Combining thermodynamic and trace element modeling – A tool to quantify mineral reactions and trace element budgets during metamorphism

MATTHIAS KONRAD-SCHMOLKE[1], THOMAS ZACK[2] AND PATRICK J. O'BRIEN[1]

[1]Institut für Geowissenschaften, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany, (mkonrad@geo.uni-potsdam.de)

[2]Institut für Geowissenschaften, Universität Mainz, Becher Weg 21, 55128 Mainz, Germany

Devolatilisation reactions in a subducted slab control the amount and composition of liberated fluids that interact with the host rocks, the overlying slab-mantle interface and the mantle wedge. Thus, quantification of mineral reactions during subduction and the associated fractionation and devolatilisation processes are a key to understand elemental and isotopic signatures in subduction-related volcanics and in ocean island basalts.

With a combination of thermodynamic modeling and mass-balanced trace element distribution among the modeled phases it is possible to quantify trace element budgets within the slab and in the liberated fluids.

Thermodynamic forward modeling, utilising Gibbs energy minimisation with consideration of element fractionation, yields precise information about modes and major element compositions of stable phases at any pressure (P) and temperature (T) condition along a P-T path of interest. At any calculated P-T point selected trace elements are distributed among the modeled stable phases based on bulk rock composition and distribution coefficients. Elements that are incorporated into phases that undergo fractional crystallisation or that are assumed to leave the system (e.g. fluid) are subtracted from the effective bulk rock composition.

With that method we can correlate complex rare earth element (REE) pattern observed in many high and ultra-high pressure (UHP) garnets with distinct devolatilisation reactions and fractionation processes in the subducted slab. The calculations enable us to predict REE concentrations in coexisting phases and to detect thermodynamic and chemical disequilibrium during mineral growth.

Further our models yield precise information about the complex interplay between mineral reactions, fluid flux and the budget of fluid-mobile trace-elements and thus enable us to distinguish between open- and closed-system behaviour of certain trace elements.

A model for CO_2 solubility in silicate melts

ALEXANDER KONSCHAK AND HANS KEPPLER

Bayerisches Geoinstitut, 95440 Bayreuth, Germany (Hans.Keppler@uni-bayreuth.de)

The importance of CO_2 in magma generation was first demonstrated by Peter Wyllie. In a series of seminal papers (e.g. [1-3]), he showed that CO_2 has little effect on the melting temperature in felsic systems, while it causes a strong depression in the solidus temperatures of basic silicate melts and of carbonatites. These differences must be related to large differences in CO_2 solubility in silicate melts, which in turn may be caused by differences in solubility mechanism.

We have studied the speciation of CO_2 in silicate melts by *in situ* infrared spectroscopy in externally-heated diamond anvil cells using synchroton infrared radiation. We found that the enthalpy of the reaction $CO_2 + O^{2-} = CO_3^{2-}$ systematically increases with decreasing NBO/T. Based on this observation, we developed a general model of CO_2 solubility in silicate melts which describes CO_2 dissolution by two equilibria: (1) CO_2 (gas) = CO_2 (melt) , with the equilibrium constant $K_1 = c(CO_2, \text{melt}) / f(CO_2, \text{gas})$ and (2) $CO_2 + O^{2-} = CO_3^{2-}$, $K_2 = c(CO_3^{2-}) / c(CO_2)$. The temperature dependence of K_1 and K_2 is described by $\ln K_i = a_i (1000K/T) + b_i$. K_2 was determined from the *in situ* infrared measurements and K_1 by fitting a large number of solubility data from the literature to this model. We found that a_1, a_2, b_1, and b_2 are linear functions of NBO/T, with $a_1 = 21.03$ NBO/T + 0.84; $b_1 = - 11.09$ NBO/T – 13.96; $a_2 = 38.81$ NBO/T + 1.48; $b_2 = 21{,}38$ NBO/T – 2.69.

The model outlined above correctly predicts the solubility of CO_2 in silicate melts over a very wide range of temperature, pressure and composition. It also explains why the diffusion coefficient of CO_2 varies little between felsic and basic melts at temperatures around 1400°C, because at these temperatures, the effect of composition on CO_2 speciation is relatively small. The influence of composition, however, becomes much stronger at temperatures close to the solidus and there a strong dependence of CO_2 diffusivities on melt composition is expected.

[1] Wyllie P. J. and Tuttle O. F. (1959) *Am. J. Sci.* **257**, 648-655. [2] Wyllie P. J. and Tuttle O. F. (1960*) J. Petrol.* **1**, 1-46. [3] Wyllie P. J. and Huang W. L. (1976) *Contrib. Mineral. Petrol.* **54**, 79 – 107.