Chapter 1: Introduction

1.1 BACKGROUND

Most magmatic differentiation processes occur in regions within the Earth that are inaccessible to direct study. Crystal fractionation, partial melting, magma mixing, assimilation, and transport may occur simultaneously as magmas evolve, yet surficial exposures of their products frequently provide our only clues as to how these processes progress and interact at depth. Trace elements are particularly useful recorders of petrogenetic and geochemical histories due to equilibrium partitioning behavior independent of their concentrations. Unfortunately, knowledge of trace element partition coefficients (D_i^j, defined as [concentration of i in mineral j]/[concentration of i in coexisting melt]) in magmatic and fluid systems remains incomplete, and experimental determination of D values for all geologically relevant elements, compositional systems, pressures, and temperature conditions is not feasible. In the absence of more specific knowledge of partitioning behavior, partition coefficients are often assumed constant throughout simulated igneous processes. Such gross approximations, while reasonable representations of partitioning in some systems, can severely limit understanding of processes in others. Therefore theoretical models of magma evolution should account for the dynamic dependence of D values on both intensive and extensive magmatic system variables.

Partition coefficients can be complex functions of pressure, temperature, and phase composition, and covariances amongst these variables frequently obscure their respective influences on partitioning. This is illustrated in literature compilations of partitioning between silicate melts and olivine (Bedard, 2005) and plagioclase (Bedard, 2006), where efforts to relate *D* values to various parameters such as melt MgO and SiO_2 contents yield relatively loose correlations, suggesting more complex controls on partitioning behavior. In particular, efforts to separate the effects of the two most important variables, anorthite content (An) and temperature, in data for $D^{\text{plagioclase}}$ tend to show a considerable amount of scatter (Blundy and Wood, 1991). Many partitioning studies note empirical correlations between partition coefficients and various melt parameters (e.g., Kohn and Schofield, 1994; Mysen and Virgo, 1980; Toplis and Corgne, 2002), but such observations often have limited relevance for predicting absolute *D* values in other systems. Isolating the contribution of melt composition to partitioning behavior requires a targeted study that varies composition of the liquid phase while holding *T*, *P*, and mineral composition constant. Resulting systematic variations in *D* values then may be attributed to melt composition and rationalized in terms of an appropriate thermodynamic melt model.

1.2 THESIS APPROACH AND SCOPE

This work was motivated by a continuing need to systematically quantify the role of melt thermodynamics on trace element partitioning behavior between mineral and coexisting liquid phases in order to more accurately model magma differentiation. Formulating a general model of equilibrium partitioning applicable to any magmatic system requires rigorous treatment of both the liquid and solid phases. This study builds its explicit thermodynamic treatment of melt major oxide activities and trace element activity coefficients on the lattice strain model of Blundy and Wood (1994), which relates partition coefficients to temperature and an expression for crystal lattice strain energy proposed by Brice (1975). The lattice strain model relegates any melt compositional effects, along with mineral fusion and trace element energetics aside from lattice strain in the mineral phase, into a single fit parameter, the pre-exponential term D_o of equation (2.1). Our objective here is to specifically quantify the role of melt composition on partitioning behavior and possibly further elucidate the physical meanings of parameters used in the lattice strain model of partitioning.

This thesis is composed of two principal parts: (1) experimental determination of partition coefficients in a simple system to develop a general partitioning model explicitly accounting for melt thermodynamics, and (2) testing model predictive capabilities by comparing calculated anorthite/melt radium partition coefficients with actual measurements of D_{Ra}, for which no experimental data have been hitherto available. The experimental study of alkaline earth element partition coefficients (Mg, Ca, Sr, and Ba) for anorthite and a range of CMAS liquids described in chapter 2 calibrates a proposed general formalism for partitioning, equation (2.11), that augments existing crystal chemical modeling. Chapter 3 provides details of the Berman (1983) CMAS liquid thermodynamic model reoptimization used in chapter 2 and documents its improved performance in the 40–50 wt. % SiO_2 composition space of interest.

In the second part of this work we undertook the first-ever experimental study of radium partitioning between anorthite and a CMAS liquid. Chapter 4 describes a multi-step gas flow line built for containing radon and other radioactive daughter products emitted over the course of ^{226}Ra-bearing dynamic crystallization experiments. Also discussed are results of γ-spectroscopic analyses evaluating the extent of radium volatilization, which were conducted upon completion of the experimental work. Chapter 5 describes measurement of ^{226}Ra experimental run products by ion microprobe and compares the partitioning results with model predictions. The 1600 year half-life of ^{226}Ra makes it an important chronometer of relatively recent (<8000 years) magmatic processes, and ^{226}Ra excesses relative to its radioactive parent ^{230}Th, where the activity ratio (^{226}Ra/^{230}Th)>1, have been recorded for young volcanics across a wide range of geologic environments (Turner et al., 2001). The significance of these data for radium transport and storage in plagioclase-bearing systems are discussed, as are implications for model predictions of radium partitioning behavior between clinopyroxene and melt within the mantle melting column. Proposed directions for future work are outlined in chapter 6.

Appendix material is divided into six sections. Appendix 1 provides additional description of the experimental design and analytical approaches adopted for the study of chapter 2. Partitioning data from compositions doped at different concentrations of Ba and measured at different locations within anorthite crystals (centers vs. edges) are compared. Ion microprobe data for Be^{2+} partitioning are presented and contrasted with previous D_{Be} plagioclase/melt measurements (Bindeman et al., 1998). Appendix 2 shows the complete data set, in the form of two-dimensional (2-D) compositional maps of crystal transects and surrounding glass, used to calculate D values reported in chapter 2. Appendix 3 documents the crystal growth dynamics throughout the controlled cooling experiments of chapter 2 with analyses of experiments quenched at intermediate times during the cooling history. Extent of anorthite crystallization and evolution of melt heterogeneities are tracked, and important anorthite trace element (Mg, Sr, and Ba) contents in glass adjacent to crystals have been mapped to investigate the possibility of concentration gradient development. Since crystals can incorporate elevated, nonequilibrium amounts of trace elements into their structures under rapid cooling conditions (e.g., LaTourrette, 1993; Watson and Liang, 1995), anorthites were grown from three representative compositions of chapter 2 by lowering furnace temperature 20 °C/hr to determine the effect of cooling rate on alkaline earth element partition coefficients in these systems. *D* values from those experiments are slightly higher than those from the 2 °C/hr cooling experiments considered in chapter 2, but the effect of cooling rate is minimal.

Appendix 4 presents anorthite/melt partitioning data from a CAI (meteoritic Ca, Al-rich inclusion)-like CMAS+Ti composition based on that of Simon et al. (1994) and compares results with those of composition 2b-2 in chapter 2. The presence of 2 wt. % titanium in the melt apparently has little impact on divalent element partitioning behavior. Pronounced cathodoluminescence was observed by scanning electron microscope (SEM) in anorthites grown from the CMAS+Ti composition and investigated with a series of doping experiments, but attempts at replicating the phenomenon proved unsuccessful. Appendix 5 consists of data from a preliminary study that measured anorthite/melt divalent element partition coefficients grown from liquids ranging from 40 to 60 wt. % SiO_2. Erratic Na and increasing Si solid solution in anorthite run products rendered these experiments unsuitable for isolating melt effects on partitioning but produced discernable systematic partitioning trends. A complete list of experiments discussed in the text of this thesis is provided in appendix 6.