

Mesoarchaean copper deposits of Dharwar Craton, India: Evidence for hydrothermal vent activity

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The Kalyadi polymetallic copper deposit occurs within the Mesoarchaean (≥ 3.0 Ga), medium-grade Kalyadi schist belt which consists of ultramafic-mafic lavas interbedded with chemogenic chert, detrital high Al-Mg pelites and siliceous sediments. This sedimentary exhalative type ore-body is the only copper deposit hosted in cherts in the western Dharwar craton, southern India. The ultramafic komatiites of Kalyadi define an Sm-Nd isochron age of 3284 ± 310 Ma [1]. The Kalyadi supracrustal rocks are intruded by tonalite-trondhjemitic gneisses (~ 3.0 Ga) and late-stage K-rich granite (~ 2.6 Ga). The Kalyadi copper deposit is polygenetic in nature. The primary ores represented by disseminations of pyrite and chalcopyrite \pm magnetite essentially along the bedding lamination of the metachert are referred to as the metamorphosed chert-sulphide rhythmites of a primary stratiform type. The ore is of low-grade and records imprints of at least two events of deformation. Pyrite is characterised by high-Co values (262 to 4524 ppm) and high \pm Co/Ni ratios (3.0 to 19.7). Rare earth element patterns of the primary ores and the host metacherts are identical, characterised by La enrichment, absence of Eu anomalies and flat to depleted HREE patterns with $\delta^{34}\text{S} = -0.8\%$. The secondary (remobilised) ores are structurally controlled occurring as veins and stringers discordant to the bedding lamination or schistosity. The constituent ores are chalcopyrite-pyrite-pyrrhotite with minor pentlandite. These sulphides with low-Co/Ni ratios (0.87 ± 1.80), have either a strong positive or negative Eu anomaly and show slight HREE enrichment. The $\delta^{34}\text{S}$ value ranges from $+2.64$ to -4.29% . It is interpreted that the primary stratiform ores and the cherts were derived from volcanogenic hydrothermal fluids as syngenetic/chemical deposits in a deep sea environment. The secondary epigenetic mineralisation is related to subsequent migmatization, deformational events and granitic activity.

[1] Jayananda M, Kano T, Peucat JJ, Channabasappa S (2008). *Precambrian Research*, **162** (1-2): 160-179.

XAS-based characterization of thioarsenates and their transformation to thioarsenites in acidic synthetic solutions

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Recent *ab initio* calculations predict that As(III)- and As(V)-thioanions can occur simultaneously in sulfidic environments at ambient pH. However, unambiguous structural characterizations for the two homologue series of thioarsenites or thioarsenates are still missing. In the present study, the molecular structures of synthesized mono-, di-, and tetrathioarsenate were characterized by XRD and XAS in their solid state and in alkaline or near-neutral solution. The determined As(V)-S and As(V)-O bond distances of 2.13-2.18 Å and 1.70 Å, respectively, are consistent with the theoretical expectations for thioarsenates and can be clearly differentiated from the corresponding As(III)-bonds, with lengths of 2.24-2.34 Å and 1.78 Å, respectively. The XANES edge positions of the individual thioarsenates (mono- 11871 eV, di- 11870 eV, and tetrathioarsenate 11869.5 eV) lie between those of As₂O₅ (11872.3 eV) and As₂O₃ (11868.2 eV) and reveal that increasing sulfur substitution decreases bond energies and, consequently, absorption edge energy. Thioarsenates can be clearly distinguished from the species formed upon acidification of tetrathioarsenate to pH < 6.3. These species were identified as thioarsenites. Their XANES edge energy lies ca. 1 eV below that of As₂O₃, confirming the redox-state change from As(V) to As(III), which is also reflected in the increased As-S distance of 2.23-2.28 Å, corresponding to As(III)-S species. Our results indicate that in synthetic solutions, thioarsenites can form as intermediate species between dissolved thioarsenates at near-neutral pH and AsS-precipitates formed under acidic conditions.