NEW MEDIA: SOFTWARE

Igneous Petrology

Glenn A. Gaetani

Within the Earth, the generation, migration, and crystallization of magma is an important mechanism for mass and energy transfer. The ages and properties of magmas that have erupted at the surface (lavas) or cooled slowly within the crust (intrusive rocks) provide direct information on the chemical and thermal evolution of Earth's interior over geologic time. The principles of physical chemistry were first used to help decipher the igneous rock record in the early part of this century, when petrologists began performing phase equilibrium experiments on geologic materials (*1*). More recently, there has been a need for quantitative, thermodynamically based models capable of simulating igneous processes not readily reproduced in the laboratory. When combined with field and laboratory studies, these models can illuminate the processes that shape the solid Earth.

MELTS
by M. S. Ghiorso, R. O. Sack, M. Hirschmann, P. D. Asimow
http://gneiss.geology.washington.edu/~ghiorso/MeltsWWW/Melts.html

MELTS is a thermodynamically based software package developed by Mark Ghiorso and co-workers (*2*, *3*) to model chemical mass transfer in magmatic systems. Given the bulk composition and conditions [pressure (*P*), temperature (*T*), oxygen fugacity (f_{O_2}), and so forth] of a magmatic system, MELTS determines the identities, proportions, and compositions of the equilibrium phases through an optimization of one of the thermodynamic potentials of the system [Gibbs free energy (*G*), enthalpy (*H*), entropy (*S*), and so forth]. In the case where pressure, temperature, and bulk composition for a given magmatic system are specified, MELTS would minimize the Gibbs free energy according to

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

where V is volume, μ_i is the chemical potential of system component i, and n_i is the number of moles of system component i.

The MELTS software package incorporates models for the compositional dependencies of the thermodynamic potentials of solid phases and magmatic liquids (solution models) as functions of pressure and temperature. Each of these models, as well as the thermodynamic database used in MELTS, can be directly accessed through the MELTS supplemental calculator (*4*). MELTS was formulated to be applicable to a wide range of petrologic compositions and processes and has been applied to problems as diverse as cooling and crystallization of magmatic liquids within the parent bodies of meteorites (*5*) and the crystallization of granitic liquids (*6*). MELTS is equally well suited to simulating the generation of magmas through the melting of preexisting rocks or the crystallization of magmas as they cool in the crust, because it determines the equilibrium phases for a reversible process (in which a system is taken from one equilibrium state to another along a path connecting intermediate equilibrium states).

The broad range of MELTS' utility comes at a price, however, and in some cases its accuracy is surpassed by models designed for specific petrologic applications. Several recent studies have compared the results of MELTS calculations to the results from experiments or from other models, illustrating the range of MELTS' applicability as well as its limitations.

The partial melting of peridotite, a rock that constitutes the bulk of Earth's upper mantle, is a mechanism by which the mantle cools and changes composition. At ocean-floor ridges, tectonic forces pull the plates apart and mantle peridotite ascends to fill the void, a process known as passive upwelling. As the peridotite decompresses, it partially melts, generating basaltic magmas that rise and cool to form new oceanic crust. Initially, it was assumed that basalt remained in chemical equilibrium with its solid peridotite residue until partial melting was complete (batch melting) (*7*, *8*). High-pressure experiments are well suited to simulate batch melting, and the compositions of peridotite partial melts have been determined with both the forward approach, in which a peridotite is partially melted, and the inverse approach in which basalts that crystallize a peridotite mineral assemblage at high pressures are identified experimentally (*9–17*). Over the past decade, however, recognition of the existence of systematic compositional variations in ocean floor basalts globally (*18*) and in situ determinations of the trace element compositions of the minerals in residual peridotites (*19*) have shown that partial melting is not a batch process. It is, instead, a dynamic process in which magmas segregate from their solid residue almost as soon as they form. Basalts erupted onto the ocean floor represent a blend of partial melts, formed over a range of upper mantle conditions, from peridotites with variable bulk compositions. This type of polybaric partial melting is a complex process that cannot be reproduced in the laboratory. Models that accurately predict the composition of a peridotite partial melt as a function of pressure, temperature, and peridotite bulk composition, however, would allow direct constraints to be placed on the melt generation process.

To test the accuracy of MELTS when used for this type of calculation, Hirschmann *et al.* (*20*) compared the results from isobaric batch melting calculations, with MELTS to the results from peridotite partial melting experiments performed at 1.0 GPa (*14*, *15*). There are significant discrepancies between the calculated and experimentally determined partial melt compositions although, in general, the compositional trends are similar. At a given percentage of partial melting the MELTS calculations predict temperatures that are systematically high by ~100°C (see the figure, panel A), a significant fraction of the 140°C experimental temperature range. The SiO_2 concentrations predicted by MELTS are systematically low by ~3 weight % (panel B), whereas the predicted concentration of MgO is systematically high by the same amount (panel C). There is reasonable agreement between the calculations and the experiments for the concentration of FeO* (total Fe as FeO), but MELTS is low with respect to Al_2O_3 and high with respect to Na_2O (panel C). The most probable explanation for these discrepancies is a tendency for MELTS to overestimate the amount of the mineral orthopyroxene [$(Mg,Fe)_2Si_2O_6$], at the expense of the mineral olivine [$(Mg,Fe)_2SiO_4$], in the residue from melting (*20*). In another study (*17*), peridotite melting experiments were compared to the results from calculations with MELTS and to the models of Niu and Batiza (*21*) and of Kinzler and Grove (*13*, *22*), both of which were designed specifically to model peridotite partial melting. As in the previous example, this study (*17*) found that there were significant discrepancies between the MELTS calculations and the experiments with respect to oxide concentrations, but that the relative compositional trends agreed. The authors concluded that the model of Kinzler and Grove (*13*, *22*) provides the most accurate peridotite partial melt compositions.

In addition to the complexities associated with the partial melting process, nearly all magmas experience some amount of cooling and crystallization during their ascent to Earth's surface. The compositional path followed by a magmatic liquid during crystallization (liquid line of descent) may reflect either a closed system process, in which crystals and liquid remain in equilib-

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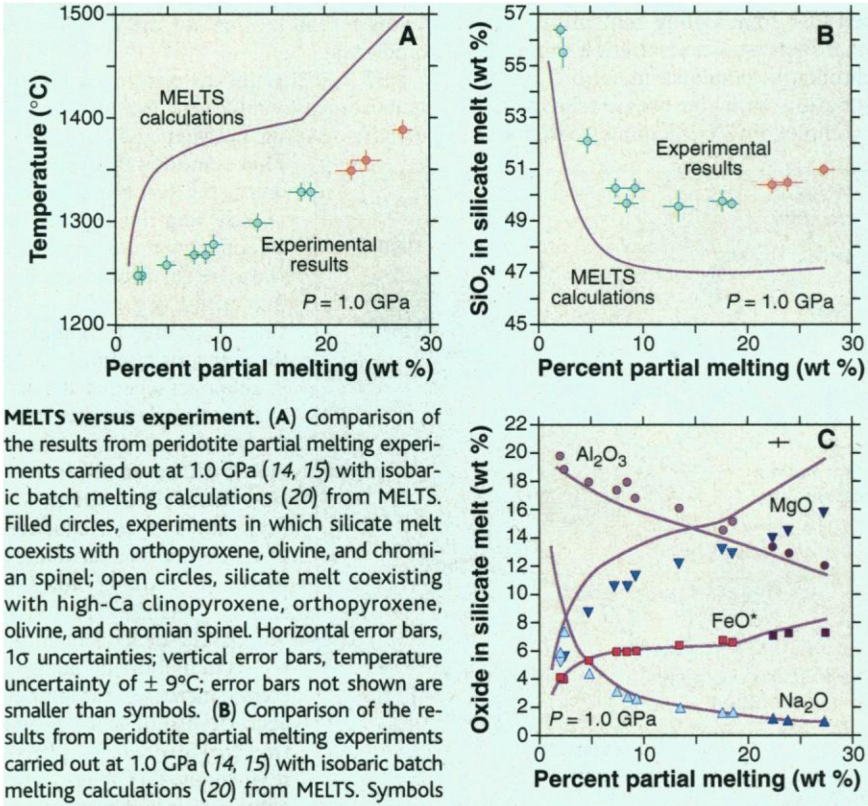
The author is in the Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180, USA. E-mail: gaetag@rpi.edu

rium during cooling, or an open system process, in which the crystals are continuously removed from contact with the liquid as they form (fractional crystallization). Models capable of accurately calculating low-pressure liquid lines of descent are necessary to constrain both the conditions under which magmas crystallize and the nature of the partial melting process that produced them (*18*, *23*). MELTS can model both open- and closed-system crystallization. Yang *et al.* (*24*) compared the results from open system calculations carried out with a number of different models, most of which were developed specifically for liquid line of descent calculations. They found that the results from the MELTS calculations indicate higher concentrations of SiO_2 and CaO, and lower FeO at a given MgO content relative to the results from the other models. Identifying the model that gives the most accurate result is difficult because most are designed to simulate fractional crystallization, which is hard to reproduce experimentally.



MELTS versus experiment. (A) Comparison of the results from peridotite partial melting experiments carried out at 1.0 GPa (*14*, *15*) with isobaric batch melting calculations (*20*) from MELTS. Filled circles, experiments in which silicate melt coexists with orthopyroxene, olivine, and chromian spinel; open circles, silicate melt coexisting with high-Ca clinopyroxene, orthopyroxene, olivine, and chromian spinel. Horizontal error bars, 1σ uncertainties; vertical error bars, temperature uncertainty of ± 9°C; error bars not shown are smaller than symbols. **(B)** Comparison of the results from peridotite partial melting experiments carried out at 1.0 GPa (*14*, *15*) with isobaric batch melting calculations (*20*) from MELTS. Symbols are as in (A). **(C)** Al_2O_3, MgO, FeO*, and Na_2O in silicate melts, comparing the results from peridotite partial melting experiments carried out at 1.0 GPa (symbols) (*14*, *15*) with isobaric batch melting calculations (*20*) from MELTS (solid curves). Error bars at upper right represent average 1σ uncertainties.

There are calculations for which MELTS or the MELTS supplemental calculator are uniquely suited. Within its limitations, MELTS has been used successfully by Asimow and co-workers to carry out rigorous thermodynamic calculations for complex natural systems, providing insights into the energetics of phase transitions in mantle peridotite (*25*), and the rate at which partial melt is produced during decompression of mantle peridotite (*26*). In another study the partial molar volume of SiO_2 in silicate melts at pressures up to 3.5 GPa was assessed experimentally by determining the pressure-dependent change in the solubility of quartz in a silicate melt at constant temperature (*27*). This calculation requires knowledge of the chemical potential of SiO_2 in β-quartz at the conditions of each experiment, and of the chemical potential of SiO_2 in the melt at 0.1 MPa, as a function of composition, both of which were calculated with the MELTS supplemental calculator. The uncertainties associated with these calculations are small enough (± 400 to 500 J/mol) to allow accurate determination of the partial molar volume of SiO_2 in silicate liquids at upper mantle conditions (*27*).

Despite its accuracy limitations for certain applications, the MELTS approach has some significant advantages over models that are less thermodynamically rigorous. First, the fact that MELTS is an internally consistent model that allows magmatic phase equilibria to be related to thermodynamic variables gives it some unique capabilities. Peridotite partial melting beneath oceanic spreading ridges, for example, is thought to occur at constant entropy, and only a model in which phase compositions are related directly to the energetics of the system is capable of simulating this process correctly. Second, because it is based on thermodynamically valid functions, it should have predictive capabilities for magmatic systems that fall outside of the pressure, temperature, and compositional range of existing experiments. This means that in principle MELTS could be used to model any magmatic system for which high-quality thermochemical data and solution models are available. In practice, however, there may be alternative models available that are more accurate than MELTS for carrying out certain types of calculations. In summary, it is too early to know whether a single thermodynamic model that can be applied to all magmatic systems represents the future of igneous petrology, but MELTS, and models like it, represent an ambitious step toward understanding the processes that shape the solid Earth.

References and Notes

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