

# The thermodynamics of mineral-melt equilibria in the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>

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## Introduction

The system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> is widely used as an analogue to naturally occurring basaltic liquids. Existing phase equilibria studies cover only a fraction of the range over which liquids and crystals coexist in this system. The power of a thermodynamic model is to permit interpolation of these limited experimental data to predict phase equilibria over the entire range of temperatures and compositions. The experimental data needed to calibrate the model have been derived from a variety of different sources, including calorimetric and phase equilibria studies.

The chemical equilibrium of a particular bulk composition is determined by minimising its total Gibbs energy with respect to the amount and composition of phases present. Thus by expressing the Gibbs energy of each phase as a function of its composition and temperature, computer minimisation techniques can be used to predict stable phase assemblages. Thermodynamic data for minerals and melts in the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> have been derived, and calculations of mineral-melt equilibria at one atmosphere are presented here. Our model has been applied not only to low-pressure differentiation of basaltic magmas, but also to high temperature slag formation, and other industrial situations.

## Theoretical approach and results

Thermodynamic data for 28 solid phases have been assessed for consistency with known phase equilibria. In the study of melting reactions it is necessary to take account of non-stoichiometry in mineral compositions, in a way that has not been attempted in databases such as those of Berman (1988) or Holland and Powell (1990). In the present work the necessary data for each pure phase are the standard state enthalpy and entropy, and the heat capacity as a function of temperature. For phases showing solid solution, these data are

necessary for each end-member in the solution, and Redlich-Kister interaction parameters are used to describe the mixing properties of each pair of elements on each site in the crystal lattice (Barry *et al.*, 1992). Such solution models have been included for the olivines, the pyroxenes, the spinels, the melilites, mullite, and halite (the generic phase name for the MgO–CaO solid solution).

The melt is modelled as consisting of non-ideally interacting species (Barry *et al.*, 1993; Sommer, 1982; Chuang and Chang, 1982). The choice of the composition of the melt species is to some extent arbitrary. Even though they usually correspond in composition to crystalline phases that melt congruently, they are fictive and do not constitute an attempt to model the structure of the melt. For example in the binary system CaO–SiO<sub>2</sub>, the species used are CaO, SiO<sub>2</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, and CaSiO<sub>3</sub>. In the ternary system CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> a species corresponding to anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) has been added. The amount of each species varies with temperature and bulk composition. The relative stabilities of the species are determined mainly by the value of the Gibbs energy of each of the species, but also by the non-ideal interactions between them. The energy of each interaction has been assessed to ensure consistency with the liquidus surface and thermochemical data, where this has been experimentally determined.

This is a substantial increase in scope over previous attempts to model melts (e.g. Berman and Brown, 1984). The liquidus surface at one atmosphere pressure is reproduced to within twenty degrees, and the composition of the invariant points is also usually well matched.

## References

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