Ordering sumperimposed to unmixing in the $CaSO_4 \cdot 2H_2O$ – $CaHPO_4 \cdot 2H_2O$ system

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SO_4^{2-} and HPO_4^{2-} ions can substitute for each other within the structures of brushite ($CaHPO_4 \cdot 2H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$). The present work assesses the extent of such substitution in the $Ca(SO_4,HPO_4) \cdot 2H_2O$ system at 25°C, the presence of ordering/unmixing processes, and crystallization behaviour by means of solution calorimetry measurements, precipitation experiments, and crystallization in gels. The experimental results reveal that the $Ca(SO_4,HPO_4) \cdot 2H_2O$ solid solution has very limited miscibility, since the phosphate and sulphate groups tend to occupy specific lattice sites, as reflected by the structure of ardealite ($Ca_2SO_4HPO_4 \cdot 4H_2O$). Crystal aggregates of the solid solution grown in silica gel (Figure 1) display phosphate-rich cores, which reveal a stronger partitioning of phosphorus towards de solid phase, in accordance to the lower solubility of the brushite endmember.

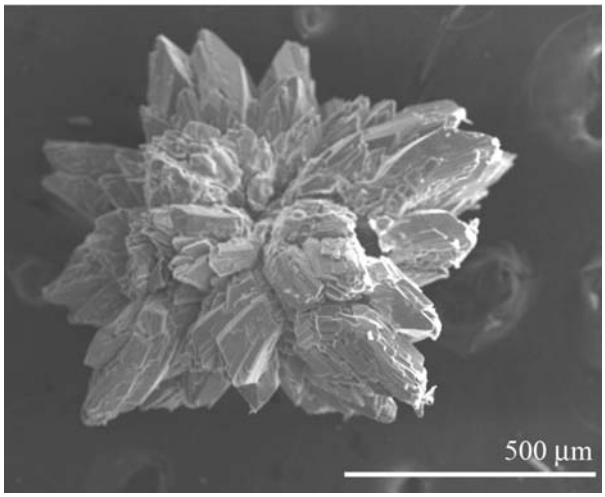

Figure 1: SEM micrograph of an aggregate of $Ca(SO_4, HPO_4) \cdot 2H_2O$ solid solution crystals, grown in silica gel.

Linking North and South Atlantic deep water circulation using Nd isotopes

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Neodymium isotope (ε_{Nd}) records measured on Fe-Mn oxide leaches from marine sediment cores have been used to reconstruct changes in Atlantic deep water mixing and structure [1,2]. However, use of this proxy has two uncertainties: firstly, whether Nd isotopes conservatively trace bottom water flow on long path-lengths today and in the past or are changed by addition of Nd from local sources [3]; and secondly, whether the Nd isotopic composition of seawater can be reliably extracted from sediments. We present new tests of marine Nd extraction, and new widely distributed records.

A new high resolution ε_{Nd} record from deep Eastern Atlantic core BOFS 8K (52.5°N 22.1°W, 4045 m) shows prominent variations during H1, the Bolling-Allerod and Younger Dryas, as well as an oscillation during the early Holocene which may correspond to the 8.2 kyr event. Though it is closer to sites of deep water formation in the North Atlantic, the deglacial change is 3.0 to 3.5 ε_{Nd} units in magnitude, identical to records from the Western North Atlantic [2], South Atlantic, and Indian Ocean. New South Atlantic data using a more specific leaching method to extract past seawater Nd isotopic composition also records this same deglacial change. The Younger Dryas ε_{Nd} changes in the deep North Atlantic BOFS 8K are similar in magnitude and shape to those in the South Atlantic Cape Basin record. This suggests similar changes in the proportion of NADW and AABW at all of the Atlantic sites, likely through a change in water mass stratification, and is further evidence against the propagation of an North Atlantic endmember change. Taken as a whole, these records provide a coherent reconstruction of glacial Atlantic deep circulation, which is consistent with benthic $\delta^{13}C$ reconstructions, and thus far does not indicate significant local addition of Nd along deep water flow.

[1] Piotrowski *et al.* (2005) *Science* **307** 1933-1938. [2] Gutjahr *et al.* (2008) *EPSL* **266** 61-77. [3] Lacan and Jeandel (2005) *Geochem., Geophys., Geosys.*. **6(12)** 1-20.