# The Behavior of Chalcophile and Siderophile Elements during Magmatic Differentiation as Observed in Kilauea Iki Lava Lake, Hawaii

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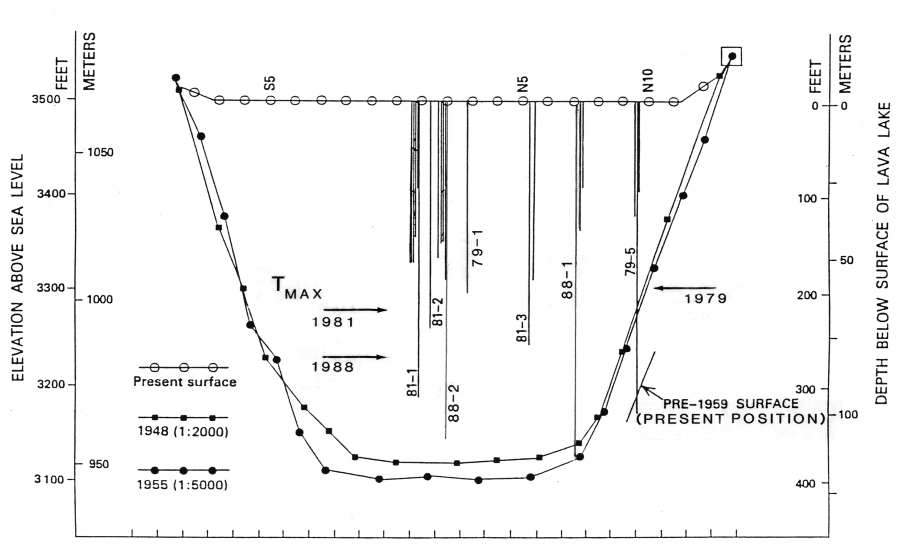
## Motivation

- Determine how strongly chalcophile elements partition into sulfur bearing phases in a basaltic melt
- Understand the cycling of chalcophile elements in the crust and mantle
- Illuminate processes of magmatic differentiation and crustal evolution
- Gain a better understanding of ore formation at various tectonic settings

Here, the behavior of eleven chalcophile and siderophile elements (Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl, and Bi) is examined in a differentiated basaltic lava lake using high precision whole rock and *in-situ* phase analyses.

## Kilauea Iki Lava Lake

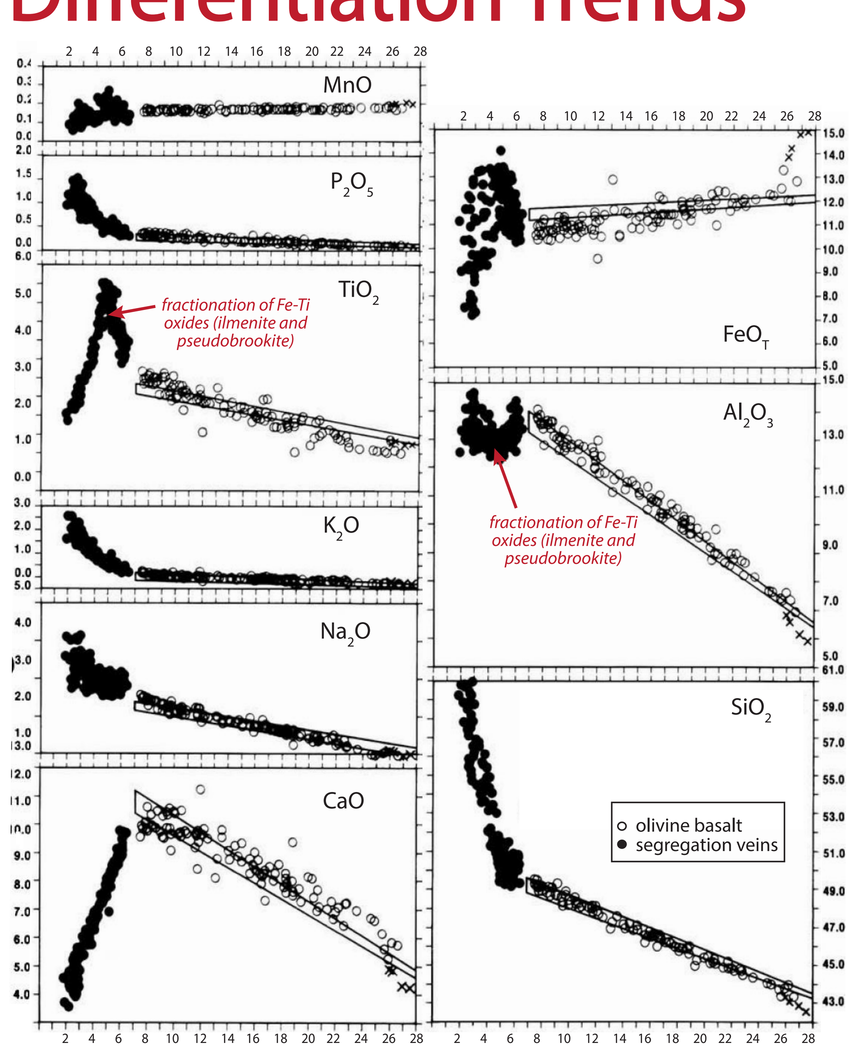
- Formed in 1959 as basaltic lava ponded in a pre-existing crater
- Differentiated and cooled over four decades while being cored by the USGS
- Primarily composed of olivine basalt, but also contains internal differentiates (segregation veins and bore-hole oozes) that formed as evolved melt was segregated from the basalt
- KI is an excellent and well characterized natural laboratory for studying magmatic differentiation




A cross section of the lake depicting the locations of drill cores. The lake was drilled between 1967 and 1988. Figure from Helz, 2012.

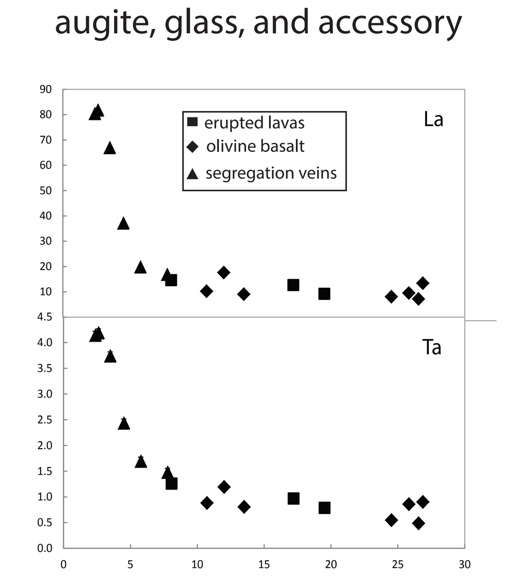
The surface of Kilauea Iki after the 16th eruption episode in 1959. A total of 17 episodes of filling and draining lava formed the lake. Photo taken by J.P. Eaton, USGS

## Differentiation Trends



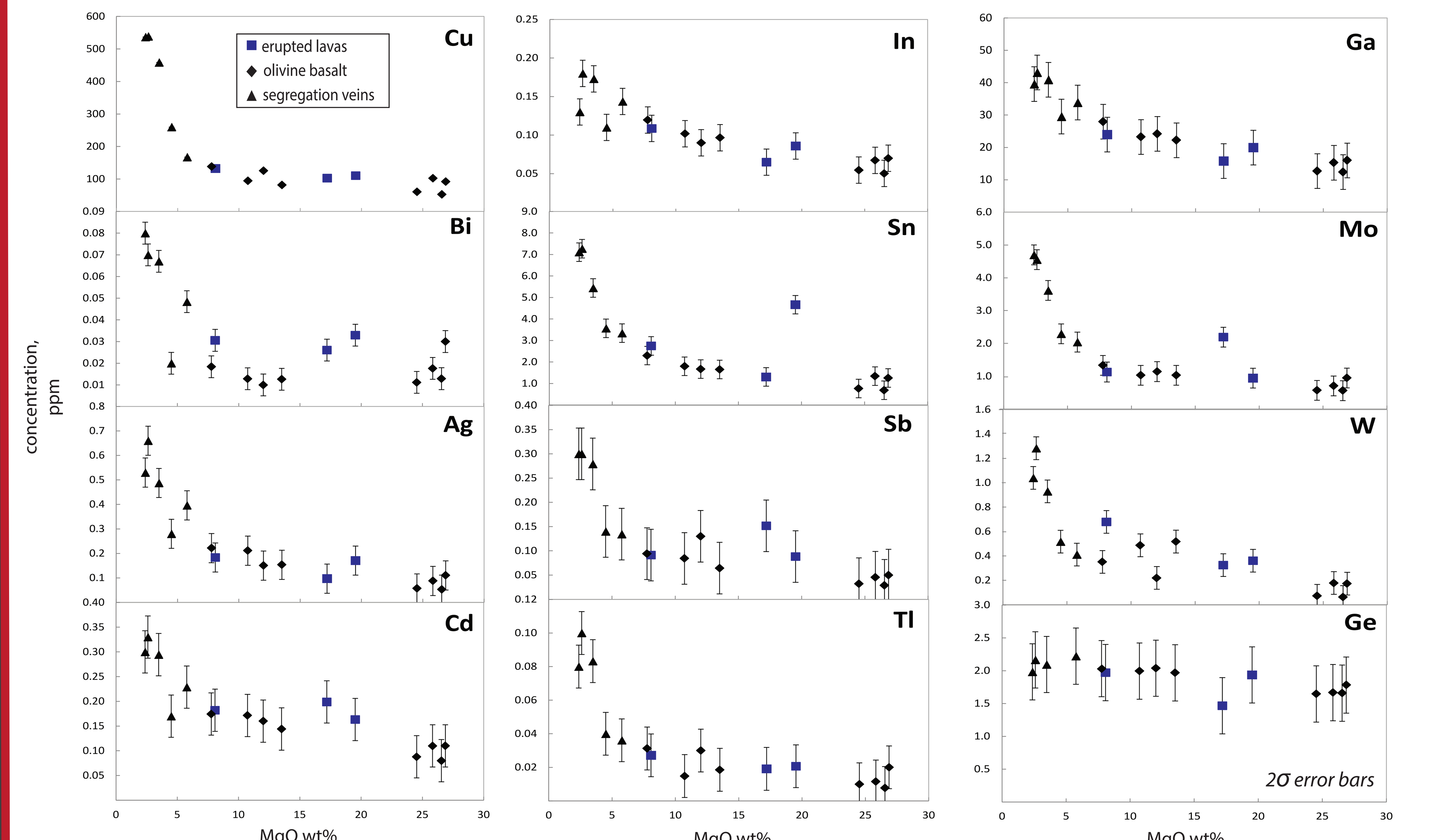

Major element oxide variation with MgO, modified from Pitcher et al. (2009)

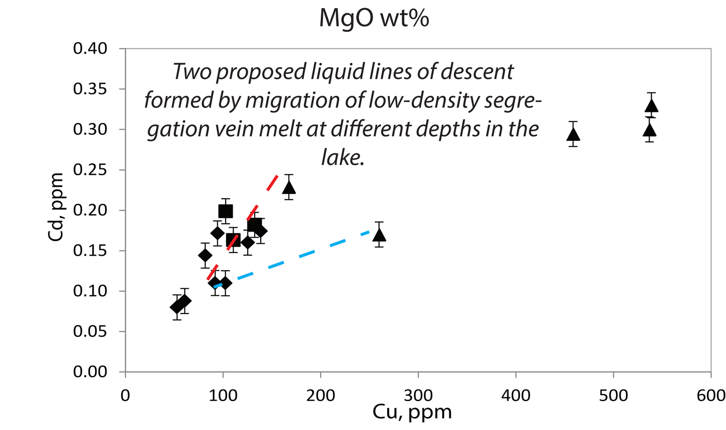
- 28 to ~7 wt.% MgO: Olivine and chromite vary in abundance
- 7 to 2 wt.% MgO: Internal differentiates contain plagioclase, Fe-Ti oxides, augite, glass, and accessory




Harker diagrams from this study displaying trends typical of incompatible elements in the system. 2σ values lie within the data points.

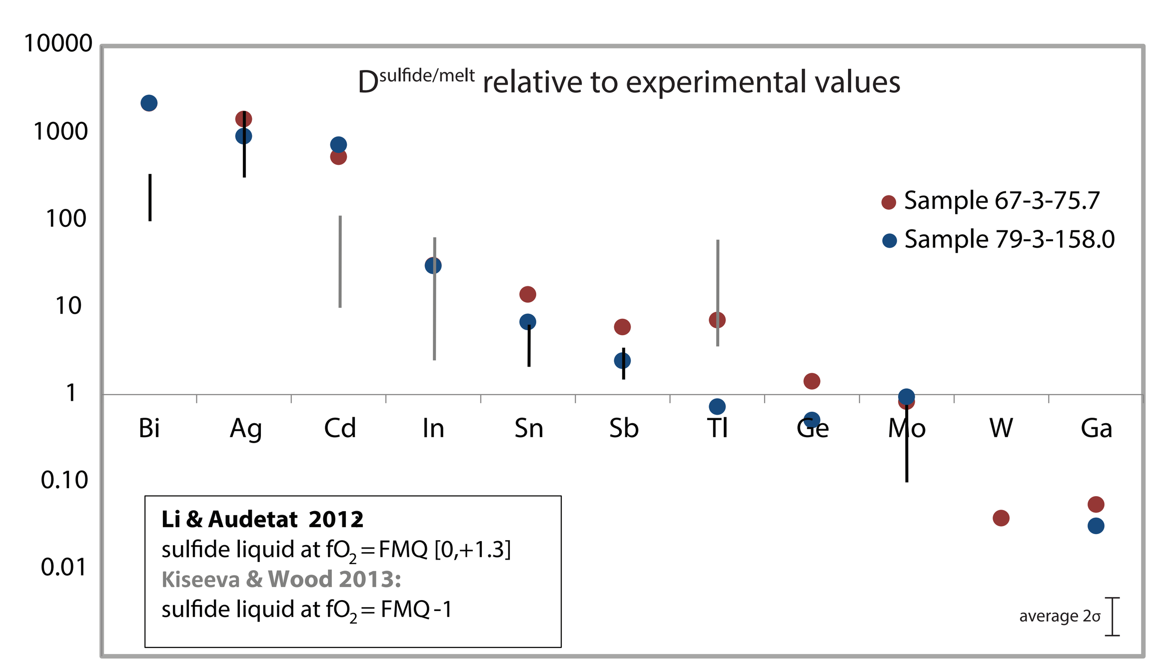
## Chalcophile Element Behavior during Differentiation

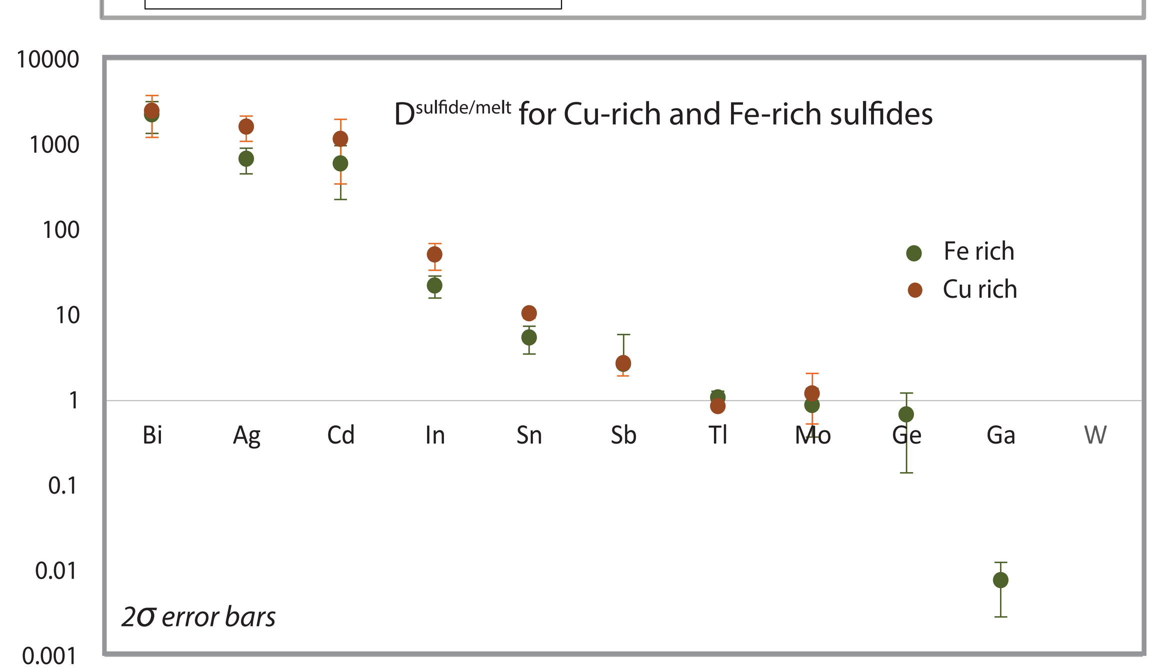



- Cu appears incompatible, but is a major constituent of Cu-Fe sulfide blebs that form at ~13 wt% MgO; apparently these blebs did not fractionate
- Scatter in some elements may reflect divergent liquid lines of descent as low-density melt migrated through the lake.
- Extreme enrichments (Bi, Sn, Mo, Sb) in the two erupted lavas may be associated with sample contamination and initial processing

## Partition Coefficients




*Conditions in Kilauea Iki:*
$fO_2$: -1< ΔNNO< 0
T = 925 - 1030 °C
Sulfide composition: Fe-Cu-S solution.
Cu ranges between 30 and 55 wt%.

**Left:** Partition coefficients measured between immiscible sulfide blebs and glassy matrix in two segregation veins. Sample 79-3-158 is more differentiated (4.5 wt% MgO) than 67-3-75.7 (5.8 wt % MgO).

Chalcophile = Bi, Ag, Cd, In, Sn, Sb
Weakly to non-chalcophile = Tl, Ge, Mo
Not chalcophile = W, Ga

**Left:** The difference in partition coefficients between sulfides in segregation vein sample 79-3-158. Ge, Ga, and W concentrations were below detection limit in one or both sulfides.

Fe rich sulfide average = 38 wt% Fe, 30 % Cu, 32 % S
Cu rich sulfide average = 24 wt% Fe, 37 % Cu, 29 % S

Most elements show similar partitioning behavior, however Ag, In, and Sn are significantly enriched in the Cu-rich sample, suggesting their partitioning is dependent on Cu abundance.

## Petrography

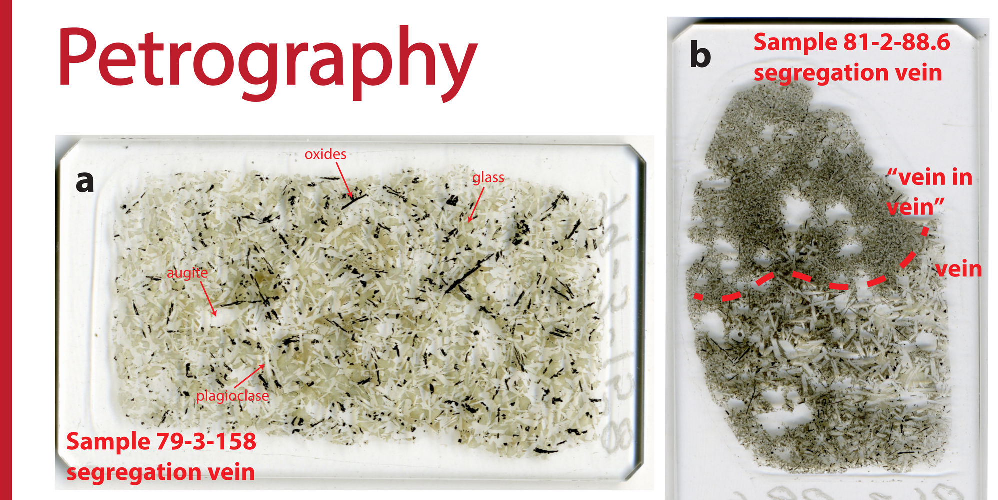



**Figure a:** Thin section scan of a segregation vein. Mineralogy: opaque ilmenite and pseudobrookite, clear plagioclase laths, euhedral augite (clear), greenish glassy groundmass, and microscopic sulfides and apatite needles.

**Figure b:** Thin section scan of an internally differentiated vein whithin a segregation vein. Mineralogy is the same as above.

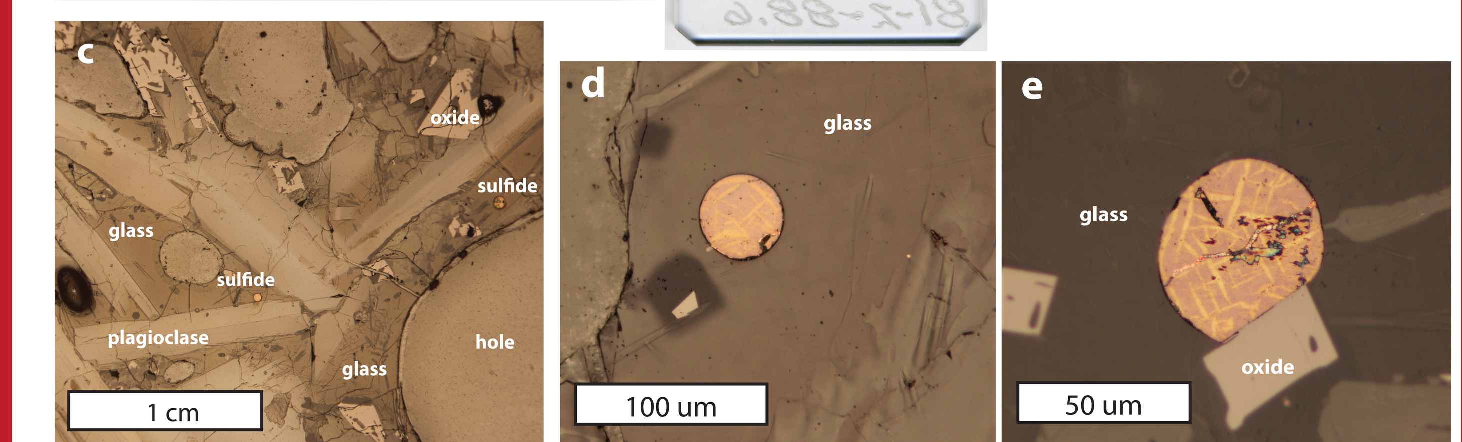
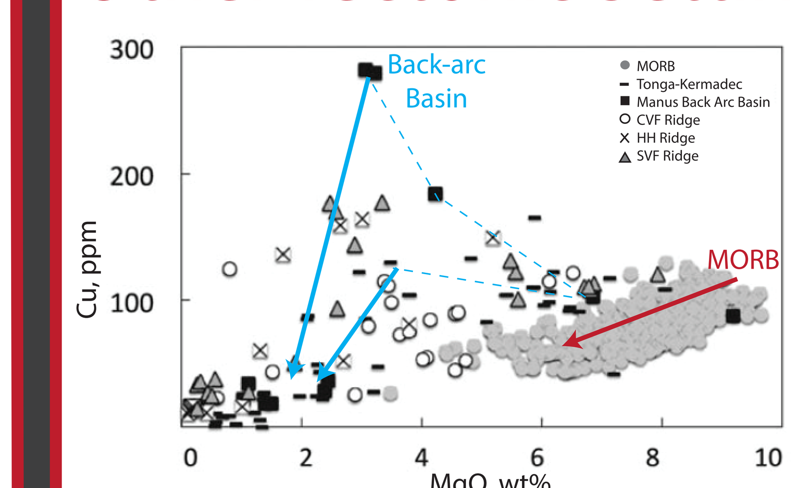



**Figure c:** Photomicrograph of a segregation vein showing immiscible sulfide blebs.
**Figures d and e:** Photomicrographs of immiscible sulfide blebs hosted in the glassy matrix of a segregation vein. The blebs show exolution textures as a Fe-rich sulfide phase exsolves from Cu-rich sulfide. Photos are taken in reflected light.

## Other Tectonic Settings




Cu-MgO variation diagram from Jenner et al. (2015) showing sulfide saturation and fractionation out of a melt for MORB (grey circles) and various arc settings.

- In MORB, sulfides saturate at ~10 wt% MgO
- In back-arc settings sulfides saturate between 2 and 4 wt% MgO.

Kilauea Iki reaches sulfide saturation at ~13 wt% MgO but they do not fractionate out of the system (see Cu-MgO diagram)

## Main Findings

- In the Kilauea Iki Lava Lake, sulfides form at 13 wt.% MgO, but do not fractionate from the evolving melt as do olivine and Fe-Ti oxides. This may be due to the sulfides sticking to other crystals, inhibiting removal.
- Sulfide saturation occurs earlier than is observed in MORB and arc settings
- Sulfides are observed to fractionate from MORB and arc lavas. This suggests that sulfide and, thus chalcophile element behavior, is dependent on tectonic setting.
- "Chalcophile elements" display a range of affinity for the sulfide phases. Bi, Ag, Cd, In, Sn, Sb are strongly chalcophile, Tl, Ge, and Mo are weakly chalcophile, while W and Ga are not chalcophile.
  - Mo and Ge display slight compatibility in Fe-Ti oxides (Mo may substitute for Ti and Ge for Fe).
  - Tl, W, and Ga are lithophile in this system.
- Ag, In, and Sn partitioning behavior depends on the abundance of Cu in sulfide phases.

## References

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