

**Uranyl phosphate sheet
reconstruction during dehydration of
metatorbernite
[Cu(UO₂)₂(PO₄)₂•8H₂O]**

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The metatorbernite structure comprises well-known autunite-type sheets of corner-sharing uranyl square bipyramids and phosphate tetrahedra, with the interlayer region occupied by Cu²⁺ ions and molecular water [1]. Previous studies have shown that upon heating, water evaporates and the basal spacing (sheet to sheet) decreases in discrete increments [2]. The structures of the lower hydrates have not been determined because suitable single crystals of these phases cannot be prepared.

We have discovered a major reconstruction of the sheets using synchrotron powder x-ray diffraction data collected during *in situ* continuous heating of powdered metatorbernite. Rietveld refinement of several possible structures for each of the lower hydrates revealed that although the autunite-type sheets remain intact through the first dehydration event above room temperature (102° C), the second (138° C) triggers a transformation to uranophane-type sheets, composed of chains of edge-sharing uranyl pentagonal bipyramids linked to one another by sharing edges and vertices with phosphate tetrahedra. This transformation enables the structure to overcome steric constraints on the minimum possible basal spacing while maintaining Cu within the interlayer.

Minerals of the meta-autunite group, including metatorbernite, are significant sinks for uranium in both natural and anthropogenically contaminated environments. Understanding the full range of possible structures under a variety of physical and chemical conditions is essential to both phase identification and long-term prediction of the fate of uranium at contaminated sites. As presented here, *in situ* heating experiments and the Rietveld method provide fundamental insights into the crystal chemistry and structural behaviors of this important mineral group.

[1] Locock and Burns (2003) *Can. Min.* **41** 489-502. [2] Suzuki *et al.* (2005) *Am. Min.* **90** 1308-1314.

**Late Quaternary variability of
Mediterranean Outflow Water based
on neodymium and lead isotopes**

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Mediterranean Outflow Water (MOW) is a warm and highly saline water mass, which enters the eastern North Atlantic Ocean at the Strait of Gibraltar at ~1 Sverdrup. Because of its higher density than North Atlantic surface waters, MOW sinks from a sill depth of 286 m (Strait of Gibraltar) to water depths between 500 – 1400 m and spreads in several branches along the Portuguese margin and in westerly directions across the North Atlantic, where it contributes to preconditioning water masses forming North Atlantic Deep Water.

During the Late Quaternary MOW in the North Atlantic has been strongly influenced by sea level changes and by variations of the hydrology of the Mediterranean Sea and the eastern North Atlantic gyre. This resulted in shifts of the flow paths and water depths of the different branches of MOW. To reconstruct the evolution of MOW, radiogenic neodymium (Nd) and lead (Pb) isotope signatures of past seawater were determined. Water masses in the ocean are labeled with distinct radiogenic isotope signatures through weathering processes on the adjacent continents. Neodymium isotopes are not fractionated by biological processes and past bottom water signatures can be extracted from early diagenetic ferromanganese coatings of bulk sediments applying a reductive leaching technique. Pb isotopes provide additional information on local weathering inputs.

Numerous surface sediment samples from the eastern North Atlantic were analysed to compare and calibrate the extracted signatures to the present hydrography and the few available water column isotope data in the area. Time series of Nd and Pb isotopes were obtained from three sediment cores located within modern MOW and below in the Gulf of Cadiz and along the Portuguese margin.

The measured Nd isotope ratios ($\epsilon_{Nd} = -8.4 - -9.4$) represent a mixed signal between more radiogenic Mediterranean Sea and less radiogenic Atlantic Ocean endmembers. Downcore variations in Nd isotope ratios suggest a change in MOW flow path or depth. The results are consistent with a generally deeper MOW during the Last Glacial Maximum.