Thermodynamic Controls on the Concentration of Indium in Sphalerite

John R. Nance – Advisors: Philip Candela and Philip Piccoli – Geology 393

Abstract

Indium has become an increasingly important metal over the past two decades. Indium in the form of indium tin oxide (ITO) is used as a capacitive sensor in a wide array of high-tech. Primarily, indium is a by-product of zinc mining. Sphalerite is the most important indium-bearing mineral; indium is incorporated into sphalerite by way of a coupled substitution, $Cu^{I}+In^{III} \leftrightarrow 2Zn^{II}$.

I performed experiments in evacuated and sealed, fused silica tubes. An experimental assemblage of pyrite, pyrrhotite, sphalerite, chalcopyrite, indium, sulfur, and LiCl-KCl salt flux are loaded into the fused silica tubes and sealed. The silica tubes were then placed into a vertical furnace at 500° C and experiments of varying duration (7 – 14 days) were performed to demonstrate time invariance, which can be used to demonstrate equilibrium.

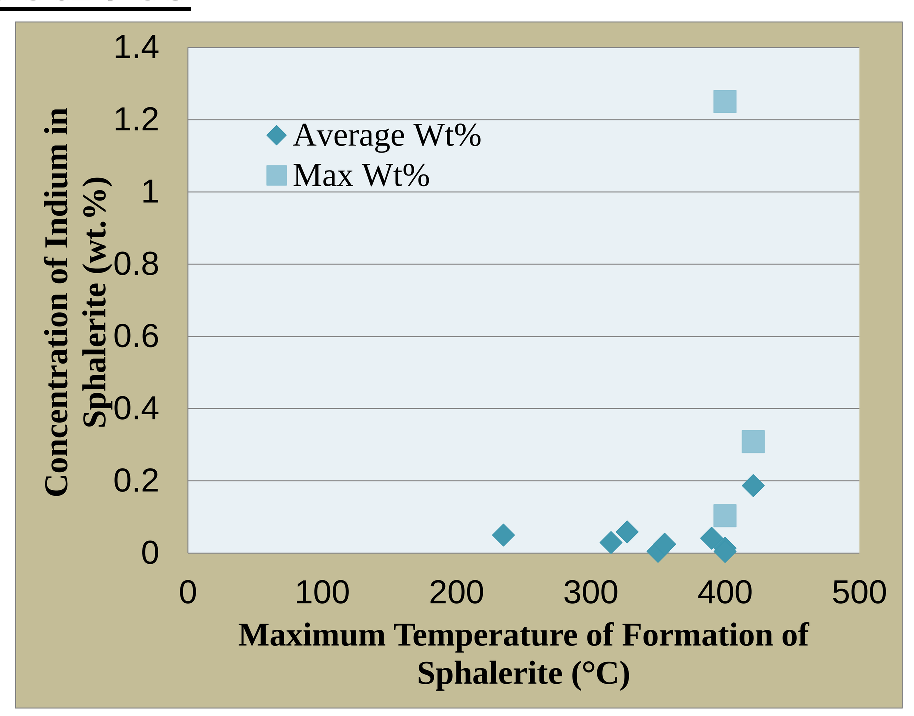
Experiments were terminated by quenching in water bath. The run products were extracted, cleaned, mounted in epoxy, and polished for analysis by electron probe microanalyzer (EPMA). The analyses provided composition and concentration data of the minerals. Reconnaissance experiments have shown that indium tends to form indium sulfide minerals and indium is also incorporated into sphalerite by the proposed coupled substitution at the weight % levels, as well as in chalcopyrite.

Hypothesis

The maximum indium concentration in sphalerite reported in the literature, at a given formation temperature, represents the maximum permitted at the given temperature and fugacity of sulfur.

Objectives

- Resolve if there is an experimentally-determinable maximum indium concentration that can occur in sphalerite and the optimal temperature and sulfur fugacity (i.e. mineral assemblage) at which this occurs.
- Determine if the reported concentrations in the literature actually represent the highest concentration or if higher concentrations are possible.



Plot showing indium concentrations in sphalerite as a function of temperature of formation (Murakami, and Ishihara, 2013). Higher temperatures are associated with higher concentrations of indium.

Thermodynamics

Three possible equilibria are considered below. Equilibrium 1 describes a low variance system with sulfur fugacity internally controlled by the coexistence of pyrite and pyrrhotite. Sulfur fugacity is related to the chemical potential of sulfur in a given system. Equilibrium 2 contains only pyrite and describes a higher sulfur fugacity system. Equilibrium 2 shifts to the products side as sulfur fugacity is increased. Equilibrium 3, containing only pyrrhotite, describes a lower sulfur fugacity system. Equilibrium 3 shifts to the reactants side as sulfur fugacity is increased.

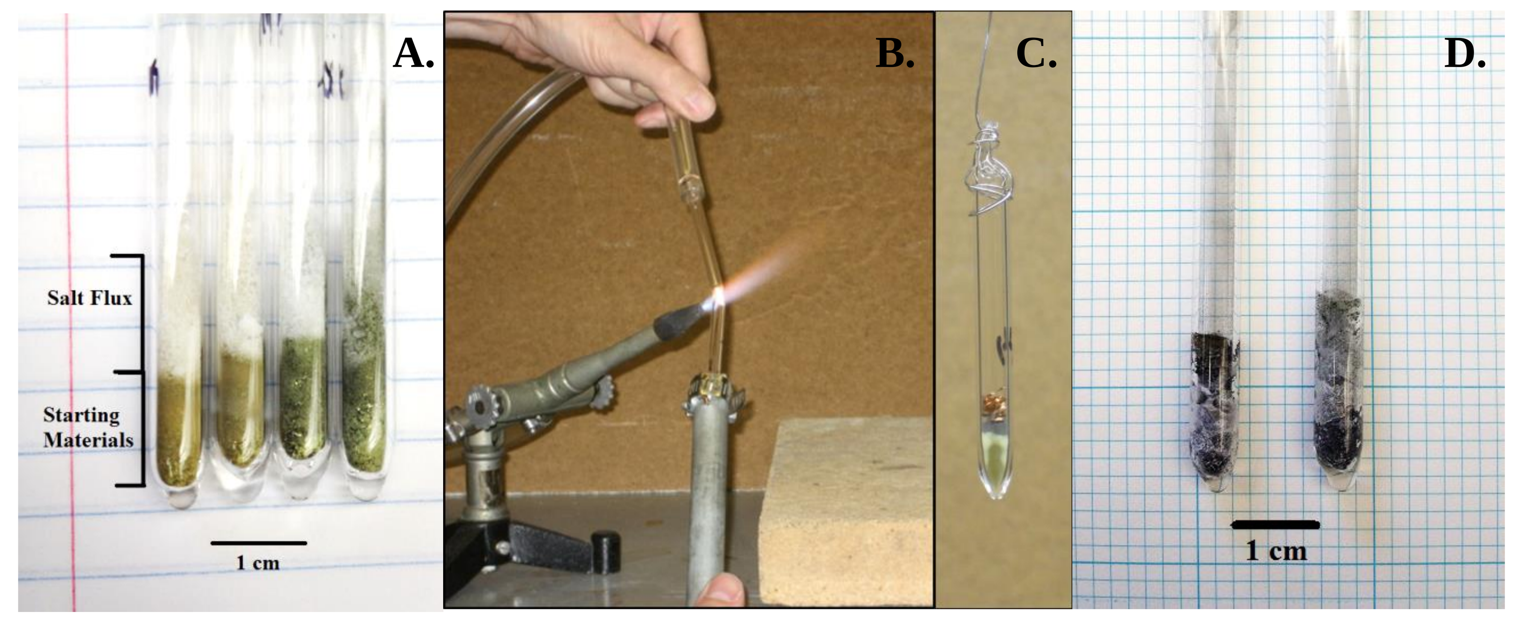
Equilibrium 1	$2CuFeS_2^{Ccp}+In_2S_3= 2CuInS_2^{Sp}+FeS^{Po}+FeS_2^{Py}$
Equilibrium 2	$\frac{1}{2}S_2^{(g)}+2CuFeS_2^{Ccp}+In_2S_3= 2CuInS_2^{Sp}+2FeS_2^{Py}$
Equilibrium 3	$2CuFeS_2^{Ccp}+In_2S_3= 2CuInS_2^{Sp}+2FeS^{Po}+\frac{1}{2}S_2^{(g)}$

Experimental Design

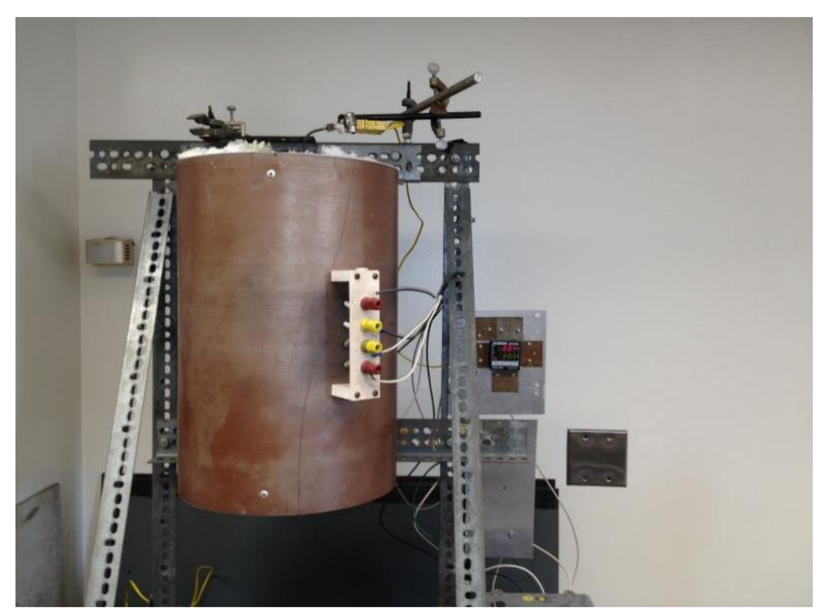
Exp.	Starting Material (mg)								Duration	Grain size of sulfides
	Chalcopyrite	Pyrite	Pyrrhotite	Sphalerite	Indium	Zinc	Sulfur	LiCl-KCl	hours (days)	
#1	0.16	0.05	0.04	0.09	0.10		0.04		168 (7)	≤ 1 mm
#2	0.16	0.05	0.04	0.08	0.10		0.04	0.20	163 (~7)	~50 µm
#3	0.16	0.05	0.04	0.09	0.10		0.04	0.18	163 (~7)	~50 µm
#4	0.16	0.05	0.04		0.10	0.06	0.07	0.20	331 (~14)	~50 µm
#5	0.16	0.05	0.04		0.10	0.06	0.07	0.18	331 (~14)	~50 µm

Experimental starting materials and recorded weights (determined by using a Mettler Toldeo analytical balance). The grain size of sulfides is the initial grain size.

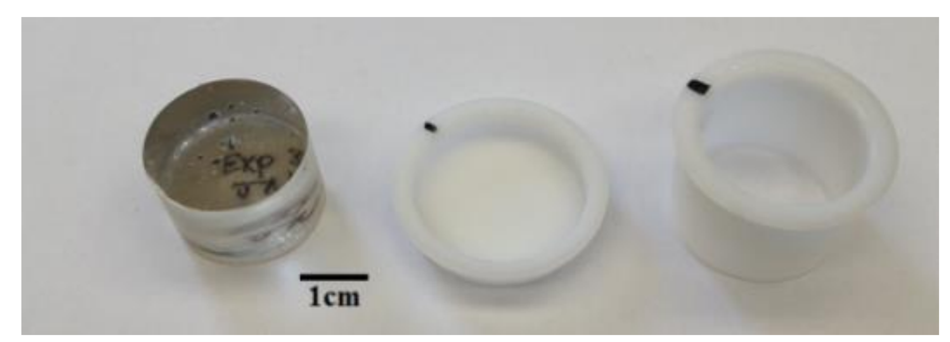
All experiments were run at 500°C. The LiCl-KCl salt flux is added to catalyze the reaction by (variably) dissolving reactants and transporting them to sites of reactions at mineral grain surfaces. The addition of salt does not promote diffusion through the minerals; that problem is solved only by reducing the diffusion distance (i.e. reducing the radius of the grains) at a given temperature.



A. Starting materials loaded into open end of silica tube. B. The loaded tube, under vacuum, being held in a methane/oxygen flame; tube is heated to pinch off and seal the tube. C. Completely sealed tube ready for the furnace. D. Run products from experiments 2 and 4 (left to right).



Fused silica tubes are suspended by chromel wire in the furnace. The experiments are run for a set period of time (7 – 14 days). The wire is then cut to release the tube which is then dropped into a water bath to quench.

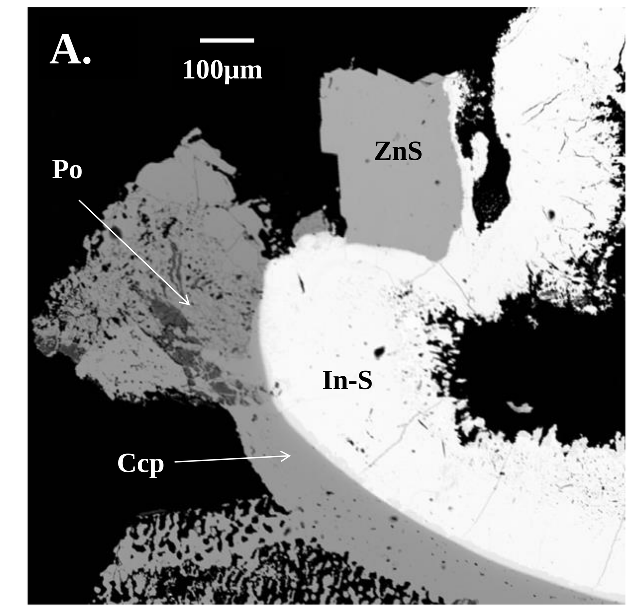


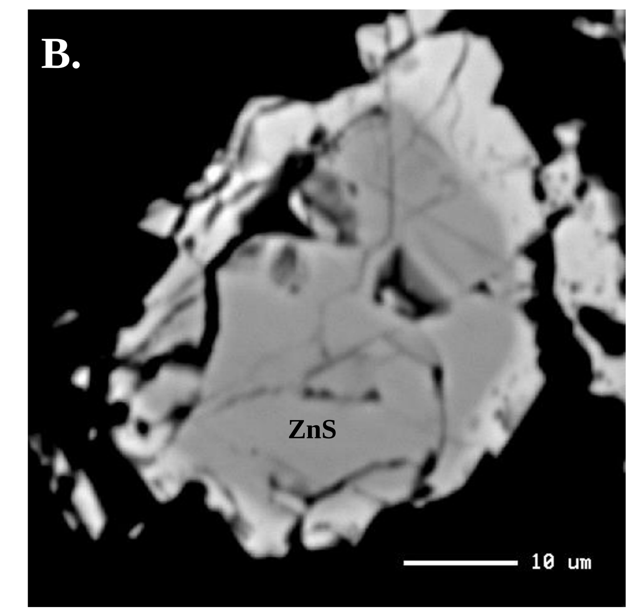
Picture of cured epoxy mount and plastic mold. Buehler© EpoFix epoxy is mixed with the hardener in a 15:2 ratio (by volume). The epoxy/hardener is mixed vigorously for 5 minutes. The epoxy is then slowly poured into the plastic mold and allowed to cure for at least 24 hours.

A thin carbon coat (200-300Å) is thermally evaporated onto the surface of the epoxy mount. The mounts are loaded into the sample exchange port, and after approximately 4 minutes when the vacuum is appropriate (2 x 10-6 torr), loaded into the instrument. An electron beam with a potential of 20 kV is focused on the sample (~1 um in diameter).

http://www.nanocenter.umd.edu/labs/NISP/images/microprobe.jpg

Results





Backscattered electron images showing textures and compositions. A. Experiment 1 – Grain 3 with all phases present. B. Experiment 2 – Grain 7 sphalerite with Cu+In – rich rim, on Cu+In – poor core.

Sphalerite analyses from experiments 1 and 2 (in weight %)

		In	Fe	S	Cu	Zn	Total	Location
Experiment 1	Grain 2	b.d.l.	0.27	33.07	0.03	66.51	99.87	Core
		b.d.l.	0.26	33.40	0.04	66.59	100.30	Core
		b.d.l.	0.34	33.08	0.11	66.83	100.36	Core
		b.d.l.	0.24	33.39	0.04	66.95	100.62	Core
	Grain 3	b.d.l.	0.15	32.99	b.d.l.	67.33	100.48	Core
		b.d.l.	0.16	33.04	b.d.l.	67.19	100.39	Core
		0.0102	0.16	33.12	0.03	66.77	100.10	Rim
		0.0370	0.18	33.02	0.04	66.25	99.53	Rim
	Grain 4	b.d.l.	0.21	32.94	b.d.l.	66.68	99.83	Core
		b.d.l.	0.21	33.15	b.d.l.	66.73	100.09	Core
		b.d.l.	0.23	32.15	b.d.l.	66.55	98.92	Rim
		b.d.l.	0.23	32.70	b.d.l.	67.18	100.11	Rim
		0.0023	0.21	33.34	b.d.l.	67.09	100.64	Rim
		b.d.l.	0.20	33.22	b.d.l.	66.93	100.35	Rim
	Grain 5	b.d.l.	0.16	33.02	b.d.l.	66.52	99.69	Core
		b.d.l.	0.17	32.70	b.d.l.	66.57	99.44	Core
		b.d.l.	0.18	32.29	b.d.l.	66.44	98.90	Rim
		b.d.l.	0.17	32.88	b.d.l.	66.90	99.96	Rim
	Grain 6	b.d.l.	0.13	32.66	b.d.l.	66.95	99.74	Core
		b.d.l.	0.11	33.08	b.d.l.	67.13	100.32	Core
		b.d.l.	0.17	32.10	b.d.l.	66.43	98.70	Rim
		b.d.l.	0.14	33.11	b.d.l.	67.03	100.29	Rim
Experiment 2	Grain 1	0.0240	1.99	33.53	0.25	62.95	98.74	Core
		0.0278	2.02	33.56	0.25	63.07	98.93	Core
		0.0343	2.04	33.50	0.29	62.95	98.81	Core
		23.44	7.97	30.69	14.14	23.46	99.70	Rim
	Grain 6	0.026	1.44	33.90	0.26	64.64	100.27	Core
		4.059	4.91	33.47	2.34	55.04	99.82	Core
		8.586	6.32	32.94	5.38	45.95	99.17	Core
		19.02	7.75	31.37	11.54	29.81	99.49	Rim
		19.75	8.27	31.25	12.31	27.49	99.06	Rim
	Grain 7	0.026	1.26	33.91	0.33	63.00	98.53	Core
		2.060	4.11	33.34	1.52	57.27	98.29	Rim
		6.522	5.50	32.94	3.90	49.72	98.59	Rim
		17.45	7.15	31.30	10.68	32.59	99.16	Rim

Future Work

Next semester, experiments will be performed at different temperatures and with different mineral assemblages (and therefore different sulfur fugacities). These assemblages will be: pyrite without pyrrhotite; and pyrrhotite without pyrite. Additionally, small sphalerite grains with a given roquesite ($CuInS_2$) mole fraction will be synthesized at 800° C in salt flux; these will be used as starting materials in subsequent experiments so as to reduce the time to reach equilibrium.

Take Home Message

A salt flux was added to experiments to increase reaction rates. Initial experiments at 7 days were found to be sluggish. Adding a salt flux and/or extending run time resulted in increased Cu+In in sphalerite; maximum Cu+In in experiment 1 was 0.04±0.01 weight % copper and 0.0370±0.002 weight % indium; maximum Cu+In in experiment 2 was 14.14±0.04 weight % copper and 23.44±0.01 weight % indium. Therefore significant indium can be added to sphalerite at the temperature and sulfur fugacity of the experiments, demonstrating feasibility.

Bibliography

- Murakami, H., and Ishihara, S., 2013, Trace elements of Indium-bearing sphalerite from tin-polymetallic deposits in Bolivia, China and Japan: A femto-second LA-ICPMS study: Ore Geology Reviews, v. 53, p. 223–243
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