Supersolidus and subsolidus equilibria in indium-bearing magmatic-hydrothermal systems

P.A. CANDELA*, P.M. PICCOLIAND, S.M. KAYSER
AND J.R. NANCE

Laboratory for Mineral Deposits Research, Dept. of Geology, University of Maryland, College Park, MD USA

Indium demand has increased due to its use as a capacitive sensor in touch screens. The metal is commonly a by-product of mining of VMS, granite-related, and other ores, wherein the most common host mineral is sphalerite. Murakami and Ishihara [1] report sphalerite analyses from indium deposits that range up to In/Zn ~ 0.006 by weight (0.35 wt % In). At current metal prices, the contribution of these two commodities to revenue are equal for In/Zn ~ 0.003; that is, in some cases, indium revenue can exceed zinc revenue. We suggest that deposits with significant indium require a suitable mineralogical host (e.g., zinc or tin sulfides), and higher temperatures of formation. Coupled substitution of Cu(I)+In(III) for 2Zn (defining $CuInZn_{-2}$, the roquesite (rq) exchange component) accounts for indium incorporation into sphalerite.

Defining the fugacity of In (metal) in the 5 component ore system Cu-Fe-Zn-In-S, the subsolidus low-variance assemblage:

$CuFeS_2$(Ccp) + FeS_2(Py) + In (System) =
$CuInS_2$(Sp) + 2FeS(Po),

can be written in terms of chemical potentials at a given P&T. Consideration of the sulfur fugacity–dependence of the associated higher variance Po-absent, and Py-absent equilibria suggest that, for a given fugacity of In, increasing sulfur fugacity leads to increasing rq component in Sp. Incorporation of In into Po ($FeS\text{-}Fe_2S_3$ ss) is hypothesized to occur along the $InFe(III)_{-1}$ exchange vector, and, in Cu-bearing Po, as $Cu(I)In(III)Fe(II)_{-2}$.

Reconnaissance experiments have been performed to evaluate the behavior of In in the supersolidus and subsolidus realms. Cold-seal experiments were performed at 800ºC and 100MPa, durations of 5-15 days, and activity of In metal = 0.05 to ~1, to evaluate the partitioning of In between Po and rhyolite melt. Results of the experiments demonstrate the affinity of In for Po (i.e. sulfides) relative to silicate melts (D~ 2-20). Subsolidus experiments were performed in sealed silica tubes at T = 500ºC for the starting assemblage of pyrite, pyrrhotite, chalcopyrite, sphalerite and indium sulfide. Results are consistent with In concentrations: Sp > Ccp ~ Po, including wt % levels of In in Sp

[1] Murakami & Ishihara (2113) *Ore Geol. Reviews* **53**, 223-243.

Sulfate was a trace constituent in the oceans of the early Earth

DONALD E. CANFIELD[1]*SEAN A, CROWE[1,2]
CARRIAYNE C. JONES[1,2] GUILLAUME PARIS[3]
JESS F. ADKINS[3] ALEX L. SESSIONS[3]
JAMES FARQUHAR[4] AUBREY ZERKLE[5] SANG-TAE KIM[6]
AND SULUNG NOMOSATRYO[7]

[1]Nordic Center for Earth Evolution (NordCEE) and Institute of Biology, University of Southern Denmark, 5230 Odense M, Denmark *(corr: dec@biology.sdu.dk)
[2]Department of Microbiology and Immunology, Univ. of British Columbia, Vancouver, BC, Canada, V6T 1Z3
[3]Division of Geological and Planetary Sciences, Caltech, Pasadena, California, 91125, USA
[4]Department of Geology, University of Maryland, College Park, Maryland, 20742, USA
[5]Earth and Environmental Sciences, University of St. Andrews, St. Andrews, Fife, Scotland, KY16 9AJ
[6]School of Geography and Earth Sciences, McMaster University, Hamilton, ON, Canada, L8S 4K1
[7]Cibining Science Centre, Cibnong Bogor, 16911, Indonesia.

Bo Barker Jørgensen has contributed more than anyone to uncovering the secrets of the microbial sulfur cycle, and this work provides the foundation for explorationing sulfur cycle evolution through time. Here, we report on the sulfur biogeochemistry of Lake Matano, South Sulawesi, Indonesia, whose low sulfate concentrations, clear waters and ferruginous conditions provide an analogue to the nature of ocean chemsitry during much of the Archean Eon (≥2.5 billion years ago). We focused in on the fractionations associated with sulfate reduction in the anoxic water column of the lake, using a newly developed MC-ICP-MS technique [1] to obtain sulfate $\delta^{34}S$ values at sulfate levels as low as 1 micromolar. Within the chemocline of the lake, the $\delta^{34}S$ of sulfate varied from 7 per mil to 40 per mil, yielding fractionations of >25 per mil at sulfate concentrations down to ≤ 5 micromolar. These fractions are greater than previously observed at such low sulfate levels. The $\delta^{34}S$ of sulfides in the chemocline varied from 7 per mil to -15 per mil, and this range is comparable to the range of values observed in shales from the Paleo- and Mesoarchean Eons. We conclude that seawater sulfate concentrations through this time were probably less than 20 microlar most likely < 5 micromolar based on independent modelling of the Archean sulfur cycle. There is an increase in the range of shale $\delta^{34}S$ values in the Neoarchean Eon, suggesting greater fractionations accompanying higher sulfate levels associated with mild oxygenation of the surface environment.

[1] Paris, G *et al* (2013) *Chemical Geology*, **345**, 50-61.

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