

Stable Isotope Geochemistry of Copper Carbonates at the Northwest Extension Deposit, Morenci District, Arizona: Implications for Conditions of Supergene Oxidation and Related Mineralization

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Abstract

Stable isotope analyses were performed on 39 copper carbonate samples from the Las Terrazas fault zone of the Northwest Extension copper oxide deposit, Morenci district, Arizona. The $\delta^{18}\text{O}$ values of azurite (23.3–25.5‰, SMOW) and malachite (21.0–23.5‰, SMOW) indicate formation in supergene conditions from meteoric water. Oxygen isotope thermometry suggests oxidation occurred at temperatures between 20° and 34°C, with lower temperatures representing ambient air temperatures, and higher temperatures reflecting minor heat production by exothermic oxidation of sulfides. For malachite, a relationship between higher temperatures and higher local oxide copper grade suggests in situ formation from oxidizing copper sulfides, whereas for azurite, the lack of such a relationship and field evidence suggest formation from copper transported along major structures.

Azurite $\delta^{13}\text{C}$ values range from –4.2 to –10.7 per mil and exhibit isotopic enrichment with increasing height above the supergene enrichment blanket (paleowater table). This evidence suggests that azurite samples received significant amounts of organic carbon resulting from the oxidation of bacteria known to be instrumental in supergene sulfide enrichment processes adjoining the water table, with upward diffusive enrichment producing the observed enrichment in ^{13}C with height above the water table. Malachite $\delta^{13}\text{C}$ values range from –9.6 to –11.1 per mil and suggest a carbon source from oxidation of surface vegetation and/or dissolution of primary or secondary carbonate by a rising water table during supergene processes.

Detailed investigation of millimeter-scale isotopic profiles across azurite veins suggests a carbon source that is initially lighter than whole-vein sample measurements with progressive isotopic enrichment of the carbon source or reservoir during vein formation. This, as well as the fact that partial pressures of CO_2 must exceed atmospheric levels for azurite formation, indicates that these veins formed in a system that was at least partially closed to the atmosphere. Oxygen isotope thermometry indicates many of the veins formed at temperatures up to 10°C above ambient temperatures, with a drop to ambient temperatures during final vein growth.

Isotopic and field evidence indicate that the Northwest Extension oxide deposit formed when a shallow, early-stage, copper-sulfide enrichment blanket was stranded above the water table. Relatively low temperature oxidation of these sulfides produced copper-rich solutions that were transported along major structures, and azurite formed when the fluids intersected pockets of high P_{CO_2} , possibly produced by seasonal oxidation of supergene-related bacteria above the water table. Over time, oxidation and related mineralization reduced permeability along major structures, and bacterial populations waned as deeper sulfide enrichment processes slowed. Lower P_{CO_2} and reduced transport potential produced in situ and highly localized oxidation, centered on the high-grade zones of the early sulfide blanket remaining in the oxidation zone, with malachite as a dominant phase.

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