Chapter 6: Future Work

A logical next step in extending this work might be assessing its performance modeling natural liquids using a thermodynamic melt activity model such as MELTS (Ghiorso and Sack, 1995) at 1 atm, where the most literature partitioning data are available and the MELTS model is best constrained. However, continued progress towards a universal model of partitioning that incorporates lattice strain treatment for crystal chemistry depends on addressing several key issues.

(1) Clarifying the physical meaning of lattice strain parameters. As discussed in chapter 2, the parameters r_o (site ideal ionic radius) and E (effective Young's modulus of the site) were originally postulated to be purely crystal chemical properties (Blundy and Wood, 1994; Brice, 1975). More recent work has suggested an apparent additional dependence of these parameters on melt chemistry (e.g., Blundy and Dalton, 2000; Prowatke and Klemme, 2005; van Westrenen et al., 2000), a potentially considerable complication that could preclude use of the lattice strain formalism as a simple representation of mineral structure controls on partitioning. While parameterizations in chapter 2 demonstrate that the anorthite-CMAS melt partitioning data presented in this work can be modeled with r_o and E remaining solely crystal chemical parameters, systematic investigations into the nature of these parameters in other systems are necessary to fully appreciate their physical significance and determine their role in constructing more universal partitioning models.

(2) A tricky challenge to full thermodynamic descriptions of trace element chemistry in both solid and liquid phases lies in the paucity of thermodynamic data for endmembers at the trace element-rich end of mineral solid solutions series and for trace element bearing melt species, the identities and abundances of which may be unknown (Hess, 1995). Existing high quality melt thermodynamic models for natural (such as MELTS (Ghiorso and Sack, 1995) and its subsequent variations) and simple systems (Berman, 1983; Berman and Brown, 1984) only address the mixing behaviors of major and minor element constituents, leaving the behavior of many trace species uncharacterized. Our results demonstrate how the partitioning model presented in chapter 2 may be applied to obtain measurements of melt trace constituent activity coefficients in carefully designed experiments. However, calculating *D* values from this model in other systems requires independent knowledge of trace element energetics. This lack of thermodynamic data on trace species remains a hurdle to using the partitioning model presented in chapter 2 to predicting trace element *D* values in systems where activity coefficients are unknown. Poor accuracy of some major species activity coefficients is a problem in some parts of melt composition space, as well.

(3) Due to relative experimental ease, the data set for partitioning behavior at 1 atm is large compared to that at higher pressures. Silicate melts are over an order of magnitude more compressible than silicate minerals (Lange and Carmichael, 1990), but discerning how this influences partitioning requires separating the effects of pressure, temperature, and melt composition. The hazards of failing to explicitly account for pressure effects in some cases may be mitigated by the fact that temperature and pressure, which both

increase with depth below the Earth's surface, often have opposite effects on partitioning. Nonetheless, pressure effects have been identified (e.g., Bedard, 2006; Blundy and Wood, 2003b; Colson and Gust, 1989; Fujinawa and Green, 1997) and adjustments to existing simple partitioning models have been proposed, such as in the case of plagioclase (Vander Auwera et al., 2000). Oxygen fugacity is another intensive variable not addressed by models that consider only homovalent substitutions but could be incorporated into a broader treatment of partitioning using the Wood and Blundy (2001) expressions for *D* dependence on cation valence state.

(4) As the multiple site occupancy of Mg^{2+} in anorthite (chapter 2) demonstrates, further development and calibration of partitioning models based on crystal lattice strain theory will require careful consideration of cation site occupancy. Fitting model expressions to partitioning data ideally constrains the shape of the Onuma curve (Onuma et al., 1968) with cation radii both larger and smaller than the ideal site size, and should be based on more data points than the number of variables being parameterized. In the cases of minerals where a limited number of isovalent cations may substitute onto a given site, quantifying the population of a cation that predominately prefers a different site, yet still is present in low abundance, can increase the data set available for modeling partitioning on the site of interest. Likewise, correct identification of substituting cation valence state is an important consideration when calibrating lattice strain models to experimental partitioning data sets. Advances in spectroscopic methods such as EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge

Structure) may offer new information about such cation behavior within both crystalline and amorphous phases that will improve partitioning model precision.