Partitioning of Indium Between Pyrrhotite and Silicate Melts

Sean Kayser
GEOL 393
Advisors: Dr. Philip Candela and Dr. Philip Piccoli

Introduction

Indium is used in many electronic devices including touch screen cell phones, LCD's, and solar cells. The ability for indium to behave as a capacitive sensor in touch screens has increased the demand for indium. Indium occurs in economic concentrations in a wide variety of ore deposits. Of these ore deposits, granite-related, vein-type deposits, skarn-type deposits and vein and disseminated ore deposits are the important sources for indium. These ore deposits are thought to have been formed by magmatic-hydrothermal processes. In magmatic-hydrothermal systems, fluids generated during the crystallization of a shallowly emplaced magma can transport metals to sites of ore deposition. By studying the partitioning of indium between silicate melts and selected crystalline phases, geologists may better estimate the quantity of indium that may be available for partitioning into a magmatic aqueous, ore forming fluid during crystallization of the ore-related magma.

Objectives

- determine the partitioning of indium between pyrrhotite and silicate melts in order to gain a better understanding of how sulfides can affect the concentration of indium in silicate melts
- evaluate the effect of copper addition to pyrrhotite on indium partitioning between pyrrhotite and silicate melts
- evaluate the effect of indium-chloride complexes in the melt on the partitioning behavior of indium between pyrrhotite and silicate melts

Why Pyrrhotite?

Pyrrhotite has been found to be a dominant sulfide mineral in shallowly emplaced arc magmas (Candela and Holland, 1986). Pyrrhotite has been found, in numerous studies (e.g., Jugo et al., 1999), to be responsible for the sequestering of ore metals in arc magmas.

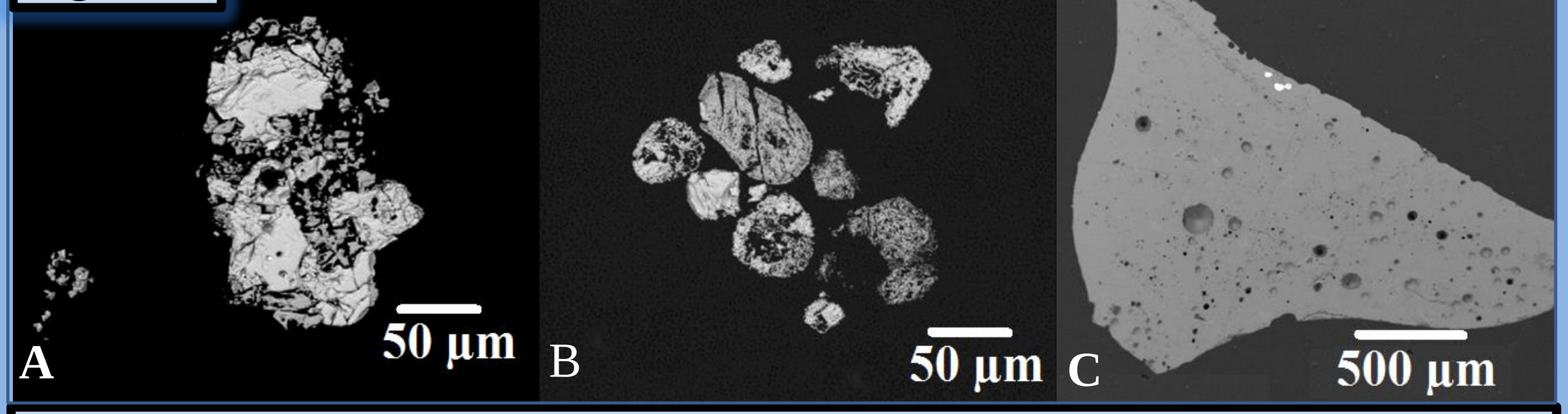
Why Indium-Gold Alloy?

Initial experiments failed due to pure indium alloying with the outer gold capsule (Figure 1). To overcome this a indium-gold alloy was created containing 5 wt% indium and 95 wt% gold.

Hypothesis

In a pyrrhotite-saturated silicate melt, indium will behave as a compatible element due to the effect of pyrrhotite alone, as is the case for copper.

Figure 3



Backscattered electron images of experimental run products. (A) Run product pyrrhotite from run 109. (B) Run product pyrrhotite from run 107. (C) Run product glass from run 104

Table 1. Summary of Experimental Conditions

Run	Aqueous solution	Duration (s)	log fS_2 ± 1σ
		[s x 10^5)]	
101	H_2O	4.3	-
102	H_2O	4.3	-
103	H_2O	4.3	-
104	H_2O	4.3	-0.40 ±0.18
105	H_2O	4.3	-0.58 ± 0.18
106*	H_2O	8.6	-
107	1.01 M Cl solution	4.3	0.32 ± 0.18
108**	H_2O	13.0	-
109	1.01 M Cl solution	13.0	0.82 ± 0.18

All experiments performed at 800° C and 100 MPa.

*A partition coefficient for experiment 106 could not be calculated due to incomplete analysis of the pyrrhotite.

**EDS analysis of experiment 108 showed that all of the pyrrhotite was transformed to magnetite rendering the experiment useless.

Table 2.

Run	[In] in pyrrhotite	[In] in glass	$D=[In]_{Po}/[In]_{Melt}$
	wt% ± 1 σ (n*)	wt% 1σ (n*)	$D_{In}^{Po/Melt} \pm 1\sigma$
104	0.29 ± 0.06 (3)	0.044 ± 0.002 (6)	6.43 ± 1.45
105	0.16 ± 0.03 (8)	0.0067 ± 0.0015 (5)	23.92 ± 6.69
109	0.16 ± 0.05 (5)	0.072 ± 0.007 (8)	2.25 ± 0.79

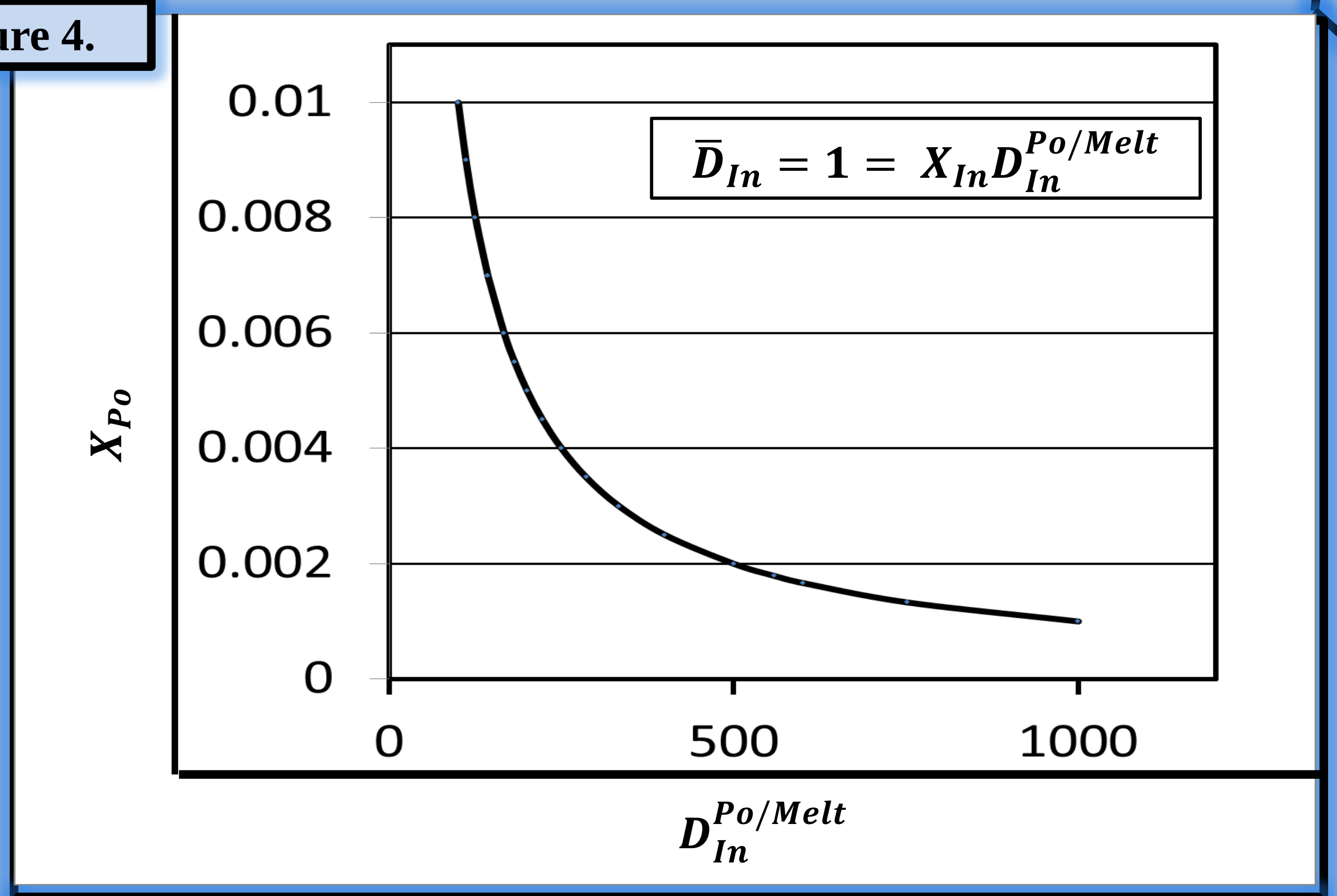
***(n) = number of analysis performed**

Indium concentrations and calculated partition coefficients for indium between pyrrhotite and melt.

Figure 1.

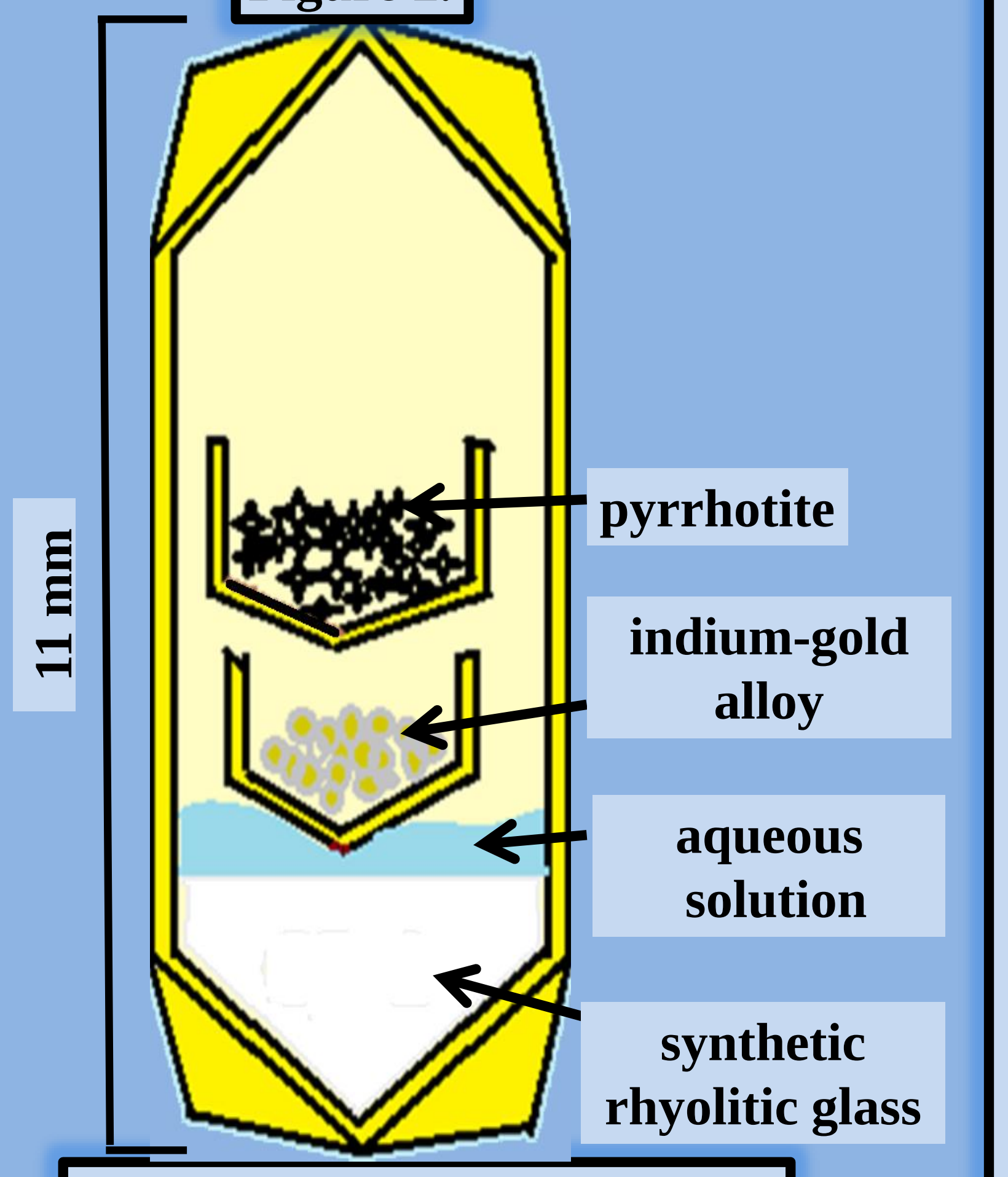
Experimental gold capsule with hole near center created due to indium alloying with the gold capsule during experiment

Figure 4.



Calculated hypothetical pyrrhotite/liquid partition coefficients for indium plotted against weight fraction of pyrrhotite (X_{Po})that yields a bulk partition coefficient equal to 1.

Figure 2.



Cartoon of loaded gold capsule

Experiments

Cold seal experiments were performed with synthetic rhyolite, synthetic pyrrhotite, and indium-gold alloy as the solid phases, and an aqueous solution. Experiments were performed in gold capsules, at 100 MPa and 800° C, and for durations of 5 to 15 days. Figure 2 illustrates a loaded gold capsule. Electron probe microanalysis was performed to measure the concentration of major and minor elements in the pyrrhotite and the glass, and partition coefficients were calculated. Figure 3 shows backscattered electron images of experimental run products . A summary of experiments performed is presented in Table 1.

Further experiments will be carried out in which copper will be added to the pyrrhotite. The starting iron/sulfur ratio in the pyrrhotite can be changed resulting in a change in the sulfur fugacity within the experiment, possibly changing the partition coefficient of indium between pyrrhotite and the silicate melt.

Further, a brine solution (NaCl, KCl, HCl) will be added to the experiment instead of distilled water. The addition of a brine solution containing NaCl, KCl and HCl can lead to the formation of indium chloride complexes in the melt, possibly stabilizing indium in the melt phase. Indium chloride complex in the aqueous phase could potentially speed up the kinetics of the indium exchange between pyrrhotite and melt. The former effect could potentially change the partition coefficient for indium between pyrrhotite and silicate melt, whereas the latter effect will not change the partitioning behavior.

Partition Coefficients

Partition coefficients are used to model the behavior of trace elements in magmatic-hydrothermal systems. The equation that is used to approximate the partitioning of trace elements between coexisting phases is the Berthelot-Nernst equation: $D_i = \frac{C_i^{Solid}}{C_i^{Liquid}}$ where C_i^{Solid} is the concentration of *i* in the solid, C_i^{Liquid} is the concentration of *i* in the liquid and D_i is the partition coefficient. To better understand the evolution of a magma the bulk partition coefficient ($\bar{D}_i$) is calculated. The bulk partition coefficient is defined as: $\bar{D}_i = \sum X_i D_i^{\frac{solid}{melt}}$ where: X_i is the weight fraction of mineral *i* in the products of crystallization and $D_i^{\frac{solid}{melt}}$ is the partition coefficient for the trace element in mineral *i*. Figure 4 presents calculated hypothetical pyrrhotite/liquid partition coefficients for indium as a function of the wt% pyrrhotite required to yield bulk D equal to 1.

Summary

Indium demand continues to grow as the applications for indium are developed. I propose to determine the partitioning of indium between pyrrhotite and silicate melts in order to gain an understanding of how pyrrhotite can affect the concentration of indium in silicate melts. Preliminary data presented in Table 2 indicate the partition coefficient for indium between pyrrhotite and silicate melt is between 2 and 20

Acknowledgments

I thank my advisors, Dr. Philip Candela and Dr. Philip Piccoli for their guidance and patience in the writing of this proposal. I thank them both for taking their time to answer and explain the multitude of questions I asked.

References

Candela, P.A. and Holland, H.D., 1986, A mass transfer model for copper and molybdenum in magmatic hydrothermal systems; the origin of porphyry-type ore deposits: Economic Geology, v. 81, no. 1, p. 1-19.

Jugo, P. J., Candela, P.A., and Piccoli, P.M., 1999, Magmatic sulfides and Au: Cu ratios in porphyry deposits: an experimental study of copper and gold partitioning at 850 C, 100 MPa in a haplogranitic melt–pyrrhotite–intermediate solid solution–gold metal assemblage, at gas saturation: Lithos, v. 46, no. 3, p. 573-589.