

## Raman and IR spectroscopy of Monazite-type ceramics for the nuclear waste management

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Lanthanide monazite-type ( $LnPO_4$ ) ceramics are promising candidate materials for the immobilisation of minor actinides resulting from reprocessing of spent fuel. Particularly with regard to the long-term safety in a deep geological repository, monazite-type ceramics present a good alternative to the widely used borosilicate glasses for the specific conditioning of actinides. In terms of their crystal structure (SG  $P 2_1/n$ ) they offer outstanding properties concerning radiation resistance and chemical stability. Their normalised dissolution rates are several orders of magnitude lower than these of glasses [1-4]. This behaviour can also be confirmed by their natural analogues (no metamictisation occurs).

Therefore we investigated different monazite-type phases as potential waste forms for minor actinides. We prepared and characterised  $SmPO_4$ - $TbPO_4$  and  $SmPO_4$ - $CaTh(PO_4)_2$  solid solutions, using wet-chemical synthesis routes like precipitation at room temperature and solid state reactions (1600 °C), respectively. The presented data obtained by Raman and IR spectroscopic investigations will be discussed in conjunction with X-ray powder diffraction data as well as thermal analyses within a comparison to the available literature. An increasing distortion of the  $PO_4$  tetrahedra should be demonstrated with increasing Th-substitution of the  $Ln$ -position. Additionally, the monazite-cheralite solid solution data will be compared to that of a Thorium containing natural monazite sample. Completely new data could be generated for the solid solutions. Results of temperature dependent Raman spectroscopic investigations on the partly metastable  $(Sm,Tb)PO_4$  solid solutions will be presented, where depending on the composition one-two exothermic phase transitions are expected.

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## Searching for evidence for Mo isotope fractionation in the mantle

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Molybdenum is a highly siderophile element which was strongly depleted in the mantle by the process of core formation. Its mantle inventory is therefore strongly influenced by the addition of material during the late veneer when highly siderophile elements were enriched in the mantle after core formation.

Recent experimental data suggest that molybdenum isotopes are fractionated during metal-silicate equilibration, with lighter isotopes preferentially entering the silicate phase [1]. Therefore the mantle should be isotopically lighter than the chondritic material which is presumed to have accreted to form the Earth as heavy isotopes were concentrated into the core. However, the addition of the late veneer may have somewhat obscured the isotopic signature of core formation.

We describe two approaches taken to investigate the isotopic composition of the mantle relative to chondrites in an attempt to verify these experimental findings. Firstly, we measure a range of ~3.8Ga samples from Greenland which have been shown to retain an isotopic signature of the mantle prior to the addition of the late veneer [2].

Secondly, we measure the Mo isotopic composition of mid-ocean ridge basalts (MORBs) which we compare to chondrite samples in an effort to detect residual fractionation of molybdenum isotopes associated with core formation post late veneer.

MORB samples are known to carry some signature of recycling; however we suggest that they are sufficiently representative of the mantle for our purposes. Whilst scatter in both the MORB and chondrite datasets currently prevents the identification of a resolvable difference, we find a tantalising offset of 0.1 permil between the most primitive MORB sample and the least altered chondrite.

[1] Hin *et al*, AGU Fall Mtg, abs #P11A-1588 [2] Willbold *et al*, (2011) *Nature* **477**, 195-198