



Copper and lead isotope study of sedimentary copper and manganese mineralization

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In this work, we show how the use of the Cu and Pb isotope systems provides a powerful method for determining the environmental conditions and sources of sedimentary hydrothermal mineralization. The Timna Valley of southern Israel exposes sedimentary copper and manganese mineralization that has evolved since the Cambrian. Copper sulphides formed in the Cambrian by the interaction of copper and sulphide solutions during dolomite diagenesis, where the source of the metals was weathering of the Precambrian igneous basement. Copper silicate minerals formed under oxidizing conditions in sandy lithofacies [1] while pyrolusite-hollandite manganese nodules (Type A nodules) formed in oxidizing conditions at the sediment-water interface [2]. Post-Cambrian secondary remobilization led to the in-situ formation of coronadite ($\text{Pb}_{1-2}\text{Mn}_8\text{O}_{16}$)-rich Mn-nodules (Type B nodules)[2] and the development of copper sulphide concretions in Lower Cretaceous sandstones [1] unconformably overlying the Cambrian sediments. Lower Cretaceous sandstone hosting copper sulphide concretions are also found at other locations (Amram, Eilat) in southern Israel, but unlike the Timna Valley, copper and manganese minerals are not exposed in the adjacent Cambrian rocks.

Pb isotope ratios ($^{207}\text{Pb}/^{204}\text{Pb}$; $^{208}\text{Pb}/^{206}\text{Pb}$; $^{208}\text{Pb}/^{204}\text{Pb}$ $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$) of the Cambrian copper minerals and for the Type A manganese nodules[3] in the Timna Valley plot on identical linear isotopic trends interpreted to represent mixing between radiogenic and non-radiogenic end-members. The radiogenic Pb end-member could reflect Pb, U and Th contributions from plutonic rock weathering to the Cambrian Sea exposed at the time of deposition. Correspondingly, the Pb isotopic compositions of the Lower Cretaceous copper minerals overlap with those of the epigenetic Type B nodules, forming a tight group of samples with non-radiogenic values. These strong overlaps establish a genetic connection between the metal-bearing fluids involved in the Cambrian copper mineralization and formation of Type A manganese nodules and between the fluids that remobilized copper into the Lower Cretaceous sandstones and altered Type A Mn -nodules to epigenetic Type B nodules. The Pb isotope compositions of copper sulphide concretions at Amram and Eilat differ from those of the concretions and Type B nodules at Timna; their trends instead suggest that the source of copper was direct remobilization from igneous basement.

$\delta^{65}\text{Cu}$ values of copper sulphides in the Cambrian Timna rocks are -2.04 ± 0.44 ‰. These negative $\delta^{65}\text{Cu}$ values, relative to igneous source rocks values of about 0 ‰ reflect the formation of copper sulphides through chemical reduction reactions. Using fluid speciation modeling calculations first developed for the sulphur isotope system [4], mildly reducing solution conditions of $Eh \approx 0.55$ V ($\log f\text{O}_2 \approx -23$ bars) at pH = 4, are deduced for the copper sulphide formation [5]. In contrast, the Cu-isotopic compositions of all Lower Cretaceous samples define a regional bimodal distribution with $\delta^{65}\text{Cu} = -0.91 \pm 0.51$ ‰ and -3.32 ± 0.29 ‰. Representative calculated Eh values are 0.45 and 0.65 V ($\log f\text{O}_2 \approx -29$ and -19 bars), respectively. These differences are attributed to variations in redox solution conditions during supergene copper remobilization brought about by change in the levels of the water table. Given the identical Pb isotope ratios in the Timna Valley, formation of Type B manganese nodules may also be related to these redox variations, which also brought about leaching of uranium from the Type A nodules [2].

[1] Shlomovitch et al. (1999) *Isr. J. Earth Sci.* 48, 195-208; [2] Bar-Matthews (1987) *Geol. Mag.* 124, 211-229; [3] Ehrlich et al. (2004) *Applied Geochem.* 19, 1927-1936; [4] Ohmoto (1972) *Econ. Geol.* 67, 551-578; [5] Asael et al. (2009) *Chem. Geol.* 262, 147-158.