Heavy boron isotopes in secondary olivine from the HP Voltri Massif: implications for the boron cycle in subduction zones

J.C.M. DE HOOG[1]* AND K. HATTORI[2]

[1]Grant Institute, School of Geosciences, Edinburgh, United Kingdom EH9 3JW (*correspondence: ceesjan.dehoog@ed.ac.uk)

[2]Dept. of Earth Sciences, University of Ottawa, Ottawa, Canada (khattori@uottawa.ca)

The Erro-Tobbio peridotite (Voltri Massif, Ligurian Alps, Italy) contains high-pressure rocks that have been subducted to peak conditions close to the upper stability limit of serpentine (650°C at 25 kbar; [1]). Secondary olivine occurs in partially dehydrated serpentinites in association with Ti-clinohumite (Ti-Chu). It has high Mg# (Fo86-87), MnO (0.3-0.4 wt%) and NiO (0.2-0.3 wt%) and contains magnetite inclusions attesting to its secondary origin. Olivine has variable but very high H_2O (up to 0.7 wt%) which correlates with high TiO_2 (up to 0.85 wt%) and F contents (5-51 ppm). FTIR spectroscopy indicates a high proportion of Ti-Chu-like defects in the olivine as the cause of high H_2O, F and TiO_2. Olivine also has very high B (8-20 ppm) and Li (3-70 ppm) contents, but these are not correlated with H_2O contents. Antigorite from the same sample has lower B (8-10 ppm) and Li (0.1 ppm) contents than olivine while F contents are comparable (15-47 ppm).

In-situ boron isotope analysis (Cameca 1270 SIMS) shows that olivine is enriched in heavy B ($\delta^{11}B_{SRM951}$ = +17 to +23‰). No difference exists between Ti-rich and Ti-poor olivine. These high values are nearly identical to those of whole-rock high-pressure serpentinites from the same area ($\delta^{11}B$ = +17 to +24‰; [2]). This indicates that little B isotope fractionation occurs during subduction dehydration of serpentine. Moreover, the high B and F contents of secondary olivine imply that these elements remain in the rock during serpentine dehydration. Hence, subduction of ultramafic rocks may introduce significant B isotope anomalies and fluorine into the deeper mantle.

[1] Scambelluri *et al*.. (1995) *Geology* **23**, 459-462. [2] Scambelluri and Tonarini (2012) *Geology* **40**, 907-910.

Evaluation of the corrosion behaviour of potential plutonium wasteforms under conditions relevant for geological disposal

G. DEISSMANN[1,2*], F. BRANDT[1], S. NEUMEIER[1], G. MODOLO[1] AND D. BOSBACH[1]

[1]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK-6: Nuclear Waste Management and Reactor Safety, 52425 Jülich, Germany (*correspondence: g.deissmann@fz-juelich.de)

[2]Brenk Systemplanung GmbH, 52080 Aachen, Germany

One important component of a safety case for a geological disposal facility for radioactive waste is to demonstrate an understanding of the corrosion behaviour of and the consequent radionuclide release from the disposed wastes. Plutonium is generated during the operation of nuclear reactors from uranium present in the nuclear fuels through capture of neutrons and can be recovered during reprocessing. Although the current preferred policy on the long-term management of separated civil plutonium in the UK is reuse as MOX fuel, at least a part of the UK plutonium inventory is likely to be designated for geological disposal. However, experimental data on the durability of plutonium wasteforms under repository conditions is rather limited to date and a detailed understanding of relevant processes that govern long-term radionuclide releases from the wasteforms on a molecular level is still missing [1].

On behalf of the NDA RWMD, we performed a review on the performance of plutonium wasteforms under conditions relevant for geological disposal in the UK. This work included the elicitation of corrosion rate data for the potential wasteforms, based on available experimental data and analogue evidence from other nuclear wasteforms, such as HLW-glasses and spent nuclear fuels. Generic candidate plutonium wasteform types addressed in this study comprised nuclear waste glasses (i.e. borosilicate glasses and phosphate glasses), ceramic wasteforms, and low-specification "storage" MOX. Due to the character of the current UK disposal programme, which is in a generic stage where no preferred disposal concept or type of host rock has yet been selected, a range of possible environmental conditions in the repository near-field were considered. The elicited ranges and distributions of the corrosion rates for the various wasteforms can be used in Post-Closure Safety Assessment models to calculate performance measures such as mean annual individual risks related to plutonium disposal with time.

[1] Deissmann *et al*.. (2012) *MinMag*, **76**, 2911–2918.

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