History and significance of ABX_3 crystal chemistry investigations

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There is substantial interest among the mineralogical and related communities in phase transitions involving materials with the general formula, ABX_3, e.g., $MgSiO_3$, $CaSiO_3$, $FeTiO_3$, $FeGeO_3$, $NaMgF_3$, Al_2O_3, Fe_2O_3, Gd_2S_3, and many others. The interactions of elements in these specific configurations provide an interesting framework for analysis of many different, but related properties. Although some of these phases are not considered to be major constituents of Earth's mantle, knowing their crystal-chemical behavior is considered to be essential for understanding overall mineralogical character and, in particular, how they react to changing environmental conditions. Recent developments based on synchrotron-related experiments provide powerful new tools, especially those that give new information on high-pressure, high-temperature mineral properties.

Copper isotope ratios of Kupferschiefer Shales and generated oils by hydrous pyrolysis

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Stable isotope ratios of transitional metals assist in understanding the source of metals and processes responsible for concentration changes. Variations in Cu isotopes of up to 9‰ are known in some natural systems, but the processes for Cu fractionation are not well understood [1]. We subjected three immature, organic carbon-rich, subsurface samples from different locations of the Kupferschiefer shale to hydrous pyrolysis (at 330° and 355°C for 72 hours) [2]. The shale samples varied in copper concentration from 0.2 to 18 wt. %. Cu isotope ratios were measured on the original samples, the pyrolyzed shales, the associated waters, and oils generated. The Cu isotopic composition from a naturally generated oil from the Kupferschiefer was also determined for comparison to the experimentally generated oil. Cu isotopic composition of the shales ranged from -0.14 ±0.16 ‰ 2σ to 0.49 ±0.30‰ for original samples, 0.06 ±0.43‰ to 0.44 ±0.19‰ for the shales heated to 330°C, and 0.01 ±0.17‰ to 0.44 ±0.28‰ for the shales heated to 355°C. Preliminary Cu isotopic composition for the natural crude oil averaged -0.09 ±0.18‰ which is similar to the Cu isotopic composition of the original shale from the same area of the Kupferschiefer. The small range in Cu isotopic composition suggests that fractionation of Cu isotopes is minimal at high temperatures and Cu isotopic composition may provide insight to oil source correlation, though the migration of Cu to the oil and water fraction was in the low ppm to ppb range.

[1] Larson *et al*. (2003) *Chemical Geology* **201**, 337-350. [2] Lewan *et al*. (2008) *Geochim. Cosmochim. Acta* **72**, 4069-4093