Carbonate stability in the Earth's lower mantle and redox melting across the 660 km discontinuity

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The formation of the deepest melts in Earth's mantle is likely to be related to small degree carbonatitic melting [1]. The critical variables are (a) the solidus temperature of carbonate bearing peridotite and, (b) the oxygen fugacity (fO_2) conditions in the mantle. fO_2 determines whether or which volatile phase or species is present in the mantle (i.e. C vs. CO_2, in presence of H_2O also CH_4) and therefore strongly influences the peridotite solidus temperature.

Here we determined the solidus temperature of carbonate bearing fertile mantle and the fO_2 position of redox equilibria controlling carbonate stability in the mantle relative to solid state oxygen buffers. Experiments were performed in Walker type multianvil presses at ETH Zürich using 14/8 and 10/3.5 assemblies.

The solidus temperature of a CO_2 enriched mantle composition at 13.6 and 23 GPa is considerably lower than extrapolation of lower pressure data [1] would predict. The solidus temperatures at the investigated pressures are in the range of a normal mantle geotherm implying that small degree carbonatitic melting would be feasible at transition zone and lower mantle P–T conditions. To investigate the stability of carbonate with regard to oxygen fugacity, we have equilibrated a fertile peridotite composition containing 5 wt.% CO_2 with Fe–FeO, Ni–NiO, and Re–ReO_2 solid state buffer assemblages at 13.6 GPa, 1450°C and 23 GPa, 1600°C. The result is that at fO_2 conditions lower than NNO-3 all CO_2 is reduced to diamond and magnesite is unstable. In view of increasingly reducing conditions in the Earth's mantle with increasing depth [2–5], carbonate induced melting is unlikely as long as the capacity of ferric/ferrous redox buffers exeed the capacity of the carbon/carbonate buffer. However, in upwelling mantle containing fragments of previously subducted carbonate-enriched oceanic lithosphere, redox melting across the lower/upper mantle boundary or within the transition zone is likely to occur.

[1] Dasgupta & Hirschmann (2006) *Nature* **440**, 659-662. [2] Ballhaus (1995) *EPSL* **132**, 75-86. [3] Woodland & Koch (2003) *EPSL* **214**, 295-310. [4] Frost *et al.* (2004) *Nature* **428**, 409-412. [5] Rohrbach *et al.* (2007) *Nature* **449**, 456-458.

Comparison of iodine and selenate retention mechanisms onto cementitious materials

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Cementitious materials are commonly used to stabilise radioactive wastes prior to their deposition in different types of repositories. The degradation of these materials produces highly alkaline leachates, whose interaction with the surrounding host-rock can produce a chemically disturbed zone. Iodine and selenate exhibit high solubility and poor sorption onto these materials, and its retention mechanism is still poorly understood. This work presents experimental and modelling results on the uptake of I^- and SeO_4^{2-} by mortar and concrete in contact with artificial cement pore water.

Batch and dynamic experiments results suggest that, under similar conditions, selenate is more retained than iodine. In batch experiments at S/L ratios = 100 g/L, Rd values obtained for selenate are between $9{\cdot}10^{-3}$ and $3{\cdot}10^{-2}$ m^3/kg for all the initial selenate concentrations studied ($1{\cdot}10^{-7}$M to $1{\cdot}10^{-4}$ M). Iodine Rd values are lower and decrease as the initial I^- concentration increases. In dynamic (column) experiments, higher selenate retardation is observed.

Several authors have previously suggested the possibility of incorporation of these anions into AFt- (ettringite) or AFm- (monosulfate) cement phases instead of SO_4^{2-} [1], [2], [3]. Results obtained in the present work indicate that the incorporation of SeO_4^{2-} into secondary AFt- phases can be a suitable retention mechanism for selenate. Iodine/sulfate substitution seems to be lower.

[1] Toyohara *et al*. (2002) *J. Nucl. Sci. Technol.* **39**(9), 950-956. [2] Bonhoure *et al*. (2002) Radiochim. Acta **90**, 647-651. [3] Ochs *et al*. (2002) *Radiochim. Acta* **90**, 639-646.