Alkaline Earth Element Partitioning in Simplified Magmatic Systems

Thesis by

Sarah Ann Miller

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2007

(Defended December 6, 2006)

© 2007

Sarah Ann Miller

All Rights Reserved

Acknowledgments

First and foremost, I would like to thank my research advisors Paul Asimow and Don Burnett for their guidance, support, and mentorship during my time at Caltech. Their continued enthusiasm for the fundamental nature of the work we were doing was inspiring and motivating. I also benefited from their willingness to undertake the more adventurous project of radium partitioning, which required more attention to safety considerations than the typical geoscience experimental investigation. Thanks to my thesis committee (Paul Asimow, Don Burnett, Ed Stolper, George Rossman, and John Eiler) for attending TAC meetings over the years and their casting sharp eyes over this thesis document. I am grateful to George Rossman, my academic advisor, for always keeping his office and lab doors open for questions of all sorts and generously making his analytical equipment available. I would also like to extend a special note of appreciation to George and John Eiler; it was a pleasure to TA the classes they taught and observe their distinctive, effective pedagogical styles. They deserve recognition not only for engaging teaching but their behind-the-scenes availability and support of the TAs with whom they work. Thank you to all the attendees of Petrology Reading Group over the years for the memories-watch out for sediments on the Earth's core and guard your papers closely if you don't remember what is in them!

Julie Heather was a constant source of experimental and analytical know-how; I am also thankful for the expertise shared by Ma Chi, John Beckett, Mike Baker, Jed Mosenfelder, Harold Connolly, Jr., Liz Miura Boyd, Caroline Seaman, and Lindsey Hedges. Haick Issaian and André Jefferson in the Safety Office went above and beyond the call of duty to help handle and characterize the radium source material. By the same token, I am grateful to our collaborators Ian Hutcheon and Doug Phinney at Lawrence Livermore National Laboratory for hosting the radium analytical work. Thanks also go to Ric in the Machine Shop, the Bio stockroom, and the Carpentry Shop. Jan Haskell, Carolyn Porter, Marcia Hudson, Michelle Medley, and Terry Gennaro made getting things done within the division infinitely easier.

A special thank you goes out to all the friends I made at Caltech, both inside and out of GPS, during my time here and who know who they are. I also thank my family and Nathan Lamarre-Vincent, husband and new father extraordinaire, for his unflagging confidence and support as well as his strength of character, raw determination, keen scientific mind, generous spirit, and sense of humor, all of which are a constant source of inspiration to me. Nothing is written.

-Lawrence of Arabia (1962)

Abstract

Trace element distributions between mineral and melt phases have proven to be important recorders of igneous differentiation histories, but this utility depends on thorough understanding of their partitioning behavior. We propose a theory for crystalmelt trace element partitioning that considers the energetic consequences of crystal-lattice strain, of multi component major-element silicate liquid mixing, and of trace element activity coefficients in melts. We demonstrate application of the theory using newly determined partition coefficients for Ca, Mg, Sr, and Ba between pure anorthite and seven CMAS liquid compositions at 1330 °C and 1 atm. By selecting a range of melt compositions in equilibrium with a common crystal composition at equal liquidus temperature and pressure, we have isolated the contribution of melt composition to divalent trace element partitioning in this simple system. The partitioning data are fit to Onuma curves with parameterizations that can be thermodynamically rationalized in terms of the melt major element activity product $(a_{A12O3})(a_{SiO2}^2)$ and lattice strain theory modeling. Residuals between observed partition coefficients and the lattice strain plus major oxide melt activity model are then attributed to non-ideality of trace constituents in the liquids. The activity coefficients of the trace species in the melt are found to vary systematically with composition. Accounting for the major and trace element thermodynamics in the melt allows a good fit in which the parameters of the crystal lattice strain model are independent of melt composition.

We also present the first experimental measurements of mineral-melt radium partitioning. Ion probe analyses of coexisting anorthite and CMAS glass phases produce a molar $D_{Ra} = 0.040 \pm 0.006$ and $D_{Ra}/D_{Ba} = 0.23$ at 1400 °C and 1 atm. Our results indicate that lattice strain partitioning models fit the divalent (Ca, Sr, Ba, Ra) partition coefficient data of this study well, supporting previous work on crustal melting and magma chamber dynamics that has relied on such models to approximate radium partitioning behavior in the absence of experimentally determined values.

Table of Contents

Acknowledgmer	nts	iii
Abstract		vi
Table of Content	ts	viii
List of Figures a	nd Tables	ix
Chapter 1	Introduction	1
Chapter 2	Determination of Melt Influence on Divalent Element Partitioning between Anorthite and CMAS Melts	6
Chapter 3	Reoptimization of the Berman (1983) CMAS Liquidus Model in Anorthite Phase Space	51
Chapter 4	Experimental Techniques for Radium Partitioning Measurements	64
Chapter 5	Experimental Study of Radium Partitioning between Anorthite and Melt at 1 atm	86
Chapter 6	Future Work	99
Appendix 1	Experimental Design	103
Appendix 2	Crystal Selection	112
Appendix 3	Crystal Growth Dynamics	123
Appendix 4	CAI Composition: Divalent Element Partitioning and Cathodoluminescence	147
Appendix 5	Anorthite-Melt Partitioning and Varying Melt Silica Contents	158
Appendix 6	Thesis Run Table	167
References		170

Figures and Tables

Chapter 2		Page
Figure 2.1	Study liquid compositions within the CMAS tetrahedron	12
Table 2.1	Glass compositions from controlled cooling experiments	23
Table 2.2	Anorthite compositions from controlled cooling experiments	23
Figure 2.2	Back-scattered electron image of representative sample 2b-3-2	24
Table 2.3	Normalized CMAS melt compositions and alkaline earth element partition coefficients	26
Figure 2.3	Relationship between D^{m}_{MgO} and melt activity product for Mg^{2+} partitioning onto IV and VIII anorthite coordination sites	31
Figure 2.4	Prediction of Mg fractionation between IV (T) and VIII (M) sites in anorthite	32
Figure 2.5	Comparison of model parameterizations to molar partition coefficients between anorthite and seven melt compositions	36
Table 2.4	Comparison of measured data with model parameterization predictions of anorthite/melt partition coefficients	39
Figure 2.6	Calculated melt γ_{BaO} and γ_{SrO} values plotted with γ_{CaO} for the seven liquid compositions	42
Figure 2.7	Exchange partition coefficients for Ca-Sr, Ca-Ba, and Sr-Ba.	44
Figure 2.8	Relationship between D ^m and optical basicity	46

Chapter 3

Page

Table 3.1	Anorthite and liquid oxide component standard state properties and heat capacity equation coefficients	56
Figure 3.1	Literature anorthite-CMAS melt liquidus data	58
Figure 3.2	Reduction of $(\Delta T_L)^2$ as a function of Margules parameter adjustments made during reoptimization	60
Table 3.2	Reoptimized Margules parameters for a portion of the anorthite liquidus field in CMAS	61
Figure 3.3	Comparision of (ΔT_L) versus melt X CaO for experimental and predicted anorthite liquidus temperatures before and after reoptimization	62

Chapter 4

Figure 4.1	²³⁸ U decay series ending in stable ²⁰⁶ Pb	66
Figure 4.2	Flow line configuration for activated charcoal heating pre- treatment under vacuum prior to sample runs in furnace	76
Figure 4.3	Flow line for ²²² Rn removal from gas exiting furnace	78
Figure 4.4	Geiger counter and γ -spectrometry measurement of post- experiment ²²⁶ Ra activity with furnace thermal profile	81

Chapter 5

Figure 5.1	Back-scattered electron image of experiment 2-1*-Ra	89
Figure 5.2	Ion probe mass scan over region surrounding mass 226 for glass of radium-free and radium-bearing samples	91
Table 5.1	Starting material, standard, radium-free, and radium-bearing compositions and alkaline earth element partition coefficients	95
Figure 5.3	Onuma curve (D vs. ionic radius) of Ca, Sr, Ba, and Ra molar partition coefficients	97

Figure A1.1	Crystals grown isothermally and by dynamic crystallization	103
Figure A1.2	Controlled cooling path of dynamic crystallization experiments	104
Table A1.1	Comparison of three CMAS2 anorthite/melt molar partition coefficient data sets for Ba, Sr, and Be	106
Figure A1.3	Anorthite/silicate melt divalent element partitioning of tetrahedral and octahedral coordination site occupancy	109
Figure A1.4	Major element rim to rim CMAS2b crystal traverses	111

Appendix 2

Figure A2.1	BSE imaging of locations of CMAS2b crystal 2-D grid analyses	112
Figure A2.2	Sample 2b-1-2; MgO, SrO, BaO maps (wt. %)	114
Figure A2.3	Sample 2b-2-2: MgO, SrO, BaO maps (wt. %)	115
Figure A2.4	Sample 2b-3-2: MgO, SrO, BaO maps (wt. %)	116
Figure A2.5	Sample 2b-4-2: MgO, SrO, BaO maps (wt. %)	117
Figure A2.6	Sample 2b-5-2: MgO, SrO, BaO maps (wt. %)	118
Figure A2.7	Sample 2b-6-2: MgO, SrO, BaO maps (wt. %)	119
Figure A2.8	Sample 2b-7-2: MgO, SrO, BaO maps (wt. %)	120
Figure A2.9	Transects summarizing zoning trends in the A2.2 crystals	122

Figure A3.1	BSE crystal images quenched at three intermediate time points	123
Table A3.1	Starting compositions of glasses fused for three hours	124
Table A3.2	CMAS glass compositions at three intermediate time steps	125
Table A3.3	Final melt compositions after 96.5 hours	125
Figure A3.2	Crystal fraction increases as a function of time and temperature	126
Figure A3.3	Heterogeneity index (HI) for melt major element oxide contents	129
Table A3.4	Melt Al ₂ O ₃ variations relative to analytical error	130
Figure A3.4	BSE images of melt grid locations for runs quenched at 67 hours	132
Figure A3.5	Sample 2b-1-5: grid melt maps of MgO, SrO, and BaO data	133
Figure A3.6	Sample 2b-4-5: grid melt maps of MgO, SrO, and BaO data	134
Figure A3.7	Sample 2b-7-5: grid melt maps of MgO, SrO, and BaO data	135
Table A3.5	JEOL JXA-8200 and JEOL 733 electron microprobe analytical error for MgO, SrO, and BaO	137
Figure A3.8	BSE imaging of 2-D grid areas for 20 °C/hr cooling experiments	137
Figure A3.9	Sample 2b-1-7: MgO, SrO, BaO maps (wt. %)	138
Figure A3.10	Sample 2b-4-7: MgO, SrO, BaO maps (wt. %)	139
Figure A3.11	Sample 2b-7-9: MgO, SrO, BaO maps (wt. %)	140
Figure A3.12	Trace element summary transects from 20 °C/hr cooling runs	141
Table A3.6	Comparison of 20 °/hr to 2°/hr Mg, Sr, Ba D rim values	142
Table A3.7	Cpx-melt D_{U} and D_{Th} for $\ 0.1 \ ^{\circ}C/hr$ and $1.7 \ ^{\circ}C/hr$ cooling	143
Table A3.8	Lattice strain parameterizations for 2 °C/hr and 20 °C/hr cooling	144
Figure A3.13	D vs. ionic radius curves for 2 °C/hr and 20 °C/hr cooling data	146

Table A4.1	Glass and anorthite compositions for 224SAM run products	147
Table A4.2	D values and lattice strain parameterization of anorthite/melt data of CAI (CMAST) and run 2b-2-2 (CMAS) compositions	148
Figure A4.1	SEM cathodoluminescence intensity of 224SAM21 anorthite	151
Figure A4.2	224SAM21 anorthite correlation plots against MgO content	152
Table A4.3	Summary table of cathodoluminescence reconnaissance study	153
Figure A4.3	SEM CL intensity images of Ti- and Eu-bearing experiments	155
Figure A4.4	SEM-CL intensity images of Ti+Eu-, Mn-, and Ge-bearing runs	156
Figure A4.5	SEM-CL intensity of anorthites with varying excess silica	157

Appendix 5

Figure A5.1	CMAS1 melt compositions projected onto the CAS ternary	159
Table A5.1	Initial CMAS1 melt compositions	160
Table A5.2	CMAS1 anorthite compositions	160
Table A5.3	CMAS1 final glass compositions	161
Figure A5.2	Excess silica component []Si $_4O_8$ in CMAS1 anorthites	161
Figure A5.3	Glass Na ₂ O content change as a function of time in furnace	162
Figure A5.4	CMAS1 D^{molar}_{MgO} and melt activity products relationship for Mg ²⁺ partitioning onto IV and VIII anorthite coordination sites	164
Table A5.4	Anorthite/melt partitioning in CMAS1 compositions at ~1400 °C	164
Table A5.5	Lattice strain model parameterization of CMAS1 divalent element (Mg, Ca, Sr, Ba) partitioning data	166
Figure A5.5	CMAS1 alkaline earth element D vs. ionic radius curves	166

Table A6.1Thesis run table

167