Contrasting style of Iron formations deposited before and after the GOE

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Iron Formations are typically interpreted to indicate anoxic deep-water conditions before the rise of atmospheric oxygen and ocean ventilation. However, deposition of iron formations continued after the Great Oxidation Event (GOE) in shallow-marine conditions above the fairweather wavebase. Their deposition on several continents at ca. 1.89 Ga has been linked to a mantle plume breakout event and indicates development of the shallow-water redoxcline in the global ocean separating deep-water, anoxic and ferruginous conditions from shallow-water oxic and well-mixed environments. Iron oxidation at the dynamic redoxcline has been linked to iron-oxidizing microbial ecosystems, oxygenic photosynthesizers, and abiotic iron oxidation. In contrast, Archean iron formations were typically deposited below the storm wavebase and lack indicators of wave or storm activity. Conspicuous absence of Archean iron formations with granular structures and Fe-coated grains might indicate lack of mechanisms for quantitative iron oxidation in Archean shallow-marine settings, suggesting that oxidizing conditions and a strong redoxcline were lacking even in highly productive shallow-marine settings. Iron isotope values of Archean and Paleoproterozoic iron formations are also consistent with non-quantitative Fe-oxidation in the Archean oceans arguing against a significant role of oxygenic photosynthesis in deposition of Archean iron formations. It seems therefore likely that anoxygenic photosynthesis in depositional settings with low sedimentation rates is responsible for deposition of Archean iron formations. The prediction from the contrasting style of deposition of iron formations before and after the GOE is that deposition of iron formations occurred at lower sedimentation rates before the rise of atmospheric oxygen. If this is the case, it has implications for scavenging capacity of iron oxyhydroxides and thus interpretation of geochemical records of iron formations.

Ge, related trace elements, and Ge isotopes in sphalerite from the Saint-Salvy deposit (France) by LA-ICP-MS and MC-ICP-MS.

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The recent increasing worldwide demand in germanium (Ge) encourages research for the understanding its geological cycles and the factors controlling its concentration in minerals. Ge occurs in a wide variety of geologic environments and though it averages 1.6 ppm in the Earth's crust, high Ge contents may occur in both oxide and sulphide minerals (up to 100–3000 ppm), especially sphalerite so that Zn ores represent a major source of Ge, with coal. The Ge-bearing sphalerite of the Saint-Salvy Zn-Ge-Ag-(Pb-Cd) vein-type deposit was subjected to an integrated mineralogical, geochemical and Ge isotopic study in order to understand the mechanisms and processes that conduct Ge and related minor/trace elements (e.g. Cu, In, Ga, Ag, Sb, Sn) to be enriched in sphalerite regarding source, transport, and deposition conditions.

In situ analyses of trace elements using LA-ICP-MS, coupled with optical and electron microscopy and multivariate statistics, pointed out an opposite distribution of Ge between compositional zoning types in sphalerite, with contents ranging from 15 to 2580 ppm. In *rhythmic bandings,* Ge anticorrelates with Fe, Cd, In and Sn, and averages 500 and 200 ppm within light brown and dark brown bands, respectively. In *sector zonings*, Ge is enriched and correlates with Cu, Ga, Sb, Ag and As, and averages 1100 ppm. Cu would enhance the incorporation of trace elements, beeing involved in many coupled substitution mechanisms, among which the most notable: $2Zn^{2+} \leftrightarrow Cu^{+} + Sb^{3+}$. In addition, the main coupled substitutions $3Zn^{2+} \leftrightarrow Ge^{4+} + 2Ag^{+}$ and $3Zn^{2+} \leftrightarrow In^{3+} + Sn^{3+} +$ also occur. Trace element features of the sphalerite from Saint-Salvy compared with those of other deposits worldwide revealed to be efficient to discriminate among genetic types of ores, which may find interests in exploration guidance. Bulk Ge isotope analyses by MC-ICP-MS showed $\delta^{74}Ge_{NIST3120a}$ ranging from -1.97 to +1.01‰ (±0.25‰ 2σ SD) that positively correlate with Ge content and highlight large sub-surface fractionation processes during sulphide precipitation in low temperature hydrothermal open system.

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