FINAL TECHNICAL REPORT

Grantee: UNIVERSITY OF CALIFORNIA, SANTA BARBARA
Institute for Crustal Studies
Santa Barbara, CA 93106

Grant: DE-FG03-01ER15210

Title: Mesoscale Molecular Dynamics of Geomaterials: The Glass Transition, Long-range Structure of Amorphous Silicates and Relation between Structure, Dynamics and Properties of Geomaterials at Elevated Temperature and Pressure

Principal Investigator: Frank J. Spera
805-893-4880; Fax 805-893-8649
E-mail: spera@geol.geol.ucsb.edu

Objectives: Our aims were (1) Large particle-number Molecular Dynamics (MD) simulations of molten silicate and aluminosilicate geomaterials (e.g., $\text{CaAl}_2\text{Si}_2\text{O}_8$, MgSiO_3 , Mg_2SiO_4) with emphasis on understanding the connection between atomic structure and properties at temperatures and pressures characteristic of Earth's mantle (2) Study of the transport properties and equations of state for silicate liquids based on the MD results (3) Development of geochemical models for the evolution of crustal magma bodies undergoing simultaneous assimilation, fractional crystallization, periodic recharge and periodic eruption and application to magmatic systems (4) Study of current-day rates of generation and eruption of magma on earth

Results: (1) The MD code was modified to take account of a variety of interatomic potentials. These include Born-Mayer-Huggins forms, van der Waals forms and valence angle three body terms. The code is optimized to run on massively parallel environments; systems with 10^5 - 10^6 particles can be simulated for durations up to 10 nanoseconds. (2) Subsidiary codes have been written to (a) develop comprehensive first coordination sphere statistics for all atoms around all other atoms for each state point (circa 60 per composition) for each composition (b) compute tracer diffusivities of all atoms for each MD simulation (c) calculate shear viscosity based on Green-Kubo relations for temporal decay of the off-diagonal stress auto-correlation function. This procedure was developed by based on high-resolution MD simulations of molten NaCl because its laboratory properties are well-known and an excellent pair potential is available (3) Completion of MD simulations using 10^4 particles for 10 nanoseconds for the compositions Mg_2SiO_4 and MgSiO_3 using the transferable potential from Matsui (1982 and 1984 versions), $\text{CaAl}_2\text{Si}_2\text{O}_8$ and MgSiO_3 using the potential of Oganov. The pressure-temperature range of the simulations covers the region 2500-6000 K and 10^{-4} -140 GPa for each composition. About 60 state points (P, T) are computed for each composition studied (4) Modification of code to computationally handle modeling of

shock wave propagation (5) Development of method to study liquid-liquid (amorphous state) phase transitions and search for such transitions in molten MgSiO_3 and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (6) Derivation of macroscopic thermodynamic equation of state of all liquids studied by MD method. This facilitates the application of MD data to real geochemical problems (7) Development of magma chamber models to account for fractional crystallization, magma recharge and assimilation during magma body evolution. Detailed results are presented in the following list of peer-reviewed publications. Currently, additional manuscripts based on the results from this research are being prepared for submission to international peer-reviewed journals.

Publications:

Fowler, S., Bohrsen, W., and F.J. Spera, 2004, Magmatic Evolution of the Skye Igneous Centre, Western Scotland: Modeling of Assimilation, Recharge and Fractional Crystallization. *Journal of Petrology*, 45, 2481-2505.

Bohrson, W. A. & Spera, F. J. (2003). Energy-constrained open-system magmatic processes IV: Geochemical, thermal and mass consequences of energy-constrained recharge, assimilation and fractional crystallization (EC-RAFC). *Geochemistry, Geophysics, Geosystems* 4(2), 2002, doi: 10.1029/2002GC000316.

Spera, F., Bohrsen, W., 2004, Open-System Magma Chamber Evolution: an Energy-constrained Geochemical Model Incorporating the Effects of Concurrent Eruption, Recharge, Variable Assimilation and Fractional Crystallization (EC-ERAXFC) part 1, *Journal of Petrology*, 45, p2459-2480

Bohrson, W., F.J. Spera, 2004, Open-System Magma Chamber Evolution: an Energy-constrained Geochemical Model Incorporating the Effects of Concurrent Eruption, Recharge, Variable Assimilation and Fractional Crystallization: part 2, *Journal of Petrology*, 45, p.2480-2501.

White S. M., J. A. Crisp, F. J. Spera, 2006, Long-term volumetric eruption rates and magma budgets, *Geochem. Geophys. Geosyst.*, 7, doi:10.1029/2005GC001002.

Bohrson, Wendy A., Spera, Frank J., Fowler, Sarah J., Belkin, Harvey E., De Vivo, Benedetto, Rolandi, Guiseppe, "Volcanism in the Campania Plain: Vesuvius, Campi Fleggeri and Ignimbrites" which will be published by Elsevier in the Series "Developments in Volcanology" (De Vivo B., Edt), 2005.

Spera, F., Yuen, D., Giles, G., 2006, Tradeoffs in Chemical and Thermal Variations in the Post-perovskite Phase Transition: Mixed phase regions in the Deep Lower Mantle? *Physics of Earth and Planetary Interiors*, in press, 2006

Fowler, Sarah J., Spera, Frank J., Bohrsen, Wendy A., Belkin, Harvey, De Vivo, Benedetto, 2006, "Phase Equilibria Constraints on the Chemical and Physical Evolution of the Campanian Ignimbrite", *Journal of Petrology*, in Press

Spera, F., Bohrsen, W, Till, C., Fowler, S., 2006, Partitioning of trace elements among coexisting crystals, melt and supercritical fluid during isobaric fractional crystallization and fractional melting, *American Mineralogist*, submitted May, 2006

Spera, F., Nevins, D., Ghiorso, M, 2006, Equation of state for molten silicates: MgSiO_3 , Mg_2SiO_4 , $\text{CaAl}_2\text{Si}_2\text{O}_8$ based on Molecular Dynamics simulations, to be submitted *Geochimica et Cosmochimica Acta*

Cutler, I, 2005, Thermodynamical, Structural, and Transport Properties of MgSiO_3 : A Molecular Dynamics Study, MS thesis, University of California, Santa Barbara, 123p.

Nevins, D, Spera, F., The computation of shear viscosity using Molecular Dynamics, to be submitted to *Molecular Simulation*