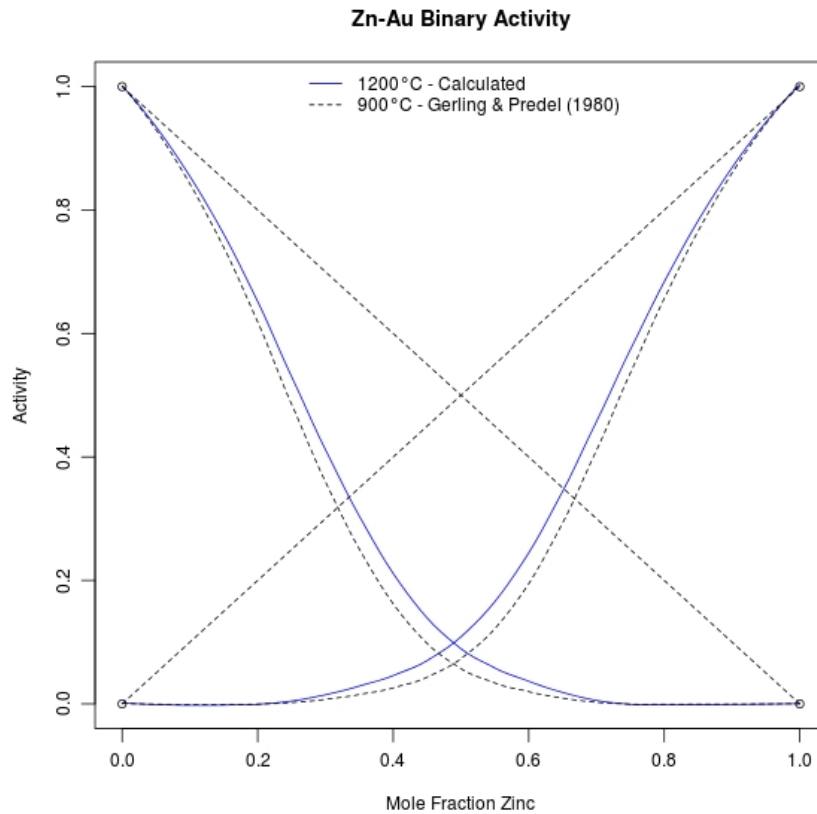


FIGURE 32: ZN-AU BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

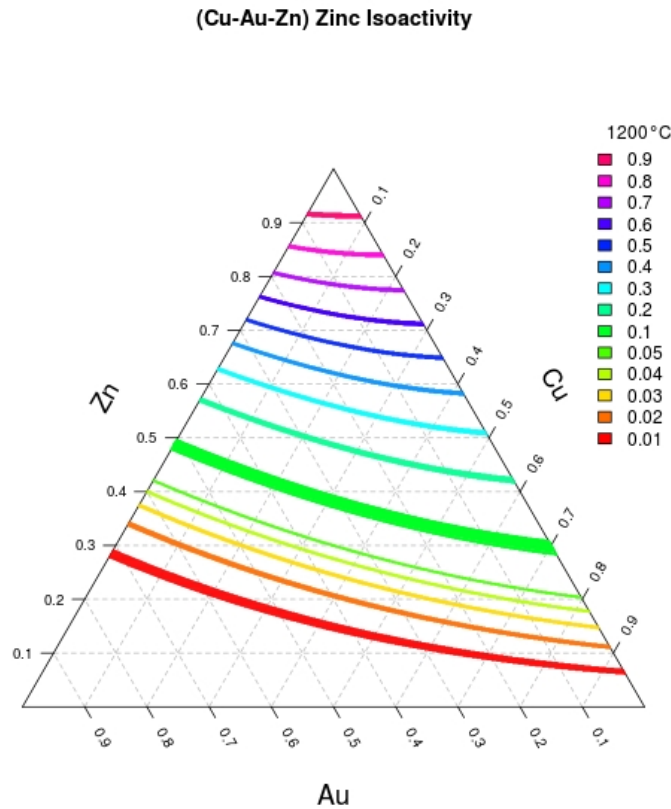


FIGURE 33: CU-AU-ZN (ZINC ACTIVITY)

Calculations of the activity of each component shows that zinc sharply decreases when gold is added to the Cu-Zn system, gold remains initially steady and decreases at high zinc content, and copper increases with both added zinc and gold. The isoactivity of zinc is shown in Figure 34 and indicates that even small amounts of gold increase its affinity to the Cu-Au binary. This behavior suggests that a Cu-Au alloy used in the calamine process would likely result in a higher percentage and more easily attained brass. Measurements by Surapunt *et al.* (1994:1995) at 802°C using the isothermal isopiestic method confirm the calculated deviation of zinc in the ternary system. On a related note, comparison of the zinc activity to the previously discussed Cu-Ag-Zn ternary system shows far more negative deviation because of

the greater electronegative difference between Au-Zn than Ag-Zn, which furthermore obeys the Hume-Rothery rules in the solid phase (Gerling and Predel, 1980; Surapunt *et al.*, 1994). The attraction force between gold and zinc is also stronger than that of copper and zinc.

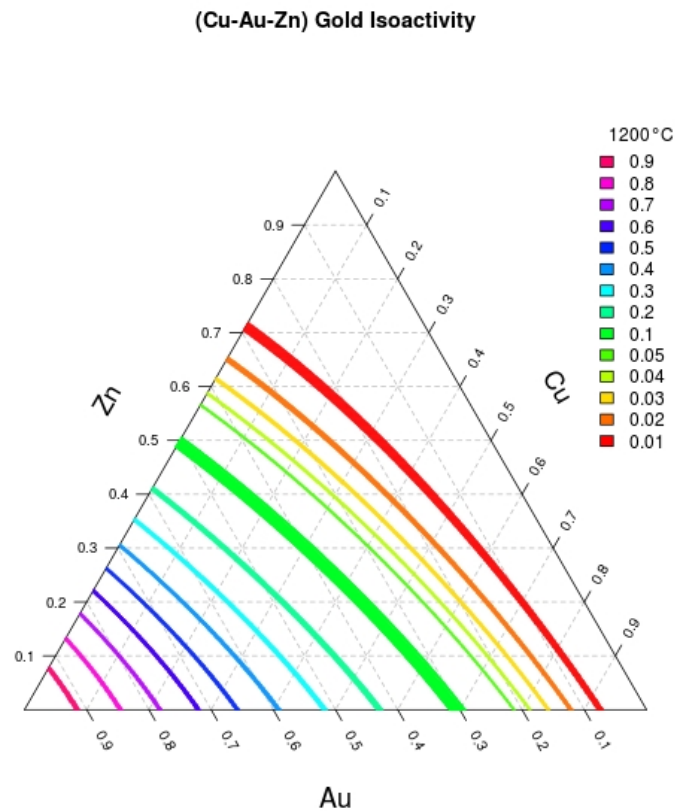


FIGURE 34: CU-AU-ZN (GOLD ACTIVITY)

The activity of gold (Fig. 35) is extremely low in the region of interest, and continues to decrease as more zinc is added reflecting the highly attractive force between gold and zinc atoms. Because of gold's extremely low vapor pressure and volatility coefficient according to Table 1 and 2, and its inability to form stable oxides, its perseverance and enrichment through copper recycling is assured. As for zinc, its loss by volatilization would be lessened through re-melting as more gold was added. However, ancient copper-based metals rarely reach more than

trace amounts of gold, perhaps nearing percentages similar to silver through enrichment, so unless it were purposely added it is unlikely that gold plays a significant role in either zinc absorption or loss. Oxidative losses, on the other hand, of gold, as mentioned, would be none, but of course zinc losses would occur rapidly as both pure Zn(g) and its oxide (Kyllo and Richards, 1998).

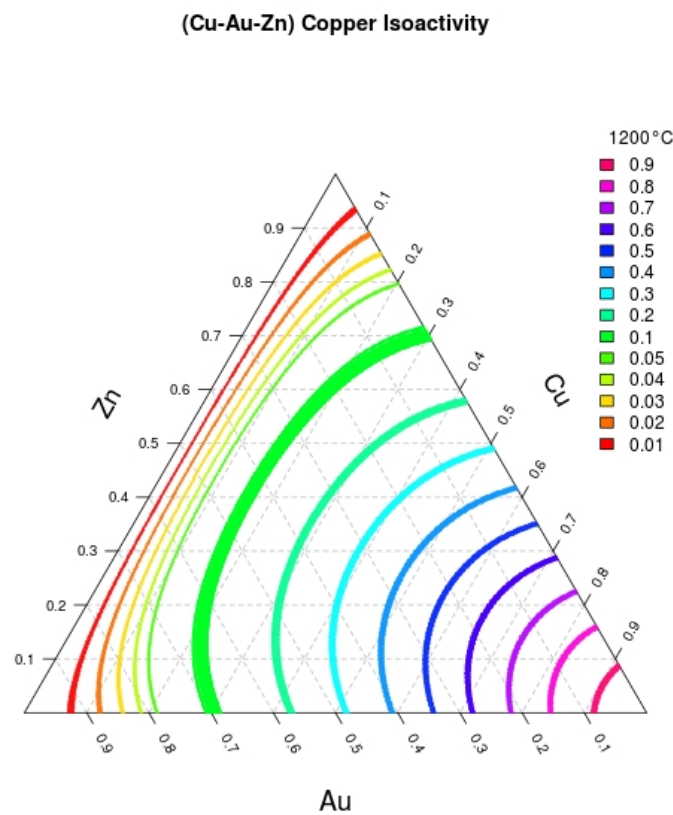


FIGURE 35: CU-AU-ZN (COPPER ACTIVITY)

Figure 36 shows the isoactivity of copper. Again its behavior indicates a small increase in vapor pressure, but it remains comparatively low compared to the other components. The concentric circular pattern of the activity of copper is interesting, formed by the similarities in the activities of copper in the Cu-Zn and Cu-Au binary systems, and the symmetry of the Zn-Au system. In

all, the comparison of these calculated activity values for zinc, gold, and copper, agree in trend and value of those measured by Surapunt *et al.* in the liquid phase despite the difference in temperature. The closeness of these values is caused by the small changes in the scale of the activity after extrapolation of the binary activity data to 1200 °C.

Table 8: Cu-Au-Zn Binary Parameters

Parameter	Cu-Au	Au-Zn	Zn-Cu
B	-2.34	-6.36	-2.2
C	0	-0.3	0
D	0	0.8	0.1

7.2.5 Cu-Bi-Zn

Binary activity data for the Zn-Bi system from Katayama *et al.* (1997) at 650 °C using the E.M.F method was used, with the Cu-Bi and Cu-Zn systems discussed in Chapter 3, to calculate the activity of each component in the Cu-Bi-Zn ternary system. Their experiment was designed to find the upper temperature limits of the miscibility gap in this system, which is seen in both the activity (Fig. 37) and corresponding phase diagrams (Appendix A.4). Their activity data for bismuth shows the gap approximately between 0.05 and 0.4 mole fractions bismuth creating a characteristically recognizable phase changing activity increase, and corresponding increase in the activity of zinc. Extrapolation of their data to 1200 °C, since the gap does not exist above their experiment's temperature, is somewhat problematic; however, the binary parameters eliminate most of the discrepancy through least squares fitting (Table 9). The binary data indicate decreasing activity with increasing temperature, owing to the mixture of these two unlike atoms and increased solubility at higher temperatures.

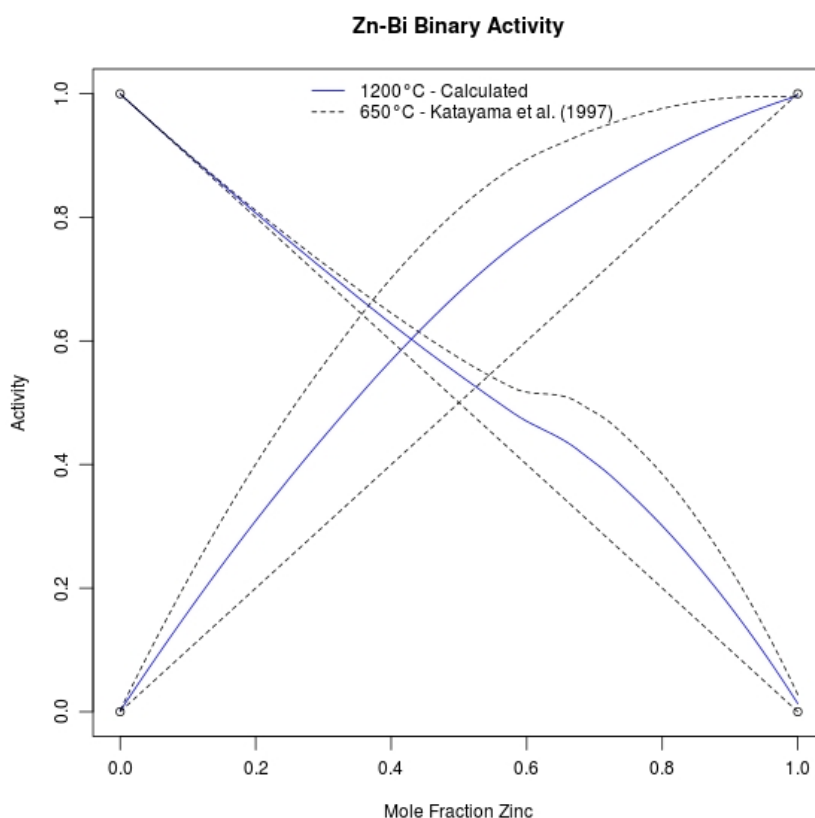


FIGURE 36: ZN-BI BINARY ACTIVITY

Zinc activity in the Cu-Bi-Zn system (Fig. 38) increases with an increase in bismuth, however, like gold, it is usually only found in trace amounts making its influence on zinc losses ancient brass of little significance except in rare instances. Yet if significant bismuth were present in copper, it would reduce the rate of zinc absorption during the calamine process. Loss of zinc through volatilization, as discussed previously, would be rapid, and with increased speed with the addition of bismuth.

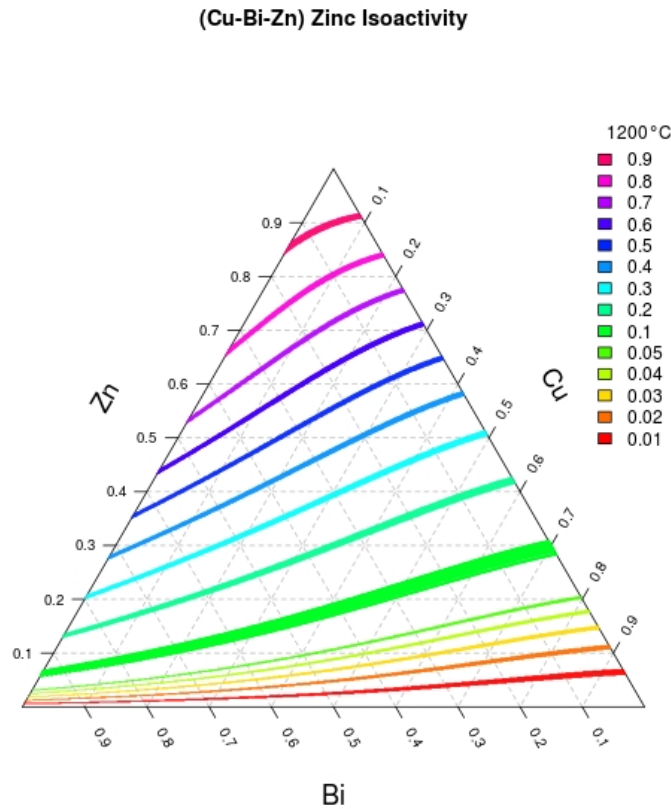


FIGURE 37: CU-BI-ZN (ZINC ACTIVITY)

For bismuth itself, its activity shows a similar concentric circle pattern comparable to copper in the Cu-Au-Zn system (Fig. 39). This patterning is caused by the similarity of the activity in the Cu-Bi and Zn-Bi systems, and symmetry of the Cu-Zn system. In low bismuth and increasing zinc compositions, the activity of bismuth changes insignificantly so that its losses in this ternary, through volatilization as Bi and Bi₂ as discussed in Chapter 4 and Table 3, would be unchanged compared to that of the Cu-Bi system. Finally, the copper activity increases with increasing bismuth and decreases with zinc in the Cu-Zn and Cu-Bi systems, respectively, but like the other systems shows relatively little change overall being unaffected in terms of evaporative losses (Fig. 40). In terms of oxidation, zinc much more favorably forms oxides over that of both bismuth and copper as discussed in Chapter 4.

(Cu-Bi-Zn) Bismuth Isoactivity

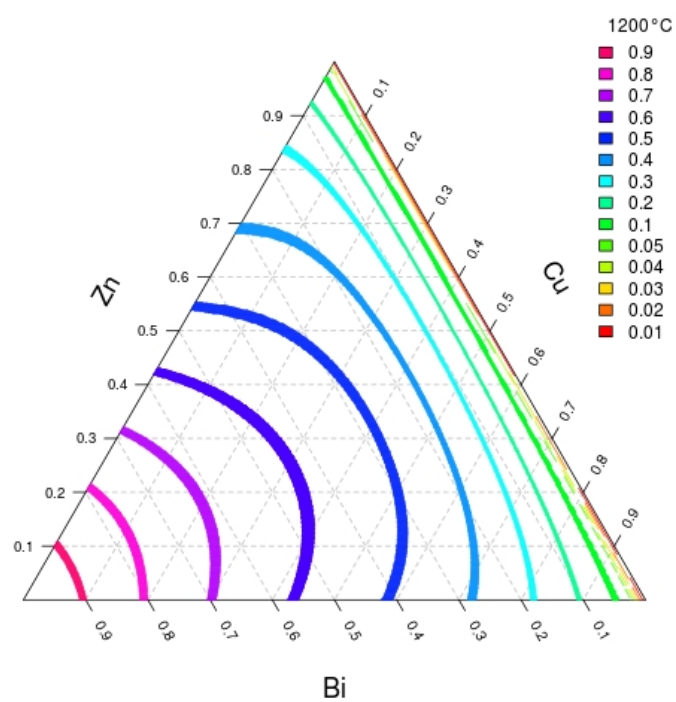


FIGURE 38: CU-BI-ZN (BISMUTH ACTIVITY)

(Cu-Bi-Zn) Copper Isoactivity

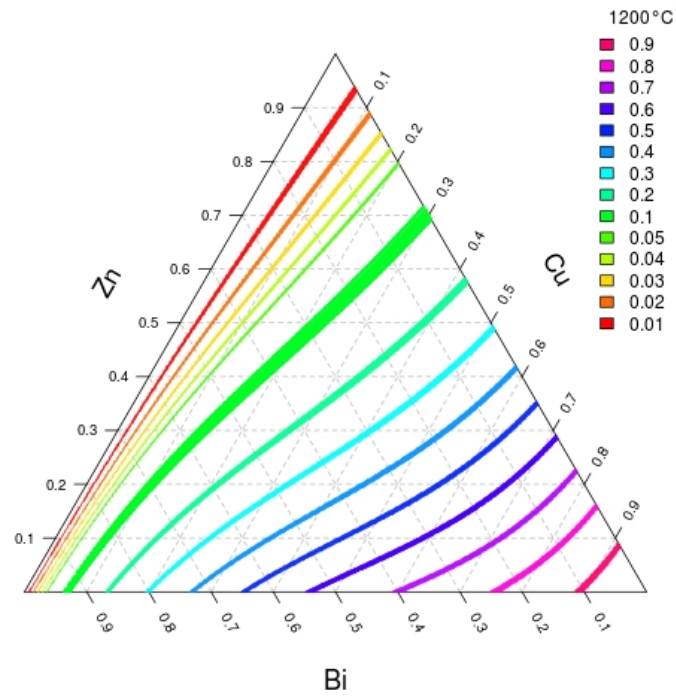


FIGURE 39: CU-BI-ZN (COPPER ACTIVITY)

Table 9: Cu-Bi-Zn Binary Parameters

Parameter	Cu-Bi	Bi-Zn	Zn-Cu
B	0.68	0.72	-2.2
C	0.26	-0.44	0
D	-0.14	0.24	0.1

7.2.6 Cu-Co-Zn

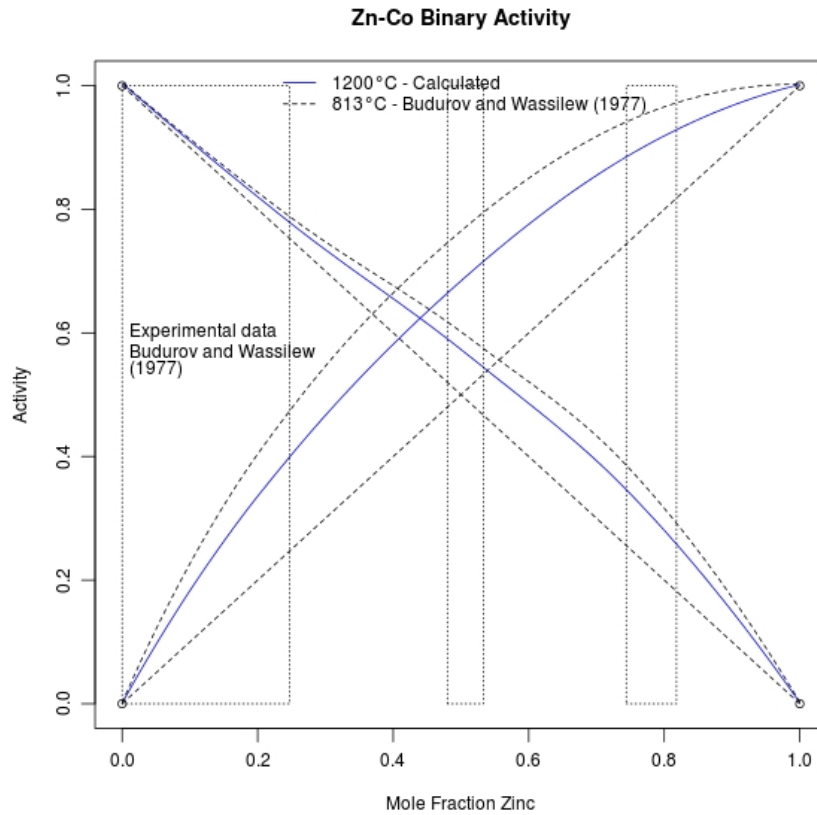


FIGURE 40: ZN-CO BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

For the Cu-Co-Zn system, the measured activity data of the Zn-Co system was taken from Budurov and Wassilew (1977), who, using the dew point method at 813°C measured the activity in the β and γ phases (Appendix A.4). They produced partial data, shown in Figure 41 within the dotted rectangles, requiring interpolation of the curve performed using the loess regression function built into the R software stack. After the data were connected across the entire system, they were extrapolated to 1200 °C, and show that cobalt activity decreases with higher temperatures. Interaction parameters are provided for this system in Table 10.

For zinc, its activity in the Cu-Co-Zn ternary system increases with added cobalt (Fig. 42), which is not unexpected given the positive deviation and thus repulsion of unlike atoms seen in the Zn-Co activity diagram. Cobalt, like other low concentration elements found in copper, is usually only in trace amounts making its influence on zinc absorption during the calamine process minimal, as well as in the loss modeling of zinc in ancient brass. At dilute concentrations elements obey Henry's law and follow both activity trend in pattern in both the binary and ternary diagrams.

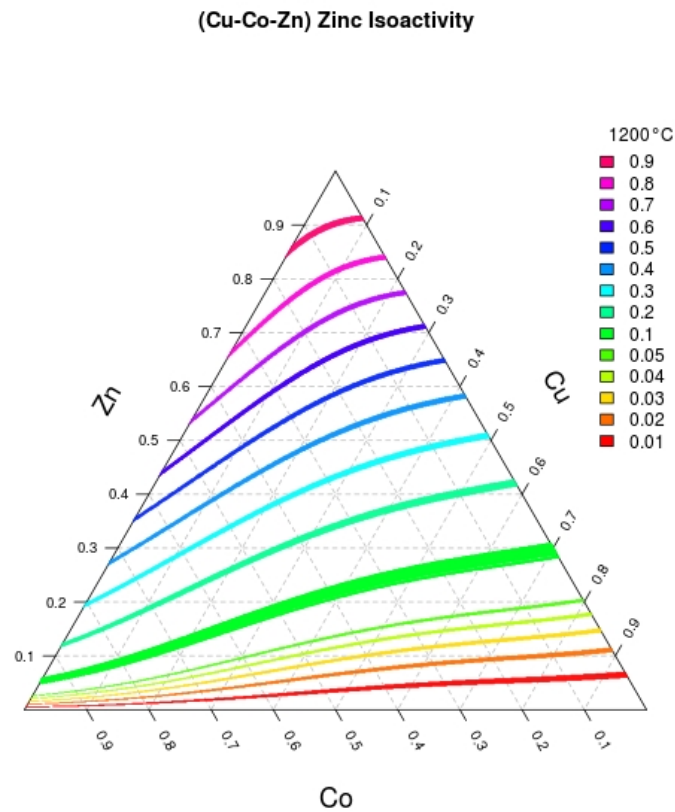


FIGURE 41: CU-CO-ZN (ZINC ACTIVITY)

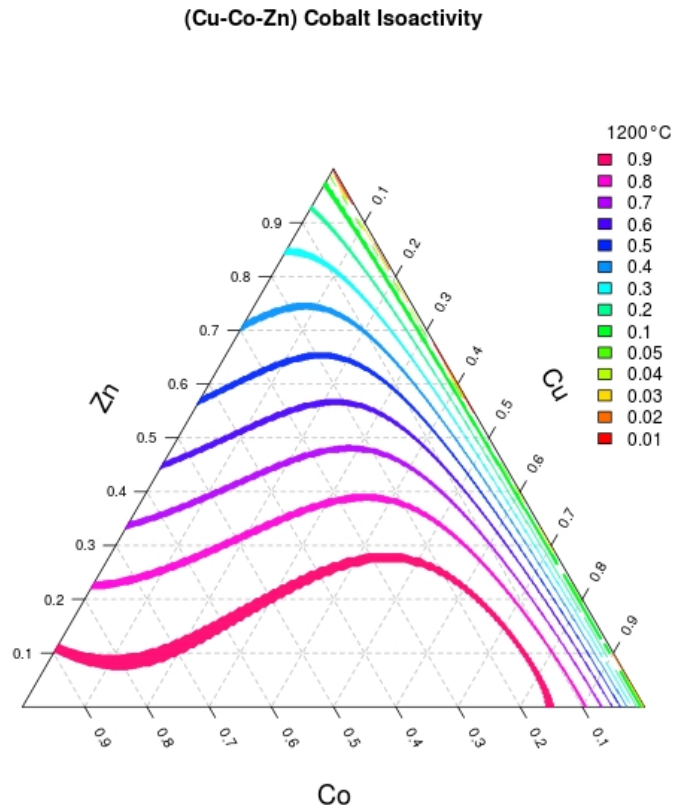


FIGURE 42: CU-CO-ZN (COBALT ACTIVITY)

The activity of cobalt is unlike other systems described thus far (Fig. 43). The immiscibility of copper and cobalt in the binary, in the region of constant activity, brings an abrupt end to the usual smooth curve of the ternary isoactivity diagrams (Fig. 10). The compression of the isoactivity lines into the bottom right corner of the Cu-Co-Zn diagram is caused by the extreme positive deviation of the binary Cu-Co system. In such cases parameter fitting is possible with the methods used for all other systems, but ideally each should be evaluated separately between regions of constant activity. As separated regions the isoactivity lines would end where constant activity begins in the binary, be straight across the concentration regions of immiscibility, and reconnect on the other side where there is a phase change. Future

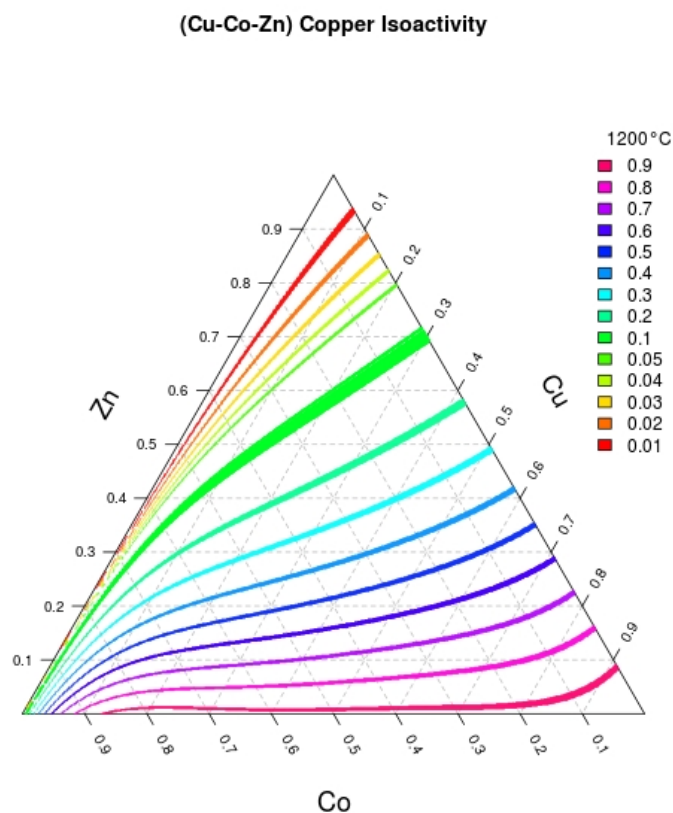


FIGURE 43: CU-CO-ZN (COPPER ACTIVITY)

research into this ternary system, and those like it, will more accurately correct for phase change, however, as they are drawn satisfactorily represent the cobalt activity at all compositions.

The activity of copper (Fig. 44), like that of cobalt, is strongly influenced by the extreme positive deviation of both components in the Cu-Co binary system, which similarly results in the compression of the isoactivity lines in the bottom left region of the ternary. These activity data indicate that copper loss, as in the other ternaries, would be negligible.

In both the copper and cobalt isoactivity diagrams one can see where immiscibility begins and ends in the corresponding binary activity diagrams, where the isoactivity lines are compressed and parallel. Lining up the Cu-Co binary activity diagram according to the description of isoactivity diagram arrangement (Fig. 24) clearly shows the influence extreme deviation has on calculated activity. These extrema have profound influence on the loss modeling prediction of each component. The low volatility coefficient and activity of cobalt precludes it from evaporative losses, but it can be removed as a non-volatile oxide. After zinc it is the second most likely to oxidize of all the considered elements in this thesis, yet given the extremely negative Gibbs free energy of formation of zinc, it is unlikely to be oxidized except after the loss of zinc as either volatile elements or oxides.

Table 10: Cu-Co-Zn Binary Parameters

Parameter	Cu-Co	Co-Zn	Zn-Cu
B	2.46	0.78	-2.2
C	-0.04	-0.36	0
D	0.48	0.3	0.1

7.2.7 Cu-Fe-Zn

Tomita *et al.* (1981) measured the activity of zinc at 800 °C using the transportation method and calculated for the activity of iron using the Gibbs-Duhem relationship. Their data were extrapolated to 1200 °C, and shown in Figure 45 taking into consideration regions of immiscibility shown in the corresponding phase diagram (Appendix A.4). This results in regions of surprising constant activity due to the widening of phases at higher temperatures.

The calculated activity of zinc in Figure 46 agrees with experimental data measured by Surapunt and Hino (1995) who used the transportation method and quenching technique at 1200 °C. They observed that below 70 wt% zinc exists two phases, a liquid Cu-Zn and a solid iron, which is reflected in this thesis' calculated isoactivity lines. Furthermore, the activity coefficient of zinc decreases with increasing iron content in the region below 60 wt% zinc, and above it

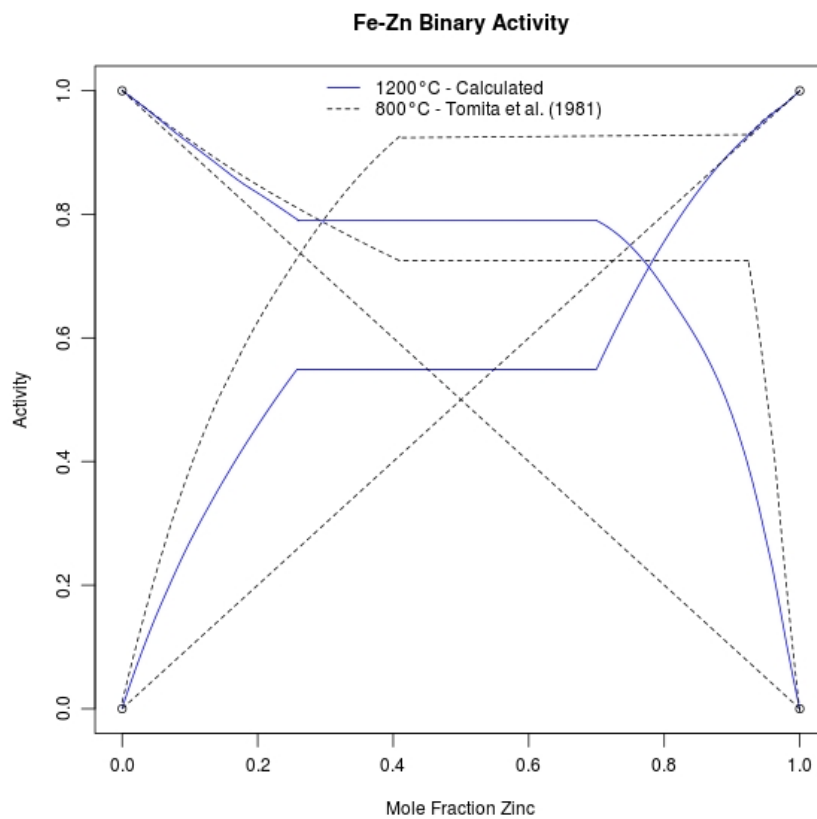


FIGURE 44: FE-ZN BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

increases, which again matches the calculations in Figure 46 according to the calculated binary system parameters in Table 11. More precisely, the calculated activity of zinc agrees well with those measured by Surapunt and Hino in the liquid phase, and roughly correlate in the liquid + solid phase where the influence of the steep activity slope of iron and copper from the Cu-Fe

binary activity diagram is evident. In compositional ranges of constant activity in the binary, and liquid + solid solution in the ternary, straight lines of activity and isoactivity, respectively, connect from the edges of the liquid to solid solution regions. The isoactivity contour lines of zinc are similar to those discussed in the Cu-Co-Zn system.

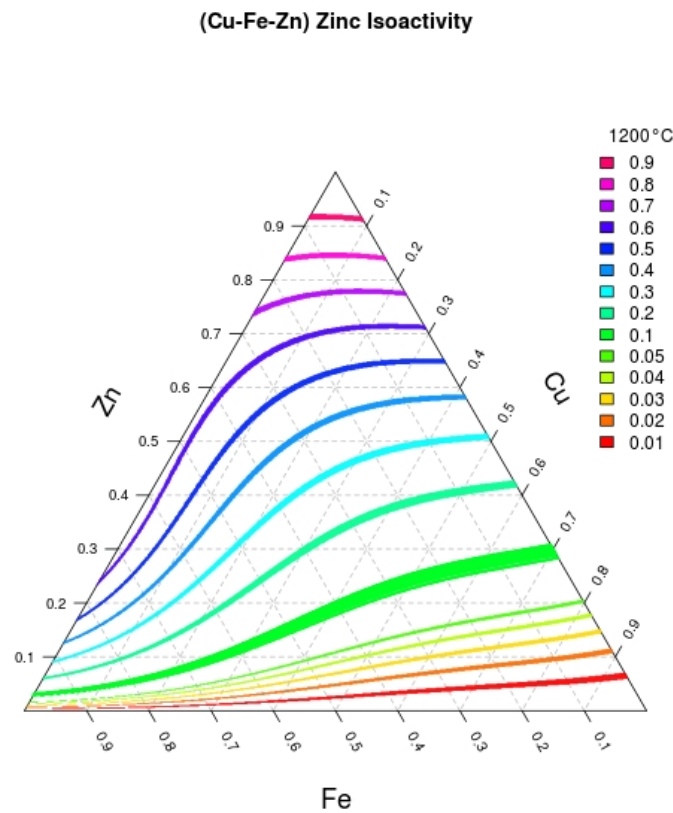


FIGURE 45: CU-FE-ZN (ZINC ACTIVITY)

Figure 47 shows the activity of iron that is calculated based on two binary systems, the Cu-Fe and Fe-Zn systems, which both have regions of constant activity. This results in the compression of the isoactivity lines in the bottom right corner, and the parallel lines on the left. This ternary system in fact has two regions of immiscibility that are evident by the trend and position of the isoactivity lines, which show that iron is highly repulsed by both copper and zinc components. Meanwhile, the copper activity, shown in Figure 48, shows compressed isoactivity

(Cu-Fe-Zn) Iron Isoactivity

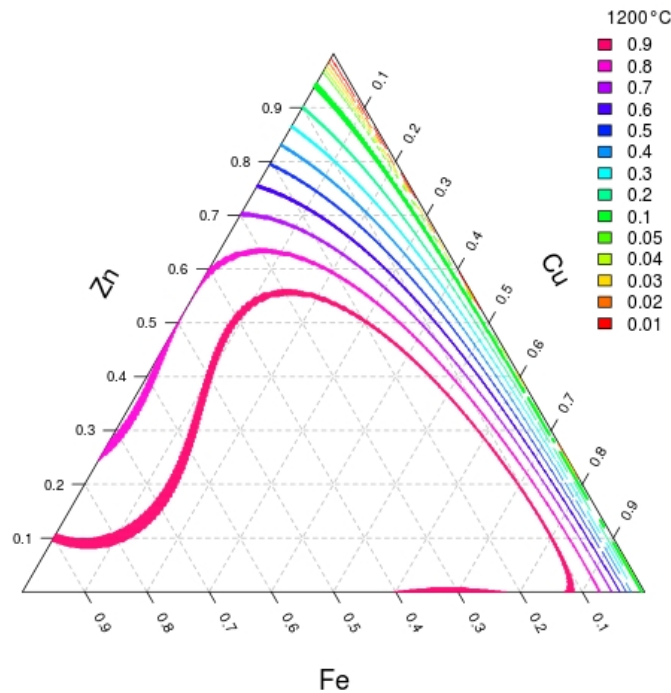


FIGURE 46: CU-FE-ZN (IRON ACTIVITY)

lines in high iron concentrations due to the extreme positive deviation of the Cu-Fe system. Small additions of iron to a brass increases the activity of copper, but results in negligible change.

Predictive loss modeling of these three metals suggests that though volatilization, unsurprisingly, zinc would be lost slightly faster than in the Cu-Zn binary system. The oxides of iron, on the hand, are non-volatile and would remain even after the complete loss of zinc. Its losses without oxidation or volatilization, may come about during casting, where iron, being less dense than copper, floats on top of the melt. However, the surface tension of copper is in fact lower than iron, which suggests that unless iron forms an oxide it will remain in the copper melt bulk.

(Cu-Fe-Zn) Copper Isoactivity

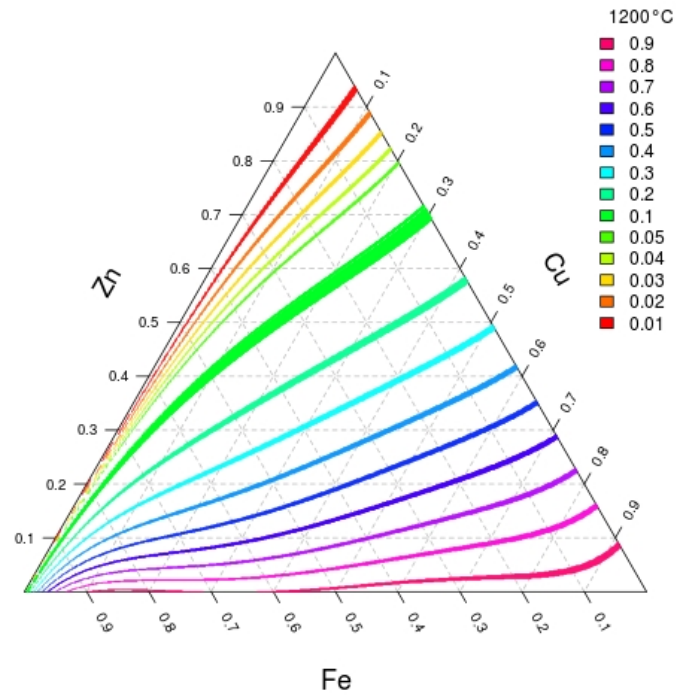


FIGURE 47: CU-FE-ZN (COPPER ACTIVITY)

Table 11: Cu-Fe-Zn Binary Parameters

Parameter	Cu-Fe	Fe-Zn	Zn-Cu
B	2.46	1.4	-2.2
C	-0.02	0.5	0
D	0.72	-0.74	0.1

7.2.8 Cu-Ni-Zn

Activity calculations for the Cu-Ni-Zn system were made using data from Hultgren (1973) given at 1100 °C and extrapolated to 1200 °C (Fig. 49), and the Cu-Ni and Cu-Zn binaries

already described in Chapter 3. The activity data from the Ni-Zn system indicates strong negative deviations and an increase in activity with increasing temperatures. Parameters for each binary system are given in Table 12, which were used to determine the isoactivity lines of each component.

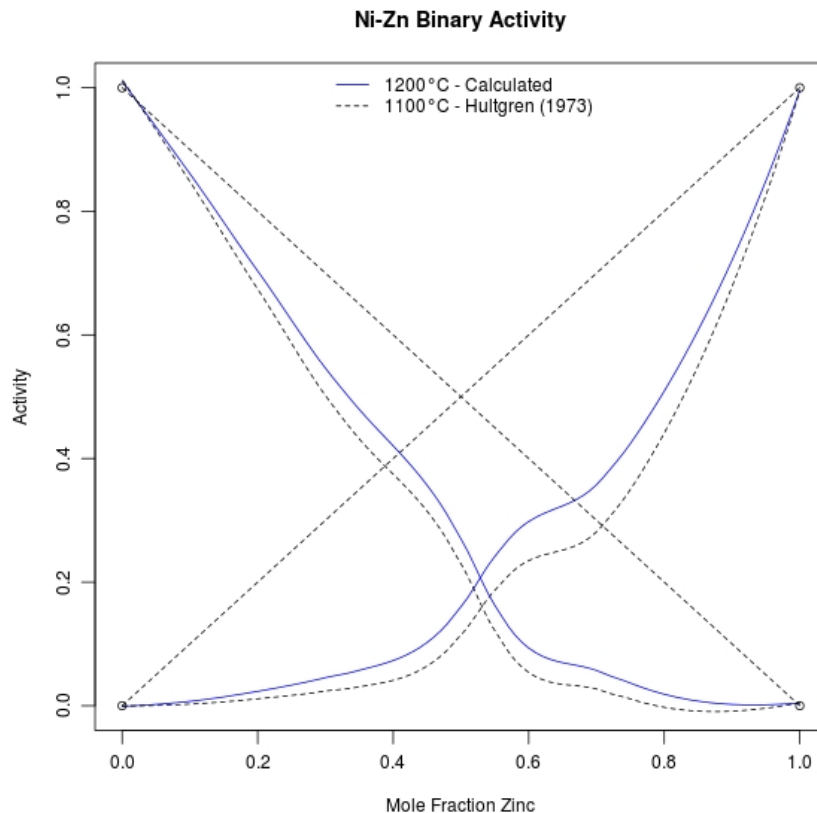


FIGURE 48: NI-ZN BINARY ACTIVITY. THE MEASURED AND CALCULATED ACTIVITY GIVEN ABOVE NOTABLY PASS THROUGH METASTABLE PHASES

For zinc, the activity shows (Fig. 50) a slight decrease with the addition of nickel to the binary Cu-Zn system in agreement in trend with the calculated results by Jiang *et al.* (2005) using the CALPHAD approach at 727°C. The activity values for zinc at the same mole fraction are offset by temperature difference. The implications of added nickel to the Cu-Zn system is that it lessens zinc losses through volatilization by increasing the affinity of zinc to the melt.

Given greater affinity the absorption of zinc would be better facilitated if a Cu-Ni alloy were used in the calamine process.

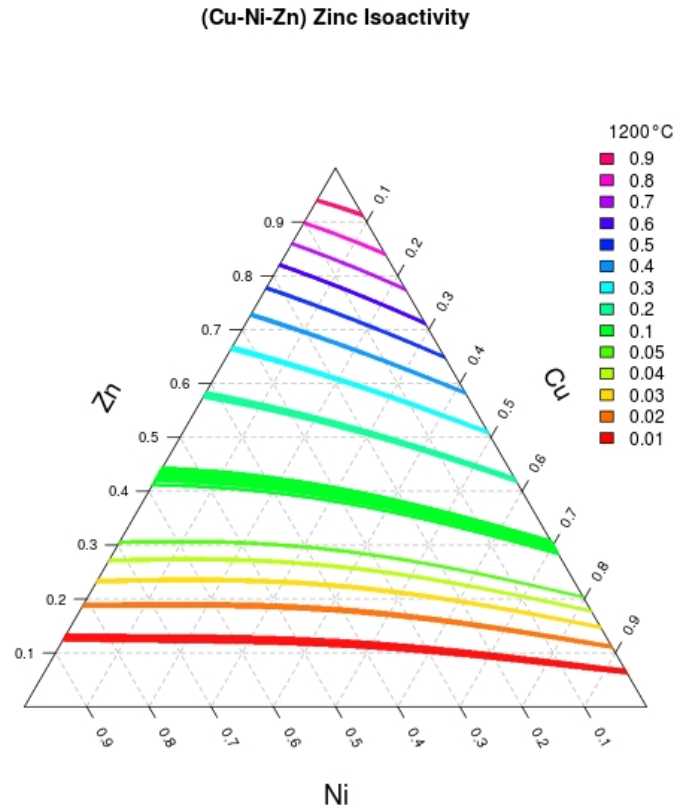


FIGURE 49: CU-NI-ZN (ZINC ACTIVITY)

For nickel and copper, their isoactivities (Figs. 51 and 52) decrease with added zinc, and copper increases with nickel, in the region of interest. Nickel in the Cu-Ni binary already has very low vapor pressure and volatility coefficient resulting in its unlikely loss during recycling by evaporation. It can, however, form stable oxides that may be removed during casting or slagging.

(Cu-Ni-Zn) Nickel Isoactivity

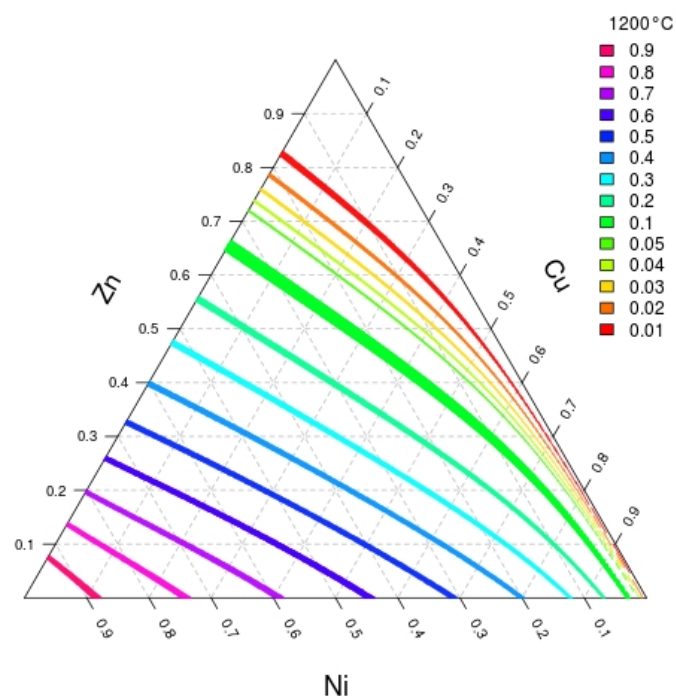


FIGURE 50: CU-NI-ZN (NICKEL ACTIVITY)

(Cu-Ni-Zn) Copper Isoactivity

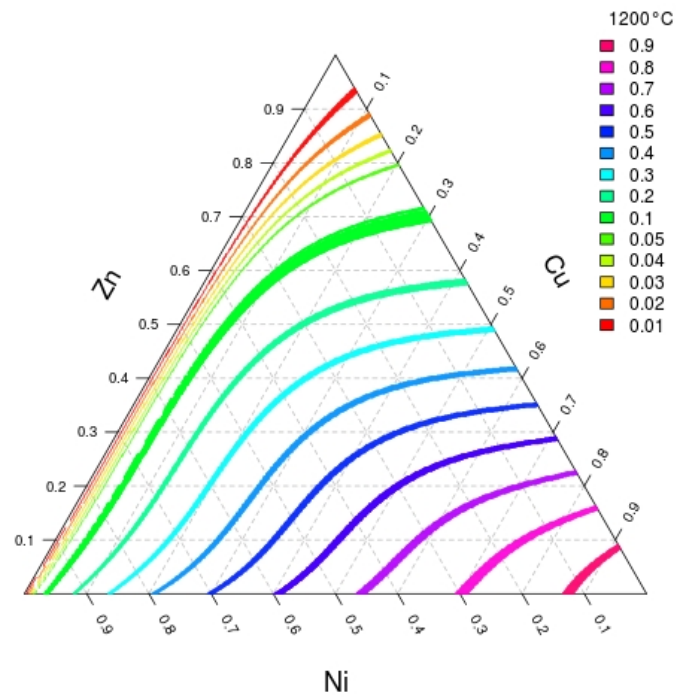


FIGURE 51: CU-NI-ZN (COPPER ACTIVITY)

Table 12: Cu-Ni-Zn Binary Parameters

Parameter	Cu-Ni	Ni-Zn	Zn-Cu
B	1.08	-3.82	-2.2
C	0.1	1.32	0
D	0.16	-1.14	0.1

7.2.9 Cu-Pb-Zn

Kozuka *et al.* (1965) measured the Pb-Zn binary activity at 1050 °C using the E.M.F. method. Their data were extrapolated to 1200 °C and used to calculate isoactivity lines in the Cu-Pb-Zn ternary system. Both the original and extrapolated activity data are shown in Figure 53, which indicate strong positive deviation and repulsion of unlike atoms approaching ideality with increasing temperatures. Each binary systems parameters, for Cu-Zn, Cu-Pb, and Pb-Zn, used for the calculation of individual component activity are given in Table 13.

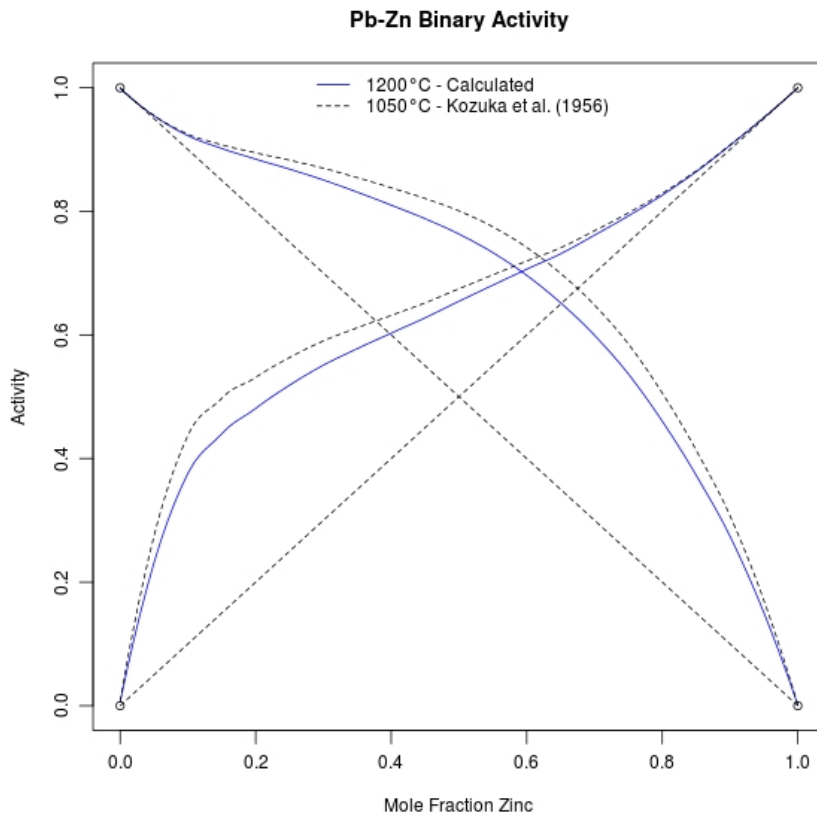


FIGURE 52: PB-ZN BINARY ACTIVITY

The calculated activity of zinc, shown in Figure 54, indicates an increase in zinc vapor pressure due to the positive deviation carried over from the Pb-Zn binary. The presence of lead

in copper during the cementation process would therefore impede zinc absorption over pure copper, or copper containing arsenic, silver, gold, or nickel. Decreased zinc absorption in the presence of lead is also noted by Bayley (1998). These calculations also show strong agreement in trend with values reported by Surapunt *et al.* (1994; 1995) at 802°C using the isothermal isopiestic method. Furthermore, comparison of the calculated activity and trend at 1200 °C of zinc activity measurements by Surapunt *et al.*, and Jantzen and Spencer (1998), show strong agreement in the liquid phase despite the difference in temperature. Activity values for lead and copper in this system were unfortunately not measured.

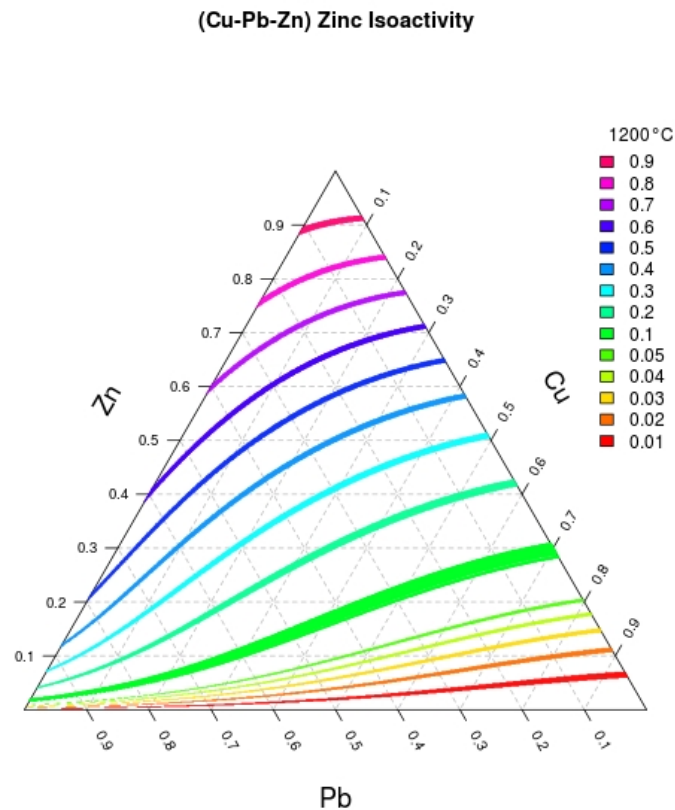


FIGURE 53: CU-PB-ZN (ZINC ACTIVITY)

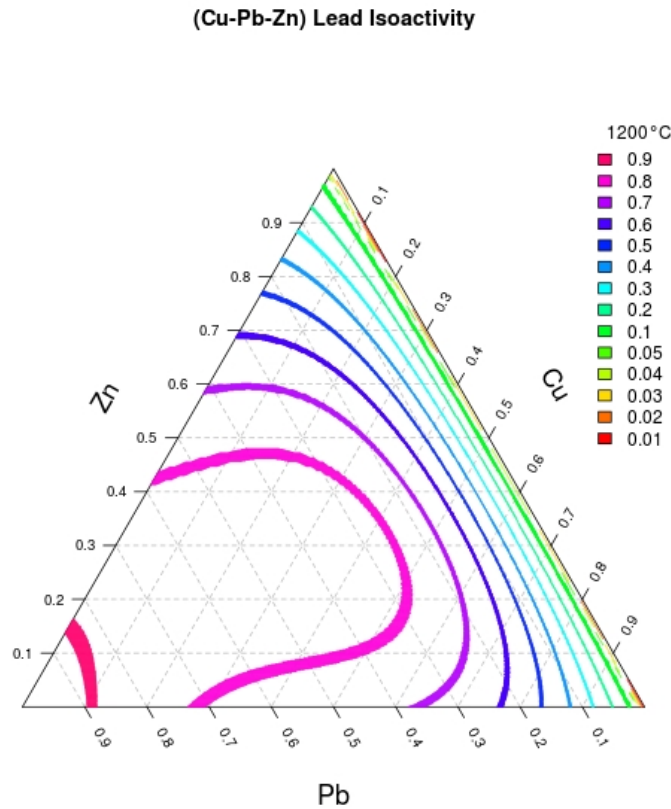


FIGURE 54: CU-PB-ZN (LEAD ACTIVITY)

According to Figure 55, lead activity increases with added zinc. Furthermore, its activity from the diagrams right and top corners show closely aligned values due to the steep slope of the lead activity in the respective binaries. Overall the similarity of the contour lines from these corners is caused by the somewhat comparable Cu-Pb and Zn-Pb binary activity values. Copper activity also increases with added lead, and decreases with zinc, in agreement with the respective Cu-Pb and Cu-Zn binary activity diagrams, but the vapor pressure of copper, regardless, remains low in the region of interest (Fig. 56). Interesting to note for this system is that lead has very low surface tension comparable to zinc (Lu and Jiang, 2005), however the vapor pressure of zinc is

far greater suggesting the more rapid, but concurrent with lead, volatilization of zinc. Oxidative losses, similar to other ternary systems previously discussed, would be ordered beginning with zinc and followed by lead.

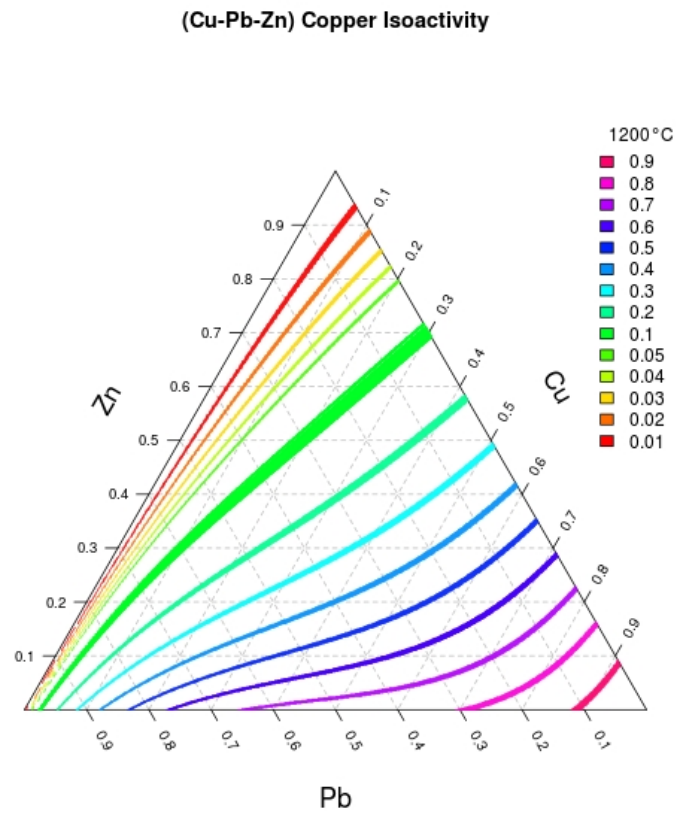


FIGURE 55: CU-PB-ZN (COPPER ACTIVITY)

Table 13: Cu-Pb-Zn Binary Parameters

Parameter	Cu-Pb	Pb-Zn	Zn-Cu
B	1.58	1.36	-2.2
C	0.02	0.32	0
D	-0.14	0.14	0.1

7.2.10 Cu-Sb-Zn

Activity calculations of the Cu-Sb-Zn system were performed using the previously discussed activity data for the Cu-Sb and Cu-Zn systems, and that provided by Hultgren (1973) at 623 °C for the Sb-Zn system, which shows near ideal behavior approaching Raoult's law with increasing temperatures (Fig. 57). The isoactivity lines for zinc, calculated at 1200 °C, reflects this ideality as a steady horizontal line across most of the ternary system (Fig. 58). The data,

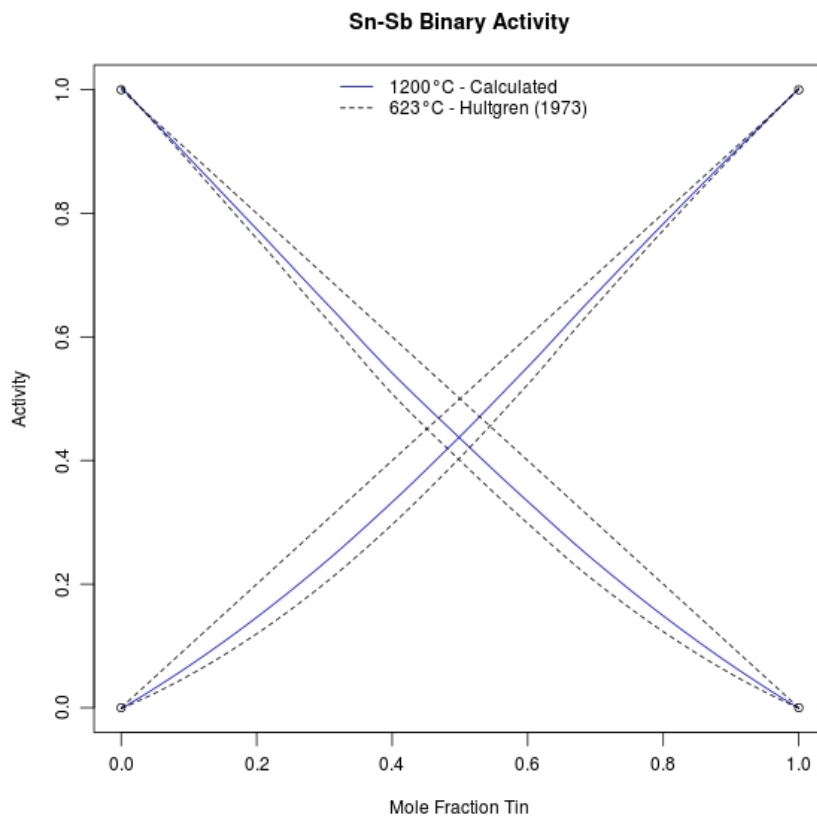


FIGURE 56: SN-SB BINARY ACTIVITY

according to the binary parameters given in Table 14, indicate that antimony increases the activity of zinc resulting in less absorption during cementation if using a Cu-Sb alloy, and more rapid losses during recycling and re-melting through volatilization. The seemingly repulsive

effects of antimony are the result of the comparably positive deviation of the Sb-Zn to Cu-Zn systems.

The activity of antimony and copper increases as zinc is added to the Cu-Sb system (Fig. 59); while copper, in the Cu-Zn system, decreases with antimony (Fig. 60). Despite the increased volatility of antimony, its vapor pressure is still far lower than zinc, so one should expect its enrichment through recycling. Oxidative losses of these three components according to the altered Gibbs free energy of formation based on activity, would proceed; first, with zinc, having the most negative free energy, followed by antimony, and finally copper.

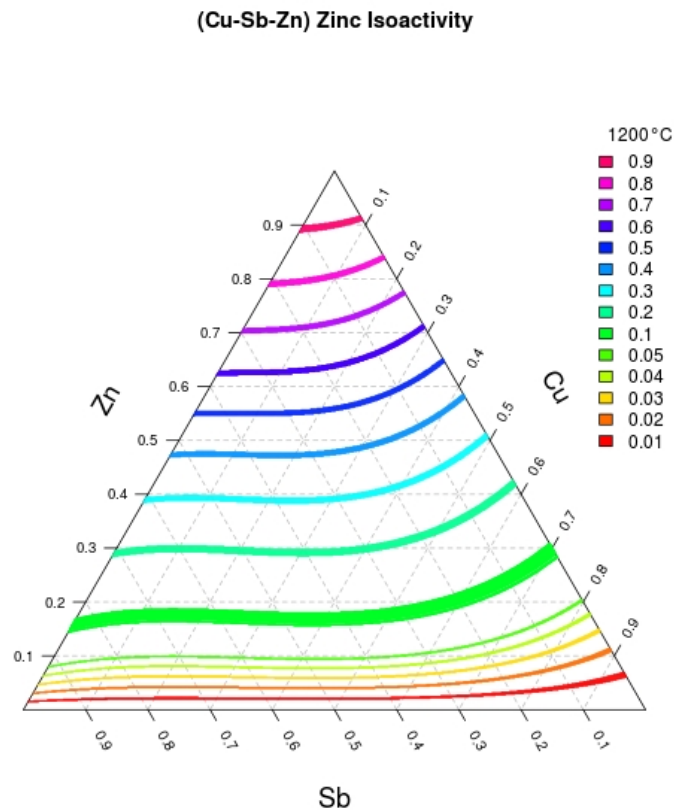


FIGURE 57: CU-SB-ZN (ZINC ACTIVITY)

(Cu-Sb-Zn) Antimony Isoactivity

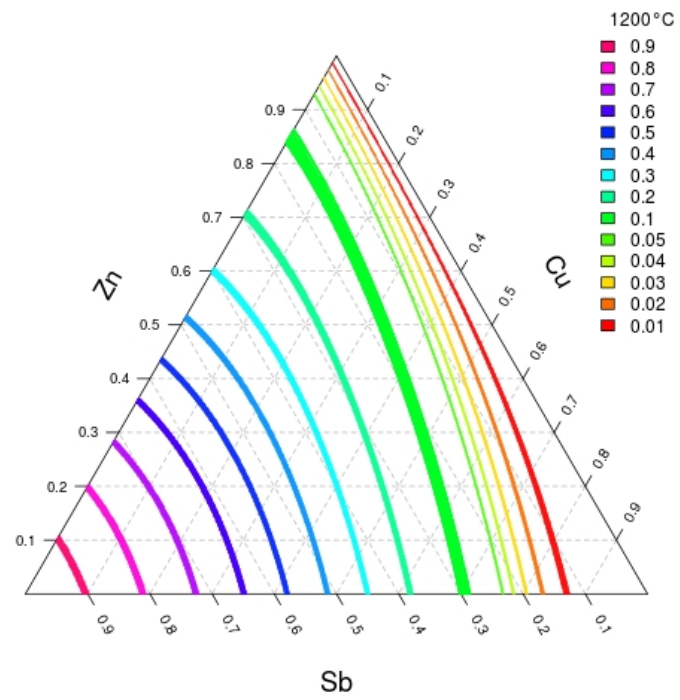


FIGURE 58: CU-SB-ZN (ANTIMONY ACTIVITY)

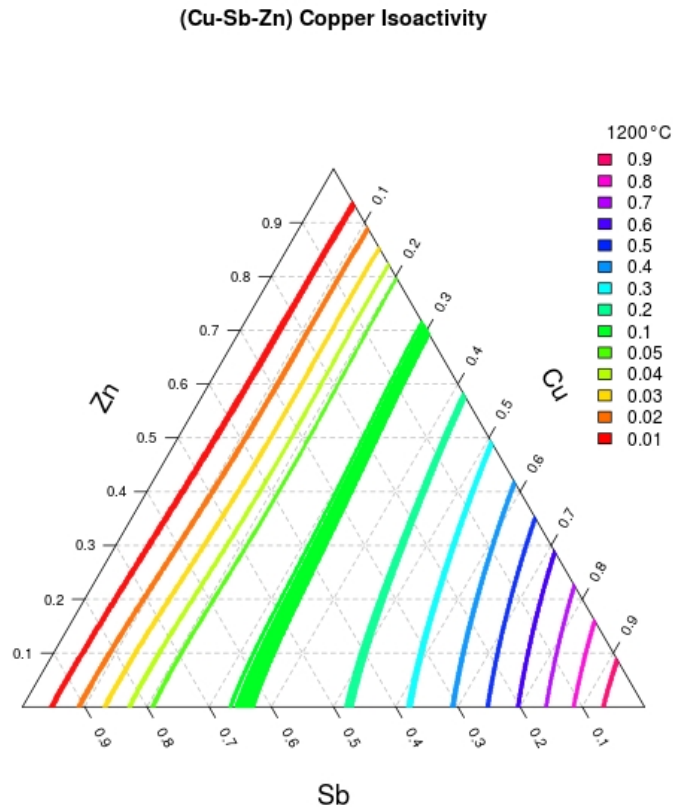


FIGURE 59: CU-SB-ZN (COPPER ACTIVITY)

Table 14: Cu-Sb-Zn Binary Parameters

Parameter	Cu-Sb	Sb-Zn	Zn-Cu
B	-2.6	-0.64	-2.2
C	-1.48	-0.08	0
D	-0.46	0.34	0.1

7.2.11 Cu-Sn-Zn

Calculations for the Cu-Sn-Zn system were made using data given by Sheil and Müller (1962) at 600 °C, which were extrapolated to 1200 °C (Fig. 61). These data show slight positive deviation nearing ideality with increasing temperatures (Table 15). Figure 62 shows that the activity of zinc increases sharply with the addition of tin to the binary Cu-Zn system. Like that of

the Cu-Sb-Zn ternary system, the difference in zinc activity is due to difference in the zinc activity between the Zn-Sn and Cu-Zn binaries. These calculations are confirmed by Sugino *et al.* (1986) experimental results using the isopiestic method at 1100 °C and 1150 °C in low mole fractions zinc (<0.08) and tin (≤ 0.08). Sugino *et al.* similarly concluded that even small amounts of tin increase the activity of zinc citing agreement with the same findings by Jantzen and Spencer (1998) and Miettinen (2002). The repulsive force caused by tin would therefore make tin bronzes highly unsuitable for use in the calamine process as it would impede zinc absorption substantially, which has been noted by Dungworth (1997) and Bayley (1998). Similarly, copper-based artifacts that contained both zinc and tin would more readily lose zinc during re-melting and recycling.

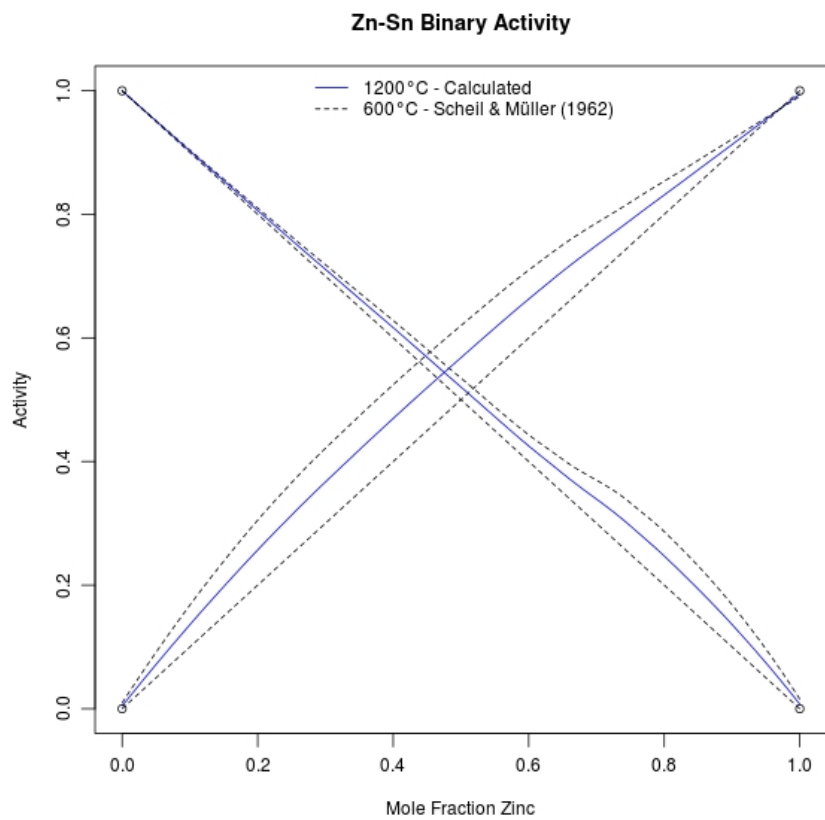


FIGURE 60: ZN-SN BINARY ACTIVITY

(Cu-Sn-Zn) Zinc Isoactivity

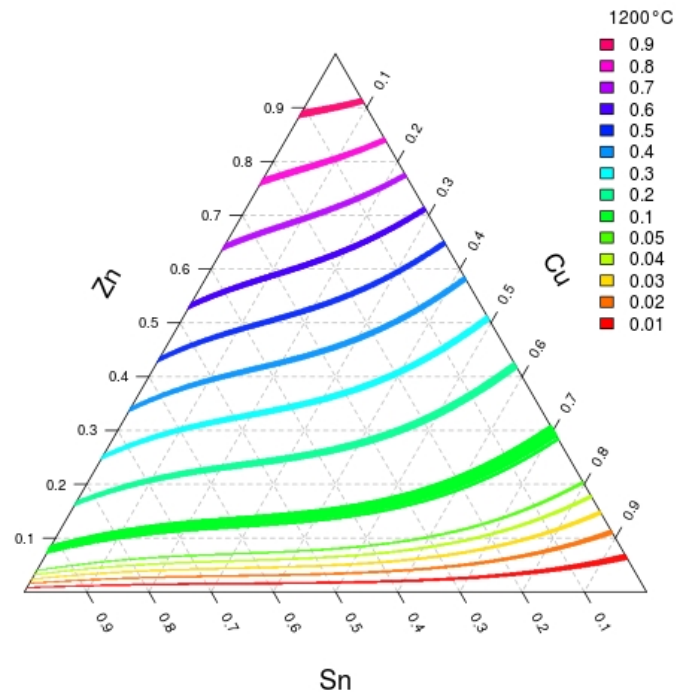


FIGURE 61: CU-SN-ZN (ZINC ACTIVITY)

In tin bronzes the addition of zinc, according to Figure 63, increases the activity of tin and copper (Fig. 64). However, noticeable losses of tin through volatilization, as explained in Chapter 4, would only occur as oxides and after the oxidation of zinc.

(Cu-Sn-Zn) Tin Isoactivity

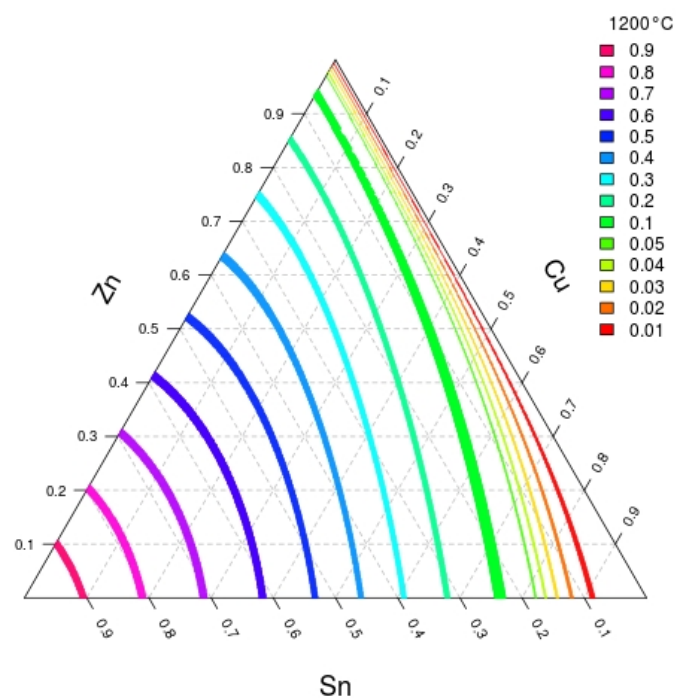


FIGURE 62: CU-SN-ZN (TIN ACTIVITY)

(Cu-Sn-Zn) Copper Isoactivity

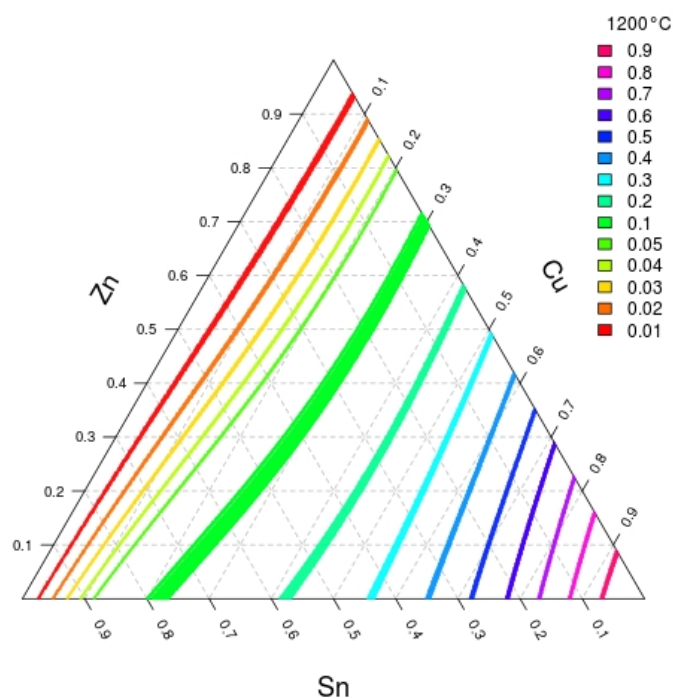


FIGURE 63: CU-SN-ZN (COPPER ACTIVITY)

Table 15: Cu-Sn-Zn Binary Parameters

Parameter	Cu-Sn	Sn-Zn	Zn-Cu
B	-1.56	0.34	-2.2
C	-1.2	-0.18	0
D	-0.62	0.08	0.1

7.2.12 Cu-Sn-Pb

Prominent in databases of 1st millennium CE Britain copper-based objects (Caple, 1986; Blades, 1995; Dungworth, 1995; Butcher and Bayley, 2004), leaded bronze, one of the most common alloys in antiquity, must be considered in addition to ternary systems containing zinc in this thesis. The modeling of the ternary Cu-Sn-Pb system is both informative in interpreting

temporal trends and in tracking the flow of copper-based metals. In the absence of quaternary system calculations including zinc, it is, nevertheless, useful to better understand brasses in the network of metal compositional change present at the time.

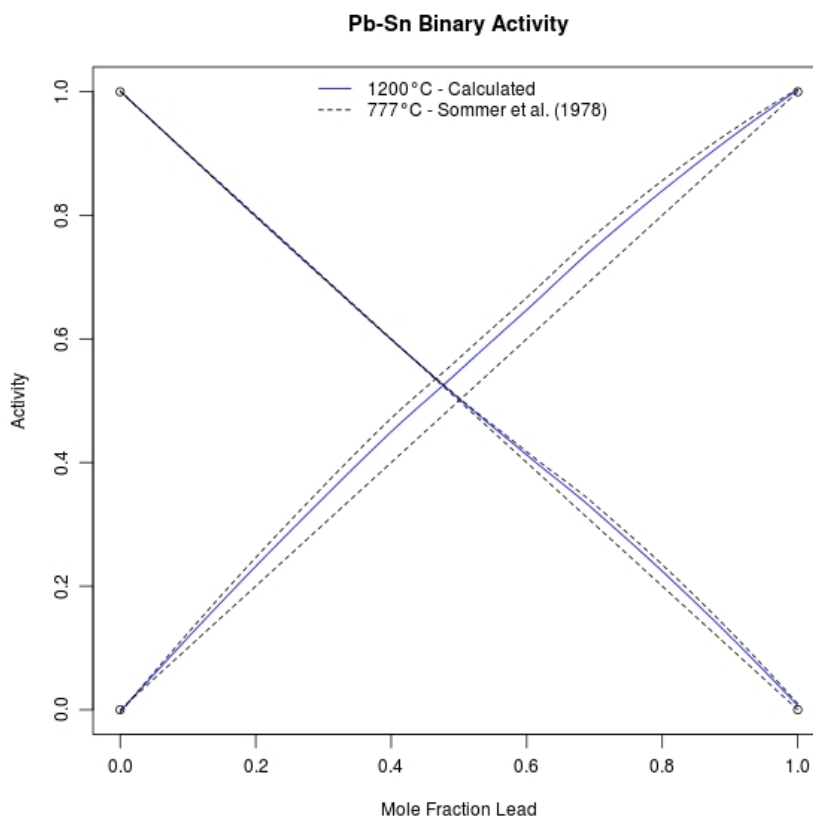


FIGURE 64: PB-SN BINARY ACTIVITY

Calculation of the Cu-Sn-Pb ternary systems component isoactivities were made with activity data from Sommer *et al.* (1978), who using Knudsen effusion at 777 °C, observed slight positive deviation of the binary Pb-Sn system. This behavior is expected given the segregation of the unlike atoms of tin and lead due to differences in their atomic radii. Extrapolated activity of the Pb-Sn binary system to 1200 °C shows decreasing deviation with increasing temperatures nearing Raoult's law (Fig. 65).

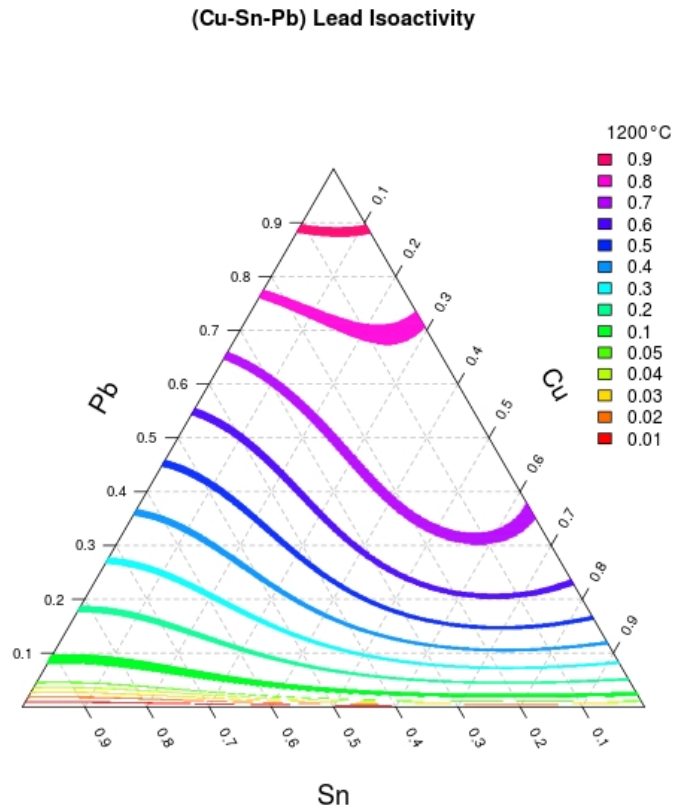


FIGURE 65: CU-SN-PB (LEAD ACTIVITY)

Ternary calculations were completed using a combination of the Pb-Sn system, and Cu-Sn and Cu-Pb systems from Chapter 3. Unlike those ternary systems containing zinc described above, the Cu-Pb binary requires reversal of the odd C parameter (compare Tables 13 and 16) according to the derivations from Chapter 6 after Barker (1953) and Rowlinson (1969, 122). Lead activity (Fig. 66) shows little change with the addition of tin to the Cu-Pb binary system in the region of interest at ≤ 0.1 mole fractions lead. Above 0.1 mole fractions, the activity of lead is slightly positive to approximately 0.3, where it increases dramatically due to the difference in lead activity seen in the binary Pb-Sn and Cu-Pb systems.

Figures 67 and 68 show that both tin and copper activity increases with added lead, and copper decreases with tin. The behavior of tin and copper with lead is the result of the interaction of unlike atoms, in accordance with the radii sizes listed in Table 5, and that of copper because of the affinity of tin and copper shown previously in Chapter 3.

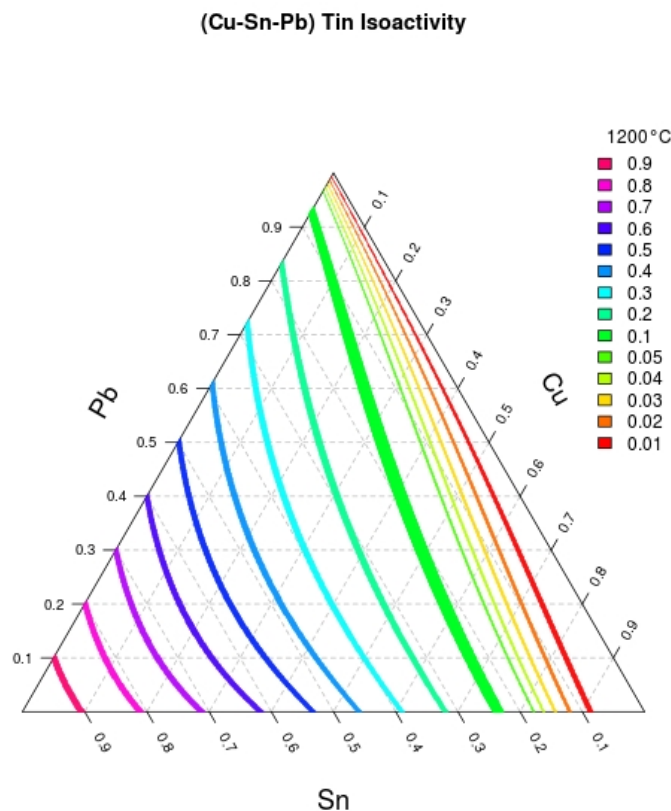


FIGURE 66: CU-SN-PB (TIN ACTIVITY)

The calculated results of each component suggests that for lead in concentrations above 0.3 because of the repulsive effects of the Cu-Sn melt, and given its standard state vapor pressure, it would rapidly volatilize; behavior of which is supported by its extreme volatility coefficient indicating that its losses though evaporation would proceed quickly and level off below 0.3 mole fraction being comparable to losses in the Cu-Pb binary. Tin, with its low vapor

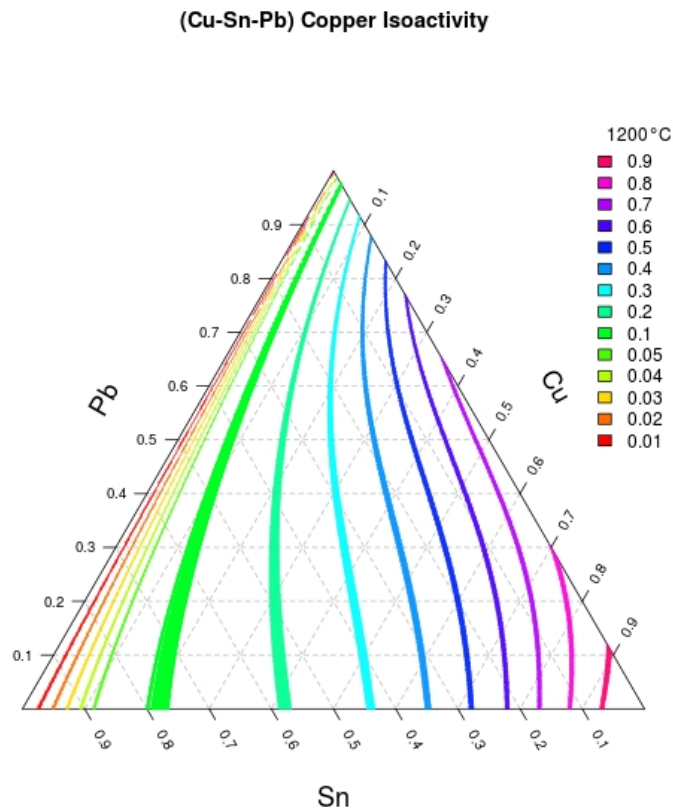


FIGURE 67: CU-SN-PB (COPPER ACTIVITY)

pressure and Gibbs free energy of formation, would not be significantly lost through elemental evaporation despite its increased activity. Instead it would be lost as an oxide, which reduces both lead and copper. Loss of volatile tin oxides (SnO), the most probable means of tin loss in antiquity, also requires reducing conditions, provided by charcoal, in order to convert nonvolatile SnO₂. Copper is unchanged because it is both least likely to oxidize or volatilize.

Table 16: Cu-Sn-Pb Binary Parameters

Parameter	Cu-Sn	Sn-Pb	Pb-Cu
B	-1.56	0.2	1.58
C	-1.2	-0.18	-0.02
D	-0.62	0.1	-0.14

7.2.13 Cu-Sb-As

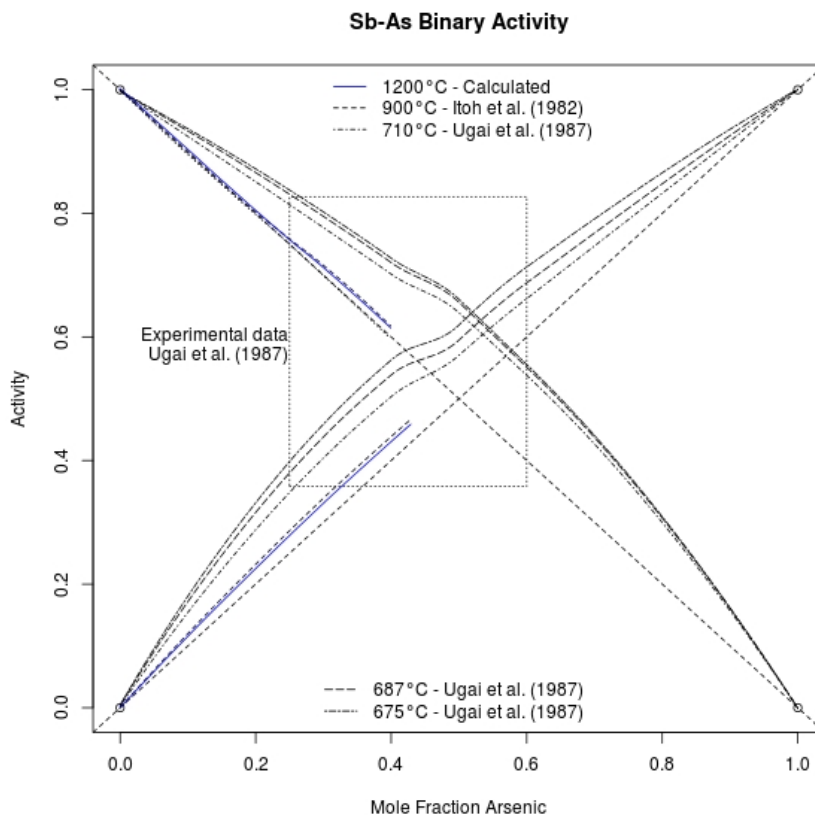


FIGURE 68: SB-AS BINARY ACTIVITY

Figure 69 shows binary activity data from Itoh *et al.* (1982) and Ugai *et al.* (1987) for the Sb-As binary system, both of which provide partial activity data but at different concentrations. Activity data given by Ugai *et al.* was measured within the confines of the dotted rectangle, outside which the activity was interpolated using loess regression. The data from both sources extrapolated to 1200 °C confirm that activity decreases with increasing temperatures, however, only data by Itoh *et al.*, using the E.M.F method, were used to calculate the Sb-As interaction parameters as the experimental temperature was closer to the defined standard (Table 17). Their data also sufficiently covers the range of arsenic and antimony in ancient copper-based artifacts and shows near agreement with Raoult's law.

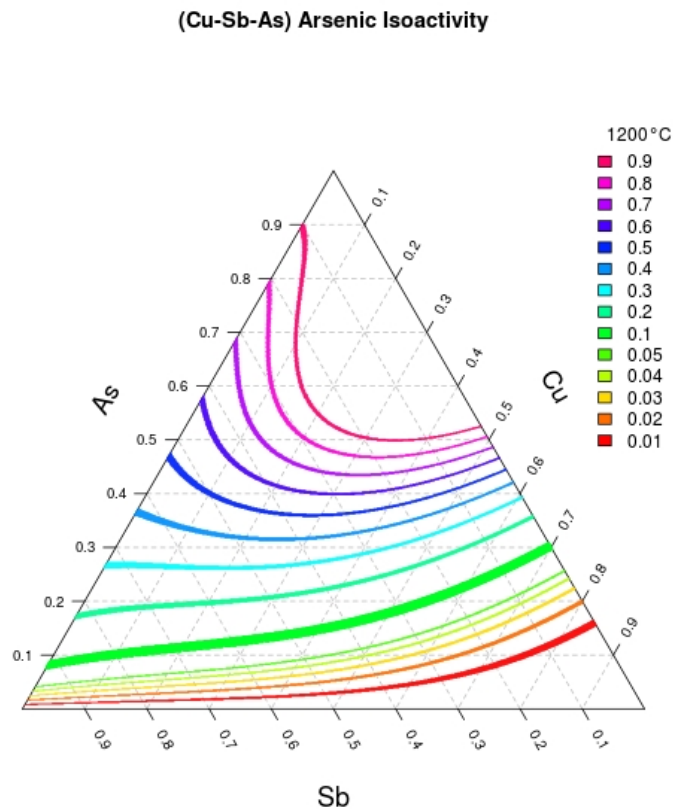


FIGURE 69: CU-SB-AS (ARSENIC ACTIVITY)

Calculations of the ternary systems required sign reversals of the odd Cu-As binary parameter, C (compare to values given in the Cu-As-Zn subsection), showing that arsenic activity increases as antimony is introduced to the Cu-As binary (Fig. 70). Its activity is influenced by the difference in the combined arsenic activity from the Cu-As and Sb-As systems. Antimony activity similarly increases (Fig. 71), but because of the near ideal mixing of antimony and arsenic, there is little change in their loss likelihood due to volatilization compared to their respective copper binaries. Copper activity also shows little change with either added arsenic, to the Cu-Sb, or antimony to the Cu-As systems (Fig. 72).

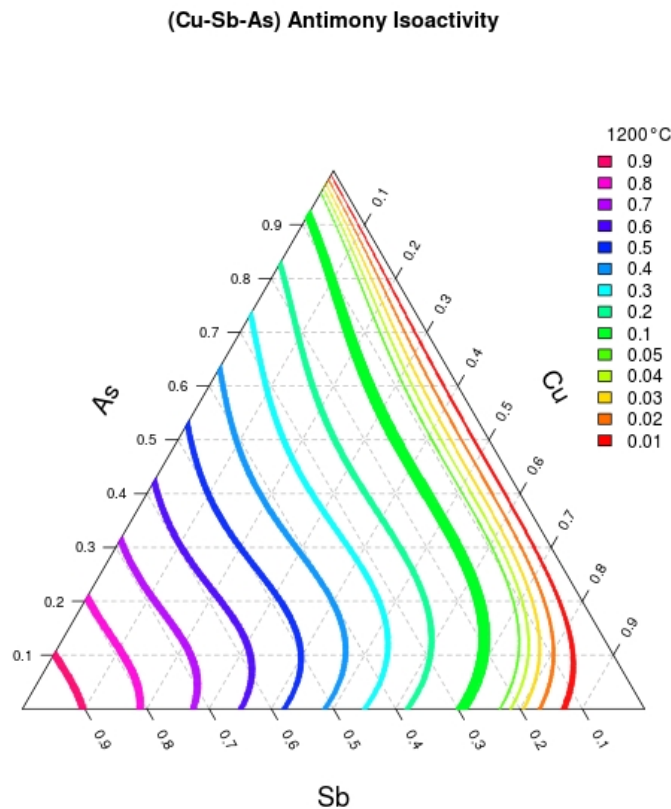


FIGURE 70: CU-SB-AS (ANTIMONY ACTIVITY)

Losses through volatilization and volatile oxides of antimony and arsenic are of particular importance to archaeometallurgical studies, and, in particular, to the Cu-Sb alloys found in Roman Britain. The volatility of arsenic is primarily the cause for its loss being much greater (Table 1) than antimony. More specifically, arsenic losses are primarily due to volatilization of oxides, as discussed in Chapter 4, and while both arsenic and antimony have predominate AsO and SbO volatile species, oxidation of arsenic at the surface of the melt is more prevalent than for antimony being first volatilized as the As₂ dimer, oxidized to 2(As₂O₃), and dissociated into the predominant AsO molecule at melting temperatures as oxygen is added to the system. Simultaneously forming are antimony oxides Sb₂O₃, which dissociate into highly volatile SbO, but antimony is given less opportunity to do so until arsenic losses are sufficient; that is until the

arsenic partial vapor pressure is low enough to allow for liquid-gas mass transfer of antimony atoms.

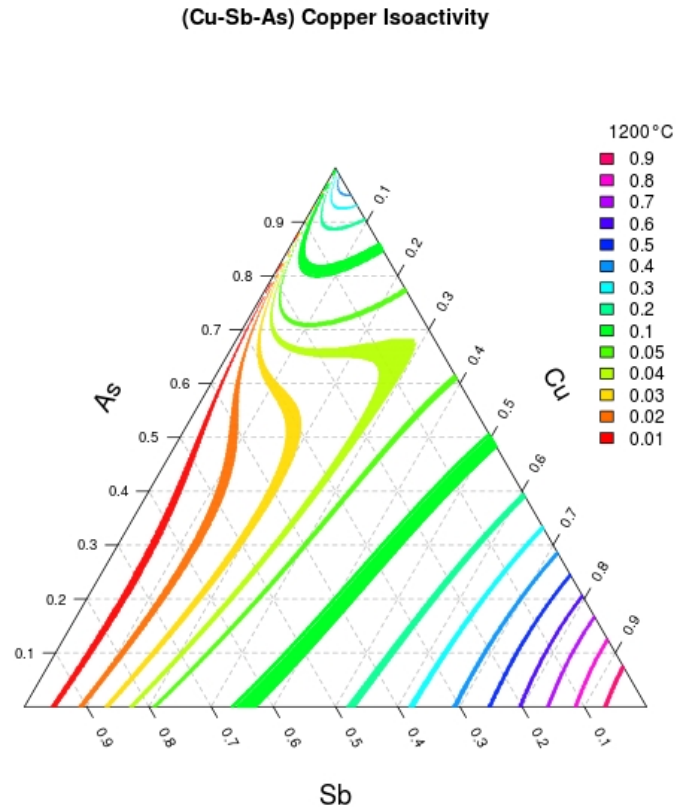


FIGURE 71: CU-SB-AS (COPPER ACTIVITY)

Table 17: Cu-Sb-As Binary Parameters

Parameter	Cu-Sb	Sb-As	As-Cu
B	-2.6	0.22	-2.48
C	-1.48	0	4.2
D	-0.46	0	2.26

7.3 Summary

To understand the influence of tertiary components in binary copper systems that were variably present in the manufacture of brass in the ancient calamine process, and loss modeling of zinc and other metals from brass due to recycling and re-melting, ternary metals systems of Cu-M-Zn were thermodynamically modeled using the well-established methodologies that have been discussed throughout this thesis. By combining the calculated thermodynamic behavior of molten binary metal systems, in the form of interaction parameters, calculations for the activity of zinc and other system components have been given. For zinc, its volatility increases with additions of iron, bismuth, lead, cobalt, antimony, arsenic, and tin; and decreases with nickel, gold, and silver. The first group of elements therefore retard zinc absorption if present during the calamine process, while the second enhance it. For zinc losses the calculated results show that the first set repulses zinc resulting in its greater loss during recycling due to volatilization, and the second help retain zinc reducing its volatility. In addition to zinc-containing ternary systems, the Cu-Sn-Pb and Cu-Sb-As ternary systems were modeled since they are present in the soon to be assessed chemical datasets mentioned in section 7.1, and in related discussions by Pollard *et al.* (2015). In these ternary systems, tin activity increases with added lead, and both antimony and arsenic show increased activity with either added arsenic or antimony. Lead shows little change except at higher mole fractions above 0.1, which may account for the somewhat ubiquitous presence of lead at lower concentrations in archaeological artifacts. Furthermore, since lead concentrations above 0.1 mole fractions are lost more readily, and if ancient metalsmiths noticed less of it after metals were recycled, it may have been frequently added to copper alloys to displace its loss.

Chapter 8 expands upon Chapter 7 by applying the results of the Cu-Sn-Zn, Cu-Pb-Zn, Cu-Sn-Pb models, and information from all other chapters, to give the behavior of individual elements. The behavior is in terms of likelihood of loss or gain, rather than precise amounts, which would require experiment and rate loss calculations.

8. Comparison of Artifact Chemical Data to the Thermodynamic Models

The thermodynamic explanations, especially those from Chapters 6 and 7, provide for individual-element evaporative and oxidative loss-behavior evaluations in binary and ternary molten-metal systems. With this information it is now possible to make informed evaluations of artifact chemical datasets that contain these systems through groupings of artifacts of similar chemical composition and type, and their chemical change over time. Included in this thesis in the previous chapter are thermodynamic system descriptions for all possible combinations of ancient copper-based binary and Cu-Zn-M, Cu-Sn-Pb, and Cu-Sb-As ternary systems, some of which are not present in the current chosen artifact datasets. They have been included, however, to ensure the existence of a complete reference set of thermodynamic assessments for future archaeometallurgical research into ancient brass by this and other scholars. Such a complete reference set should also prove useful in other regions of the world where varying ancient alloy combinations undoubtedly exist.

Returning to the thermodynamic evaluation of the chemical datasets by Caple (1986), Blades (1995), Dungworth (1995), and Bayley and Butcher (2004), this chapter integrates the defined terminology and interpretations of these data that have been compiled and discussed by Pollard *et al.* (2015). In their work they defined a system that, instead of modern cut-off values for metals types, uses 1 wt% for tin, lead, and zinc; and the abbreviated metal type names C (copper), LC (leaded copper), B (bronze), LB (leaded bronze), BR (brass), LBR (leaded brass), G (gunmetal), and LG (leaded gunmetal) to categorize ancient alloys. These changes shift the artifact chemical-data metal-type categories out of the confines of modern predetermined alloy percentages and into ones more suitable for understanding ancient recycling, according to what they unassumingly are rather than what they are commonly predetermined to be according to

modern standards. In other words, there seems to be no reason to assume parity between ancient and modern copper-alloy chemical percentages, other than for mechanical properties, if they were at all sought, when in fact ductility and hardness may have only played a secondary role to qualities such as color and castability in influencing alloy choices. This thesis considers the conclusions and finding of Pollard *et al.*, and goes a step further by not defining cutoff values in favor of a dynamic system of interpreting object composition. The thermodynamic models created here, after all, are dynamic, varying with both composition and temperature, providing insight into the entire compositional range of each system.

Applying the models to the available artifact chemical datasets is, however, not without issue. The datasets themselves are at first inspection vast; however, they contain unreliable chemical data -attained using a variety of analytical campaigns and techniques- and results, placement of artifacts in broad or likely incorrect time periods, and often grossly unequal numbers of artifacts representing different time periods and object types. Yet, despite these shortcomings, enough viable data exists, and, in combination with the thermodynamic models unbound by cutoff percentages, it is possible to make informed assessments of recycling and mixing trends and metal flow. These datasets are summarized below after Pollard *et al.*:

- Caple (1986) analyzed 445 mounted copper alloy pins using X-ray fluorescence (XRF) variably dated between 400 and 1600 CE from 14 sites for, quantitatively, Cu, Zn, Pb, Sn, Ni, Fe, Mn, Sb, and, semi-quantitatively, Ag, As, and Au. It consists of the following samples: 72 Roman, 52 Saxon (mostly poorly dated), 33 early medieval, 120 late medieval, and 105 post-medieval.
- Dungworth (1995) published 2,600 objects analyzed using EDXRF from polished surfaces or drilling samples from 83 sites from the 1st to the 4th century CE for,

quantified, Cu, Zn, Pb, Sn, Fe, Ni, Mn, As, Co, and unreliably, Sb. These objects are from northern Britain between Manchester and Edinburgh, consisting of personal ornaments (~25%), household (~27%), military equipment (~8%), transport-related (~13%), waste (~5%), and other or uncertain objects (~22%).

- Blades (1995) reported data for 1,235 samples dating from approximately 400–1600 CE analyzed using inductively coupled plasma optical emission spectrometry (ICP-AES) for Cu, Zn, Pb, Sn, Fe, As, Bi, Cd, Sb, Co, Ni, Cr, P, S, Mn, Ag, Au, and V. These data are from 18 sites south of West Heslerton, representing brooches, pins, and sheets.
- Bayley and Butcher (2004) published approximately 3,500 Roman brooch analyses, with 1,092 chemical analyses for Cu, Zn, Pb, Sn, Ag with 1,018 analyzed using atomic absorption (AAS) and the remainder derived from Dungworth (1995). The remainder of the 3,500 (-1,092) are ignored in this thesis since they are qualitative XRF analyses on unpolished surfaces. Eliminating the majority of these data, the remaining are dated typologically, with 10 from the Late Iron Age (pre-conquest: 100 BCE–50 CE), 368 from 1–70 CE (Late Iron Age to Roman conquest), 91 from 43–70 CE (conquest), and 296 from 70–170 CE (post-conquest).

Of these available datasets, only those given by Dungworth (1995) and Blades (1995), a total of 2,646 object analyses, were viable, which include those data discussed by Pollard *et al.* (2015). Within the rejected datasets many analyses lacked firm dates and/or associated site information.

Plotting Dungworth and Blades data, it is clear that three main elements persist, other than copper, throughout. These are zinc, lead, and tin, and are shown in Figure 73 from the Late Bronze Age to post-medieval periods. Also immediately apparent is that after the 4th century CE,

beginning in Blades's Roman (RMN) data, the composition of objects increases in variation to include gold, silver, cobalt, antimony, bismuth, and increased amounts of arsenic over earlier time periods. It is possible that the presence and increased percentages of these elements in later dated artifacts was the result of the choice of analytical technique -ICP-AES compared to XRF-, an influx of fresh metal with trace amounts of these impurities, the eventual buildup of silver from the recycling and mixing of lead and leaded objects, or, according to Blades (1995), the use of debased silver coins as scrap. Given the unlikely loss of silver and gold, as discussed in Chapters 3 and 4, and the ability of ICP-AES to detect elements at parts-per-billion (ppb), it is most probable that the supposed increased ubiquity in both gold and silver was at least partly due to a combination of metal nobility and analytical technique rather than the recycling of coinage. Unfortunately, Dungworth's earlier period data does not include gold and silver measurements, and was furthermore collected using XRF; the former of which for those elements that were assessed is far less sensitive to low concentrations and often incapable of detecting trace amounts. Influenced by the elements themselves and matrix structure, XRF also often precludes the detection of some elements in low concentrations altogether. Blades's conclusions, and his reiterated findings (e.g., Fleming, 2012), illustrate well the difficulty in interpreting data from different analytical methods, especially without knowing the thermodynamic consequences of recycling.

Furthermore, the detector type used in Dungworth's analyses is not reported, which is crucial to determining the validity and accuracy of his analytical results. What useful information is provided, however, is limited to the voltage, a low 20kV, and that no filter was used. Under these conditions, regardless of the detector type, identification of some elements is severely limited by peak overlap and the lack of sufficient excitation of electrons. Thus, despite the use of

deconvolution software to sort and eliminate peak overlap, several elements were simply not detected by the employed method, and as a result there was in fact nothing to deconvolute. Later publications that used the same instrument (Link Analytical XR200) have confirmed these issues and its inability to detect several trace amounts of elements, namely Sb, Au, and Ag (Dungworth, 1997).

Meanwhile, arsenic appears in almost every time period and in both datasets, but at low amounts compared to those measured by Blades. An increase in arsenic, if not simply an artefact of analytical technique, would undoubtedly be the result of the strong affinity of arsenic for copper and its survival through recycling according to the oxidation order calculated in Chapter 2. Another possibility for the supposed increase in arsenic ubiquity and percentages, and although EDXRF and ICP-AES results are on average statistically comparable (Lyubomirova et al., 2014), is the overlap of arsenic and lead peaks in XRF spectra (Lutz and Pernicka, 1996). At excessively high concentrations of lead compared to arsenic, such that are present in the vast majority of the analyses, quantification of arsenic using XRF is unreliable and becomes increasingly less so with increasing lead percentages. In fact, arsenic percentages below 0.5% are difficult to quantify, which explains both the absence of arsenic in many of Dungworth's analyses compared to Blade's. Therefore, an influx of copper from a new source may explain the overall increase in arsenic in Blades' data in later periods, however, overlap of peaks in XRF analyses may be the single cause, or at least a significant contributing factor, to the discontinuity between datasets. Dungworth (1995, 104) even comments on the high ubiquity of arsenic in his Iron Age artifact analyses, however, in many of these artifacts the presence of arsenic is often recorded where lead is not detected (Appendix B.3). Therefore, the lack of earlier silver and gold analyses, and later questionable arsenic ubiquity and concentrations, precludes the interpretation

of recycling practices of these metals before the Roman period with these data. As a result, the ternary Cu-As-Zn system modeled in Chapter 7 will not be discussed in any great detail.

Fortunately, zinc, lead, and tin appear in all analyses, and in great enough percentages and high enough accuracy, to allow for their thermodynamic interpretation. These elements alone are sufficient for this pilot study.

The combined data shown in Figure 73 were ordered chronologically according to the dating schemes found in Appendix B.2, and by site (Appendix B.1), with careful interpretation of poorly dated objects, which were considered separately rather than rejected completely. The time periods include those defined by Dungworth (1995): LBA (Late Bronze Age), EIA (Early Iron Age), IA (Iron Age), LIA (Late Iron Age), C1AD (1st century AD), C2AD (2nd), C3AD (3rd), C4AD (4th), EROM (early Roman), MROM (middle Roman), LROM (late Roman), ROMN (Roman), and by Blades (1995): RMN (Roman).¹⁰ These data are plotted into broadly and more specifically dated time periods, and are interpreted separately. It is important to note the existence of the MIA (middle Iron Age) that is thought to be evidenced by the chemical composition of bronze objects that contain no lead (e.g. Dungworth, 1995, 68-90), however, no data, or data that has been more finitely dated beyond their general placement within the IA, have been reported in the examined datasets.

In regard to the mechanical properties of the alloys contained within the selected datasets, and therein the objects as they were intended for use before recycling, it is important to note that control was exercised by the Romans over their composition to achieve particular attributes. These attributes have already been discussed in detail by scholars (e.g. Blades, 1995, 30ff), but

¹⁰ See Appendix B.3 and the attached DVD for the combined chemical datasets used in this thesis.

are briefly summarized here as these properties suggest an initial use application and intended future trajectory. The trajectory was likely directed by categorization and controlled recycling efforts of brasses and bronzes whereby imprecise but recognizable physical attributes were recognized and sought systematically.

In summary after Blades (1995), tin bronze with up to 10 wt% tin is suitable for wrought fabrication and casting, while above this amount it should only be used for casting since the alloy becomes too hard. Tin content upwards of 20-25 wt% was suitable for mirrors that could be polished to achieve a reflective surface, which is seen in the combined datasets for early Roman (C1AD) mirrors with decreasing tin and increasing lead in later ones. Up to 25 wt% tin was also used for bells, but was found to be excessive and cause fracturing. The amount of lead used in bells was later decreased to 15-20 wt% in the Medieval period. With increasing tin content, the color of bronze changes from red-brown to whitish.

Comparably, brass is also suitable for casting and wrought fabrication. Adding zinc to copper results in a yellowish metal that is ductile and malleable. However, compared to tin bronzes, brasses may have often contained twice as much zinc as tin in tin bronzes because more zinc is required to acquire the same working properties. During the Roman periods, bronze and brass objects seem to scale towards this workability metric with decreasing zinc and increased mixing of brass and bronze moving forward to the Early Saxon period.

A combination of the alloys of brass and bronze, the ternary Cu-Sn-Zn, is suitable for wrought working, but it is inferior to brass in this respect. Brasses of up to 30 wt% zinc and 1-2 wt% of lead or tin were used for wrought items and small castings such as pins and wires, and handles and buckets, respectively. Later, 14th century brasses contained 15-20 wt% zinc, rising

to up to 33 wt% by the 16th century (Cameron 1974), which was a trend also seen in other brasses and the datasets in this thesis. Medieval leaded and unleaded gunmetals were used for small castings, and high leaded bronzes of up to 25 wt% lead and 10 wt% tin were common for large cast vessels.

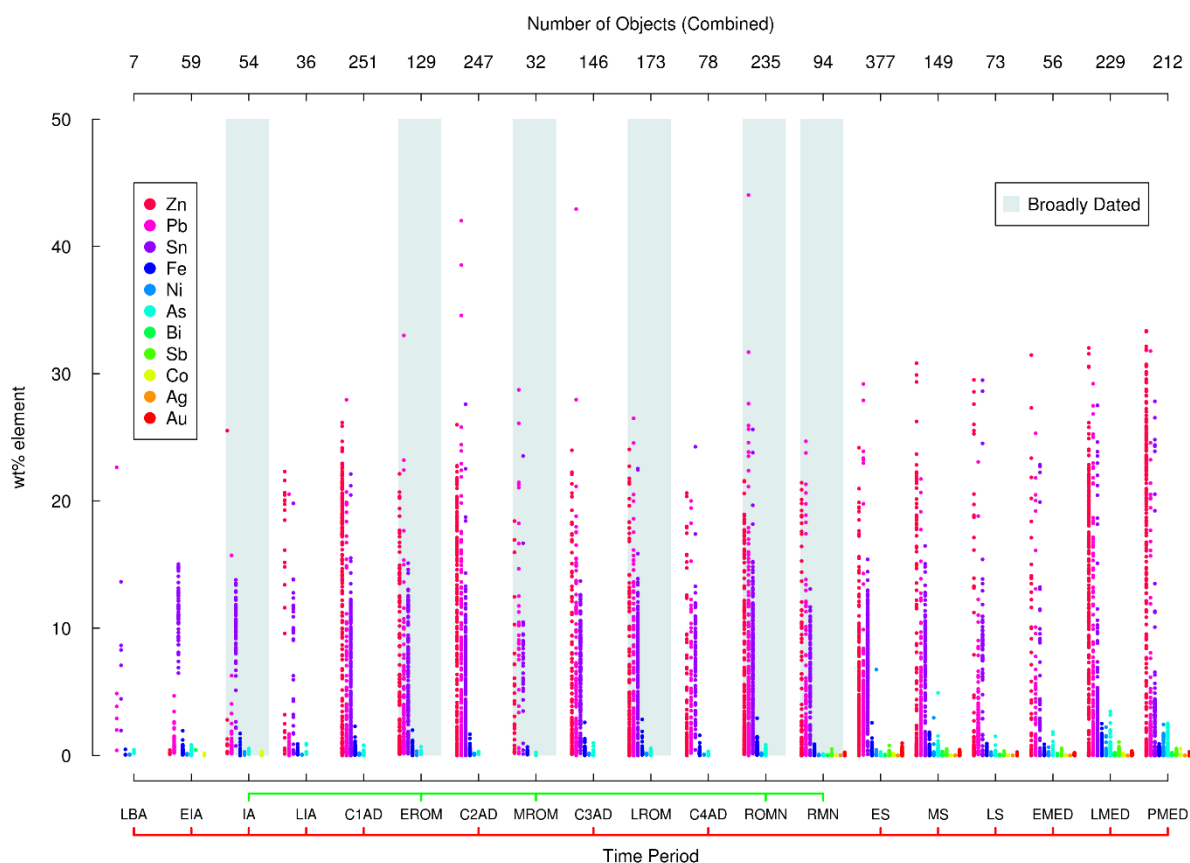


FIGURE 72: TIME PERIOD AND ARTIFACT CHEMICAL COMPOSITION

8.1 Visualizing and Discussing Recycling, Metal Flow, and Thermodynamic Changes

Understanding metal flow and the underlying thermodynamics of the alloys from Late Bronze Age (LBA) to post-medieval (PMED) Britain is best achieved by visual representations of the data in conjunction with the ternary diagrams completed in Chapter 7. Figures 74, 75, and 76 give wt% comparisons of all 2,646 copper alloy objects with associated dates and sites from

the Late Iron Age (LIA) to PMED periods in combinations of [Cu]-Sn-Zn, [Cu]-Pb-Zn, and [Cu]-Sn-Pb systems. From Figures 74, 75, and 76,¹¹ viewed together, it is clear that in the Late Bronze Age (LBA) Sn seems to predominate, and that there are few instances of low lead (~4% or less), with one exception, and only trace amounts of zinc, a trend which carries over into the Early Iron Age (EIA). In the LIA, zinc spikes to over ~20% at Redcliff (RDCL) for the majority of objects that also contain low percentages of tin, which varies inversely and proportionally with zinc. All objects contain low lead (~1%), while at Tofts Field (TOFT) in the same time period there is leaded bronze (LB) and no objects containing zinc. Following in the 1st century CE (C1AD), brass (BR) and leaded brass (LBR) spike at Castleford (CASD), showing the same inverse relationship at a time that roughly coincides with the Roman incursion into Britain, and at sites as far north as the later built Hadrian's Wall (Blackfriars (CABL), Castle Street (CACA), Annetwell Street (CAAN)). Of the objects at CASD, some contain the highest zinc yet (>25%), while others contain lesser amounts of zinc along with lead and tin in an inverse relationship. Instances with lesser zinc percentages that are not primary brass -brass containing only copper and zinc with little lead- are probably evidence of the mixing and recycling of LBR with LB from previous time periods. This pattern of mixing begins in the LIA, but a lack of site correlation and sufficient prior data prevents any direct comparison. At TOFT, in the 1st century CE both primary brass as well as LB simultaneously exist, and similar patterns emerge at Edinburgh Castle (ELGN), Dragonby (DRAG), Old Wintringham (OLDW), and especially Stanwick Hoard (STAN). What seems to be occurring is the mixing of BR with either lead, or leaded copper (LC) and LB, and that lead is added to the general metal flow from either source.

¹¹ See attached DVD for higher resolution figures.

More importantly, when lead and/or tin are present, less zinc occurs in the produced object. Both tin and lead have been shown in Chapter 7 to increase the activity of zinc, resulting in zinc in a Cu-Sn-Pb-Zn alloy more likely to evaporate, which accounts for the inverse relationship mentioned earlier. Furthermore, while zinc and tin show increased activity, lead does not, and given the volatility of zinc and tin oxides, outlined in Chapter 4, lead is less affected by interaction in the quaternary system. It should be expected, then, according to the lines of isoactivity shown in Chapter 7, that low lead will prevail throughout the flow and recycling of metal. For the LBA it must be noted, like all other time periods, but especially those that are pre-Roman, that limited analytical data and represented sites for each period restricts their interpretation accordingly. The discussions of recycling in this thesis therefore focus on periods later than the LBA. Of the few objects from Redcliff with more than 10% Zn, 12 are brooches, suggesting this early site was a gateway for materials and production, as has been suggested by Dungworth (1995, 218).

In the 2nd century CE (C2AD), at the same sites as those from the 1st century, the same pattern continues and, especially at Vindolanda (VIND), some objects contain only copper and tin. The pattern is also seen at Welton Wold (WEWO) and Walton-le-Dale (WLDL), and in the 3rd century CE (C3AD) throughout each site, with the clearest distinction at Brougham (BRHM). Primary brass is still being produced at these sites, and added to a continuous flow of fresh metal until in the 4th century (C4AD) when all analyses contain zinc, lead, and tin, indicating indiscriminate mixing of BR and bronze (B), and thus the decrease of zinc and tin in greater proportions. Leaded gunmetal (LG) becomes the most prevalent metal type owing to the convergent evolution of mixing, which began unrestricted by metal type in C3AD. The presence of LG, in agreement with Pollard *et al.* (2015), is undoubtedly due to recycling.

What is evident is that up until the 4th century, there was an attempt to keep two metal types that were simultaneously in circulation in separate recycling groups -BR and B-, perhaps for reasons of retaining color, castability, or working properties, and that, evidenced by the dataset compilation, decorative items were often made of LBR or LB. In fact, in brass, because of the high vapor pressure of zinc and its continuous and steady evaporation, outside gases are prevented from being absorbed into the molten alloy. When brasses are cast the outgassing effect of zinc results in decreased porosity. This is just one reason ancient smiths would want to keep BR and B separate. Also, cases of high lead in LG for vessels and decorative items such as brooches occurs -the lead most likely being added to increase the alloy castability for intricate or large casts- and in either recycling group at least low percentages of lead are present. Although these two alloy groups were predominant and existed in tandem recycling efforts, use of lead and tin as alloy-modifying elements was well understood, such as in the casting of mirrors. Since the reflective attributes of mirrors required particular proportions, and since the knowledge to create them existed, smiths likely started from scratch with pure copper, lead, and tin, not knowing the exact composition of scrap metal. The same is true for primary brass, which was likely cemented using only copper and zinc oxide ores, with lead added later. So, scrap metal had its place in recycling, and especially for recasting of similar items that required high castability, for instance, but not for specialized items. It is fortunate that not many of these specialized items exist in the examined dataset.

Returning to basic interpretation of the data, looking at the broadly dated sites in the Iron Age (IA), early Roman (EROM), middle Roman (MROM), and late Roman (LROM), the same pattern emerges of coexisting metal types, and it supports the interpretation of the better dated sites above. The Roman data by Dungworth (ROMN) and Blades (RMN) lie somewhere along

the expanse of the 1st to the 4th century CE and on their own are not useful for determining metal flow; however, in the expanded contexts of continuous manufacturing, recycling, and mixing of metal from the better dated and discussed sites, their randomness begins to make sense. Objects in the ROMN and RMN categories, for instance, that contain no LG can be better dated to EROM or MROM, and those with LG to late MROM or LROM. Objects broadly dated to the IA may be similarly distributed based on alloy type if and when more data are made available. Furthermore, for the data recorded by Caple (1986) and Bayley and Butcher (2004), and those object data rejected for interpretation in this thesis in the assessed datasets, they may in the future be dated by the same means as above for ROMN and RMN datasets, as well as for Bayley's later period brooches.

Finally, in the early Saxon (ES) period, the trend from ROMN and RMN continues, but clear changes begin to take form in the MS period at the site of Brandon, continuing to sites in the PMED period, where there is a sudden drop in the percentage variability of alloying elements. The use of tin and lead appears to decrease along with indiscriminate mixing of metal types, but is more likely an indication of more intelligently used alloying techniques. After the middle Saxon (MS) period there is undoubtedly recycling of earlier period metal, but at the same time primary brass and bronze are being produced. Throughout the dataset it is clear that peaks of primary alloys of BR and B exist, indicating use of the calamine process and simple Cu-Sn alloying, that lower percentage primary alloys usually correspond with increases in other elements, and that this trend occurs from the introduction of BR in the LIA onward.

8.1.1 Thermodynamics

The above interpretations of Dungworth's (1995) and Blades's (1995) chemical datasets are derived, not from the combination and plotting of the data, but primarily from the

thermodynamic models created in Chapter 7. These models highlight the patterns seen in the data. In particular, Figures 54-56 (Cu-Pb-Zn), 62-64 (Cu-Sn-Zn), and 66-68 (Cu-Sn-Pb) dictate the limits and possibilities of the datasets' meaning, and are mentioned here briefly with reference to the lines of isoactivity plotted in the previous chapter and thermodynamic data for elements in binary systems. If there are errors in this interpretation, they lie in the fundamental weaknesses of thermodynamic theory, rather than in personal opinion.

Beginning with the Cu-Pb-Zn ternary system, it is clear that when present, lead is detrimental to the absorption of Zn(g) by solid and liquid copper. And, looking at the data, it becomes clear that cases of primary brass coincide with this fact and often contain no or very low percentages of lead (~1%), further suggesting the use of relatively pure copper ingots in the calamine process. Pure copper, as it were in antiquity, was anything but. By modern standards it was dirty, and certainly low percentages of impurities could, together, significantly influence the outcome of zinc absorption. To this point the other models given in Chapter 7, such as Cu-As-Zn and Cu-Ag-Zn, would be instrumental in determining the success of cementation where analyses for additional elements exist. Tin, likewise, in the Cu-Sn-Zn system also increases zinc activity, and in combination the positive deviation of tin and lead to zinc may be additive. Here the concept of additive influence does not suggest that the values of the lines of isoactivity are added, rather it refers to results of calculations more complex than those given in Chapter 6, which rely on the total Gibbs energy of mixing. Assuming some additive influence, however, the possibility of increased repulsion further supports the belief that clean copper was used for cementation rather than scrap or metal of unknown composition. This makes sense looking at the composition of primary brass throughout the dataset, which contains few impurities, and coincides with recipes for brass from the Middle Ages (Smith and Gnudi, 1942). This of course

suggests that any G, LG, or LBR is the result of mixing and recycling of metal types no matter how early they appear in the archaeological record. It also suggests that craftsmen were not unwittingly selecting metal types, and could at least roughly identify the metals contained in scrap.

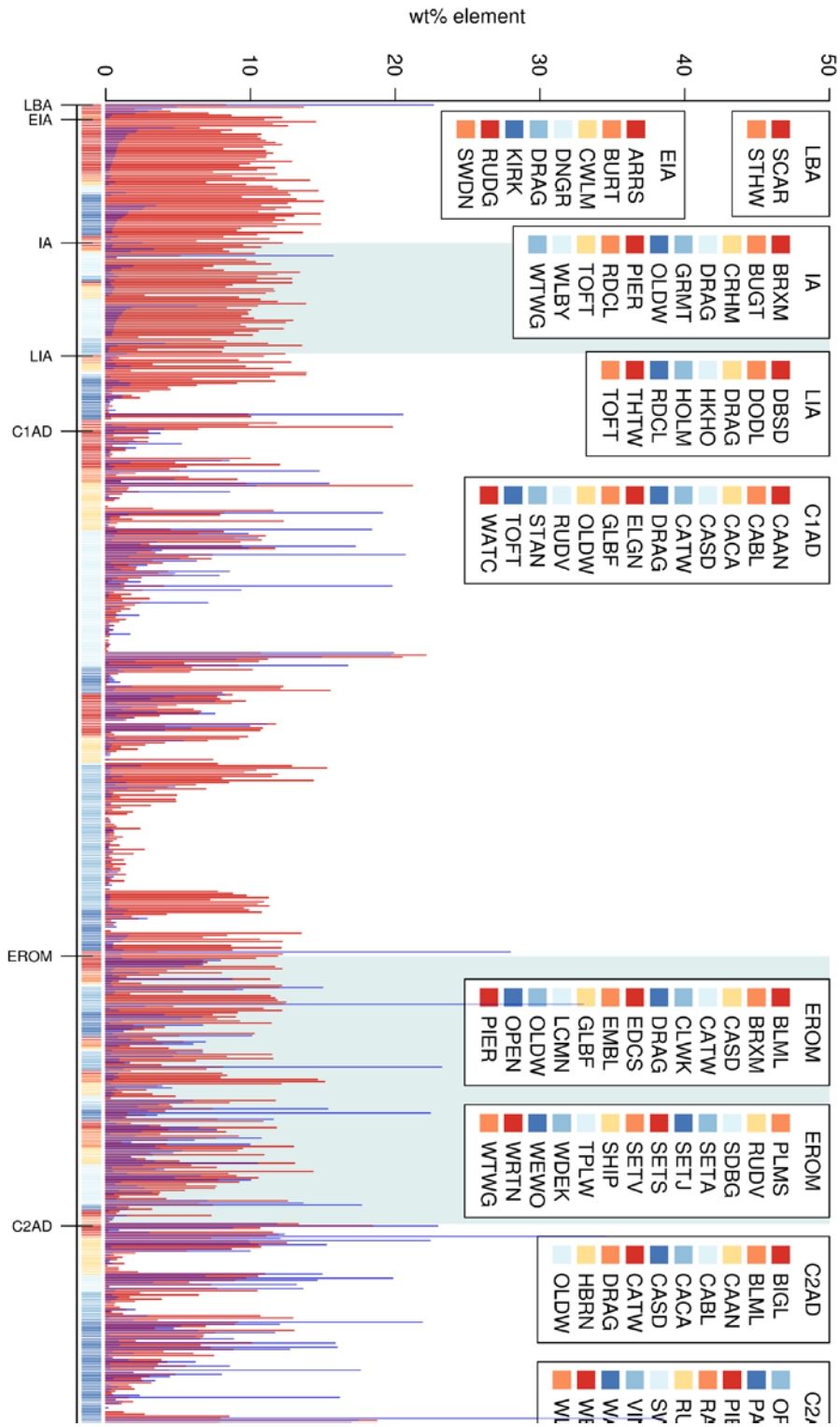
In the Cu-Pb-Zn system, lead has the largest atomic radius of the three elements, the lowest equilibrium constant, and a very high volatility coefficient in a copper melt, but one that is considerably lower than zinc. In the presence of oxygen lead oxide, the most important means of loss of lead in a binary Cu-Pb system, is slow to evaporate and unlikely to form compared to the lower Gibbs free energy of formation ZnO(g) molecules. The slow and unnoticeable evaporation of Pb(g), and rapid loss of Zn and ZnO(g), would therefore result in the apparent perseverance of lead through recycling in this ternary system, and large and noticeable decreases in zinc. Lead has the effect, as mentioned previously, of increasing the activity of zinc in a copper melt, thus resulting in the greater loss of zinc according to Figure 54. The behavior of zinc within the confines of the ternary Cu-Pb-Zn model explains the relatively low zinc in LBR compared to primary brass and the aforementioned “magic limit”. This effect, assuming it is additive, is further reason behind zinc loss according to Figure 62 and the activity of zinc in the Cu-Sn-Zn model. From the model, and data from Figures 74–76, it is shown that in cases where both lead and tin are present, zinc is at its lowest for the Cu-Zn-Sn-Pb system. Tin, according to the thermodynamic data presented, has an atomic radius satisfying the Hume-Rothery rules compared to both copper and zinc. It is not as likely to form oxides as zinc, and has a very low volatility coefficient, and combined, these traits, like those for lead, result in the rapid loss of zinc and perceived survival of tin through recycling. According to the thermodynamics, then, one should expect zinc percentages in objects to be at their lowest in the quaternary system, followed

by tin and then lead. Even though lead has a much higher volatility coefficient than tin, it is reduced by both zinc and tin, both of which form volatile oxides. The suggestions, therefore, by Pollard *et al.* (2015), that decreasing percentages of zinc were caused primarily by mixing, not volatilization as thought by Caley (1964, 99) and Dungworth (1995, 148), and the notion by Fleming (2012) that mixing of different metals types during the Roman period was unusual, are not correct or partial answers. Mixing of different metal types occurred frequently and resulted in quaternary copper alloys. Many of these alloys were the result of repeated mixing of BR and B and are partially responsible for the low-high zinc distributions in LG. They could also have simply been re-melted or mixed with relatively pure ingot metal. Mixing of alloys did contribute to the diminishing percentages seen throughout the dataset in both BR and LG, but what had at least an equal impact was the increased volatility of zinc from the combined repulsive effects of lead and tin (Sugino *et al.*, 1986; Surapunt *et al.*, 1995; 1995). So it seems that both Caley and Pollard *et al.* were correct. Mixing, especially in significant percentages above a few percent, increases the likelihood of molecular and atomic interactions in a molten metal solution, and in this case resulted in increased evaporation of zinc. These interpretations for element loss, according to predictive models from Chapter 7, are relative to the activity from their respective Cu-M binaries, which, lacking rate loss experiments, must be interpreted using the chemical data. This is of course not ideal, but it fulfills the goal of this thesis to provide the loss likelihood of elements relatable to a chemical dataset, which can later be further expanded with kinetics.

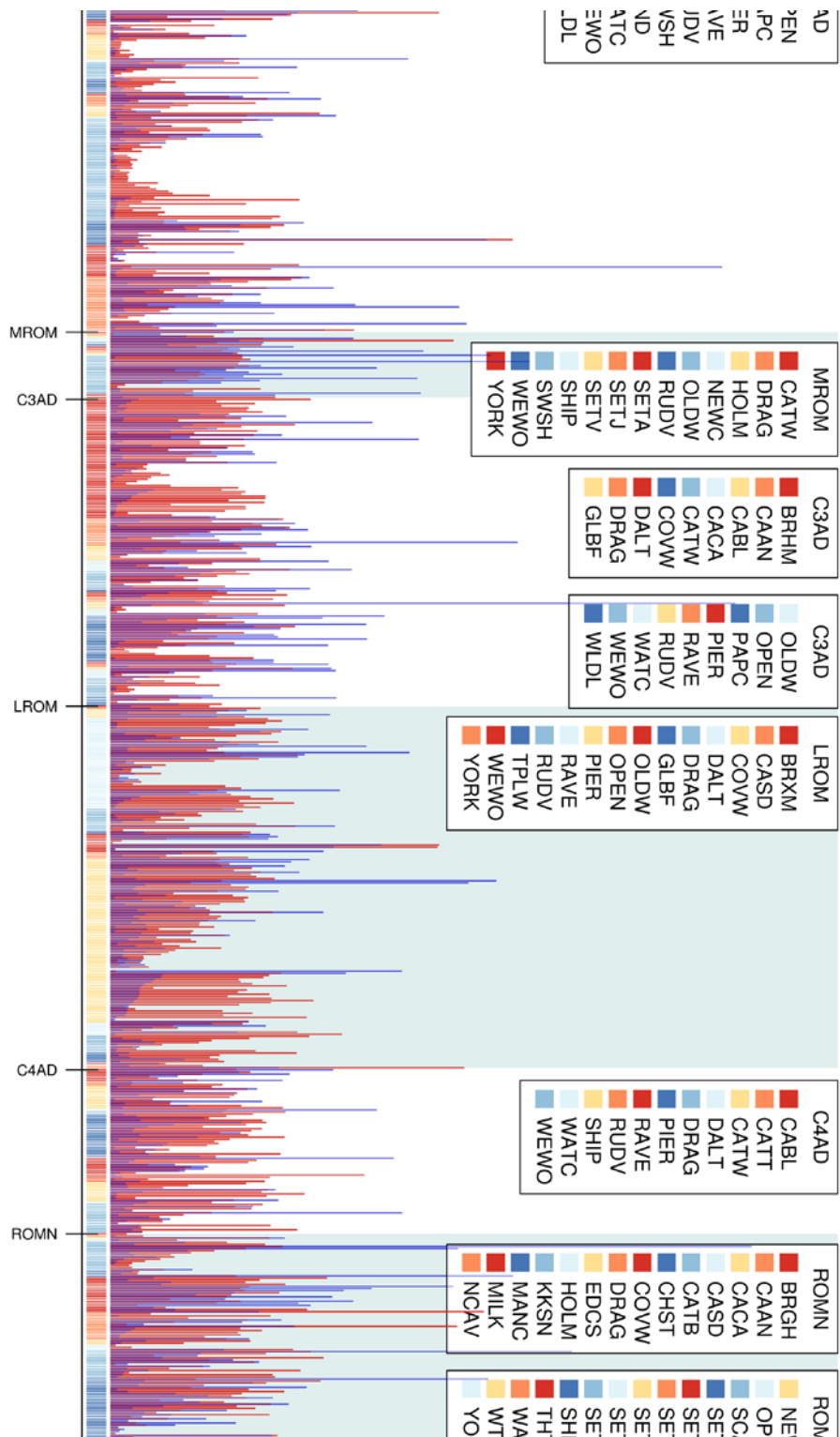
As for the behavior of lead and tin, it is shown that the repulsive behavior of copper and lead seen in the Cu-Pb binary system (Fig. 2) is carried over to the Cu-Sn-Pb ternary (Fig. 66), and is the reason why a predominantly copper melt in any regard repulses lead. The repulsion of lead has little to do with the addition of tin, as Figure 67 illustrates, and does not contribute to the

loss of lead from the system. Rather, it reinforces the conglomeration, and segregation, of lead, and tin during freezing, in the molten copper ternary and quaternary Cu-Zn-Sn-Pb systems. In this ternary system, absent zinc, tin loss would be substantial.

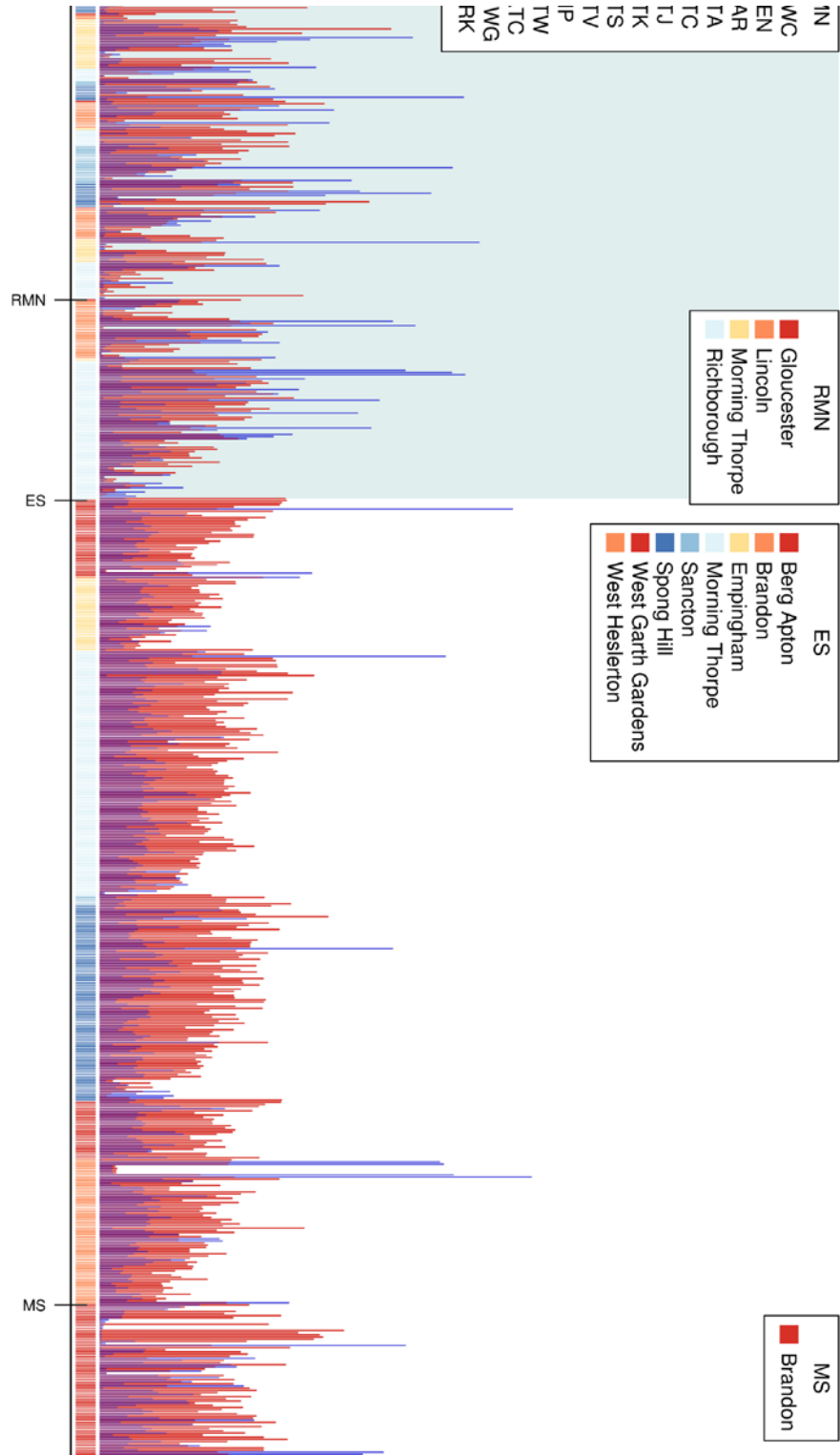
FIGURE 73: LEAD AND TIN PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS



The Dynamics of Lead a



Lead and Tin in Cu-Pb-Sn Artifacts



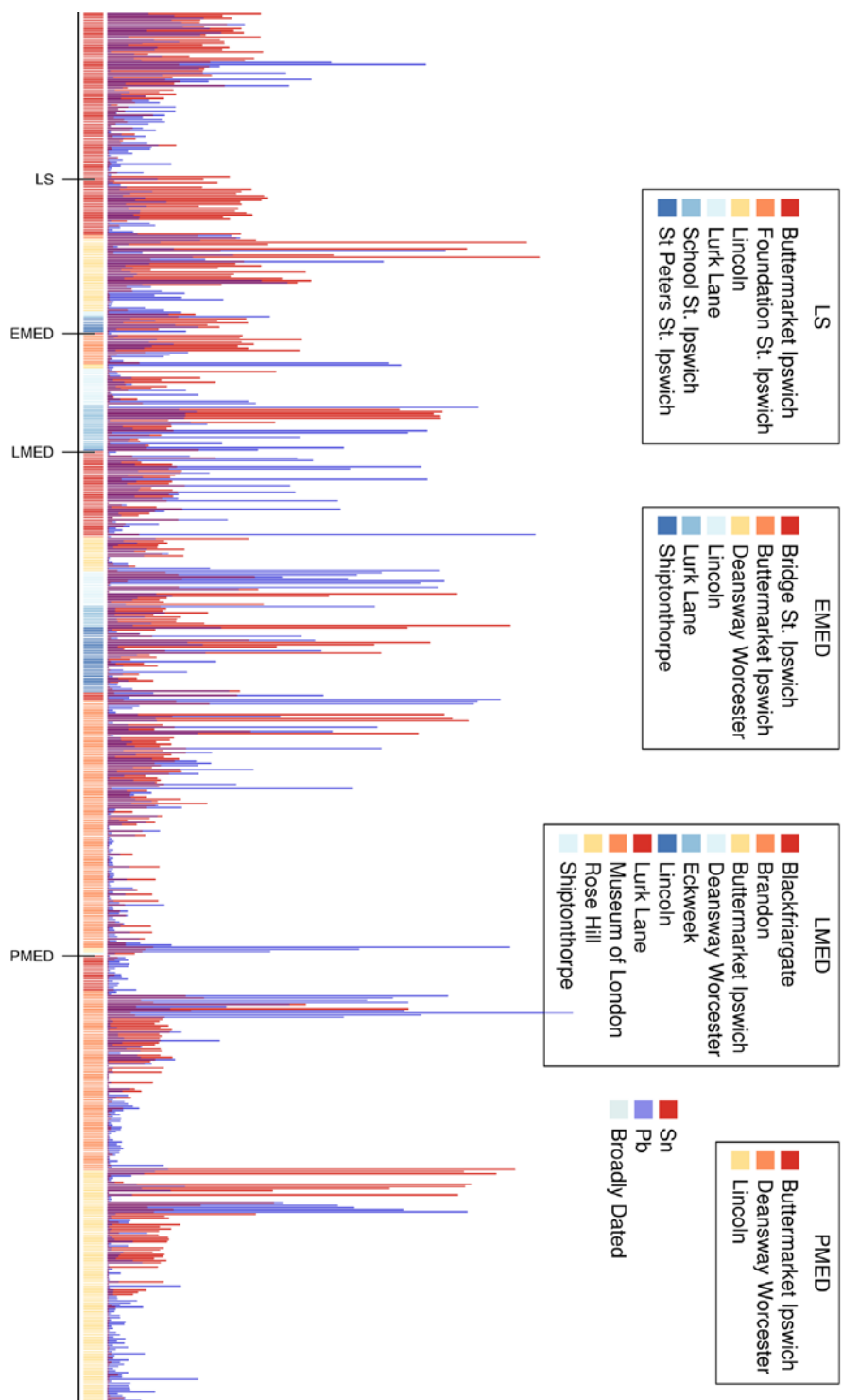
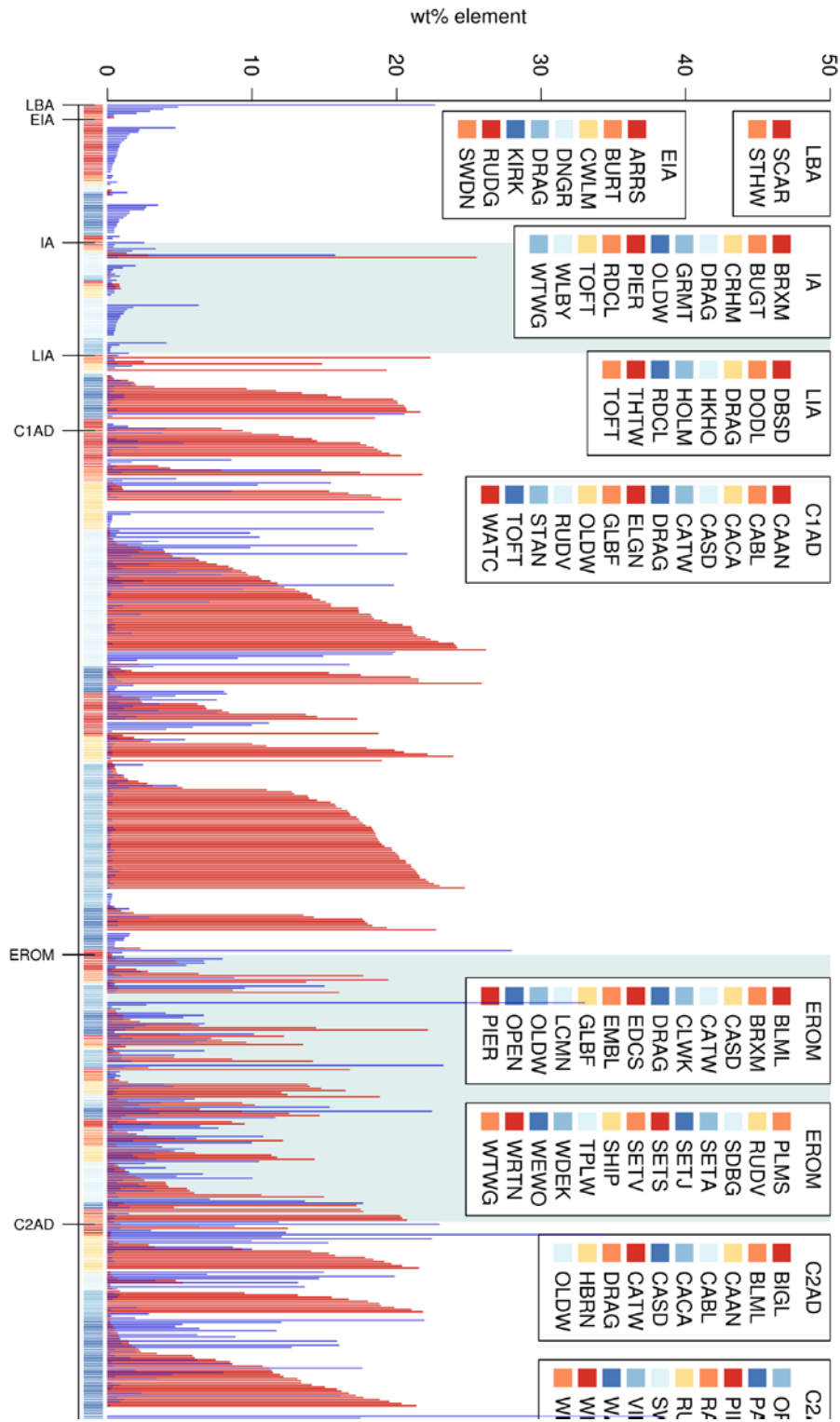
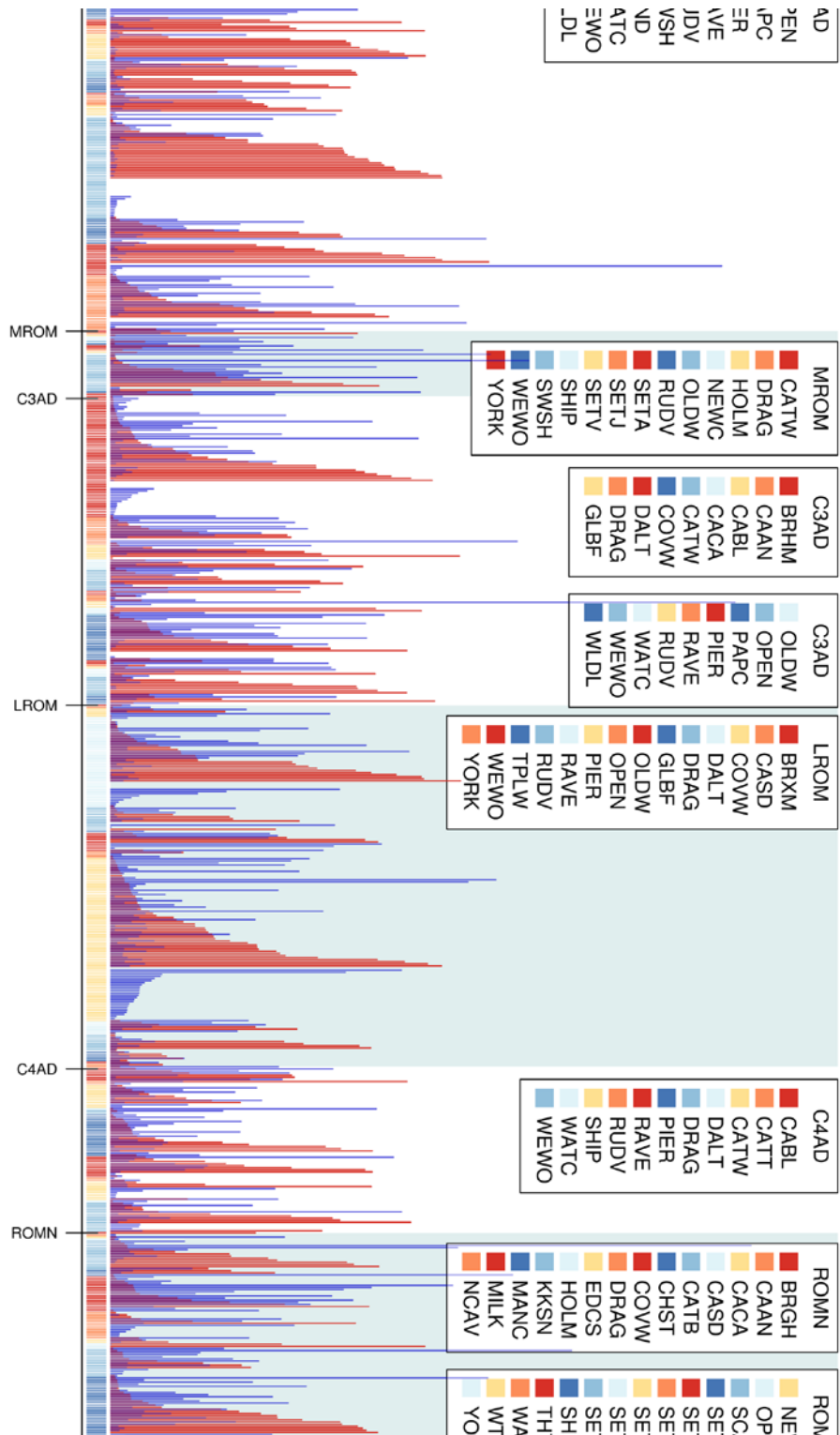


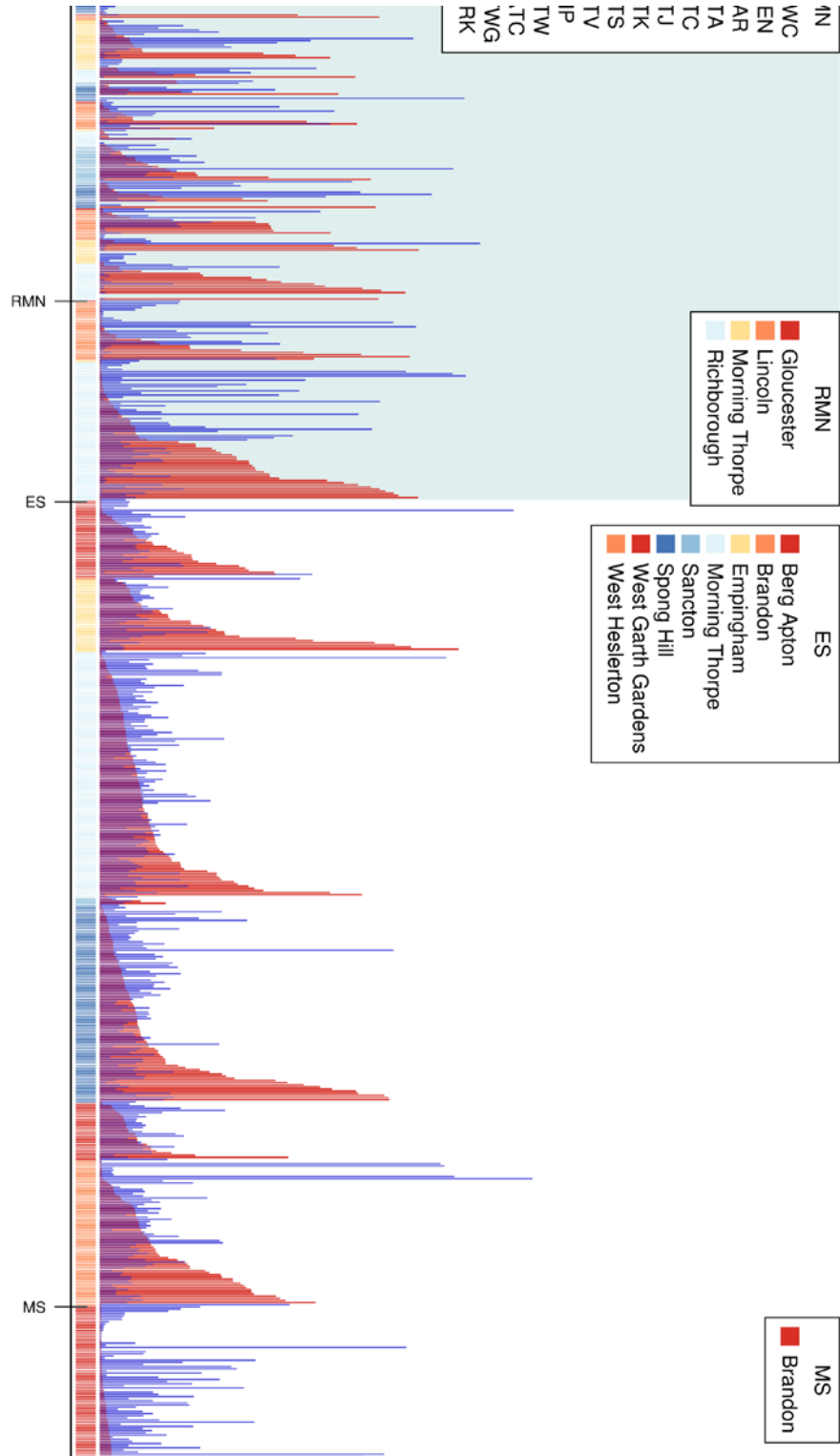
FIGURE 74: ZINC AND LEAD PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS



The Dynamics of Zinc ar



Lead in Cu-Zn-Pb Artifacts



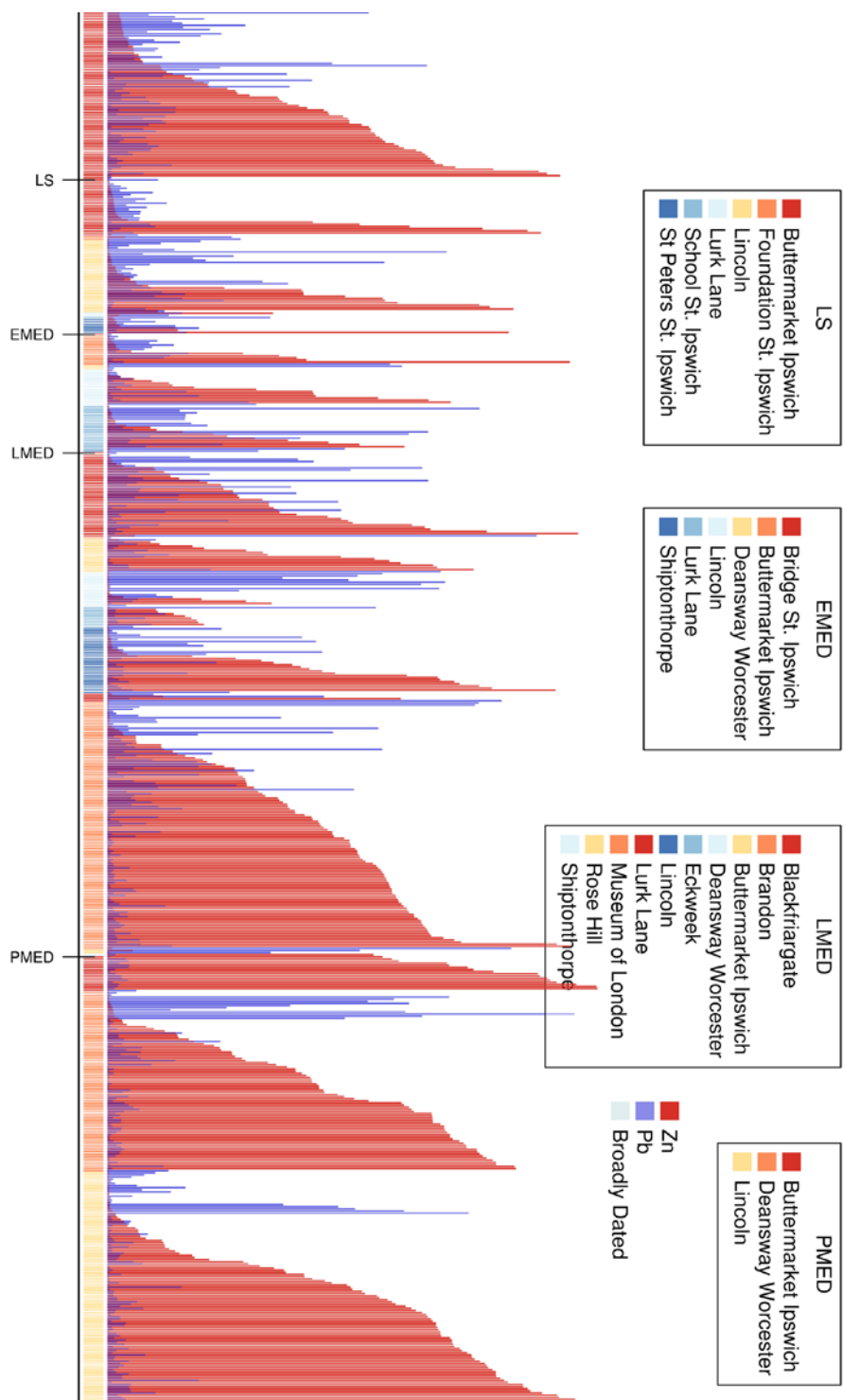
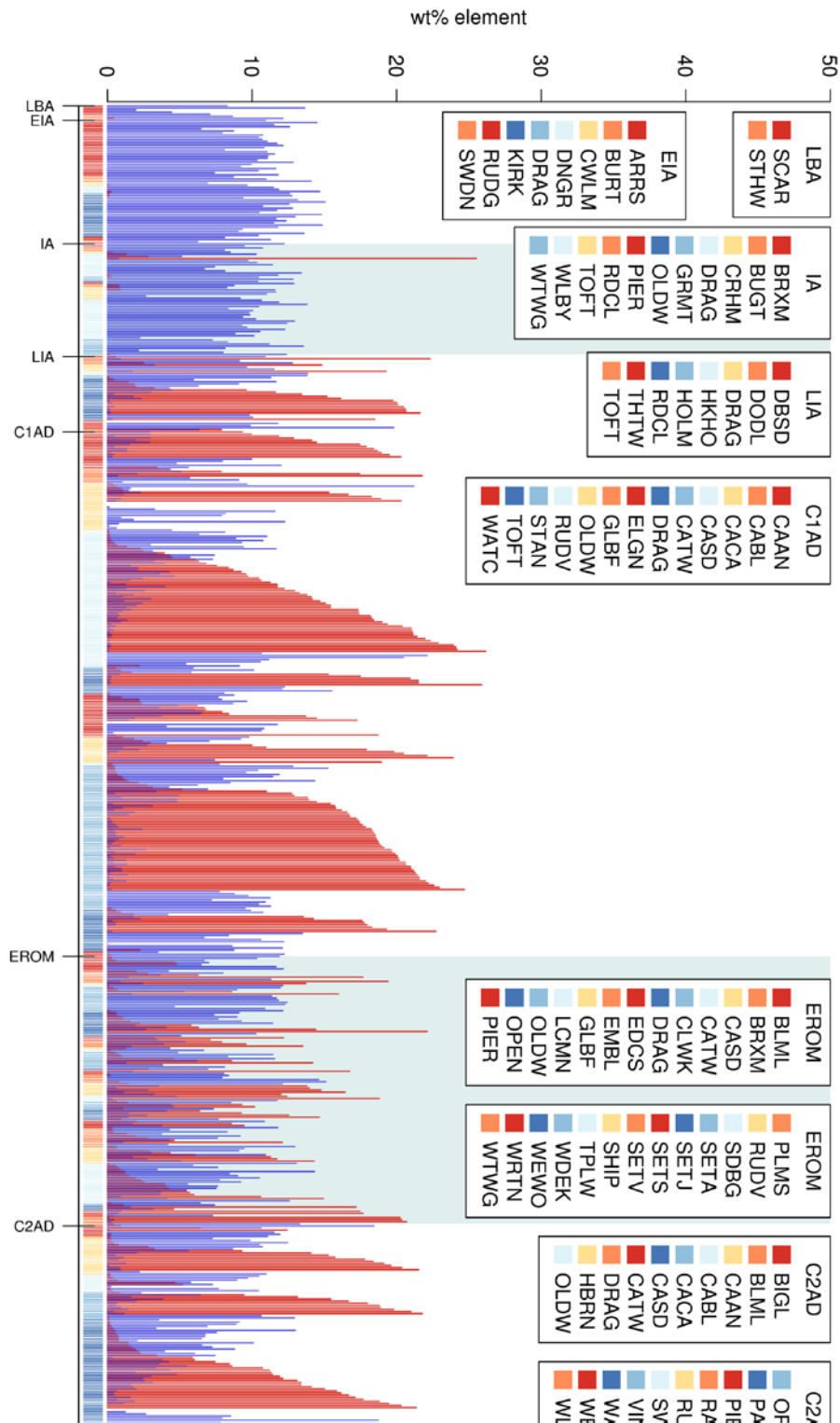
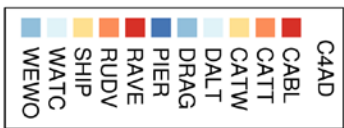


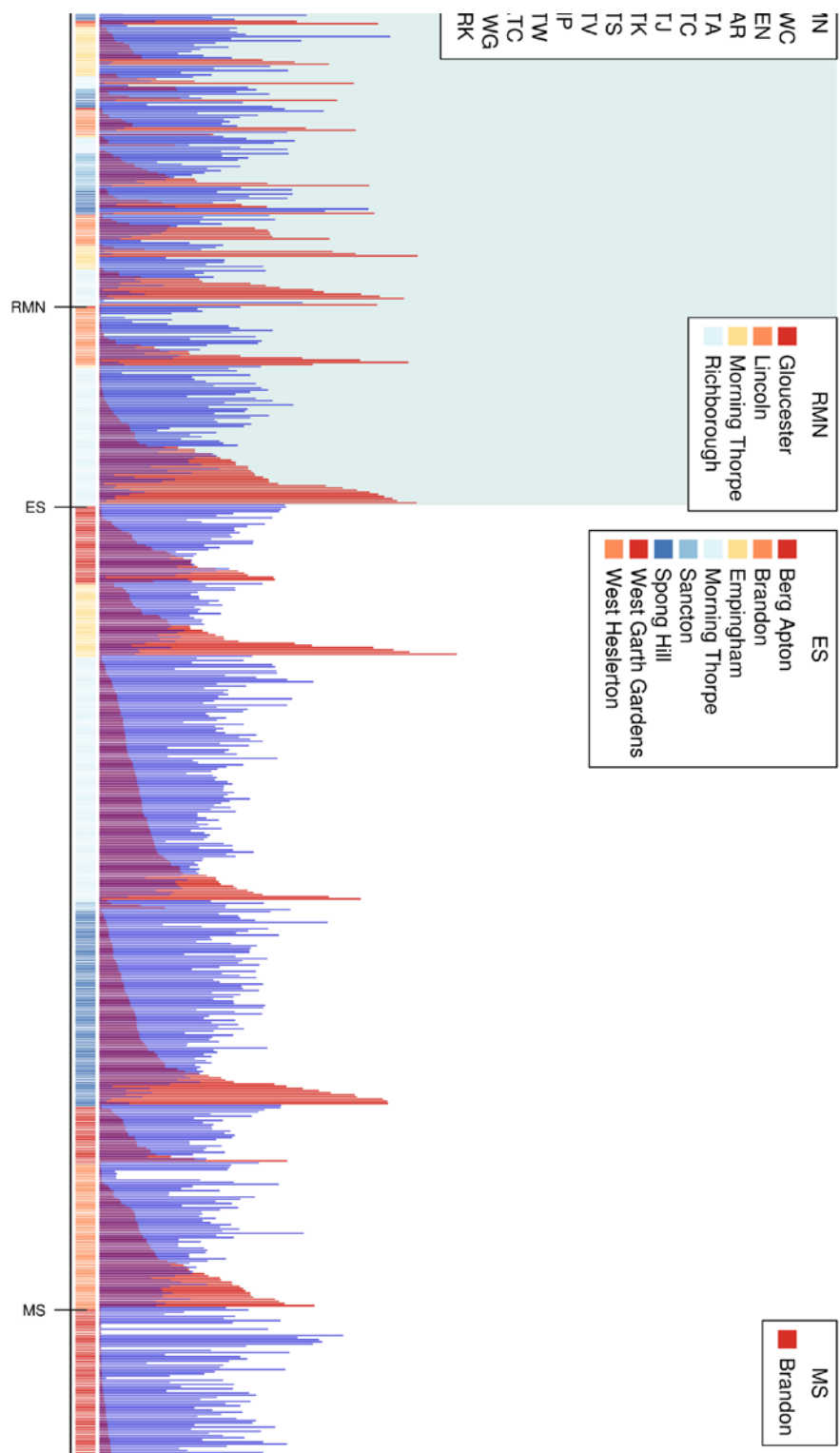
FIGURE 75: ZINC AND TIN PERCENTAGES IN LATE BRONZE AGE TO POST-MEDIEVAL COPPER ALLOYS

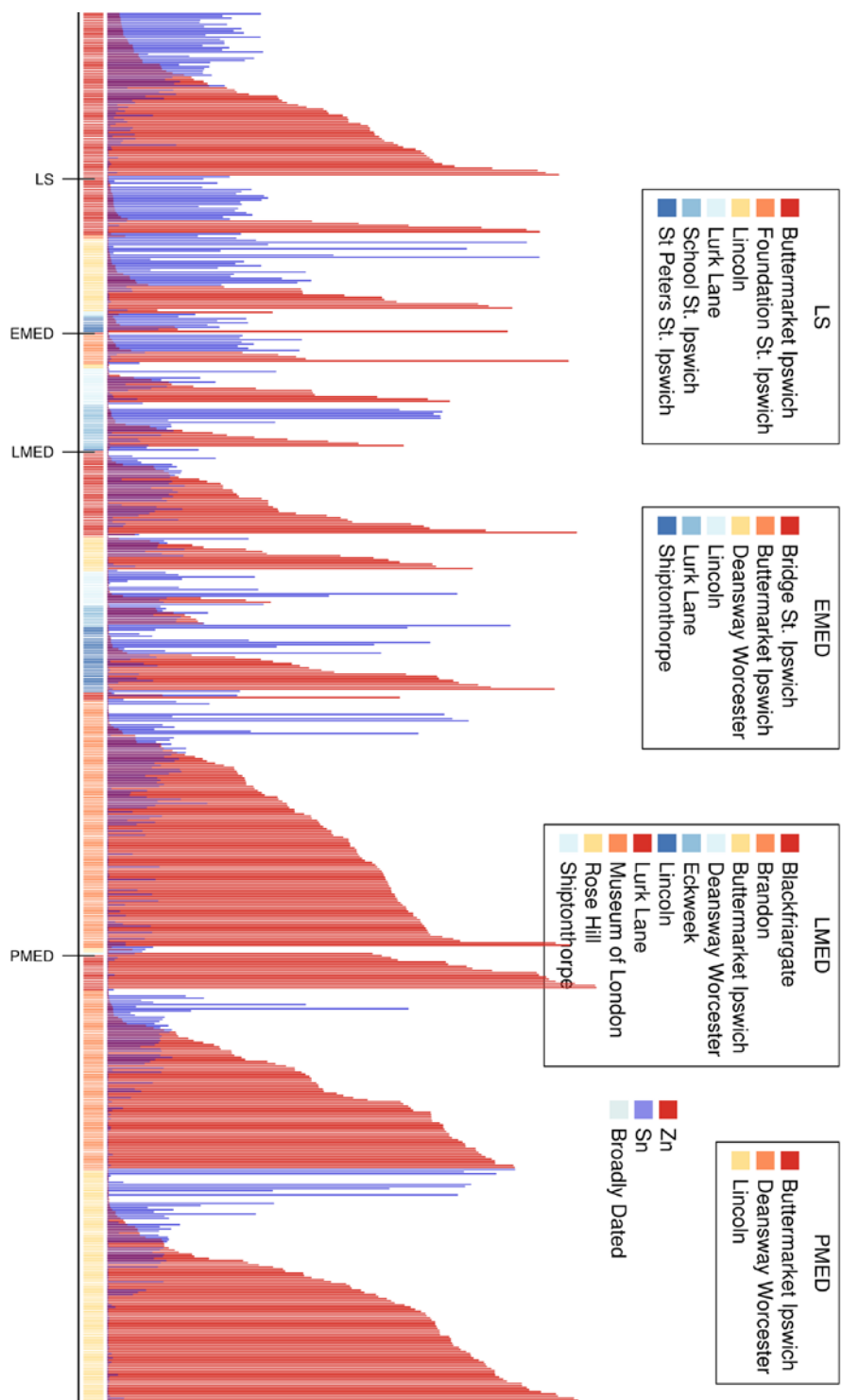


AD
PEN
PC
ER
VE
IDV
VSH
ND
ATC
WO
DL



nd Tin in Cu-Zn-Sn Artifacts





8.2 Summary

First and foremost, this chapter rigorously proves, through the combined thermodynamic theories and calculations described over the course of the entire thesis, that loss modeling of ancient alloys can add a profound understanding of ancient pyrometallurgical processes. Perhaps most importantly, it shows that decisions were made to recycle metals of different composition separately, and that the thermodynamic properties of these alloys were at least understood at a basic level. Discussed and evidenced in this chapter is the interaction of copper, zinc, tin and lead, and how these elements influence one another to promote changes seen in the chemical data reported by Dungworth (1995) and Blades (1995). Working from the bottom-up, the thermodynamic approach to ancient metallurgy, and especially recycling, is shown to be powerful and one that helps explain the metal material archaeological record of copper alloys. As part of a comprehensive study the size of atoms, the volatility of oxides and pure species, the oxidative tendencies of each component, and the interactions of elements in Cu-M binary and Cu-Zn-M ternary systems were considered. This information was used to draw conclusions regarding the compositional changes in artifacts containing zinc, tin, and lead from the Late Bronze Age to post-medieval periods in CE Britain.

9. Conclusions

9.1 Overview

This thesis has outlined key knowledge and methods pertaining to metallurgical thermodynamics as it has been applied to archaeological copper-based material culture to understand the underlying causes of change, and to predict the original and resultant chemical composition, of iterations of ancient recycled, mixed, and reused metal. This knowledge may be cautiously consulted to begin to understand primary and secondary ancient smelting. Modeling of molten metal systems of brass were assessed for the latter, with notable exceptions for sulfur and oxygen as they contribute to elemental losses as either volatile or non-volatile oxides and sulfides, while the former was left for future studies that may include ore roasting, oxidic and sulfidic smelting, and other processes and furnace implementations leading up to the casting of ingots. The modeling of the copper-based metal systems discussed in this thesis were achieved by first understanding states of equilibrium, and the various related thermodynamic properties such as activity, which were used to calculate the behavior of individual elements as they interact with copper and other elements in defined molten systems. The comprehensively described methodologies executed in this thesis to model individual elements may be applied to any ancient metals system as long as assessed thermodynamic data from baseline binary systems is available, since the properties of individual elements cannot be used to predict their behavior in multi-component systems. Only in relation to one another can individual elements be understood in the contexts of impure mixtures. In sum, the calculation of the activity based on temperature, pressure, and composition, with the extrapolation and interpolation of preexisting experimental data, was used to determine the behavior of molten copper-based systems. The preliminary binary system's activity calculations, and related activity coefficients, are imperative since they

provide the numeric behavioral value of each element at a desired temperature and varying compositions, which are carried over into far more complex system's calculations as the diversity of a given system increases with additional components. The equations for activity were also expanded to include vital information about the volatilization of elements as they relate to the molecular weight of copper in a molten system. These additional data are necessary for determining the loss or enrichment likelihood of elements, as well as to determine the rate of element evaporation in future research. Both the loss likelihood and evaporative behaviors of elements were also thoroughly detailed according to the interactions on the atomic scale in ionic melt theory, which, although not yet well understood, provides perhaps the best explanation for molten metal systems in conjunction with basic statistical thermodynamics. Individual element interactions in molten metal systems have not been observed, however, ionic melt theory provides a framework that successfully interprets activity and the resultant composition of alloys after processing. It may in fact be what occurs in practice.

Perhaps the most important part of this thesis begins in Chapter 6 where the mathematics and theory used to calculate binary and higher order systems are detailed. These equations were used to calculate the thermodynamic properties of each element hundreds of thousands of times in custom-built software across their entire compositional range, and the output was rendered as lines of isoactivity that provide easily read trends for copper-based ancient alloys. Many of these diagrams, in particular the ternary, are for alloys and element combinations only important to archaeometallurgists as they model systems that are not produced by modern industry. Some, on the other hand, were modeled in this thesis and confirmed by experimental results and alternative calculations. Ultimately, both archaeologically and modernly relevant systems were applied to understanding the reasons behind the chemical composition of archaeological finds in Britain,

and to decipher the conundrum of metal recycling and flow for copper alloys containing three major elements; lead, tin, and zinc. The methods and models described were introduced, developed, and applied to artifact datasets to showcase the importance and potential offered by thermodynamics to archaeometallurgy. In the end, it is hoped that the efforts of this author have shown that definitive interpretations of copper-based artifact chemical data are indeed possible from first-principles thermodynamics. The approach to ancient metallurgy taken in this thesis must be applied more broadly to ancient metal material culture if scholars hope to truly understand the unknown intricacies of ancient metal extraction, processing, use, and flow.

This thesis is the first of its kind highlighting the possibilities of archaeometallurgical thermodynamics as it applies to civilizations and peoples that practiced pyrometallurgy in antiquity. It is, by most every measure, likely unfamiliar to archaeologists and archaeometallurgists as it employs, for the first time, thermodynamic theories and rigorous methodologies towards the interpretation of ancient metal and metal flow. Almost no publication on the subject exists in archaeological literature, and so almost nowhere is it recognized as an important aspect to understanding ancient metallurgy. This is a curious occurrence since the field of metallurgy has always combined the theoretical and computational aspects with analytical laboratory investigations to produce informed conclusions. Archaeology has predominately utilized only laboratory observations, yet, unbeknownst to archaeologists, the laboratory and analytical and theoretical aspects are in fact inseparable in order to create a complete picture. The findings in this thesis clearly show the need, not only for further research into the thermodynamic of ancient materials and how it can be used to elucidate the past, but for acceptance and assimilation of new ideas that may substantially diverge from the common curriculum. Thermodynamics allows for, and what has been known for quite some time in

modern times, the appropriation of in-depth knowledge that quantifies the complexity of the world. This same quantification provides the starting point for archaeological and historical interpretations of alloys with a nearly unshakable foundation, which must not be ignored or underestimated.

9.2 The Future of Archaeometallurgy

This thesis is an exhaustive outline of the steps taken to explain the loss and enrichment likelihood of elements under ancient furnace conditions, but it cannot wholly describe ancient metallurgy in the scope of this PhD research project. Indeed, this thesis introduces several novel approaches and methods to archaeometallurgy, and it is pioneering in its own right; however, as noted by this thesis' title, it is comparatively but an overview of the potential of the subfield of archaeometallurgical thermodynamics. What is absolutely imperative, and what this author has encountered in discussions with colleagues and established scholars in the field, is for the extension of this work towards understanding roasting, primary and secondary smelting, and of course, the further deciphering of recycling and mixing worldwide in antiquity. Purposely this author has provided the groundwork for such an expansion, which has been periodically suggested throughout this work with mention of, for instance, the expansion of the applied polynomials and the future modeling of systems containing sulfur.

It is the hope of this researcher that future projects will include, firstly, the modeling of sulfur in ancient metallurgical contexts. Understanding the presence of sulfur in copper artifacts, where its removal is assumed to have been a priority achieved by roasting, may be inextricably linked to differences in ancient pyrometallurgical technology, or perhaps a sign of technological transition of processing methods. For sulfur, what does its presence tell us about ancient flash smelting, or direct smelting as it is sometimes called, of sulfidic copper ores? And/or could its

presence be due to yet unexplained and modeled interactions of elements in low sulfur ores that contributed to its transference all the way to finalized artifacts? To answer these questions, and many more, the modeling of ternary systems containing sulfur, as well as quaternary and higher systems such as Cu-Fe-As-S, must be performed. And in the contexts of this thesis, as was mentioned in Chapter 8, systems such as the quaternary Cu-Sn-Pb-Zn that was preliminarily assessed in terms of the divisible copper ternaries within, must be modeled for each component taken together. Only when all components are considered will it be possible to decipher ancient pyrometallurgy.

Secondly, considerably alluded to in this thesis was the question of the rate loss of elements that would have occurred in ancient furnaces. For example, the kinetics of arsenic loss from arsenical copper varies with composition, is partially controlled by the exposed surface area of the melt, and calculable given archaeological attained crucibles and fragmentary furnace remains. Again, purposely, the work done in this thesis provides the groundwork, and more precisely the variables, for making such calculations. Combining the expansion of additional models with the kinetics of elemental change in such systems, as well as continued research of simple systems not discussed here, in future research can dramatically improve both archaeometallurgical and archaeological interpretations of the past.

And third, there is a clear connection between metallurgical thermodynamics and traditional means of metal artifact investigation, which is commonly conducted through metallographic examination. These two approaches, both new and old, are parts of a bigger picture that when used together have far greater potential to elucidate archaeometallurgical questions.

10. References

- Alcock, C. B., Sridhar, R., & Svedberg, R. C. (1969). A mass spectrometric study of the binary liquid alloys, Ag-In and Cu-Sn. *Acta Metallurgica*, 17(7), 839–844.
- Arita, M., Nakamura, M., Goto, K. S., & Ichinose, Y. (1984). Activity and diffusivity measurements of copper in alpha cobalt by equilibration between solid Co and liquid Ag. *Transaction of the Japan Institute of Metals*, 25(10), 703–709.
- Azakami, T., & Hino, M. (1986). Thermodynamic studies on behavior of arsenic in copper smelting. *Metallurgical Review of MMIJ*, 3(3), 72–86.
- Azakami, T., & Yazawa, A. (1968). Activities of zinc and cadmium in liquid copper base alloys. *Nippon Kogyo Kaishi*, 84(968), 1663–1668.
- Azakami, T., & Yazawa, A. (1976). Activity measurements of liquid copper binary alloys. *Canadian Metallurgical Quarterly*, 2, 111–122.
- Baker, E. H. (1970). Vapour pressure and thermodynamic behaviour of liquid zinc-copper alloys at 1150°C. *Transaction of the Institute of Mines and Metallurgy, Sec. C*, 1–5.
- Barker, J. A. (1953). Determination of activity coefficients from total pressure measurements. *Australian Journal of Chemistry*, 6, 207–210.
- Bayley, J. (1984). Roman brass-making in Britain. *Historical Metallurgy*, 18(1), 42–43.
- Bayley, J. (1998). The production of brass in antiquity with particular reference to Roman Britain. In P. T. Craddock (Ed.), *2000 years of zinc and brass. Occasional paper number 50*. (pp. 7–23). London: The British Museum.
- Bayley, J., & Butcher, S. (2005). *Roman brooches in Britain: A technological and typological study based on the Richborough collection*. London: Society of Antiquaries of London.
- Begemann, F., Schmitt-Strecker, S., Pernicka, E., & LoSchiavo, F. (2001). Chemical composition and lead isotopy of copper and bronze from Nuragic Sardinia. *European Journal of Archaeology*, 4, 43–85.
- Blades, N. W. (1995). *Copper alloys from English archaeological sites 400–1600 AD: An analytical study using ICP-AES*. (Unpublished doctoral dissertation). University of London, London.
- Bourgarit, D., & Bauchau, F. (2010). The ancient brass cementation processes revisited by extensive experimental simulation. *Journal of Metals*, 62(3), 27–33.
- Bourgarit, D., & Thomas, N. (2011). From laboratory to field experiments: Shared experience in brass cementation. *Historical Metallurgy*, 45, 8–16.

- Bray, P. J., & Pollard, A. M. (2012). A new interpretative approach to the chemistry of copper-alloy objects: Source, recycling and technology. *Antiquity*, 86(333), 853–867.
- Budurov, S., & Wassilew, G. (1977). The thermodynamics of β - and γ -intermetallic compounds of nickel-zinc and cobalt-zinc systems. *Zeitschrift für Metallkunde*, 68(12), 795–798.
- Caley, E. R. (1964). *Orichalcum and related ancient alloys: Origin, composition and manufacture with special reference to the coinage of the Roman Empire*. New York: The American Numismatic Society.
- Cameron, H. K. (1974). Technical aspects of medieval monumental brasses. *Archaeological Journal*, 131, 215-236.
- Caple, C. (1986). *An analytical appraisal of copper alloy pin production: 400–1600 AD*. (Unpublished doctoral dissertation). University of Bradford, Bradford.
- Charles, J. A. (1967). Early arsenical bronzes-A metallurgical view. *American Journal of Archaeology*, 71(1), 21–26.
- Chaubal, P. C., & Nagamori, M. (1983). Volatilization of arsenic and antimony in copper matte converting. *Metallurgical and Materials Transactions B*, 14B(2), 303–306.
- Chaubal, P. C., & Nagamori, M. (1988). Thermodynamics for arsenic and antimony in copper matte converting—computer simulation. *Metallurgical and Materials Transactions B*, 19B(4), 547–556.
- Chen, C., Zhang, L., & Johanshahi, S. (2010). Thermodynamic modeling of arsenic in copper smelting processes. *Metallurgical and Materials Transactions B*, 41B(6), 1175–1185.
- Choudary, U. V., Lee, Y. E., & Chang, Y. A. (1977). A thermodynamic analysis of the copper-lead-sulfur system at 1473 K. *Metallurgical and Materials Transactions B*, 8B(4), 541–546.
- Coursol, P., & Stubina, N. (2005). Arsenic and lead volatilization from molten copper at high oxygen levels. *Metallurgical and Materials Transactions B*, 36B(3), 411–413.
- Craddock, P. T. (1975). *The composition of copper alloys in the classical world* (Unpublished doctoral dissertation). University of London, London.
- Craddock, P. T. (1976). The composition of the copper alloys used by the Greek, Etruscan and Roman civilizations 1. The Greeks before the archaic period. *Journal of Archaeological Science*, 3(2), 93–113.
- Craddock, P. T. (1977). The composition of the copper alloys used by the Greek, Etruscan and Roman civilisations: 2. the archaic, classical and Hellenistic Greeks. *Journal of Archaeological Science*, 4(2), 103–123.

- Craddock, P. T. (1978). The composition of the copper alloys used by the Greek, Etruscan and Roman civilisations 3: The origins of early and early use of brass. *Journal of Archaeological Science*, 5(1), 1–16.
- Craddock, P. T. (1980). The composition of Iberian bronze age metalwork in the British museum. In W. A. Oddy (Ed.), *Aspects of early metallurgy. Occasional paper number 17* (pp. 51–62). London: The British Museum.
- Craddock, P. T. (1981). The report on the composition of metal tools and weapons from Ayia Paraskevi, Vounous and Evreti, Cyprus. In Birmingham Museums and Art Gallery, *A catalogue of Cypriot antiquities in Birmingham museum and art gallery* (pp. 77–8). Birmingham.
- Craddock, P. T. (1986). Report on the composition of bronzes excavated from a middle Cypriot site at Episkopi Phaneromeni and some comparative Cypriot bronze age metalwork. In Swiny, S., Craddock, P. T., & Tylecote, R. F. (Eds.), *The Kent State University expedition to Episkopi Phaneromeni* (pp. 153–8). Nicosia: P. Åströms Förlag.
- Craddock, P. T. (1994). *Early metal mining and production*. Edinburgh: Edinburgh University Press.
- Craddock, P. (2009). *Scientific investigation of copies, fakes and forgeries*. Oxfordshire: Taylor & Francis.
- Craddock, P. T., & Meeks, N. D. (1987). Iron in ancient copper. *Archaeometry*, 29(2), 187–204.
- Dungworth, D. B. (1995). *Iron Age and Roman copper alloys from northern Britain* (Doctoral dissertation). Durham University, Durham. Available at Durham E-Theses Online (Number 1024).
- Dungworth, D. (1997). Iron Age and Roman copper alloys from northern Britain. *Internet Archaeology* (2).
- Dungworth, D. (1997). Roman copper alloys: Analysis of artefacts from northern Britain. *Journal of Archaeological Science*, 24(10), 901–910.
- Eaton, E. R., & McKerrell, H. (1976). Near eastern alloying and some textual evidence for the early use of arsenical copper. *World Archaeology*, 8(2, Climatic Change), 169–191.
- Edwards, R. K., & Downing, J. H. (1956). The thermodynamics of the liquid solutions in the triad Cu-Ag-Au. I. the Cu-Ag system. *Journal of Physical Chemistry*, 60, 108–11.
- Fleming, R. (2012). Recycling in Britain after the fall of Rome's metal economy. *Past & Present*, 217(1), 3–45.

- Fujita, Y., Pagador, R. U., Hino, M., & Azakami, T. (1997). Thermodynamic investigation on molten Cu-Ni-Fe alloys by the double Knudsen cell-mass spectrometer system. *Nippon Kinzoku Gakkaishi*, (7), 619–624.
- Gerling, U., & Predel, B. (1980). On the thermodynamic properties of liquid gold-zinc-Alloys. *Zeitschrift für Metallkunde*, 71(2), 79–84.
- Gokcen, N. A. (1960). Application of Gibbs and Gibbs-duhem equation to ternary and multicomponent systems. *The Journal of Physical Chemistry*, 64(4), 401–406.
- Gokcen, N. A. (1986). *Statistical thermodynamics of alloys*. New York and London: Plenum Press.
- Haedecke, K. (1973). Gleichgewichtsverhältnisse bei der Messingherstellung nach dem Galmeiverfahren. *Erzmetall*, 26, 229–233.
- Halleux, R. (1973). L'orichalque et le laiton. *L'Antiquité Classique*, 42, 64–81.
- Harris, R. (1984). Vacuum refining copper melts to remove bismuth, arsenic and antimony. *Metallurgical Transactions B*, 15B(2), 251–257.
- Hauptmann, A. (2007). *The archaeometallurgy of copper: Evidence from Faynan, Jordan*. Berlin and Heidelberg: Springer-Verlag.
- Hino, M. (1985). Activities in molten Cu-As, Cu-S-As and Fe-S-As alloys; thermodynamic studies of molten arsenic alloys (3rd Report). *Journal of the Mining and Metallurgical Institute of Japan*, 101(1171), 543–548.
- Hino, M. (1995). Activities of arsenic and antimony in metal and matte phases of the copper and nickel smelting. *Tohoku Daigaku Sozai Kogaku Kenkyusho Iho*, 51(1), 84–98.
- Hino, M., & Azakami, T. (1980). Activities of molten iron-arsenic and nickel-arsenic binary alloys; thermodynamic studies of molten arsenic alloys (1st report). *Journal of the Mining and Metallurgical Institute of Japan*, 96(1110), 553–558.
- Hino, M., & Azakami, T. (1981). Activities of molten copper-arsenic, silver-arsenic, gold-arsenic and iron-copper-arsenic alloys. *Nippon Kogyo Kaishi*, 97(1126), 1269–1273.
- Hino, M., & Azakami, T. (1996). Arsenic activities in the Cu-X-As (X: Ni, Co) ternary systems. *Canadian Metallurgical Quarterly*, 35(5), 427–433.
- Hino, M., & Toguri, J. M. (1986). Arsenic activities in molten copper and copper sulfide melts. *Metallurgical Transactions B: Metallurgy and Materials Transactions B*, 17B(4), 755–761.
- Hook, D. R., & Craddock, P. T. (1996). The scientific analysis of the copper-alloy lamps aspects of classical alloying practices. In D. Bailey (Ed.), *Catalogue of the lamps in the British*

- museum. Volume IV. Lamps of metal and the lampstands* (pp. 144–163). London: British Museum Press.
- Hultgren, R. R., Desai, P. D., Hawkins, D. J., Gleiser, M., & Kelley, K. K. (1973). *Selected values of the thermodynamic properties of binary alloys*. Metals Park, OH: American Society for Metals.
- Itagaki, K., Mendoza, D. G., Voisin, L., & Hino, M. (2005). Activity of arsenic in liquid Cu-Fe base alloys. *Monatshefte für Chemie / Chemical Monthly*, 136(11), 1847–1852.
- Itagaki, K., Seino, T., & Yazawa, A. (1979). Thermodynamic activity of arsenic in the liquid copper-iron-sulfur mattes. *Tohoku Daigaku Senko Seiren Kenkyusho Iho*, 35(1), 1–10.
- Itagaki, K., Voisin, L., & Mendoza, D. (2006). Phase relations and activities in the Cu-Fe-S-X and Cu-Fe-S-C-X (X = As or Sb) systems and distribution of precious metals relating to reduction smelting of copper. In F. Kongoli, & R. G. Reddy (Eds.), *Advanced processing of metals and materials (Sohn International Symposium), Volume 1, Thermo and physicochemical principles: Nonferrous high temperature processing* (pp. 289–300). Minerals, Metals & Materials Society.
- Itagaki, K., & Yazawa, A. (1983). Thermodynamic evaluation of distribution behavior of arsenic, antimony and bismuth in copper smelting. In H. Y. Sohn, D. B. George & A. D. Zunkel (Eds.), *Advances in sulfite smelting, Basic principles, Volume 1* (pp. 119–142). Warrendale, PA: Minerals, Metals & Materials Society.
- Itoh, S., & Azakami, T. (1984). Activity measurements of bismuth and antimony in liquid copper-base binary alloys by the Knudsen effusion method with electrobalance. *Nippon Kinzoku Gakkaishi*, 48(4), 405–413.
- Itoh, S., Hino, M., & Azakami, T. (1982). Activity measurements of liquid M-arsenic (M = tin, indium, antimony) alloys by the electromotive force method. *Nippon Kinzoku Gakkaishi*, 46(2), 162–169.
- Jantzen, T., & Spencer, P. J. (1998). Thermodynamic assessments of the Cu-Pb-Zn and Cu-Sn-Zn systems. *Calphad*, 22(3), 417–434.
- Jeffers, J. H., Aldhous, A. P., & Katyal, A. (1984). *Strathclyde Conference*, 45–57.
- Jiang, M., Wang, C. P., Liu, X. J., Ohnuma, I., Kainuma, R., Vassilev, G. P., & Ishida, K. (2005). Thermodynamic calculation of phase equilibria in the Cu-Ni-Zn system. *Journal of Physics and Chemistry of Solids*, 66, 246–250.
- Jones, D. G., & Philipp, D. H. (1979). Arsenic activity in copper at 1100°C. *Transactions of the Institute of Mining and Metallurgy*, 88, C7–C10.

- Kameda, K. (1987). Activities of liquid gold-zinc and silver-zinc binary alloys by E.M.F. measurements using zirconia. *Transaction of the Japan Institute of Metals*, 28(1), 41–47.
- Kang, S. Y., Oh, C. S., & Lee, D. N. (1991). A thermodynamic study on the liquid phase and copper-rich solid solution of the copper-antimony-tin system. *Taehan Kumsok Hakhoechi*, 29(3), 270–9.
- Katayama, I., Sommer, F., Hattori, Y., & Lida, T. (1997). Activity measurement of liquid Zn-Bi alloys by EMF method. *Journal de Chimie Physique et de Physico-Chimie Biologique*, 94, 1094–1100.
- Kim, H. G., & Sohn, H. Y. (1998). Minor-element behavior in copper smelting and converting with the use of tonnage oxygen. *Transactions of the Institution of Mining and Metallurgy, Section C: Mineral Processing and Extractive Metallurgy*, 107(2), 43–59.
- Koryakova, L., & Epimakhov, A. V. (2007). *The Urals and Western Siberia in the Bronze and Iron Ages*. Cambridge: Cambridge University Press.
- Kozuka, K., Nakai, Y., & Moriyama, J. (1965). Thermodynamic study of liquid Zn-Pb alloys. *Transactions of the Japan Institute of Metals*, 6(2), 92–96.
- Krapp, H., & Mann, R. (1992). Thermodynamische Betrachtungen zum frühesten Auftreten der Metalle. *Radex-Rundschau*, 1, 58–70.
- Kubista, J., & Vrest'al, J. (2000). Thermodynamics of the liquid co-Cu system and calculation of phase diagram. *Journal of Phase Equilibria*, 21(2), 125–129.
- Kulkarni, A. D., & Johnson, R. E. (1973). Thermodynamic studies of liquid copper alloys by electromotive force method: Part II. The Cu-Ni-O and Cu-Ni systems. *Metallurgical Transactions B*, 4B(7), 1723–1727.
- Kyllo, A., & Richards, G. (1998). Kinetic modeling of minor element behavior in copper converting. *Metallurgical Transactions B: Metallurgy and Materials Processing Science*, 29B(1), 261–268.
- Larouche, P. (2001). *Minor elements in copper smelting and electrorefining*. (Master's thesis). McGill University. Montreal.
- Lechtman, H. (1996). Arsenic bronze: Dirty copper or chosen alloy? A view from the Americas. *Journal of Field Archaeology*, 23(4), 477–514.
- Li, M., Du, Z., Guo, C., & Li, C. (2009). Thermodynamic optimization of the Cu-Sn and Cu-Nb-Sn systems. *Journal of Alloys and Compounds*, 477(1), 104–117.
- Li, R., & Harris, R. (1991). Vacuum refining metallurgical melts. In Minerals, Metals and Materials Society, *EPD Congress. 91: Proceedings of a Symposium Sponsored by the*

Extraction and Processing Division. Held at the TMS Annual Meeting (pp. 387–404). New Orleans, LA.

- Lu, H. M., & Jiang, Q. (2005). Surface tension and its temperature coefficient for liquid metals. *Journal of Physical Chemistry B*, 109, 15463–15468.
- Lu, X., Nakajima, K., Sakanakura, H., Matsubae, K., Bai, H., & Nagasaka, T. (2012). Thermodynamic estimation of minor element distribution between immiscible liquids in Fe–Cu-based metal phase generated in melting treatment of municipal solid wastes. *Waste Management*, 32(6), 1148–1155.
- Lutz, J., Pernicka, E. (1996). Energy dispersive x-ray fluorescence analysis of ancient copper alloys: Empirical values for precision and accuracy. *Archaeometry*, 38(2), 313–323.
- Lynch, D. C. (1980). Activity of arsenic in copper. *Metallurgical and Materials Transactions B*, 11B(4), 623–629.
- Lynch, D. C. (2009). Activity of Sb in Cu-Ni mattes. *Canadian Metallurgical Quarterly*, 48(4), 347–354.
- Lynch, D. C., & Zhong, X. (1997). Henrian values of the activity coefficient of As, Bi, Pb, and Sb in Ni-Cu mattes. In Canadian Institute of Mining, Metallurgy and Petroleum, *Proceedings of the Nickel Cobalt International Symposium* (pp. 313–321). Montreal.
- Lyubomirova, V., Djingova, R., Kuleff, I. (2014). Comparison of analytical techniques for analysis of archaeological bronze. *Archaeometry*, 1-10.
- Manasijevic, D., Minic, D., Živkovic, D., Vrešt'ál, J., Aljilji, A., Talijan, N., Todorovic, R. (2009). Experimental investigation and thermodynamic calculation of the Cu-In-Sb phase diagram. *Calphad: Computer Coupling of Phase Diagrams and Thermochemistry*, 33(1), 221–226.
- Mckerrell, H. and Tylecote, R.F. (1972). The working of copper-arsenic alloys in the early bronze age and the effect on the determination of provenance. *Proceedings of the Prehistoric Society*, 38, 209–218.
- Mendoza, D. G., Hino, M., & Itagaki, K. (2001). Phase relations and activity of arsenic in Cu-Fe-S-As system at 1473 K. *Materials Transactions*, 42(11), 2427–2433.
- Mendoza, D. G., Hino, M., & Itagaki, K. (2002). Phase relations and activities in the Cu-Fe-S-As and Cu-Fe-S-Sb systems at 1473K. *Sulfide Smelting 2002, Proc.Symp.*, 511–522.
- Merkel, J. F. (1983). Summary of experimental results for late Bronze Age copper smelting and refining. *The Journal of the Museum Applied Science Center for Archaeology*, 2(6), 173–178.

- Merkel, J. F. (1990). Experimental reconstruction of Bronze Age copper smelting based on archaeological evidence from Timna. In B. Rothenberg (Ed.), *The ancient metallurgy of copper: Archaeology, experiment, theory* (pp. 78–122). London: University College London Institute for Archaeo-Metallurgical Studies.
- Mey, S. A. (1992). Thermodynamic re-evaluation of the Cu-Ni system. *Calphad*, 16(3), 255–260.
- Miettinen, J. (2002). Thermodynamic description of the Cu-Al-Zn and Cu-Sn-Zn systems in the copper-rich corner. *Calphad*, 26(1), 119–139.
- Mikula, A., & Komarek, K. L. (1990). The Gibbs free energy in the liquid As-Cd-Zn and As-Zn system. *Zeitschrift für Metallkunde*, 81(3), 209–213.
- Nagamori, M., & Chaubal, P. C. (1982). Thermodynamics of copper matte converting: Part III. Steady-state volatilization of Au, Ag, Pb, Zn, Ni, Se, Te, Bi, Sb, and as from slag, matte, and metallic copper. *Metallurgical and Materials Transactions B*, 13B(3), 319–329.
- Newbury, B. D., Nortis, M. R., & Newbury, D. E. (2005). Revisiting the zinc composition limit of cementation brass. *Historical Metallurgy*, 39(2), 75–81.
- Northover, P. (1988). Alloy design in the Bronze Age. In J. E. Jones (Ed.), *Aspects of ancient mining and metallurgy* (pp. 44–54). Bangor: University College of North Wales.
- O’Connell, J. P., & Haile, J. M. (2005). *Thermodynamics: Fundamentals for applications*. Cambridge: Cambridge University Press.
- Oddy, W. A. (2004). Unmasking forged antiquities: How scientific techniques are used to expose fakes in museum collections. In M. Martini, M. Milazzo & M. Piacentini (Eds.), *Proceedings of the International School of Physics “Enrico Fermi”, Volume 154: Physics methods in archaeometry* (pp. 281–297). Amsterdam: IOS Press.
- Ohno, R. (1976). Rates of evaporation of silver, lead, and bismuth from copper alloys in vacuum induction melting. *Metallurgical Transactions B*, 7(4), 647–653.
- Oishi, T., Ono, K., & Moriyama, J. (1981). Thermodynamic study of liquid copper-cobalt alloys. *Nippon Kinzoku Gakkaishi*, 45(11), 1126–1129.
- Oishi, T., Tagawa, S., & Tanegashima, S. (2003). Activity measurements of copper in solid copper-nickel alloys using copper-beta-alumina. *Materials Transactions*, 44(6), 1120–1123.
- Olette, M. (1961). Vacuum distillation of minor elements from liquid ferrous alloys. In G. R. St. Pierre (Ed.), *Physical chemistry of process metallurgy, Part 2* (pp. 1065–1087). New York: Interscience.

- Ono, K., Nishi, S., & Oishi, T. (1984). A thermodynamic study of the liquid Cu-Sn and Cu-Cr alloys by the Knudsen cell-mass filter combination. *Transaction of the Japan Institute of Metals*, 25(11), 810–814.
- Ottaway, B. S., & Roberts, B. W. (2008). The emergence of metallurgy. In A. Jones (Ed.), *Prehistoric Europe: Theory and practice* (pp. 193–225). London: Blackwell.
- Padilla, R., Fan, Y., Sanchez, M., & Wilkomirsky, I. (1997). Arsenic volatilization from enargite concentrate. In B. Mishra, (Ed.), *EPD congress 1997: Proceedings of sessions and symposia sponsored by the Extraction and Processing Division, Held at the TMS Annual Meeting* (pp. 3–83). Warrendale, PA: Minerals, Metals & Materials Society.
- Pagador, R. U., & Hino, M. (1996). Arsenic and antimony activities in copper, nickel and their mattes. *Metallurgical Review of MMIJ*, 13(1), 166–185.
- Park, Y. & Gaskell, D. R. (1989). The thermodynamic activities of copper and iron in the system copper-iron-platinum at 1300 °C. *Metallurgical and Materials Transactions B*, 20(2), 127–135.
- Pei, B. (1993). Assessment of arsenic activity in molten copper. *Scandinavian Journal of Metallurgy*, 22, 24–29.
- Pernicka, E. (1986). Provenance determination of metal artifacts: Methodological considerations. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 14(1), 24–29.
- Pernicka, E. (1987). Erzlagerstätten in der Ägäis und ihre Ausbeutung im Altertum: Geochemische Untersuchungen zur Herkunftsbestimmung archäologischer Metallobjekte. *Jahrbuch des Römisch-Germanischen Zentralmuseums*, 34, 607–714.
- Pernicka, E. (1999). Trace element fingerprinting of ancient copper: A guide to technology or provenance. In S.M.M. Young et al. (Eds.), *Metals in antiquity. British Archaeological Reports International Series*, 792 (pp. 163–171). Oxford: Archaeopress.
- Pernicka, E. (2004). Archaeometallurgy: Examples of the application of scientific methods to the provenance of archaeological metal objects. In M. Martini, M. Milazzo & M. Piacentini (Eds.), *Physics methods in archaeometry* (pp. 309–329). Oxford: IOS Press.
- Pickles, C. (1998). Selective oxidation of copper from liquid copper-silver alloys. *Metallurgical and Materials Transactions B*, 29B(1), 39–51.
- Pinakin, C., & Nagamori, M. (1983). Volatilization of arsenic and antimony in copper matte converting. *Metallurgical and Materials Transactions B*, 14B(2), 303–306.
- Plascencia, G., & Utigard, T. (2003). Oxidation of copper at different temperatures. In F. Kongoll, K. Itagaki, C. Yamaouchi & H. Y. Sohn (Eds.), *Yazawa International Symposium:*

Metallurgical and materials processing: Principles and technologies; Volume 2: High-temperature metal production (pp. 359–369). Wiley.

- Pollard, A. M. (1990). Experimental smelting of secondary minerals: Implications for early Bronze Age metallurgy in Britain. In E. Pernicka, & G. A. Wagner (Eds.), *Archaeometry '90: Proceedings of the International Archaeometry Symposium* (pp. 127–136). Basel: Birkhäuser.
- Pollard, A. M., Bray, P., Gosden, C., Wilson, A., & Hamerow, H. (in press). Characterising copper-based metals in Britain in the first millennium AD: A preliminary quantification of metal flow and recycling. *Antiquity*.
- Pollard, A. M., & Heron, C. (2008). *Archaeological chemistry* (2nd ed.). Cambridge: Royal Society of Chemistry.
- Pollard, A. M., Thomas, R. G., & Williams, P. A. (1990). Experimental smelting of arsenical copper ores: Implications for early Bronze Age copper production. In C. Peter, & C. Susan (Eds.), *Early mining in the British Isles: Proceedings of the early mining workshop at Plas Tan y Bwlch Snowdonia National Park Study Centre* (pp. 72–74). Tan y Bwlch: Plan Tan y Bwlch Snowdonia National Park Study Centre.
- Pollard, A. M., Thomas, R. G., & Williams, P. A. (1991). Some experiments concerning the smelting of arsenical copper. In P. Budd, B. Chapman, C. Jackson, R. Janaway & B. Ottaway (Eds.), *Archaeological sciences 1989: Proceedings of a conference on the application of scientific techniques to archaeology* (pp. 169–174). Oxford: Oxbow.
- Porter, A. W. (1920). On the vapour pressures of mixtures. *Transactions of the Faraday Society*, 16, 336–345.
- Požega, E., Gomidželović, L., Živković, D., Trujić, V. (2010). The impurities behaviour analysis in thermodynamic simulation models in copper metallurgy. *Journal of the University of Chemical Technology and Metallurgy*, 45 (2), 189–194.
- Rapp, R. A., & Maak, F. (1962). Thermodynamic properties of solid copper-nickel alloys. *Acta Metallurgica*, 10(1), 63–69.
- Redlich, O., & Kister, A. T. (1948). Algebraic representation of thermodynamic properties and the classification of solutions. *Industrial & Engineering Chemistry*, 40(2), 345–348.
- Rehren, T. (1999). Small size, large scale Roman brass production in Germania inferior. *Journal of Archaeological Science*, 26(8), 1083–1087.
- Roine, A. (1987). Activities of As, Sb, Bi, and Pb in copper mattes— effect of O, Ni, and Co. *Metallurgical and Materials Transactions B*, 18B(1), 203–212.

- Roine, A., & Jalkanen, H. (1985). Activities of arsenic, antimony, bismuth, and lead in copper mattes. *Metallurgical and Materials Transactions B*, 16B(1), 129–41.
- Rowlinson, J. S. (1969). *Liquids and liquid mixtures* (2nd ed.). London: Butterworth & Co.
- Saunders, N., & Miodownik, A. P. (1990). The Cu-Sn (copper-tin) system. *Bulletin of Alloy Phase Diagrams*, 11(3), 278–287.
- Scheil, E., & Müller, E. D. (1962). Dampfdruckmessungen an flüssigen Zink-Zinn-Legierungen. *Zeitschrift für Metallkunde*, 35(6), 389–395.
- Seetharaman, S., McLean, A., Guthrie, R.L., Sridhar, S. (2014). *Treatise on Process Metallurgy. [electronic resource]*. Kidlington, Oxford, U.K.; Waltham, Mass.: Elsevier.
- Shibata, E., Yamamoto, K., Nakashima, K., & Mori, K. (1999). Rate of oxidation of impurity in liquid copper by the oxidizing gas. *Shigen-to-Sozai*, 115(6), 455–459.
- Smith, C., & Gnudi, M. T. (1942). *The pirotechnia of vannoccio biringuccio: The classic sixteenth-century treatise on metals and metallurgy*. New York: The American Institute of Mining and Metallurgical Engineers.
- Sohn, H. S., Fukunaka, T., Oishi, Z., Asaki, Z., & Sohn, H. Y. (2004). Kinetics of As, Sb, Bi and Pb volatilization from industrial copper matte during Ar + O₂ bubbling. *Metallurgical and Materials Transactions B*, 35B(4), 651–661.
- Sommer, F., Suh, Y. H., & Predel, B. (1978). Determination of thermodynamic activities of liquid alloys in the gallium-, indium-, and tin-lead systems using the Knudsen method. *Zeitschrift für Metallkunde*, 69(7), 470–475.
- Steinhauser, J., Vartianinen, A., & Wuth, W. (1984). Volatilization and distribution of impurities in modern pyrometallurgical copper processing from complex concentrates. *Journal of Metals*, 36(1), 54–61.
- Stewart, E. M., & Stewart, J. R. (1950). In Stewart E., Stewart J. R., & British School at Athens (Eds.), *Vounous 1937–38: Field-report on the excavations sponsored by the British School of Archaeology at Athens*. Lund: C.W.K. Gleerup.
- Sugino, S., & Hagiwara, H. (1986). Activity of zinc in molten copper and copper-gold alloys. *Nippon Kinzoku Gakkaishi*, 50(2), 186–192.
- Sugino, S., Nakamura, S., & Hagiwara, H. (1986). Effect of tin on the activity of zinc in molten copper. *Journal of the Japan Institute of Metals*, 50(5), 462–466.
- Sundman, B., Fries, S. G., & Oates, W. A. (1998). A thermodynamic assessment of the au-cu system. *Calphad*, 22(3), 335–354.

- Surapunt, S., & Hino, M. (1995). Activity of zinc in molten Cu-Zn-Fe ternary system. *Shigen-to-Sozai*, 111(7), 495–499.
- Surapunt, S., Vasquez, R. R., & Itagaki, K. (1994). Activity measurements in liquid Cu-Zn-X (X= Pb, Ag, Au) ternary alloys. *Shigen-to-Sozai*, 110(8), 631–635.
- Takeda, Y., Ishiwata, S., & Yazawa, A. (1983). Distribution equilibriums of minor elements between liquid copper and calcium ferrite slag. *Transactions of the Japan Institute of Metals*, 24(7), 518–528.
- Taskinen, T. (1982). Activities and thermodynamic properties of molten Co – Cu alloys. *Zeitschrift für Metallkunde*, 73, 445–450.
- Teppo, O., Niemelä, J., & Taskinen, P. (1990). An assessment of the thermodynamic properties and phase diagram of the system Bi-Cu. *Thermochimica Acta*, 173, 137–150.
- Thornton, C. P., & Ehlers, C. (2003). Early brass in the ancient near east. *Institute for Archaeo-Metallurgical Studies Journal*, 23, 3–8.
- Thornton, C. P., Lamberg-Karlovsky, C. C., Liezers, M., & Young, S. M. M. (2002). On pins and needles: Tracing the evolution of copper-base alloying at Tepe Yahya, Iran, via ICP-MS analysis of common-place items. *Journal of Archaeological Science*, 29(12), 1451–1460.
- Timberg, L., Toguri, J., & Azakami, T. (1981). A thermodynamic study of copper-iron and copper-cobalt liquid alloys by mass spectrometry. *Metallurgical and Materials Transactions B*, 12(2), 275–279..
- Tomiska, J. (2009). “ExTherm 2”: An interactive support package of experimental and computational thermodynamics. *Calphad*, 33(2), 288–294.
- Tomita, M., Azakami, T., Timberg, L. M., & Toguri, J. M. (1981). The thermodynamics of the Fe–Zn system. *Transactions of the Japan Institute of Metals*, 22(10), 717–722.
- Turchanin, M. A., & Agraval, P. G. (2007). Phase equilibria and thermodynamics of binary copper systems with 3d-metals. V. copper-cobalt system. *Powder Metallurgy and Metal Ceramics*, 46(1–2), 77–89.
- Turchanin, M. A., Agraval, P. G., & Abdulov, A. R. (2007). Phase equilibria and thermodynamics of binary copper systems with 3d-metals. VI. copper-nickel system. *Powder Metallurgy and Metal Ceramics*, 46(9–10), 467–477.
- Tylecote, R. F. (1970). The composition of metal artifacts: A guide to provenance? *Antiquity*, 44(173), 19–25.

- Tylecote, R. F., Ghaznavi, H. A., & Boydell, P. J. (1977). Partitioning of trace elements between the ores, fluxes, slags and metal during the smelting of copper. *Journal of Archaeological Science*, 4(4), 305–333.
- Ugai, Y. A., Semenova, G. V., Samoilov, A. M., & Goncharov, E. G. (1987). Analysis of the phase equilibria in the antimony-arsenic system. *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, 23(9), 1434–1437.
- Ullwer, H. (2008). Das alte Galmeiverfahren und die erreichbaren Zinkgehalte. *World of Metallurgy - ERZMETALL*, 61(5), 322–327.
- Valério, P., Monge Soares, A. M., Silva, R. J. C., Araújo, M. F., Rebelo, P., Neto, N., Fontes, T. (2013). Bronze production in southwestern Iberian Peninsula: The late Bronze Age metallurgical workshop from Entre Águas 5 (Portugal). *Journal of Archaeological Science*, 40(1), 439–451.
- Vecher, A. A., Nikolskaya, A. V., & Gerasimov, Y. I. (1957). *Zhurnal Fizicheskoi Khimii*, 31, 1395.
- Wayman, M. L., & Duke, M. J. M. (1999). The effects of melting on native copper. In A. Hauptmann, E. Pernicka, T. Rehren & U. Yalcin (Eds.), *The beginnings of metallurgy. Der Anschnitt – Beiheft 9* (pp. 55–63). Deutsches Bergbau-Museum
- Wayman, M. L. (1989). Determining the origin and age of metal artifacts. *MRS Bulletin*, 14(03), 31–35.
- Welter, J. (2003). The zinc content of brass: A chronological indicator? *Techné*, 18, 27–36.
- Werner, O. (1970). Über das Vorkommen von Zink und Messing im Altertum und im Mittelalter. *Erzmetall*, 23(6), 259–296.
- Witusiewicz, V. T., Hecht, U., Fries, S. G., & Rex, S. (2004). The ag-al-cu system part I: Reassessment of the constituent binaries on the basis of new experimental data. *Journal of Alloys and Compounds*, 385(1–2), 133–143.
- Wypartowicz, J. (1995). Thermodynamic properties of copper-arsenic liquid solutions. *Journal of Alloys and Compounds*, 227(1), 86–92.
- Yamaguchi, K., Mikula, A., Komarek, K. L., & Itagaki, K. (1991). Thermodynamic investigations of the liquid As-Zn and As-Cd systems by drop calorimetry. *Zeitschrift für Metallkunde*, 82(8), 591–598.
- Yazawa, A. (1974). Thermodynamic considerations of copper smelting. *Canadian Metallurgical Quarterly*, 13(3), 443–453.

- Yazawa, A. (1980). Distribution of various elements between copper, matte, and slag. *Erzmetall*, 33, 377–382.
- Yazawa, A., & Azakami, T. (1969). Thermodynamics of removing impurities during copper smelting. *Canadian Metallurgical Quarterly*, 8(3), 257–261.
- Yazawa, A., Hino, M., & Swinborne, D. R. (2000). Thermodynamics of arsenic behavior in pyrometallurgy. In *Proceedings from MINPREX 2000: International Congress on Mineral Processing and Extractive Metallurgy* (pp. 419–426). Carlton, Victoria: Australasian Institute of Mining and Metallurgy,
- Yazawa, A., & Nakazawa, S. (1998). Evaluation of non-equilibrium minor components in pyrometallurgy. In B. Mishra (Ed.), *EPD congress 1998* (pp. 641–655) Minerals, Metals & Materials Society.
- Zacharias, S. (1989). Brass making in medieval Western Europe. In M. L. Wayman (Ed.), *All That Glitters: Readings in Historical Metallurgy* (pp. 35-40). Montreal: Metallurgical Society of the Canadian Institute of Mining and Metallurgy,
- Zakeri, A., Hino, M., & Itagaki, K. (1998). Activity of silver in molten copper sulfide saturated with copper. *Materials Transactions JIM*, 39(11), 1101–1107.
- Zwicker, U., Greiner, H., Hofmann, K., & Reithinger, M. (1985). Smelting, refining and alloying of copper and copper alloys in crucible furnaces during prehistoric up to Roman times. In P. T. Craddock, & M. J. Hughes (Eds.), *Furnace and smelting technology in antiquity. Occasional Paper Number 48* (pp. 103–116). London: The British Museum.

Appendix A.1: Volume and the Derivation of the Ideal Entropy of Mixing

The number of arrangements of n_1 and n_2 ,

$$\Omega = \frac{(n_1 + n_2)!}{n_1! n_2!} \quad \text{A.1.1}$$

Application of Stirling's approximation,

$$S_{n_1+n_2} = -k \left[n_1 \ln \left(\frac{n_1}{n_1 + n_2} \right) + n_2 \ln \left(\frac{n_2}{n_1 + n_2} \right) \right] \quad \text{A.1.2}$$

Substitution of moles with mole fractions,

$$S = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad \text{A.1.3}$$

The entropy of expansion of a vapor from volume V_1 to a total $V_1 + V_2$,

$$\Delta S = R \ln \frac{V_1 + V_2}{V_1} \quad \text{A.1.4}$$

Entropy change when two vapor expand into the available volume,

$$\Delta S = R \left[x_1 \ln \frac{V_1 + V_2}{V_1} + x_2 \ln \frac{V_1 + V_2}{V_2} \right] \quad \text{A.1.5}$$

Entropy of mixing of in a given total volume for two liquids where V_{nf} denotes free volume and $V_{1f} \ll V_1$,

$$\Delta S = R \left[x_1 \ln \frac{V_{1f} + V_{2f}}{V_{1f}} + x_2 \ln \frac{V_{1f} + V_{2f}}{V_{2f}} \right] \quad \text{A.1.6}$$

Assuming free volume is the same for each,

$$V_{1f} = fV_1; V_{2f} = fV_2 \quad \text{A.1.7}$$

Where ϕ_n are the volume fractions,

$$\Delta S = R \left[x_1 \ln \frac{V_1 + V_2}{V_1} + x_2 \ln \frac{V_1 + V_2}{V_2} \right] = -R[x_1 \ln \phi_1 + x_2 \ln \phi_2] \quad \text{A.1.8}$$

And ϕ_1 in terms of mole fractions is,

$$\frac{x_1 V_1}{x_1 V_1 + x_2 V_2} = \frac{x_1}{x_1 + x_2 \left(\frac{V_2}{V_1} \right)} \quad \text{A.1.9}$$

Where x_1 is equal if $\frac{V_2}{V_1} = 1$, and assuming $V_1 = V_2$ gives the ideal entropy of mixing,

$$\Delta S_{mix} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad \text{A.1.10}$$

Appendix A.2: Mixing, Mole Fractions, and the Partial Derivative

When $n_1 + n_2 = N_A$, G and dG are identical in the alternative system,

$$dG(T, P, n_1, n_2) = dG(T, P, x_1, N_A) \quad \text{A.2.1}$$

And,

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n_1} dn_2 = \left(\frac{\partial G}{\partial x_1}\right)_{N_A} dx_1 + \left(\frac{\partial G}{\partial N_A}\right)_{x_1} dN_A \quad \text{A.2.2}$$

Keeping n_2 constant where $dn_2 = 0$ and dividing by dn_1 ,

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \left(\frac{\partial G}{\partial x_1}\right)_{N_A} \left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} + \left(\frac{\partial G}{\partial N_A}\right)_{x_1} \left(\frac{\partial N_A}{\partial x_1}\right)_{n_2} \quad \text{A.2.3}$$

Reduces to,

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \frac{(1 - x_1)}{N_A} \left(\frac{\partial G}{\partial x_1}\right)_{N_A} + \left(\frac{\partial G}{\partial N_A}\right)_{x_1} \quad \text{A.2.4}$$

Since,

$$\left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} = \frac{1}{n_1 + n_2} - \frac{n_1}{(n_1 + n_2)^2} = \frac{(1 - x_1)}{N_A} \quad \text{A.2.5}$$

And because the sum of the mole fractions are equal to N_A ,

$$\left(\frac{\partial N_A}{\partial x_1}\right)_{n_2} = 1 \quad \text{A.2.6}$$

And replacing the last term where G_m is the free energy of one mole of the mixture,

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \frac{1 - x_1}{N_A} \left(\frac{\partial G}{\partial x_1}\right)_{N_A} + G_m \quad \text{A.2.7}$$

Substituting $(1 - x_2)$ for x_2 and differentiating G_m in $\Delta G_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2)$ with respect to x_1 ,

$$\left(\frac{\partial G}{\partial x_1}\right)_N = RT(\ln x_1 + 1 - \ln(1 - x_1) - 1) \quad \text{A.2.8}$$

And,

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = RT(1 - x_1)(\ln x_1 - \ln x_2) + RT(x_1 \ln x_1 + x_2 \ln x_2) = RT \ln x_1 \quad \text{A.2.9}$$

Appendix A.3: The Activity Coefficient and Independent Variables

From Appendix A.2, rewriting A.2.7, as,

$$RT \ln \gamma_1 = \frac{(1 - x_1)}{N_A} \left(\frac{\partial G^E}{\partial x_1} \right)_{N_A} + G_m^E \quad \text{A.3.1}$$

Replacing x_2 with $(1 - x_1)$ and differentiating with respect to x_1 ,

$$\left(\frac{\partial G^E}{\partial x_1} \right)_{N_A} = B(1 - 2x_1) = B(x_2 - x_1) \quad \text{A.3.2}$$

Substituting into Equation A.3.1 gives A.3.3 in agreement with 6.8,

$$RT \ln \gamma_A = B(x_2 - x_1)(1 - x_1) + Bx_1x_2 = Bx_2^2 \quad \text{A.3.3}$$

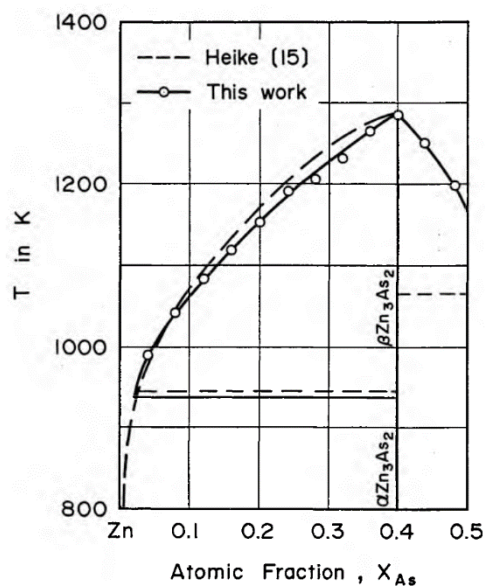
And if A.2.7 is expressed in the form,

$$RT \ln \gamma_1 = (1 - x_1) \left(\frac{\partial G}{\partial x_1} \right) - x_2 \left(\frac{\partial G}{\partial x_2} \right) + G_m \quad \text{A.3.4}$$

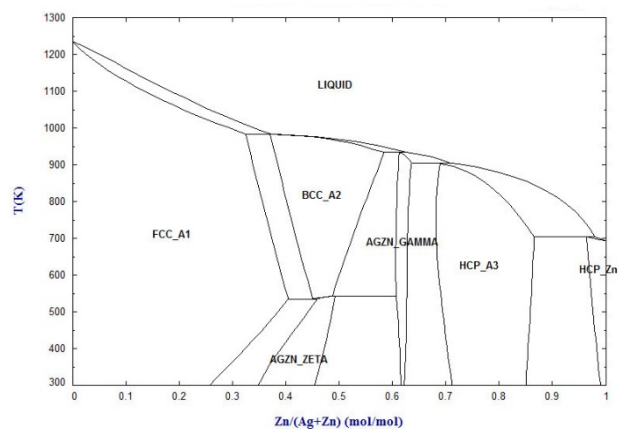
Then with substitution as before, but not replacement using x_1 and x_2 as independent variables, we get the same results confirming prior derivations,

$$RT \ln \gamma_1 = (1 - x_1)Bx_2 - Bx_2x_1 + Bx_1x_2 = Bx_2^2 \quad \text{A.3.5}$$

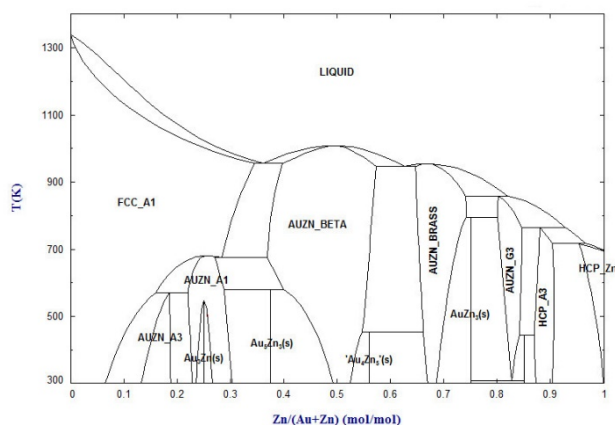
Appendix A.4: Binary Zn-M Phase Diagrams



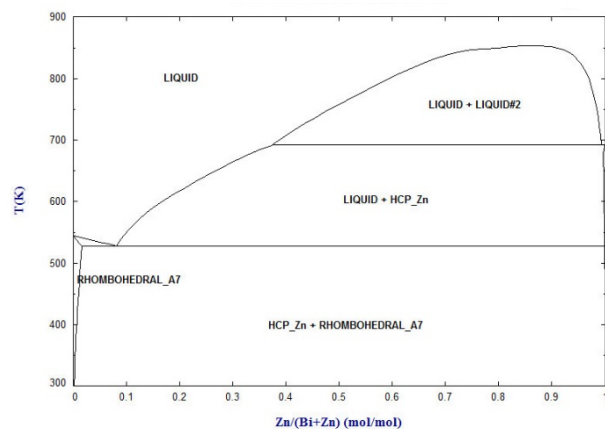
As-Zn Phase Diagram (Yamaguchi et al., 1991)



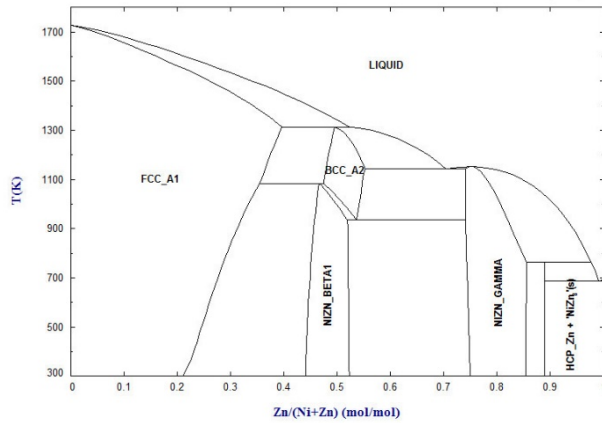
Ag-Zn Phase Diagram source:
<http://www.crtc.polymtl.ca/fact/>



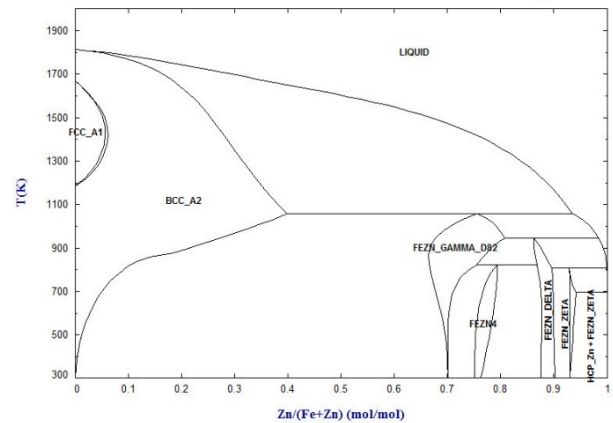
Au-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



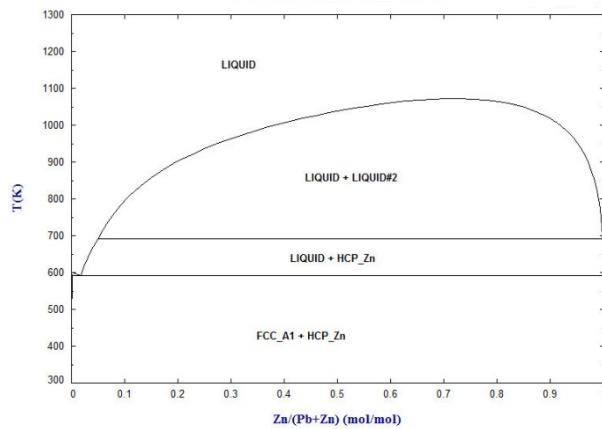
Bi-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



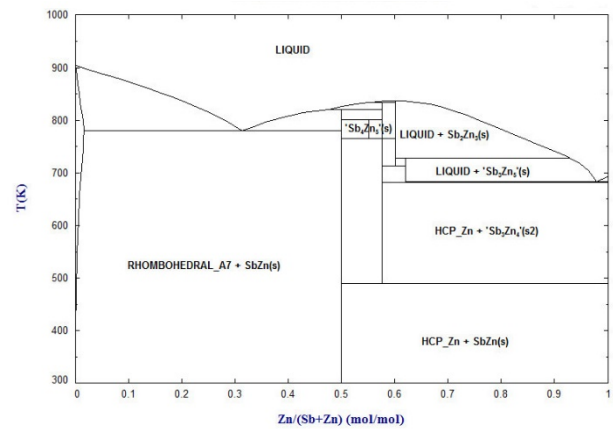
Ni-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



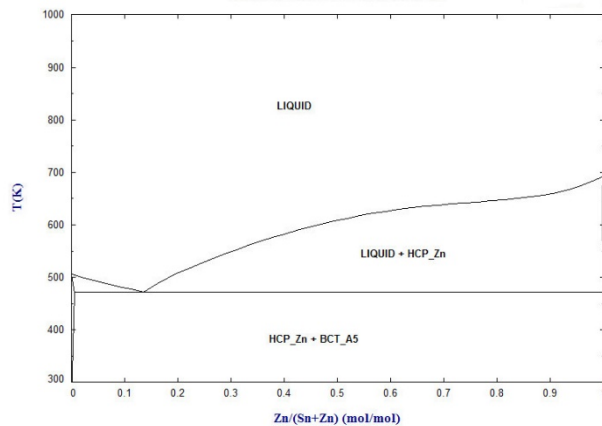
Fe-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



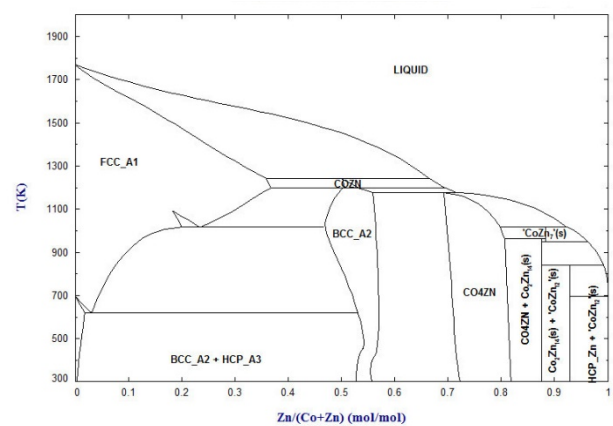
Pb-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



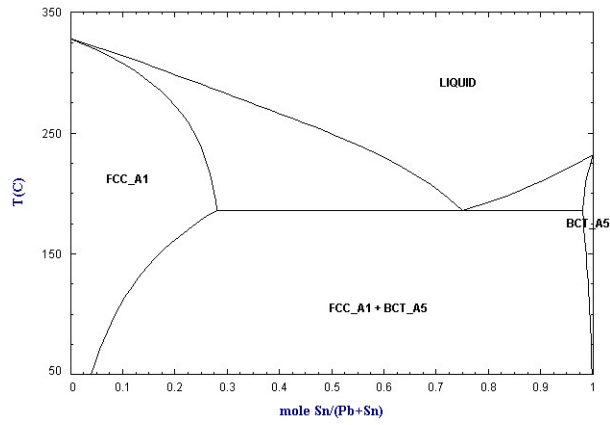
Sb-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



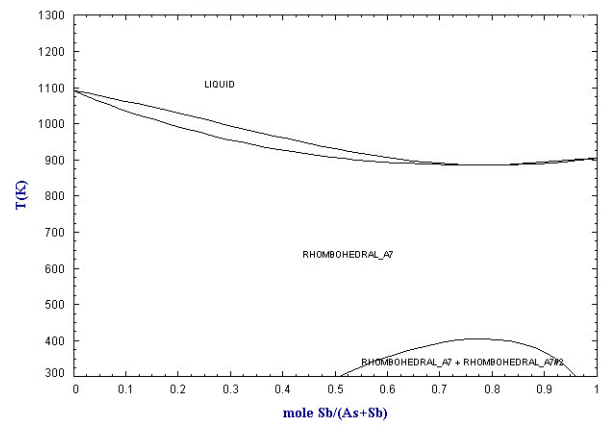
Sn-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



Co-Zn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



Pb-Sn Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)



As-Sb Phase Diagram (source:
<http://www.crtc.polymtl.ca/fact/>)

Appendix A.5: Custom Software

The software created for this thesis are in two distinct parts; one is written in R-base, a scripting language, and the other in Java, an object oriented compiled language. These parts were written piecemeal to fulfill tasks at different times by different people. The software written in Java, for instance, was originally written and designed by Dr. Robert Thomas to solve a different but related question. It was then modified by him for metal systems. Furthermore, each diagram in this thesis, including those in Chapter 8, were created using R-base scripts. Each script is itself a program that requires a multitude of inputted data, the referencing of pre-installed functions, and additional packages from R-base repositories (i.e. PLOTrix, TRIAXPLOT).

These software are, as a result, not compatible with each other in the sense that they cannot directly communicate with one another. To build the models occasional editing of program source code and data files had to be performed. They also must be run from a terminal or an integrated development environment (IDE), and often manual input, parsing of output files, and further adjustments were required. For obvious reasons the code itself is not useful to others in its current state, but, as mentioned, the equations given in this thesis may be used to achieve the same results. The equations can be used to check the validity of the models. It is hoped that the tasks performed by these software will at some point be written in a standardized programming language. Since a graphic interface is not efficient, and it is not reasonable to show higher order systems of four or more components visually, this author plans to use R-base exclusively. Absent the code itself the steps to create they binary and ternary models are outlined below.

1. Thermodynamic Data Acquisition: Activity data of each component in binary system were recorded and inputted into R-base scripts. This data is either calculated or experimentally derived and is commonly given in three forms.
 - a. Activity Data: Either listed at specific mole fractions or given in activity diagrams. Often the activity of only one component is given.
 - b. Activity Coefficient Data: Either listed at specific mole fractions or given in activity coefficient diagrams. Values nearing zero and one mole fractions are often not given.
 - c. Gibbs Excess Energy Data: Either listed at specific mole fractions or given in diagrams. This is the least common form.
2. Acquired Data Conversion: All thermodynamic data were converted in R-base scripts to activity coefficient values using the simple mathematical relationships found in this thesis.
3. Activity Coefficient Data Adjustment to 1200° C: Data given in various temperatures were extrapolated to the standardized temperature of 1200° C. Temperatures as close to the standardized temperature were chosen from the original thermodynamic data.
4. Calculation of the Secondary Component Activity: Thermodynamic data is often only given for a single component in published binary systems, however, it is possible to calculate the activity of the second using the Gibbs-duhem relationship. These calculations were performed in R-base scripts.
5. Loess Regression Plotting and Point Interpolation: The loess function in R-base is called to interpolate between data points creating a continuous smooth line between 0 and 1 mole

fractions for each component. Within each line 100 points are selected at even intervals and output with each's corresponding mole fraction as comma separated values (CSV).

6. Binary Activity Data Inputted into the 1st Java program: Inputted data is matched by least squares, and in accordance with the Gibbs-duhem relationship, to calculate three (B, C, D) binary interaction parameters. This step is repeated three times for each binary system contained within a given ternary of interest.
7. Interaction Parameters Inputted into the 2nd Java Program: Nine interaction parameters are entered (three for each binary system) into the second program that calculates the Gibbs excess energy and sums their total for each point in the system where the total mole fractions of all components is equal to 1. The results of this step are outputted into to a CSV file.
8. Data are Inputted into an R-base Script and Plotted: Data from the previous step are read into R-base scripts. They are then parsed and plotted according to user defined activity values so that the individual points are joined to form lines. This step produces the ternary activity diagrams and lines of isoactivity in the same script.

Appendix B.1: Site Names and Abbreviations

Site Name	Abbreviated Site Name
Annetwell Street, Carlisle, Cumbria	CAAN
Arras, North Humberside	ARRS
Attermire Cave, Settle, North Yorkshire	SETA
Bainese Farm, Catterick, North Yorkshire	CATB
Biglands, Cumbria	BIGL
Blackburn Mill, Cockburnpath, Lothian	BLML
Blackfriars, Carlisle, Cumbria	CABL
Brough Castle, Cumbria	BRGH
Brougham, Cumbria	BRHM
Broxmouth, Lothian	BRXM
Burton Fleming, North Humberside	BURT
Carham, Borders	CRHM
Carlingwark Loch, Dunfries & Galloway	CLWK
Castle Hill, Scarborough, North Yorkshire	SCAR
Castle Street, Carlisle, Cumbria	CACA
Castleford, West Yorkshire	CASD
Catterick, North Yorkshire (CATT, CATW)	CATT
Catterick, North Yorkshire (CATT, CATW)	CATW
Chesters, Northumberland	CHST
City of York	YORK
Coventina's Well, Northumberland	COVW
Cowlan, North Humberside	CWLM
Dalton Parlours, West Yorkshire	DALT
Danes Graves, North Humberside	DNGR
Dod Law, Northumberland	DODL
Doubtstead, Scremerston, Northumberland	DBSD
Dragonby, South Humberside	DRAG
Edinburgh Castle, Lothian	EDCS
Elginbaugh, Lothian	ELGN
Embleton, Cumbria	EMBL
Glebe Farm, Barton-on-Humber, North Humberside	GLBF
Greater Kelco Cae, Settle, North Yorkshire	SETC
Grimthorpe, North Humberside	GRMT
High Brunton, Northumberland	HBRN
Holme House, North Yorkshire	HOLM
Huckhoe, Northumberland	HKHO
Kinsey Cave, Settle, North Yorkshire	SETK
Kirk Sink, Gargrave, North Yorkshire	KKSN
Kirkburn, North Humberside	KIRK
Manchester	MANC
Milking Gap, Northumberland	MILK
Newcastle, Tyne and Wear	NEWC
North Cave, North Humberside	NCAV
Old Penrith, Cumbria	OPEN
Old Wintringham, South Humberside	OLDW
Papcastle, Cumbria	PAPC

Piercebridge, County Durham	PIER
Pilling Moss, Lancashire	PLMS
Ravenglass, Cumbria	RAVE
Redcliff, North Humberside	RDCL
Rudston, North Humberside	RUDG
Rudston, North Humberside	RUDV
Sadeberge, County Durham	SDBG
Sawdon, North Yorkshire	SWDN
Settle Caves (Jackson Collection), North Yorkshire	SETJ
Sewell's Cave, Settle, North Yorkshire	SETS
Sewing Shields, Northumberland	SWSH
Shiptonthorpe, North Yorkshire	SHIP
Stanwick Hoard, North Yorkshire	STAN
Staple Howe, North Yorkshire	STHW
Thorpe Thewles, Cleveland	THTW
Tofts Field, Stanwick, North Yorkshire	TOFT
Traprain Law, Lothian Region	TPLW
Victoria Cave, Settle, North Yorkshire	SETV
Vindolanda, Northumberland	VIND
Walton-le-Dale, Lancashire	WLDL
Warton, Lancashire	WRTN
Watecrook, Cumbria	WATC
Weelsby Avenue, Grimsby, South Humberside	WLBY
Welton Wold, North Humberside	WEWO
Wetwang and Garton Slacks, North Humberside	WTWG
Whitehills Moss, Lochmaben, Dumfries & Galloway	LCMN
Wooden Echford, Borders	WDEK

Appendix B.2: Site Dates

Dungworth (1995) Dating Scheme

LBA		Late Bronze Age / Early Iron Age
EIA		Early Iron Age
IA		Iron Age
LIA		Late Iron Age
C1AD	1 st C. AD	Roman, post 42 AD
C2AD	2 nd C. AD	Roman
C3AD	3 rd C. AD	Roman
C4AD	4 th C. AD	Roman
EROM	1 st –2 nd C. AD	Early Roman
MROM	2 nd –3 rd C. AD	Middle Roman
LROM	3 rd –4 th C. AD	Late Roman
ROMN	1 st –4 th C. AD	Roman

Blades (1995) Dating Scheme

RMN	1 st –4 th C. AD	Roman
ES	430–650 AD	Early Saxon
MS	650–850 AD	Middle Saxon
LS	850–1066 AD	Late Saxon
EMED	11 th –13 th C. AD	Early medieval
LMED	13 th –15 th C. AD	Late medieval
PMED	1600+ AD	Post-medieval

Appendix B.3: Combined Artifact Chemical Datasets

Period	Site Name	Artifact	Context	Find Number	Analyse Code	Blades P140 Page Number	Cu	Zn	Pb	Sn	Fe	Ni	As	Bi	Sb	P	S	Co	Cr	Mn	V	Cd	Ag
LEA	SCAR	ARLLET	NA	NA	NA	9972	ND	ND	22.64	82.9	0.07	ND	0.2	NA	NA	NA	NA	ND	NA	ND	NA	NA	NA
LEA	SCAR	Bronze AGE	NA	NA	NA	6558	ND	ND	22.64	82.9	0.05	0.47	0.33	NA	NA	NA	NA	ND	NA	ND	NA	NA	NA
LEA	SCAR	CHISEL	NA	NA	NA	9254	ND	ND	231	445	ND	0.08	ND	NA	NA	NA	NA	ND	NA	ND	NA	NA	NA
LEA	STHWH	CHISEL	NA	NA	NA	9085	ND	2	7.08	ND	ND	0.05	ND	NA	NA	NA	NA	ND	NA	ND	NA	NA	NA
LEA	STHWH	CHISEL	NA	NA	NA	9085	ND	2	7.08	ND	ND	0.05	ND	NA	NA	NA	NA	ND	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8858	ND	0.42	0.22	12.15	0.17	ND	0.11	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	ARLLET	HORSE BIT	NA	NA	NA	8521	ND	ND	ND	10.92	0.06	ND	0.07	NA	NA	NA	NA	0	NA	ND	NA	NA	NA
EIA	AR																						

CACA	CACD	CIAD	NA	NA	73.57	0.36	15.42	9.66	0.7	ND	NA	NA	NA	NA	NA	0.05	NA	NA
CACA	CACD	CIAD	NA	NA	9682	0.94	0.21	157	0.45	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	9686	1.04	0.32	146	0.32	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	7325	15.32	6.97	227	0.99	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	8126	15.32	0.19	ND	0.22	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	79.3	18.89	0.72	0.93	0.15	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	100	100	ND	ND	0.13	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	9987	ND	ND	ND	ND	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	8806	ND	ND	0.12	0.21	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	7273	ND	19.11	8.15	0.12	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	89.9	ND	1.56	7.88	0.11	0.13	ND	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	8878	ND	0.28	0.94	ND	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	8721	ND	0.26	12.26	0.07	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	98.96	ND	0.22	0.77	0.05	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACA	CACD	CIAD	NA	NA	99.66	ND	0.15	0.11	0.06	0.1	ND	NA	NA	NA	NA	0.01	NA	NA
CACA	CACD	CIAD	NA	NA	99.22	ND	0.15	0.62	ND	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.69	0.14	0.38	4.14	0.7	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	83.48	0.12	0.38	4.14	2.23	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	87.28	0.13	9.84	6.32	0.22	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA		0.15	0.57	11.01	0.26	ND	NA	NA	NA	NA	NA	0.02	NA	NA
CACD	CACD	CIAD	NA	NA		0.16	10.5	8.66	0.25	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	88.31	0.26	0.39	10.75	0.08	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	94.06	0.62	2.35	2.98	ND	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	71.92	1.33	17.24	9.39	0.11	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	75.47	2.25	9.85	11.67	0.77	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	90.53	2.44	3.84	3.1	0.09	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	90.33	3.92	2.12	3.4	0.11	0.11	ND	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	88.07	4.47	1.57	5.69	0.26	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	81.26	6.04	5.1	7.27	0.32	ND	NA	NA	NA	NA	NA	0.02	NA	NA
CACD	CACD	CIAD	NA	NA	88.04	6.19	0.19	0.7	0.19	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	88.54	6.94	0.31	3.19	0.31	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	87.69	7.53	2.84	1.55	0.26	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	88.81	8.35	0.56	2.11	0.17	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	88.81	9.23	8.56	4.27	0.48	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.85	9.55	4.76	3.6	0.6	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	77.56	9.69	0.82	4.62	0.31	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	86.97	10.6	0.4	1.5	0.32	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	85.61	11.24	2.4	0.14	0.24	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	84.13	11.71	10.77	3.99	0.36	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	85.22	12.2	1.09	1.25	0.24	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	74.67	12.94	9.35	2.51	0.53	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	83.84	13.8	0.22	1.74	0.29	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	82.3	14.09	0.16	10.3	0.38	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA		14.16	ND	3	0.19	0.13	ND	NA	NA	NA	NA	0.02	NA	NA
CACD	CACD	CIAD	NA	NA	83.78	14.68	ND	1.12	0.12	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	74.97	15.07	7.06	2.38	0.52	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	81.9	15.42	1.03	1.28	0.21	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	80.52	17.33	0.33	1.65	0.16	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	81.31	17.35	ND	1.02	0.26	0.07	ND	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.41	18.17	2.29	0.81	0.32	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	80.87	18.26	ND	0.64	0.23	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	79.46	18.69	0.33	0.92	0.29	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	80.3	19.35	ND	0.19	0.16	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.3	20.39	0.51	0.55	0.25	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.38	21	0.23	0.19	0.17	ND	NA	NA	NA	NA	NA	0.02	NA	NA
CACD	CACD	CIAD	NA	NA	77.98	21.03	0.49	0.44	0.13	ND	NA	NA	NA	NA	NA	0.03	NA	NA
CACD	CACD	CIAD	NA	NA	78.76	21.14	1.66	0.3	0.16	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	78.08	21.39	ND	0.25	0.36	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	77.23	22.33	ND	0.16	0.14	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	76.79	22.86	ND	0.14	0.18	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	75.54	23.08	0.29	0.19	0.38	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	75.44	24.17	ND	0	0.22	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	73.5	25.16	ND	0.12	0.09	0.06	ND	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	57.61	25.19	19.71	22.13	0.29	ND	NA	NA	NA	NA	NA	0.02	NA	NA
CACD	CACD	CIAD	NA	NA	63.12	ND	14.9	20.47	ND	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	79.71	ND	9.99	11.16	0.14	ND	NA	NA	NA	NA	NA	ND	NA	NA
CACD	CACD	CIAD	NA	NA	80.34	ND	0.58	16.26	0.07	ND	NA	NA	NA	NA	NA	0.01	NA	NA
CACD	CACD	CIAD	NA	NA	93.43	ND	0.18	9.13	0.35	ND	NA	NA	NA	NA	NA	ND	NA	NA
CATW		CIAD	NA	NA	71.62	2.19	15.72			ND	NA	NA	NA	NA	NA	0.01	NA	NA

WTWG	EROM	NA	NA	NA	78.47	20.69	0.16	0.22	0.46	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
BEL	C2AD	NA	NA	NA	73.83	0.41	11.81	13.3	0.23	0.16	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
BEL	C2AD	NA	NA	NA	57.2	0.89	22.93	18.43	0.21	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
BEL	C2AD	NA	NA	NA	73.89	6.36	ND	ND	0.16	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
BEL	C2AD	NA	NA	NA	85.03	ND	2.96	11.52	0.24	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
BLM	C2AD	NA	NA	NA	74.73	0.2	12.32	11.02	0.08	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	54.12	0.16	34.57	11.06	0.08	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.44	0.19	12.03	7.26	0.06	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	67.35	0.2	22.41	9.85	0	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	73.18	0.74	15.24	16.5	0.33	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	85.94	2.8	0.32	10.7	0.11	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	79.53	3.21	9.85	8.66	0.31	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.05	14.04	0.45	20.2	0.42	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.75	15.29	0.27	0.53	0.24	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.75	15.29	0.27	0.53	0.24	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.75	17.79	0.31	0.75	0.1	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	81.3	18.37	0.24	0	0.09	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.96	19.12	0.46	1.26	0.2	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.96	19.12	0.46	1.26	0.2	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.47	20.34	ND	0.85	0.25	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	77.31	21.52	ND	0.86	0.21	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	73.73	0.17	14.94	10.68	0.16	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	81.57	0.18	6.86	10.48	0.11	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	69.86	0.35	19.84	9.89	0.11	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	85.98	4.69	3.25	5.75	0.1	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	74.13	5.18	13.16	7.25	0.29	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.22	0.17	13.62	7.61	0.1	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	87.21	0.32	0.62	10.44	0.93	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	96.44	0.94	ND	2.33	0.4	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.27	9.43	0.42	6.4	0.11	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.49	13.13	0.84	1.62	0.73	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	79.29	15.45	0.97	3.82	0.6	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	81.09	17.99	ND	0.62	0.3	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.6	18.78	ND	0.56	0.24	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.64	19.3	2.03	1.39	0.15	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.33	20.99	0.24	0.38	0.21	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	76.94	21.78	ND	1.15	0.14	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	78.16	21.84	2.04	2.23	0.07	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	86.66	0.12	0.23	12.92	0.07	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	84.32	0.14	1.88	3.55	0.11	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	81.57	0.16	1.89	1.07	0.07	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	87.67	0.21	5.15	6.88	0.09	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	91.65	0.35	4.66	3.34	0.06	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.2	0.51	11.66	7.53	0.1	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	90.89	0.68	0.2	6.75	0.51	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	85.84	0.72	8.5	9.1	0.08	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	96.13	0.78	0.87	2.04	0.16	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	72.41	1.42	15.96	10.08	0.23	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	74.88	1.65	15.99	15.99	0.28	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	76.23	1.91	12.71	8.79	0.35	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	93.29	2.14	0.46	4.95	0.14	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	88.19	3.38	0.17	11.98	0.17	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	92.93	5.85	0.47	0.32	0.23	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	81.99	7.44	6.18	4.22	0.17	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	87.23	8.43	0.26	3.57	0.49	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	76.9	8.9	6.96	5.5	0.43	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	84	11.3	1.89	1.9	0.45	0.07	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.12	11.89	4.41	4.19	0.3	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	84.59	12.14	0.49	2.42	0.36	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.56	13.1	3.39	2.52	0.43	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	83.52	13.37	0.29	1.57	0.5	0.14	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	82.95	14.09	0.82	1.77	0.37	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.17	16.66	2.31	0.66	0.48	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	82.7	16.15	ND	0.38	0.46	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	80.17	16.66	2.31	0.66	0.48	ND	ND	NA	NA	NA	NA	NA	ND	ND	NA	ND	NA	ND	0.02	NA	NA	NA
CAIN	C2AD	NA	NA	NA	79.36	17.68	0.66	0.85	1.67																	

DALT	LROM	UNKNOWN	NA	NA	6767	4.81	13.3	12.79	1.42	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR PIN	NA	NA	7118	5.96	6.71	10.13	0.12	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	TERRET REIN RING	NA	NA	8578	5.96	0.99	0.99	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	PENANULAR BROOCH	NA	NA	8454	12.46	0.56	0.56	0.19	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SCALE HOUR	NA	NA	8267	13.66	0.66	0.66	0.32	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LIKE SHEET BUT LONGER UP TO 1mm	NA	NA	8091	13.56	2.78	2.14	0.2	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	THICK	NA	NA	851	16.82	0.63	0.63	0.33	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	7592	17.87	1.6	3.41	0.64	ND	0.54	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	RING	NA	NA	7955	19.62	0	0	0.18	ND	0.11	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	7552	21.51	1.87	1.87	0.51	ND	0.48	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	7552	21.51	1.87	0.48	0.51	ND	0.09	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHIELD	NA	NA	7233	24.05	0.83	2.04	0.32	ND	0.44	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	7417	1.263	ND	7.17	0.33	ND	0.17	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8096	ND	ND	ND	0.13	ND	0.2	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	VESEL (NOT INCLUDING PHETAE)	NA	NA	8952	ND	ND	891	0.15	ND	0.16	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8672	ND	16.71	5.96	0.05	ND	0.1	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8573	ND	7.62	5.96	0.08	ND	0.08	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMLET	NA	NA	8719	ND	1.9	0.95	0.07	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	RING	NA	NA	8953	ND	0.84	8.79	0.25	ND	0.29	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8538	ND	0.51	12.55	0.07	ND	0.11	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	9029	ND	0.32	9.1	0.19	ND	0.19	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LIKE SHEET BUT LONGER UP TO 1mm	NA	NA	8823	0.16	0.24	10.23	0.08	ND	0.05	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	THICK	NA	NA	8229	0.28	8.55	7.61	0.44	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	PIN	NA	NA	8573	0.28	8.55	7.61	0.44	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8764	0.84	4.41	5.97	0.27	ND	0.27	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMLET	NA	NA	8906	4.24	0.21	6.2	0.16	ND	0.12	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LIKE SHEET BUT LONGER UP TO 1mm	NA	NA	8779	8.14	0.38	3.37	0.32	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	THICK	NA	NA	8312	8.36	2.18	5.01	0.33	ND	0.35	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	TOILET IMPLEM	NA	NA	8288	12.94	0.71	3.03	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	8573	ND	0.55	12.94	0.16	ND	0.16	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	PENANULAR BROOCH	NA	NA	8392	ND	15.37	12.67	0.35	ND	0.35	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMLET	NA	NA	93.6	ND	0	5.36	0.24	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	8739	11.32	ND	0.8	0.18	ND	0.31	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	TOILET IMPLEM	NA	NA	7849	14.7	10.9	9.01	0.13	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	7711	17.1	11.46	9.45	0.27	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	RING	NA	NA	8158	17.45	ND	0.69	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8137	18.35	ND	0.1	0.18	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8581	ND	18.6	22.54	0.05	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SPECULUM HAND MIRRORS	NA	NA	9538	ND	0.22	0.28	0.11	ND	0.24	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	76	2.18	14.58	7.03	0.2	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	BELT PLATE	NA	NA	851	ND	0.22	0.28	0.11	ND	0.24	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	851	ND	0.22	0.28	0.11	ND	0.24	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	CALVARY HARNESS FITTING	NA	NA	8489	0.66	0.97	3.71	0.37	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8489	0.66	0.97	3.71	0.37	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LIKE SHEET BUT LONGER UP TO 1mm	NA	NA	8632	0.1	3.33	9.39	0.09	ND	0.06	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	THICK	NA	NA	7956	0.15	13.64	7.17	0.09	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LEVER	NA	NA	8019	0.29	12.36	7.17	0.09	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8353	0.32	7.37	8.13	0.13	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	7984	0.42	7.94	7.6	0.2	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8792	0.49	1.82	8.42	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	BUCKLE	NA	NA	59.4	0.61	12.92	10.25	0.27	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	851	ND	0.75	10.25	0.13	ND	0.13	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8516	0.75	10.25	9.97	0.14	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	BELL	NA	NA	8489	0.86	1.66	11.22	0.13	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	U-SECTIONED BINDING USED FOR	NA	NA	6452	0.9	26.49	7.59	0.35	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	EDGING ON WOOD...	NA	NA	6452	0.9	26.49	7.59	0.35	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8714	1.21	2.34	8.21	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	U-SECTIONED BINDING USED FOR	NA	NA	8725	1.24	1.69	9.43	0.38	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	EDGING ON WOOD...	NA	NA	8681	1.24	1.51	9.22	0.11	ND	0.05	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	7977	1.33	11.5	7.31	0.1	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8573	1.33	11.5	7.31	0.1	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8564	1.47	3.72	5.55	0.12	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	SHEET	NA	NA	8781	1.66	0.22	9.38	0.13	ND	0.12	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	PIN	NA	NA	8653	1.72	2.15	9.12	0.19	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8805	1.79	0.9	7.48	0.14	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMLET	NA	NA	8768	1.91	4.33	5.78	0.3	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	LOOPEO MOUNT	NA	NA	8768	1.91	4.33	5.78	0.3	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8922	2.02	1.79	6.77	0.19	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	CALVARY HARNESS FITTING	NA	NA	7086	2.63	14.57	11.06	0.28	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	STUD SNAILS RIVETS AND TACKS	NA	NA	8784	2.96	2.35	9.72	0.16	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA
DALT	LROM	ARMOUR	NA	NA	8543	3.42	3.42	7.3	0.21	ND	ND	NA	NA	NA	ND	NA	NA	ND	NA	NA	NA	NA	NA	NA

[illegible]

271

272

ES	WEST GARTH GARDENS	61	NA	CRUCIFORM BROOCH
ES	WEST GARTH GARDENS	13	NA	ANNULAR BROOCH (PN ABSENT)
ES	WEST GARTH GARDENS	30	NA	BUCKLE
ES	WEST GARTH GARDENS	33	NA	ANNULAR BROOCH (WITH PIN)
ES	WEST GARTH GARDENS	48	NA	WRIST-CLASP
ES	WEST GARTH GARDENS	48	NA	SMALL-LOOGE BROOCH
ES	WEST GARTH GARDENS	48	NA	WRIST-CLASP
ES	WEST GARTH GARDENS	48	NA	WRIST-CLASP
ES	WEST GARTH GARDENS	48	NA	WRIST-CLASP
ES	WEST GARTH GARDENS	51	NA	EQUAL-ARM BROOCH (WITH PIN)
ES	WEST GARTH GARDENS	51	NA	ANNULAR BROOCH (WITH PIN)
ES	WEST GARTH GARDENS	61	NA	CRUCIFORM BROOCH
ES	WEST GARTH GARDENS	7	NA	SMALL-LOOGE BROOCH
ES	WEST GARTH GARDENS	7	NA	SMALL-LOOGE BROOCH
ES	WEST GARTH GARDENS	36	NA	EQUAL-ARM BROOCH (PARASENT)
ES	WEST GARTH GARDENS	52	NA	ANNULAR BROOCH (PN ABSENT)
ES	WEST GARTH GARDENS	52	NA	SMALL-LOOGE BROOCH
ES	WEST GARTH GARDENS	55	NA	SMALL-LOOGE BROOCH
ES	WEST GARTH GARDENS	55	NA	EQUAL-ARM BROOCH
ES	WEST GARTH GARDENS	55	NA	EQUAL-ARM BROOCH
ES	WEST GARTH GARDENS	55	NA	SMALL-LOOGE BROOCH
ES	WEST HESLERTON	50	AB	BROOCH REBULA
ES	WEST HESLERTON	8	AC	ANNULAR BROOCH
ES	WEST HESLERTON	11	GT	ANNULAR BROOCH
ES	WEST HESLERTON	91	GT	ANNULAR BROOCH
ES	WEST HESLERTON	43	FO	WRIST-CLASP(F)
ES	WEST HESLERTON	43	FO	WRIST-CLASP(F)
ES	WEST HESLERTON	43	FP	WRIST-CLASP(M)
ES	WEST HESLERTON	43	FP	WRIST-CLASP(M)
ES	WEST HESLERTON	NA	FD	ANNULAR BROOCH
ES	WEST HESLERTON	NA	GW	ANNULAR BROOCH
ES	WEST HESLERTON	41	GW	ANNULAR BROOCH
ES	WEST HESLERTON	46	GR	WRIST-CLASP
ES	WEST HESLERTON	20	EH	WRIST-CLASP
ES	WEST HESLERTON	12	BE	ANNULAR BROOCH
ES	WEST HESLERTON	13	AD	ANNULAR BROOCH
ES	WEST HESLERTON	17	AD	ANNULAR BROOCH
ES	WEST HESLERTON	50	AD	BROOCH SMALL-LONG
ES	WEST HESLERTON	57	AD	ANNULAR BROOCH
ES	WEST HESLERTON	16	AA	ANNULAR BROOCH
ES	WEST HESLERTON	43	FS	ANNULAR BROOCH
ES	WEST HESLERTON	109	BU	BROOCH CRUCIFORM
ES	WEST HESLERTON	31	CS	BROOCH CRUCIFORM
ES	WEST HESLERTON	10	AK	ANNULAR BROOCH
ES	WEST HESLERTON	4	AK	ANNULAR BROOCH
ES	WEST HESLERTON	12	CA	ANNULAR BROOCH
ES	WEST HESLERTON	12	CA	RING
ES	WEST HESLERTON	14	QFO	WRIST-CLASP(F)
ES	WEST HESLERTON	96	EG	BANGLE
ES	WEST HESLERTON	31	AC	BROOCH FLAT
ES	WEST HESLERTON	34	EL	RING CRUCIFORM
ES	WEST HESLERTON	34	NA	BROOCH FLAT
ES	WEST HESLERTON	101	NA	BUCKET BINDING
ES	WEST HESLERTON	101	NA	ANNULAR BROOCH
ES	WEST HESLERTON	101	NA	ANNULAR BROOCH
ES	WEST HESLERTON	14	CR	ANNULAR BROOCH
ES	WEST HESLERTON	104	AW	ANNULAR BROOCH
ES	WEST HESLERTON	11	BK	ANNULAR BROOCH
ES	WEST HESLERTON	16	BN	ANNULAR BROOCH
ES	WEST HESLERTON	11	DN	ANNULAR BROOCH
ES	WEST HESLERTON	16	NA	ANNULAR BROOCH
ES	WEST HESLERTON	24	EL	ANNULAR BROOCH
ES	WEST HESLERTON	101	AX	ANNULAR BROOCH
ES	WEST HESLERTON	43	FT	ANNULAR BROOCH
ES	WEST HESLERTON	101	AX	ANNULAR BROOCH
ES	WEST HESLERTON	160(M)	Q	WRIST-CLASP(R)
ES	WEST HESLERTON	14	CQ	ANNULAR BROOCH
ES	WEST HESLERTON	14	NA	ANNULAR BROOCH
ES	WEST HESLERTON	100(10)	NA	ANNULAR BROOCH
ES	WEST HESLERTON	10	AEF	BANGLE
ES	WEST HESLERTON	13	AD	ANNULAR BROOCH (PN)
ES	WEST HESLERTON	12	FB	ANNULAR BROOCH
ES	WEST HESLERTON	12	FB	ANNULAR BROOCH
ES	WEST HESLERTON	16	DP	ANNULAR BROOCH
ES	WEST HESLERTON	12	QI	ANNULAR BROOCH
ES	WEST HESLERTON	12	AA	ANNULAR BROOCH
ES	WEST HESLERTON	13	AE	TWEEZERS
ES	WEST HESLERTON	13	AE	WRIST-CLASP(F)
ES	WEST HESLERTON	100(10)	NA	WRIST-CLASP(F)
ES	WEST HESLERTON	13	AE	BUCKLE (PN)
ES	WEST HESLERTON	13	AE	WRIST-CLASP(M)
ES	WEST HESLERTON	12	CC	WRIST-CLASP(M)
ES	WEST HESLERTON	12	CC	RING
ES	WEST HESLERTON	13	AA	BROOCH CRUCIFORM
ES	WEST HESLERTON	13	AA	ANNULAR BROOCH
ES	WEST HESLERTON	17	GG	ANNULAR BROOCH
MS	BRANDON	53	GG	ANNULAR BROOCH
MS	BRANDON	22(3)	NA	SPATULA
MS	BRANDON	58(6)	NA	BINDING
MS	BRANDON	256(5)	NA	BAR</

[illegible][illegible]

275

277

[illegible]

[illegible]

