

## Genesis of quartz-rich geodes from peculiar aqueous fluids in a Cu-Zn-Pb skarn (Temperino mine, Italy) and relations with ore bodies

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The Temperino deposit is an historical Cu-Zn-Pb skarn located in the the Tuscan magmatic province of Italy. It consists mainly of massive lenses of sulfide bodies, enclosed within white marble, from which chalcopyrite, sphalerite, and galena were exploited in the past <sup>1,2</sup>. These bodies occur close to trachyandesite and rhyolite porphyry dikes and within NNW-SSE trending, en-echelon and discontinuous ilvaite and hedenbergite skarn masses.

A peculiar characteristics of this deposit is the presence of quartz-rich geodes within the ilvaite and hedenbergite skarns. The geodes occur close to the sulfide lenses, have variable volumes (range: from 10-20 cm<sup>3</sup> to 2-3 m<sup>3</sup>), and are enclosed within the massive ilvaite and hedenbergite skarns. They represent the end of the main mineralizing event at Temperino. In addition to large euhedral quartz crystals (up to 15 cm in length), geodes contain ilvaite, calcite, epidote, and small proportions of ore minerals.

We determined the physical-chemical properties of the geode fluid combining microthermometry, Raman spectrometry, EMPA, CL imaging, and LA-ICP-MS of fluid inclusions entrapped at several stages of euhedral quartz growth. The crystals show alternations of 100 µm- to 1 mm-thick bands variably enriched in Al, Na, Li, Rb, Sr, Sb, Ba, Mn, B, Cs, and Zn, so they are chemically zoned. This zoning was accounted for in the determination of inclusion compositions. Fluid inclusions host two- (L, V) to five phase (L, V, and 3 solids) aqueous fluids. Despite this, their estimated bulk salinity is unexpectedly low (0.4-2.9 wt% NaCl eq.) and does not change systematically within the crystals. The *T<sub>h</sub>*(total) of all fluids is consistently in the 220-260 °C range and homogenization occurs mainly by bubble disappearance. The main inclusion components are (in order of relative abundance) Na, K, B, Sr, Sb, Ba, Mn, Rb, Cs, Zn, Pb, and Cu, *i.e.*, the same that make the quartz zoning.

[1] Vezzoni (2008) in Department of Earth Sciences 175 (MSc Thesis. University of Pisa, Italy). [2] Corsini *et al* (1980) *Economic Geology* **75**, 83-96.

## Molybdenum in ancient glacial tillites of different ages and its bearing on atmospheric oxygenation

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Molybdenum is an important redox indicator because of its ability to exist in either insoluble +4 or soluble +6 states. The abundance and isotopic composition of Mo in black shales have been used to make inferences about global atmospheric oxygenation. While an unambiguous and dramatic rise in oxygen occurred during the ~2.3 Ga Great Oxygenation Event (GOE), Mo systematics in shales suggest that the oceans and possibly the atmosphere contained “whiffs” of oxygen as early as 2.7 Ga, implying that oxidative weathering of the continents (and Mo loss) began before the GOE. Proxies for the average composition of the upper continental crust (UCC) should reflect this loss. V.M.Goldschmidt suggested that continental glacial till deposits could be such a proxy, and thus we have studied the chemical compositions of Paleozoic to Paleoproterozoic glacial tillites.

Ancient tillites from around the world show systematic changes in Mo abundances with time, regardless of location. Mo abundances for all Paleoproterozoic (2.4-2.2 Ga) samples are comparable to the upper crustal estimate (1.1 ppm) whereas post-Paleoproterozoic samples show depletions in Mo of up to an order in magnitude. This depletion in Mo is especially apparent when compared to elements with similar compatibility in igneous environments (*i.e.*, LREE) and when all samples are corrected for quartz and carbonate dilution when normalized to Y or Al. Relatively undepleted Mo contents in Paleoproterozoic tillites implies insufficient oxygen in the atmosphere at that time to preferentially mobilize Mo during glacial erosion, or for the UCC to have developed an intrinsic oxidative weathering chemical signature. Both hypotheses place limits on the presence of any Neoproterozoic whiffs of oxygen in the atmosphere. A test of these hypotheses is available in the Mo contents of Quaternary tills derived from exclusively Archean crustal terranes, as an absence of depletion in Mo would be inconsistent with both hypotheses.