

C–H–O fluid speciations under mantle conditions

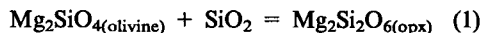
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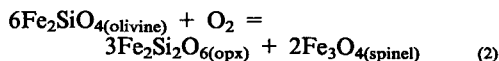
The C–H–O fluid speciation is of fundamental importance for partial melting processes in the upper mantle. If the prevailing oxygen fugacity (f_{O_2}) of the upper mantle is between a value corresponding to FMQ and FMQ-2 (two log-bar units below FMQ), as most calculations from mantle xenoliths suggest (e.g. Wood and Virgo, 1989; Ballhaus *et al.*, 1990; Ballhaus, 1993), then CO_2 and H_2O ought to be the dominant volatile species. The composition of the first melt is then likely to be rich in CO_3^{2-} and CO_2 (Brey, 1976; Wallace and Green, 1988). If, however, the prevailing f_{O_2} is at FMQ-3 or lower, CH_4 becomes a major species (Green *et al.*, 1987) and the amount of carbon that dissolves in the melt is much lower (Taylor and Green, 1987). A fundamental problem is that there is no direct means of determining the f_{O_2} of the asthenospheric mantle because there is no proper sample material available. Mantle xenoliths are likely to be all lithospheric and basaltic melts do not preserve the f_{O_2} of their source regions.

Theory demands that the asthenosphere is reduced and that f_{O_2} falls with increasing depth in the upper mantle, for two reasons:

(1) Pressure effects on f_{O_2} . In the mantle, f_{O_2} is related to the silica activity (a_{SiO_2}) and in turn sensitive to pressure effects on a_{SiO_2} . In the upper mantle a_{SiO_2} is effectively buffered by the equilibrium



Increasing pressure causes a drop in a_{SiO_2} because the $P\Delta V_r/(2.303RT)$ contribution to free energy of equilibrium (1) is negative. In a mantle where f_{O_2} is, at least in part, determined by ferriferous iron equilibria such as



this means that even if the activities of fayalite and magnetite and the bulk composition of the mantle remain constant, f_{O_2} will fall with increasing depth because a_{SiO_2} falls.

(2) Phase transitions and changes in solid solution behaviour. Any phase transition that affects the activities of the ferric iron components and/or

a_{SiO_2} also affects f_{O_2} . For example, the progressive reactions from the plagioclase- to the spinel- to garnet-stability fields dilute the ferric iron components in the mantle phases and cause a drop in f_{O_2} with increasing pressure. Within the garnet field, the solubility of the skiaegite ($Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$) endmember in almandine increases sharply with pressure (Woodland and O'Neill, 1993) until complete solid solution at ~ 9 GPa. In addition, increasing pressure along a geotherm favours the formation of a single subcalcic clinopyroxene solid solution and, at higher pressure, solid solution between garnet and pyroxene to majorite. Both reactions cause a_{SiO_2} to fall and in turn a drop in f_{O_2} . Thus, with increasing pressure ferric iron in the mantle will find an increasing reservoir of phases that can accommodate ferric iron. In consequence, the activities of the ferric iron components and f_{O_2} will fall with depth.

Provided there is no systematic bulk compositional change in the upper mantle with depth, these pressure effects cause f_{O_2} to fall relative to the FMQ buffer, by an estimated rate of 0.5 to 0.8 log-bar units per GPa unit pressure increase (Ballhaus and Frost, 1994). In consequence, the source regions to deep-seated alkaline mantle melts such as melilitites and kimberlites must be so reduced that volatiles should be well within $CH_4-H_2 \pm H_2O$ stability. This conclusion, however, is in sharp contrast to observations that deep-seated alkaline melts are usually quite enriched in dissolved CO_2 and CO_3^{2-} (Brey, 1976).

To solve this obvious contradiction between theory and reality, it is essential (1) to determine the speciation of C–H–O fluids in equilibrium with mantle phases as a function of pressure, temperature, and f_{O_2} and (2) to determine the partitioning of C–H–O volatile species between a model high-pressure basaltic melt that is quenchable at high pressure (e.g. a jadeitic composition) and a C–H–O fluid. As a first step in this direction, I have started an experimental investigation into the speciation of C–H–O volatiles in equilibrium with olivine-opx-cpx-spinel/garnet-graphite-carbonate assemblages, to clarify the lower f_{O_2} stability limit of carbonates in the upper mantle. Experiments are carried out in a belt apparatus between 3 and 7 GPa just inside the thermal

stability of carbonates in equilibrium with natural mantle olivine, opx, cpx and spinel/garnet, i.e. at the maximum activity of CO₂ in the coexisting fluid phase. The composition of the fluid is fixed by the intersection of the CCO redox equilibrium



with the carbonation reaction



which is invariant at fixed pressure and temperature. a_{SiO_2} given by equilibrium (2). f_{O_2} is monitored by an internal PdO-Fe₂SiO₄-C oxygen sensor assemblage (inside a separate graphite capsule) that reacts at pressure and temperature to a Pd-Fe alloy, Fe₂Si₂O₆, and CO₂. The composition of the equilibrium fluid is analysed by feeding the fluid after an experiment into a gas chromatograph and analysing it for CO₂, CH₄, H₂O, and H₂ to a precision better than 1 mole percent.

The experimental setup allows careful monitoring of C-H-O fluid speciations in equilibrium with graphite and natural mantle assemblages. The results allow the derivation of thermodynamic

data relevant for C-H-O mixed fluids and graphite-carbonate assemblages under upper mantle conditions.

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