Sulfur mobility in arc magma systems: Implications for porphyry ore deposits

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INTRODUCTION

Magmatic-hydrothermal porphyry deposits

- Form above active subduction zones
- Centered on intermediate porphyritic stocks
- *Deep:* porphyry Mo ± Cu ± Au
- *Shallow:* epithermal Au ± Ag ± Cu
- Also host critical metals: Pd, Te, Se, Bi Zn, Pb
- **Represent sulfur and metal anomalies**

The Bingham Canyon porphyry deposit *(usra.edu)*


Mount Pinatubo eruption in June 1991

Metal	Average crustal abundance	Typical exploitable grade	Concentration factor
Cu	27 ppm	0.2 wt%	**x 75**
Au	1.3 ppb	2 ppm	**x 1500**

Mt. Pinatubo eruption — ***~10 million tons sulfur***

Bingham Canyon — ***~1 billion tons sulfur***

The "excess sulfur problem"

$$\text{Excess S} = \frac{\text{S released to the atmosphere}}{\text{S determined by petrological estimates}}$$

Primary objective: Physically assess mass transfer across the interface during magma mixing

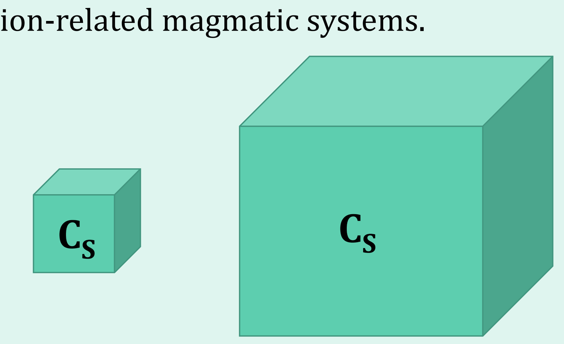
HYPOTHESIS


Angular mafic enclaves in a felsic host rock at Quizapu Volcano, south-central Chile.

Sulfur excess requires input from underplating, un-erupted mafic magma

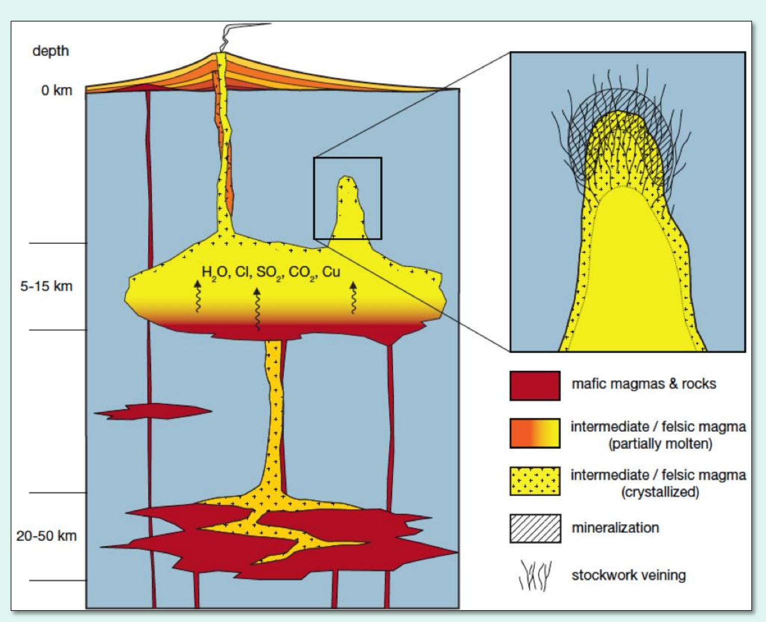
Magma mixing

A well-documented phenomenon that occurs when two chemically distinct magmas (e.g., basalt and rhyolite) mix and mingle physically and chemically in subduction-related magmatic systems.



felsic magma << mafic magma

Mafic magmas contain an order of magnitude more sulfur than felsic magmas (*Hattori & Keith 2001*)

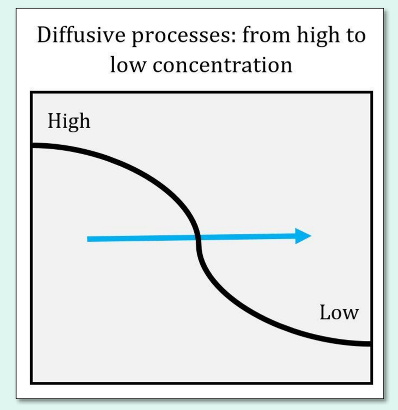


Compositionally zoned magma chamber in the upper crust that is replenished during underplating. [Audetat & Simon 2012]

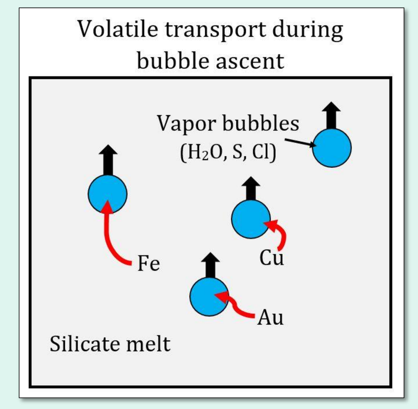
Porphyry ore deposit recipe

1) Partial melting in the asthenospheric/lithospheric mantle
2) MASH zone interactions at the base of the crust: mixing, assimilation, storage, and homogenization
3) Formation of upper crustal magma chamber
4) Repeated replenishment by ascending mafic magmas
5) Volatile exsolution, sulfur and metal transfer from melt to fluid
6) Ascent and precipitation of metal sulfides

Transport by diffusion through silicate melt or by way of magmatic volatile phases?



vs.



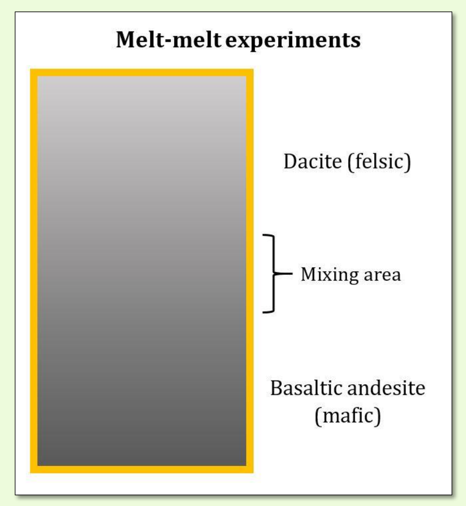
Research questions

- **R1:** Over a range of P-T-fO_2-H_2O conditions, is the transport of volatiles and metals dominated by diffusive transport via silicate melt or transfer by way of volatile phases (bubbles)?
- **R2:** As redox conditions vary from reduced to oxidized, how does the oxidation state of the melt affect the mobility of volatiles and metals?

METHODS

We performed two types of diffusion-couple experiments to investigate mass transfer during mixing of mafic and felsic magmas at upper crustal arc magmatic conditions:

1) **Melt-melt experiments** – both sides are above the liquidus temperature i.e., no mineral phases exist
2) **Crystal mush experiments** – both sides consist of a heterogeneous mixture of melt + crystals ± bubbles

1)


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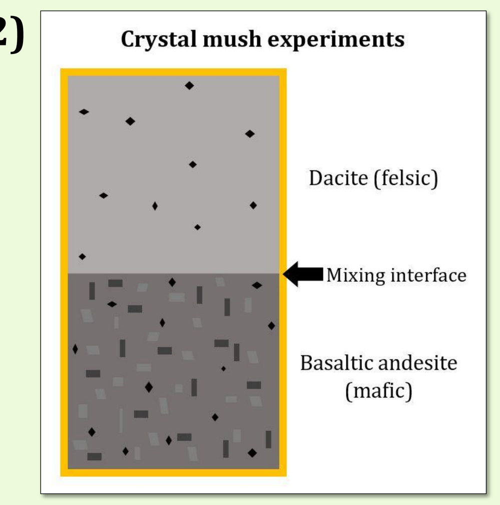


Starting materials were natural basaltic andesite and dacite from the most recent eruptions of Volcán Quizapu in Chile, the compositions of which have been fully characterized and reported (Fiege et al., 2017; Ruprecht et al. 2012). Prior to each diffusion-couple experiment, the mafic and felsic starting materials were equilibrated separately and then juxtaposed in a single capsule, with the less dense felsic material overlying the mafic material.

Experiments are designed to simulate the interaction of mafic and felsic magma in subduction zones. They are time-series: each **crystal mush series** has a 1 hr, 10 hr, and >79 hr duration @ FMQ+3 and +4, and each **melt-melt series** has 3 time durations (0 hr, 1 hr, 5 hr, 10 hr, or 20 hr) @ FMQ+0.2, +1.3, and +3.

Sulfur, H_2O, and Cl concentrations were systematically varied to represent arc magmatic compositions:

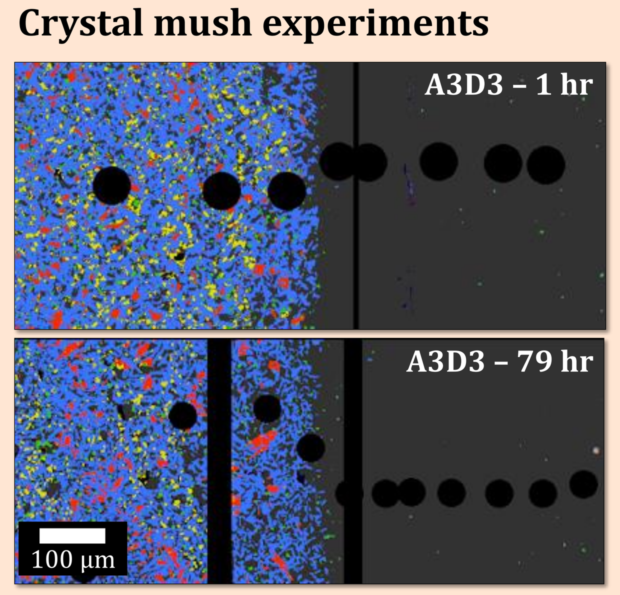
- **[H_2O]** between 0.5 – 5 wt % (dacite has more H_2O than basaltic andesite, except in A8D8 series)
- **[S]** – zero (dacite), 300 (dacite), or 1,000 (basaltic andesite) ppm
- **[Cl]** – zero (basaltic andesite), 500 (basaltic andesite), or 1,000 (dacite) ppm

↑ H_2O = volatile saturation = free bubbles form

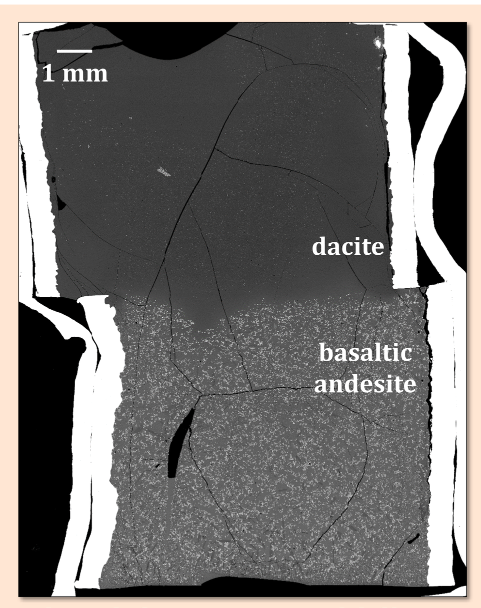
↓ H_2O = no bubbles form = higher crystallinity

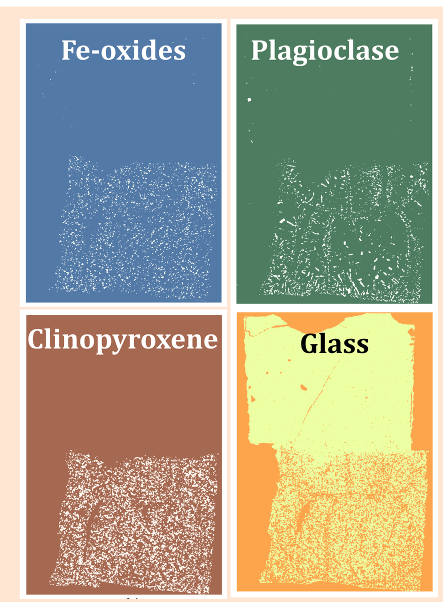
RESULTS

Crystal mush experiments



Dissolution sequence in mafic magma at the mixing interface:
cpx -> opx -> plg -> spl





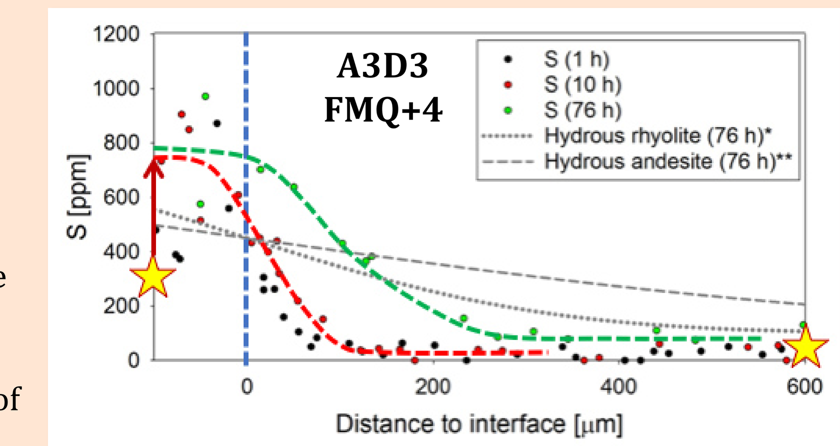
Above left: BSE image of diffusion-couple crystal mush experiment A10D10-2 showing dacite (top, mostly glass) and basaltic andesite (bottom, highly crystallized). *Above right*: Python-generated phase maps of same run. Magnification 200x

Crystal mush experiments

The sulfur diffusion profiles (right) at FMQ+4 are slower than expected based on experiments by Watson (1994) for sulfur diffusion in hydrous rhyolite and hydrous andesite at reducing conditions (near the IW redox buffer; ~FMQ-3).

Sulfur content of the interstitial melt on mafic side of diffusion couple contains less sulfur than expected based on mass balance calculations. The "missing sulfur" is most likely present in bubbles of magmatic-hydrothermal fluid. Stars = initial conc.

Sulfate diffusion profiles

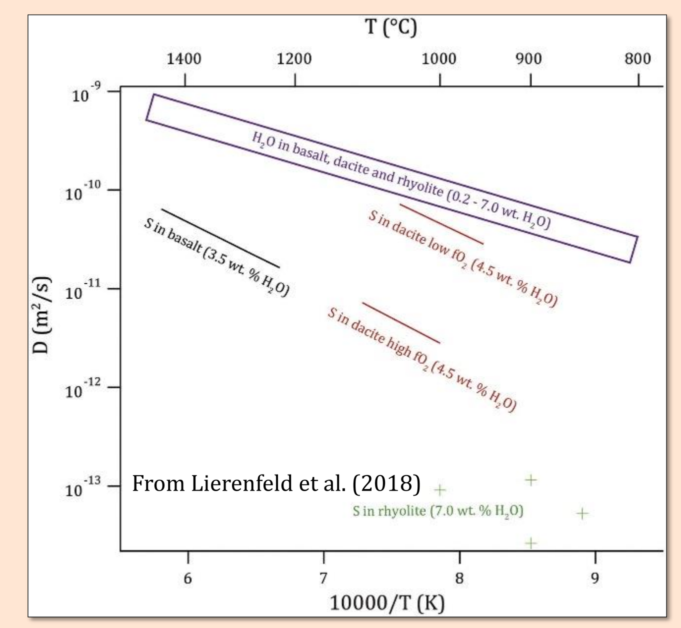


Melt-melt experiments

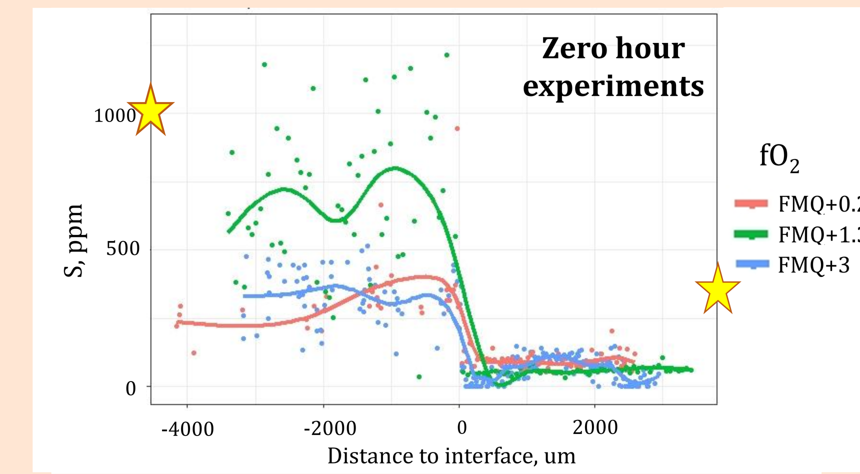
Our results reveal that diffusion of sulfur is faster in reduced melts. This is consistent with the results of Lierenfeld et al. (2018).

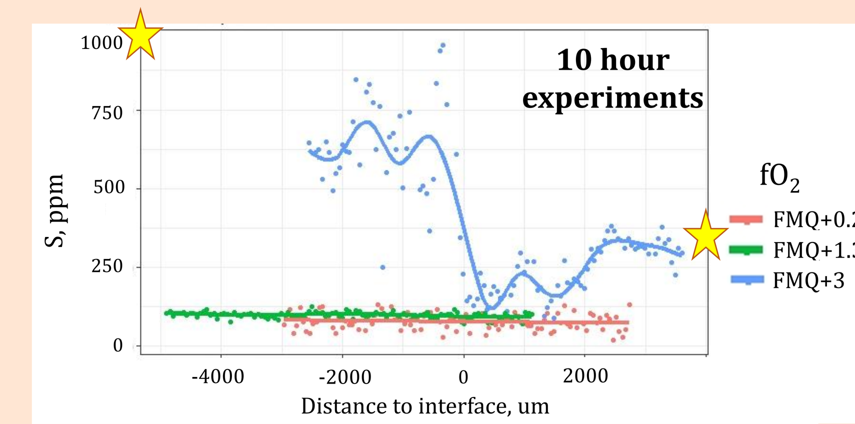
The same relationship between diffusivity and redox is observed for all elements:

↓ fO_2 = ↑ **diffusivities**

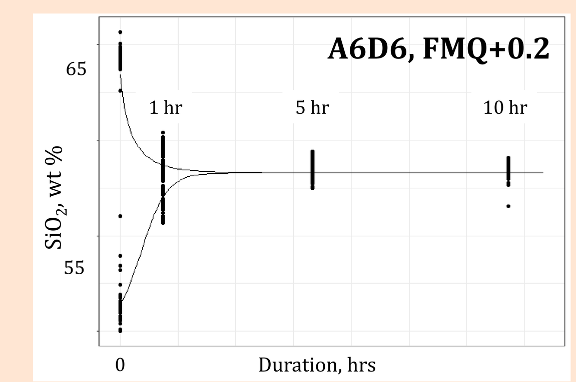


Comparison of S and H_2O diffusivities in hydrous silicate melts. In reduced dacite melt, S diffusion is nearly as fast as H_2O diffusion.





Mixing observed in the most reduced run within 5 hours. Mixing of dacite + basaltic andesite in melt-melt experiments results in an andesite.



INTERPRETATIONS

Crystal much experiments:

- Crystal dissolution rate limits major element transport
  - *Sulfur diffusion slower than expected – limited by major element transport*
- High crystallinity can hinder volatile ascent through mafic magma
  - *Can limit S and metal transfer*
- Magma mixing leads to a significant redox gradient near interface under oxidizing conditions
  - *Can lead to sulfide/sulfate precipitation or break-down*
  - *Can affect the Cu/Au ratio in melt and fluid*

Melt-melt experiments:

- Diffusion for all major elements faster under low fO_2 conditions
  - *Mixing occurred much faster in reduced experiments*
  - *Consistent with previous observations (Lierenfeld et al., 2018; Linnen et al., 1995)*

Future work: Conduct higher P, reducing crystal mush experiments to assess roles of P and fO_2 on sulfur and metal mobility

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