Mineral reactions at high pH relevant to radwaste disposal: a 15 year experimental study

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The use of cement within waste forms, engineering and potentially as backfill in the geological disposal of radioactive waste will produce a high pH (~pH 13-10) leachate plume as the geological disposal facility (GDF) evolves over hundreds to millions of years. This plume will create a chemically disturbed zone (CDZ) within the host rock causing alteration, dissolution and secondary precipitation of minerals. This has clear potential to change the rock's physical and chemical properties and affect radionuclide transport in the geosphere through alteration of flow paths or change in the host rock sorption capacity for radionuclides.

Here we describe analysis of a unique series of batch experiments which contain Borrowdale Volcanic Group (BVG) rock (quartz, orthoclase and dolomite with clay coatings) reacted in CDZ leachates at 70 ºC for 15 years. Two leachates were used: young cement leachate (pH 13.00, KOH and NaOH dominated); and evolved leachate equilibrated with a model deep groundwater (pH 12.2, $Ca(OH)_2$ and NaCl dominated)[1]. Experiments were characterised at 15 months and in this most recent work, at 15 years.

At 15 months mineral dissolution and formation of Ca-bearing silicate phases, e.g. apophyllite and Ca-K-Al silicate clays, was observed. However, recent work shows that by 15 years, extensive de-dolomitisation had occurred; here the dissolution of $CaMg(CO_3)_2$ resulted in extensive $CaCO_3$ re-precipitation and release of Mg^{2+}. By 15 years, it is apparent that this Mg^{2+} had reacted with silica in solution and clay particles on the primary mineral surfaces to produce Mg(K)(Al)-silicates of varying composition, structure and morphology as the major alteration products. The Ca-bearing silicates observed after 15 months of reaction were not present at 15 years. At all points, the alteration level was greatest in the young leachate, but the processes described occurred in both fluids.

Overall, these results demonstrate that the stability of secondary phases formed within the CDZ may change significantly over time and may affect both flow and radionuclide speciation. Clearly, this has implications for GDF safety case development.

[1] Rochelle *et al.* (1997) BGS technical report WE/97/16

Planetary scale Sr isotopic heterogeneity

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Isotopic anomalies in planetary materials may reflect both early solar nebular heterogeneity inherited from presolar stellar sources [1], and processes that generated non-mass dependent isotopic fractionations [2,3]. The characterization of isotopic variations in heavy elements among early Solar System materials brings important insight into the stellar environment and formation of the solar system, and may also provide critical information about initial isotopic ratios relevant to long-term chronological applications [4]. One such heavy element, strontium, is a central element in the geosciences due to the widespread application of the long-lived ^{87}Rb-^{87}Sr radioactive system (λ=1.393x10^{-11}y^{-1} [5]) as a chronological tool.

Through high-precision Sr isotopic measurements we show that the stable isotopes of Sr were heterogeneously distributed at both the mineral- and the planetary-scale in the early Solar System, and also that the Sr isotopic heterogeneities correlate with mass independent oxygen isotope variations. This correlation implies that most Solar System material was formed by mixing of at least two isotopically distinct components: a refractory inclusion-like component (rich in *p*-process ^{84}Sr or *s*-process ^{88}Sr, and ^{16}O), and an H-chondrite-like component (poor in ^{84}Sr or ^{88}Sr, and ^{16}O).

The heterogeneous distribution of Sr isotopes, most notably with respect to ^{84}Sr, may indicate that variations in initial ^{87}Sr/^{86}Sr of early Solar System materials reflect isotopic heterogeneity instead of having a chronological significance, as interpreted previously. For example, the corrected age difference between the formation of refractory inclusions and eucrites, as determined from Sr isotopic differences, is much shorter than previously suggested, placing the Sr chronology in agreement with other long and short-lived systems, such as U-Pb and Mn-Cr [6].

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