

Sr isotope stratigraphy of carbonate fraction in oil shales

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Oil shale is a term used for immature, organic-rich, fine-grained sedimentary rocks from which hydrocarbons can be produced. In Israel, these rocks are composed of four main components: carbonate, phosphate, organic matter, and detritus (mainly Al-Silicates). The studied oil shales sequence is dated by their stratigraphic position (Bio-Zone) to Campan-Maastricht.

The use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from marine sediments is in one of two ways: to determine the Sr isotopic composition of the ocean water at deposition time, or to determine the age of the sediment based upon ocean water $^{87}\text{Sr}/^{86}\text{Sr}$ changes with time (Sr isotope stratigraphy).

In the present study we examined the potential of calcite in oil shales to reflect the $^{87}\text{Sr}/^{86}\text{Sr}$ of the ocean water at time of formation. The absence of dolomite in the studied oil shales sequence suggests that the associated calcite was not significantly altered and therefore should reflect the isotopic composition of Sr in the ocean water at time of formation. The calcite and insoluble residue fractions in oil shales from different basins in Israel, were separated using sequential extraction and their Sr isotopic composition was determined. The numerical Sr ages of the calcite was calculated [1] and results show that the numerical stratigraphic age is in good agreement with the assigned bio-stratigraphic age. Moreover, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the insoluble residue should reflect the source of detritus transported to these basins and may shed light on their province. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the insoluble residue varies and has no correlation with the Sr isotopic ratio of the calcite. This strengthens the observation that the calcite fraction in oil shales can record the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ocean water. Furthermore, the observed strong correlations between (1) the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and 1/Sr and (2) Sr, Ca and P concentrations in the insoluble residue, indicate a mixture of two PO_4 -minerals which are likely to be of biogenic and magmatic origin.

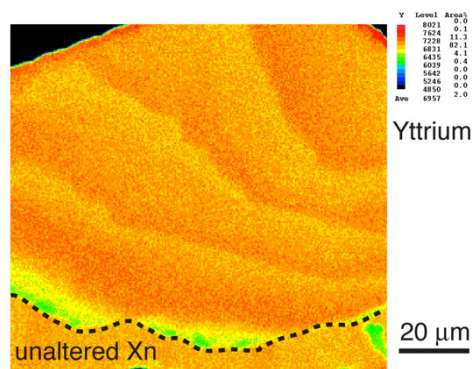
[1] McArthur, Howarth & Bailey, (2001). *Journal of Geology* **109**, 155–169. (LOWESS V5).

Experimental incorporation of U into xenotime at 900 °C, 500-1000 MPa utilizing alkali-bearing fluids

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In this study, specific areas of a natural Th-absent, low U, xenotime $[(\text{Y}+\text{HREE})\text{PO}_4]$ of uniform composition, are experimentally enriched in U + Si utilizing a NaF + H_2O fluid plus UO_2 and SiO_2 under both reducing (graphite- CO/CO_2 buffer) and oxidizing (Mt-Hm buffer) conditions. Charge and fluid were sealed in 2 cm long, 3 mm diameter Au and Pt capsules. In the reduced experiment the Au capsule was placed in the piston-cylinder apparatus (CaF_2 assembly; graphite oven; 1000 MPa; 900 °C; 8 days). In the oxidized experiment (500 MPa; 900 °C; 4 days) the Pt capsule was packed with Hm + H_2O into a 4 cm long, 5 mm diameter Pt capsule, which was placed in the gas apparatus. BSE imaging indicates that the altered areas occur as a series of curvilinear intergrowths with sharp compositional boundaries that extend from the edge of the xenotime grain into the interior. EPMA indicates that the altered areas from both experiments are enriched in U + Si via the coupled substitution $\text{U}^{4+} + \text{Si}^{4+} = (\text{Y}+\text{HREE})^{3+} + \text{P}^{5+}$. WDS element distribution maps indicate that U + Si are concentrated close to the compositional interface between the altered and unaltered xenotime with corresponding depletion in Y+HREE. Across the altered region Y occurs as a series of concentric waves of relative enrichment and depletion with contrasting depletion and enrichment in HREE (see Y element map below).



Element movement is interpreted as a consequence of fluid-mediated coupled dissolution-reprecipitation in some sort of a chromatographic column effect across the altered area. Fluid-aided incorporation of U into xenotime has implications with respect to its utilization as a metamorphic geochronometer.