

Assessing the geochemical behaviour of ceramic nuclear waste forms using natural samples

G.R. LUMPKIN¹, K.L. SMITH¹, R. GIERÉ², AND
C.T. WILLIAMS³

¹ Materials Division, ANSTO, PMB 1, Menai, NSW 2233, Australia (grl@ansto.gov.au)

² Dept. of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-1397, USA

³ Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

In addition to the direct disposal of spent nuclear fuel, borosilicate glass and polyphase or single phase ceramic waste forms have been considered as options for the disposal of nuclear waste in geological repositories. Of critical concern in the scientific evaluation of these materials is how they perform in natural systems over long periods of time (e.g., 10³ to 10⁶ years). Experience gained over the last 20 years or so has shown that laboratory experiments can be combined with studies of natural samples to provide information on both the short-term and long-term behaviour in aqueous fluids. The laboratory experiments provide data on elemental release rates under controlled conditions, but often fail to elucidate the alteration mechanisms, even when reaction products are easily observed (e.g., formation of TiO₂ polymorphs during alteration of perovskite). Studies of minerals from various geological environments, on the other hand, reveal quantitative data on the geochemical alteration mechanisms, but only limited inferences can be made concerning the reaction kinetics.

The objective of this paper is to give an overview of the current state of knowledge with regard to the aqueous durability of the major host phases for actinides (e.g., Th, U, Np, Pu, Cm) and important fission products (e.g., Sr and Cs). In the case of titanate ceramics, we are primarily concerned with the brannerite, hollandite, perovskite, pyrochlore, and zirconolite structure types. Other ceramic waste forms based on apatite, zircon, monazite, and the recently proposed zirconate pyrochlores are included for comparison. Of these structure types, natural samples exist for all but the zirconate pyrochlores. For monazite, zircon, and zirconolite, existing data demonstrate acceptable laboratory leach rates together with limited geochemical alteration in natural environments. Hollandite appears to be a highly durable host phase for radioactive Cs, but studies of natural samples are needed in order to study the long-term behaviour. Pyrochlores, both titanate and zirconate, also have acceptable leach rates, but long-term data are only available for titanate pyrochlores (together with Nb and Ta rich varieties). Further details of the aqueous durability of these phases in the laboratory and in nature will be presented, together with other aspects of the waste form selection criteria and a few comments on the future direction of this work.

Li isotope profiles in dunite to lherzolite transects within the Trinity Ophiolite

C.C. LUNDSTROM¹, M. CHAUSSIDON², P. KELEMEN³,
AND ALBERT HSUI¹

¹.Dept of Geology, University of Illinois at Urbana Champaign, Urbana IL 61801 USA lundstro@uiuc.edu

².CRPG-CNRS, BP 20 15, rue Notre Dame des Pauvres, Vandoeuvre-les-Nancy, 54 501, France chocho@crpg.cnrs-nancy.fr

³.Dept of Geology and Geophysics, WHOI., Woods Hole., MA 02543 USA peterk@whoi.edu

Recent experimental work suggests that alkali elements will diffuse from ascending magmas into surrounding peridotite wallrock due to gradients in alkali activity (Lundstrom, Nature 2000). No observational evidence for this process yet exists. In order to seek evidence for alkali diffusion as well as to test whether Li isotopes might be fractionated by diffusion, we have measured Li isotopes by ion microprobe (CRPG-Nancy) in samples from the Trinity Ophiolite (northern CA).

Because geochemical signatures argue that dunites are former pathways of melt ascent (Kelemen et al., Nature 1995), Li isotope ratios were measured in clinopyroxenes and olivines as a function of distance from dunite in several dunite to plagioclase lherzolite transects (transects TP90-20 (20m long), VB91 (20cm) and TP90-9 (2m with a gradient in REE in CPX, Kelemen et al., Nature 1992;). 3-10 analyses were made from the same thin section at a given location producing an external precision of ~2‰ for samples from harzburgite or lherzolite. All three transects show lower values of δ⁷Li (+2 to -6‰) in the harzburgite adjacent to the dunite and higher values far from the dunite (+3 to 12‰). Despite some variability in δ⁷Li and Li concentrations which is not understood at present, dunite has higher average values resulting in a trough of low δ⁷Li across the dunite-lherzolite transect.

If high Li concentrations in dunite represent the original magmatic signature, a systematic trough exists for all 3 transects which cannot result from alteration by seawater (δ⁷Li = +32‰). The observed profiles are consistent with a simple model of Li isotope fractionation by diffusion in which the ⁶Li melt diffusion coefficient is slightly greater than that of ⁷Li, reflecting the 16% mass difference in Li isotopes. Notably, the length scale of the δ⁷Li gradient is similar to the length scale of the REE gradient. If the δ⁷Li gradient is due to diffusion, then diffusivities of Li and REE are similar which is inconsistent with experimental results. Alternatively, REE concentrations result from vertical, advective melt extraction acting simultaneous to horizontal diffusion. We have investigated numerical models of diffusion with different sink terms to account for possible extraction mechanisms and to constrain the timescale needed to create the observed dunite-lherzolite profile lengths.