

MINERAL REACTIONS IN A MODEL MANTLE: PREDICTION OF MINERAL COMPOSITIONS AND ASSEMBLAGES.

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General Problem:

Despite positive attempts to calibrate mineral thermometers and barometers to evaluate physical and chemical conditions in the Upper Mantle, the possible uncertainties in data and fitting procedures can result in errors as large as 100 percent. Such uncertainties are rarely quoted if even evaluated. The difficulties arise from the existence of only a few high-variance assemblages stable over a wide range of Upper Mantle conditions, problems of defining chemical components and the minimal amount of consistent experimental, thermodynamic and chemical data. Only broad constraints upon the possible mineral associations can be supplied from observed seismic structure and viscosity limits and from inferred thermal and electrical conductivities. These bounds can be satisfied by a large range of actual and unknown rock types. Unfortunately many geochemical constraints are circularly dependent on the above properties and assumed P and T used to model the Upper Mantle. A consideration of continuous and discontinuous reactions in the $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ (CAMS) system and its compositional extensions permit the available data to be more rigorously constrained and viewed in a coherent framework.

Reactions in the CAMS compositional space:

Discontinuous and continuous reactions in CAMS are most usefully discussed with reference to the $\text{CaSiO}_3(\text{Wo})\text{-MgSiO}_3(\text{En})\text{-Al}_2\text{O}_3(\text{Cor})$ plane. The four principal compositional reactions types are

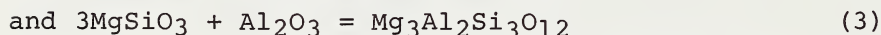
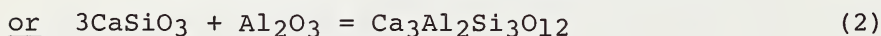
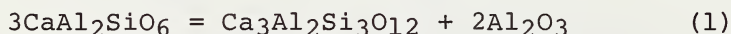
- I. in the Wo-En-Cor plane.
- II. on the SiO_2 -rich side (Wo-En-Cor-Qtz).
- III. on the SiO_2 -poor side (Wo-En-Cor-(CaO+MgO)).
- IV. crossing the Wo-En-Cor plane.

Of these types, those in the Wo-En-Cor plane control all the reactions in CAMS involving two or more of diopsidic clinopyroxene (Cpx), orthopyroxene (Opx) and garnet (Ca-rich=Gro, Mg-rich=Pyp). The compositions of the phases Cpx and Opx may be defined by the components $\text{CaMgSi}_2\text{O}_6(\text{Di})\text{-MgSiO}_3(\text{En})\text{-CaAl}_2\text{SiO}_6(\text{Ct})$ and those of the garnet phases Gro and Pyp by the components $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{Gr})\text{-Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{Py})$.

Type I reactions in the Wo-En-Cor plane:

The compositional changes of Cpx, Opx, Gro and Pyp phases may be predicted as functions of P and T from end-member reactions in CAS or MAS and exchange reactions in Wo-En-Cor. The topology in Wo-En-Cor shown by Boyd (1970, Min.Soc.Am.Sp.Pap.3, Fig.11) shows four 3-phase fields. Cor-Gro-Cpx and Cor-Pyp-Cpx occur because of continuous reactions and Pyp-Cpx-Opx and Gro-Wol-Cpx exist by virtue of the miscibility gaps between Cpx-Opx and Wol-Cpx. Without the Cpx-Opx miscibility gap a complete bundle of two-phase tie-lines would exist with orientations determined by the pyroxene structure (because $X_{Mg}^{Opx} > X_{Mg}^{Gar} > X_{Mg}^{Cpx}$). The behaviour of compositions of Cpx-Opx-Pyp with changing P and T may be predicted from the Di-En phase diagram and the effects of Cpx-Pyp and Opx-Pyp tie-line rotation. For example at constant P, increasing T causes greater mutual solubility of pyroxenes which is larger for Cpx (it is easier to put smaller Mg in larger Ca-sites) and an increase of Ca in Pyp (the net effect of the larger Cpx-Pyp tie-line rotation). Because of the inferred steep positive dP/dT for critical Cpx, these effects would be reversed though weaker for increasing P at constant T. For the most part the Ca-Mg exchange between Cpx-Opx-Pyp has a larger effect on composition than Tschermarks exchange except when Cpx is more aluminous than Ca-rich garnet (Gro).

The continuous reactions involving Cpx-Gro-Cor and Cpx-Pyp-Cor may be written as the end-member component reactions



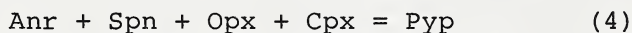
coupled with the exchange reactions between Di(or Wo)-En-Ct for pyroxenes and Gr-Py for garnets. Reaction (1) has a positive dP/dT in CAS with Gr+Cor on the high-P side, consequently Cpx in Cpx-Gro-Cor becomes enriched in Ct with increasing T at constant P and depleted in Ct with increasing P at constant T.

These arguments can be extended to include continuous reactions on both sides of the Wo-En-Cor plane (Types II, III and IV).

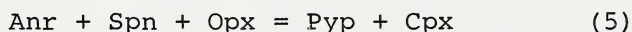
Other reaction Types (II,III and IV):

The following discussion illustrates exactly how the reaction topologies for all Type II,III and IV reactions involving two or more of Cpx-Opx-Gar are controlled by the Wo-En-Cor plane.

Because phases such as forsterite(For), spinel(Spn), Opx, anorthite(Anr), wollastonite(Wol) do not have isostructural end-members in both CAS and MAS, no end-member reactions can be written for phases in both systems. Most relevant reactions for assemblages in the ultramafic family (Cpx+Opx+Pyp+For+Spn+Anr), eclogites (Cpx+Pyp+Cor/Kya), grosspyrites (Cpx+Gro+Cor/Kya) and assemblages such as Gro+Wol+Cpx+Anr+Spn+For in calc-silicates and possibly meta-rodingites, usually involve at least two of Cpx, Opx or Gar. Consequently the exact nature of the reaction is controlled by the exchange reactions in the Wo-En-Cor plane. For example, the reaction



has this form if the garnet composition (defined in Wo-En-Cor) lies between that defined by the plane Anr+En+Spn (1/6Gr 5/6Py) and Anr+Di+Spn (1/2Gr 1/2Py). However, if the data of Akella (1976, Amer.Min., 61, p.591) hold in the P-T range for (4), the reaction will have the form



because the garnet in Pyp-Opx-Cpx is more Mg-rich than (1/6Gr 5/6Py).

CAMS compositional extensions and Upper Mantle Assemblages:

The subtleties of reaction controls in CAMS are such that certain bulk compositions may easily by-pass many of the assumed reactions. While P and T may still be estimated from compositions of Cpx-Opx-Gar many bulk compositions may not exhibit a particular reaction, or the transition interval may vary in width in P-T space. Models have been developed using the above techniques to predict how a given bulk composition will behave over a wide range of P-T conditions. These models are being used to assess the likelihood of mineral reactions being the cause of seismic discontinuities and to constrain the heterogeneity of Upper Mantle compositions.