

Gauging bottom-water ventilation in the eastern Mediterranean by combining geochemical and magnetic data from sapropel-bearing sediments

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Magnetic properties of eastern Mediterranean sediments recovered during Leg 160 of the Ocean Drilling Program (ODP) are controlled by non-steady-state diagenetic reactions associated with accumulation and degradation of organic matter in sapropels. According to their magnetic properties, we describe three types of sapropels that correspond to increasingly anoxic conditions at the time of sapropel formation. Ba and trace metal (e.g., Mo, V, Ni) to Al ratios enable determination of the relative role of productivity and bottom-water ventilation in the resulting diagenetic stage reached for the three types of sapropels. It appears that increased productivity is a prerequisite for sapropel formation and, once organic matter is available in sufficient amounts, variable efficiencies in bottom-water ventilation are more important for modulating the diagenetic context in which sapropels formed. Magnetic properties are thus more sensitive to variations in bottom-water ventilation than to productivity, and can be used to establish relative variations in bottom-water ventilation both at, and after, periods of sapropel formation. High-resolution (1 cm) magnetic results and the distribution and type of sapropels at ODP Site 966 (Eratosthenes Seamount) between 2.0 and 4.0 Ma suggest that bottom-water ventilation was modulated by the orbital eccentricity component, with ventilation being restricted during 400-kyr eccentricity maxima and enhanced during eccentricity minima. Enhanced ventilation during eccentricity minima, as indicated by magnetic data, is consistent with the occurrence of red intervals in Site 966 and other eastern Mediterranean sites drilled during ODP Leg 160, and also with astronomically-modulated variations in CaCO₃ content found in Mediterranean land-sections. This suggests that variations in eastern Mediterranean bottom-water ventilation operated at a basin-wide scale and responded to global climate, although the mechanisms responsible for such variations are unclear.

Cu Isotopes: Tracing Metal Sources in Ore Deposits

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New developments in MC-ICP-MS now allow for routine, high precision analyses of Cu isotopes in natural samples. The GeoAnalytical Laboratory at Washington State University now operates a ThermoFinnigan Neptune® MC-ICP-MS. Here, we present Cu isotope ratios for native Cu and chalcopyrite from six western hemisphere hydrothermal deposits. We employ sample-standard bracketing for analysis using NIST 976 and have undertaken an extensive machine evaluation using standards and sample-standard runs to constrain and correct ⁶⁵Cu/⁶³Cu for mass bias and machine drift. Our results show constant or negligible drift over time for standards, ensuring high in-run precision and external reproducibility of ⁶⁵Cu/⁶³Cu ratios (reported as ‰ δ⁶⁵Cu values relative to NIST 976). No molecular or isobaric interferences were detected for the analyzed minerals. Reproducibility over a one month period is better than 0.15‰. Samples of pure, hand-picked native Cu and chalcopyrite were dissolved in aqua regia and analyzed without undergoing chromatographic purification.

Our preliminary results verify heterogeneity of Cu isotopes among six ore deposits, but internal variations within individual deposits or districts may be limited. Supergene processes (weathering) apparently fractionate Cu isotopes so that their low-temperature products are enriched in ⁶⁵Cu relative to the primary hydrothermal minerals.

Samples from the six deposits range from -0.71 to 3.01‰ (n=17). Hydrothermal native Cu from 5 mines in the Michigan District yield statistically identical values from 0.26 to 0.34‰. A homogeneous source for the native Cu in this large district appears likely, without apparent fractionation during transport and deposition. Supergene native Cu from Ray, Arizona, ranges from 0.07‰ when pure, and increases with the amount of intermixed cuprite to 1.26‰, suggesting low temperature fractionation between these phases.

Chalcopyrite from four skarn deposits (Crown Jewel, WA, Empire Mine, ID, Tintaya and Las Bambas, Peru) range from -0.71 to 3.01‰. Based on our limited data set, ratios from individual deposits can vary by as much as 3‰. Heterogeneity in single deposits may be the product of any number of source, transport, or depositional variables. These include variable degrees of mixing between isotopically distinct Cu sources, and chemical processes which may fractionate Cu isotopes, such as boiling and/or redox reactions occurring during hydrothermal transport and deposition.