

Primordial mantle heterogeneities revealed by coupled ^{182}W and $^{186,187}\text{Os}$ investigations

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Subtle W isotope anomalies within the Earth's mantle have been recently evidenced by high-precision measurements for 3.8 Ga Isua rocks [1], and the 2.8 Ga Kostomuksha komatiites [2]. These samples have ~15 ppm ^{182}W excesses, which are similar to the isotope composition of the mantle prior to the arrival of late accreted materials, as estimated assuming that the highly siderophile elements (HSE) present in the silicate Earth today were derived entirely from this HSE-rich extraterrestrial contribution. However, the mantle source of the Kostomuksha komatiites had total HSE abundances ca. 80% of those estimated for the modern mantle. These observations are inconsistent with Kostomuksha komatiites being derived from a pre-late accretionary mantle reservoir. Instead, their mantle source, also characterized by coupled $^{186,187}\text{Os}$ excesses [3], must have contained a primordial component, which is argued [2] to have formed during the lifetime of ^{182}Hf (<60 Myr after Solar System formation) via either magmatic differentiation or metal-silicate equilibration. These processes were modeled [2] to have resulted in development of high Hf/W, Pt/Os, and Re/Os ratios.

Here, we report new high-precision W isotope data for ~4.3 Ga rocks from the Nuvvuagittuq supracrustal belt (Northern Quebec, Canada). These results, coupled with Os isotope and HSE abundance data, as well as published ^{142}Nd data [4], are used to further constrain the timing and the nature of processes involved in the generation of ^{182}W heterogeneities. Four samples analyzed show ^{182}W anomalies of ca. +16 ppm, whereas the other two have W isotope compositions that cannot be resolved from that of the modern mantle. Samples with positive ^{182}W anomalies have total HSE abundances between 45 and 60% of those estimated for the modern mantle. Assuming that their HSE abundances are representative of their source HSE composition, the data would indicate that a substantial proportion of the late accreted materials were delivered to Earth prior to ~4.3 Ga. This would imply that the ^{182}W anomalies of some Nuvvuagittuq rocks must have been produced by an early mantle differentiation process and provide further evidence that geochemical heterogeneities were created in the Earth's mantle while accretion was still ongoing, most likely prior to the giant impact and the formation of the Moon at ~4.50 Ga. These mantle domains were preserved until at least the late Archean. Preservation of early differentiation products during accretion events may suggest that the Earth's mantle has never been completely homogenized and/or entirely molten.

[1] Willbold M. et al. (2011) *Nature* 477, 195.

[2] Touboul M. et al., *Science*, in press.

[3] Puchtel et al. (2005) *EPSL* 206, 411.

[4] O'Neil J. et al. (2008) *Science* 321, 1828

MODELLING WATER/ROCK INTERACTIONS IN CLAY-ROCK FORMATIONS: A SYNTHESIS.

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The chemistry of pore water and its controlling mechanisms are important properties of clayrocks being considered as host rocks for long-term storage of radioactive waste. Ionic strength, pH and redox potential are key parameters for assessing the speciation and thus the mobility of radionuclides under storage conditions. Porewater-controlling mechanisms must also be known to predict the evolution of the artificial and natural barriers foreseen in storage concepts. Since pore waters in clay-rich rocks cannot generally be sampled directly from rock samples, their chemistry must be estimated using geochemical modelling constrained by laboratory-measurable properties of core samples. In parallel to modelling work, considerable efforts have been made during the last ten years to obtain pore water samples from specially equipped boreholes in Underground Research Laboratories (URLs). Some of these experiments aim at obtaining water samples with minimal perturbations in order to enable comparisons with pore water geochemical modelling. Others obtain samples under disturbed conditions (e.g. bacterial, alkaline, redox, thermal perturbations) which can be used to assess the effectiveness of predicted controlling mechanisms.

Current modelling concepts of porewater composition will be reviewed together with their ability to explain key features in experimental results from the Bure (France) and Mont-Terri (Switzerland) URLs. We will show that pH and ionic strength as well as major solutes concentrations (Na, K, Ca, Mg, Cl, SO_4 , etc.) are adequately predicted in undisturbed conditions, but that redox potential remains a difficult modelling issue. Controlling mechanisms for trace metal concentrations and their impact on radionuclides retention will be also discussed. Hereafter, we will show how the knowledge on solute parameters controls enables predicting the evolution of storage-material under various perturbation scenarios. Model uncertainties and limitations (e.g. thermodynamic database accuracy and completeness, kinetic controls, etc.) will be discussed in order to better emphasize the significance of long-term predictive modelling of storage-material evolution.