**Friedrich-Alexander-Universität** Faculty of Sciences





# Crystallisation history of magmatic sulphides in intra-oceanic arcs

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#### **Overview of sample locations**



Fig. 1 Map illustrating sample localities. Please note that the poster focuses on the results of arc samples. Mid-ocean ridge and back-arc basin samples are included for comparison.

## **Overview of host rock chemistry**



Fig. 2 Total alkali vs. SiO<sub>2</sub> diagram (TAS) of volcanic glass and whole rocks that host the studied magmatic sulphides.

## **Textures of arc magmatic sulphides**



Fig. 3 Photomicrographs in reflected light of representative magmatic sulphides showing different textures and associated minerals of arc sulphides. (a) Fe-Ti oxide acting as a nucleation site for a homogeneous sulphide consisting of pyrrhotite from Brothers volcano. (b) Homogeneous sulphide from Brothers volcano consisting of pyrrhotite with iss exsolutions. Abbreviation: iss = intermediate solid solutions, mss = monosulphide solid solution, po = pyrrhotite.

## Sulphide analysis by SEM-EDS



Fig. 4 Back-scattered electron images of magmatic sulphides. An example of a sulphide analysis by SEM-EDS. (a) Fe-Ti oxide acting as a nucleation site for a homogeneous sulphide consisting of pyrrhotite from Brothers volcano. (b) Zoned sulphide from Niuatahi consisting of chalcopyrite and cubanite. Abbreviation: iss = intermediate solid solution, mss = monosulphide solid solution, po = pyrrhotite.

## **Mappings of major elements**



Fig. 5 Back-scattered electron images and major element mappings by SEM-EDS. A homogeneous sulphide from Brothers volcano consisting of pyrrhotite with an Cu-(Ag-Au-)rich rim. Abbreviation: mss = monosulphide solid solution, po = pyrrhotite.

## **Major elements of magmatic sulphides**



Fig. 6 (a) Ternary Cu-Ni-Fe diagram showing the composition of sulphides compared to selected sulphide phases. (b) Ni vs. Ni/Cu of sulphides from intraoceanic arcs, back-arcs and mid-ocean ridges. Petrographic and chemical observations imply a different timing of sulphide saturation in mid-ocean ridge and arc magmas. sulphides in mid-ocean ridges are commonly associated with olivine and clinopyroxene, showing a higher Ni content, suggesting an early sulphide saturation. In arcs, sulphides are often associated with Fe-Ti oxides (which crystallize at approximately 60 wt.% SiO2) and have a lower Ni content, indicating a later stage of sulphide saturation.

#### **Trace element analysis by LA-ICP-MS**



Fig. 7 Sketch of a LA-ICP-MS line scan to illustrate how trace element analysis were performed. The line scan started in the host silicate material on one side of the magmatic sulphide and ended in the silicate matrix on the other side of the sulphide. This results in a bell-shaped LA-ICP-MS signal.

# Verification of line scan analysis



Fig. 8 Signal of spot analyses performed at sites of former magmatic sulphides that were previously ablated by line scans. The sharp drop in the S signal indicates that most of the magmatic sulphide was already ablated during the line scan. The increase in the Si signal indicates that the laser interacted with the microscope slide.

#### Loss of elements during degassing



Fig. 9 Sulphides of felsic arc magmas show depletion in most elements compared to mafic ones. Pyrrhotite dominates Brothers volcano samples, often with iss-rich rims and exsolutions in pyrrhotite droplets. Silicate melt likely has low iss-related element content due to iss resorption at 60-66 wt. % SiO2, followed by loss of elements like Cu, Sn, Cd, Bi, Te upon volatile saturation at >66 wt. % SiO2. This leads to highly fractionated, degassed melt depleted in iss-related elements, reducing late-stage iss formation potential. This agrees with thin Cu-rich rims and generally iss-poor character of Brothers volcano samples.

Edmonds, M., Mason, E., & Hogg, O. (2022). Volcanic outgassing of volatile trace metals. Annual Review of Earth and Planetary Sciences, 50, 79-98. (Fig. 2 in the paper).

This figure was employed to identify the volatile and chalcophile elements lost during the degassing of arc magmas.



#### Model of chalcophile element evolution in arc magmas



Fig. 10 Sulphides in subduction-zone lavas often exhibit complex geometry and mineralogy, suggesting changes in composition during cooling and solidification, either by continuous sulphide segregation or re-equilibration with the silicate melt (a). Pressure decrease during magma ascent may increase the sulphide solubility limit of the silicate melt, causing resorption or partial remelting of sulphides (b). This may particularly affect Cu-Fe-rich iss due to their lower melting temperature (<840°C) compared to related mss (>950°C). Elements dominantly hosted by iss phases (e.g., Cu, Au, Zn, Sn, Cd, Bi, Te, Ag) may be liberated to the silicate melt. Subsequent magma stagnation, fractional crystallisation, and cooling may decrease sulphide solubility, resulting in a second stage of sulphide saturation (c), possibly dominated by elements previously liberated from the iss. This may explain observed enrichments in Zn, Sn, Cd, Bi, Te, Ag, and Pd in magmatic sulphides from intra-oceanic arc basalts compared to gabbro xenoliths (Fig. 9). Sulphides from Niuatahi caldera mainly consist of iss-related phases, supporting the proposed two-stage sulphide saturation process (Fig. 6). Similarly, Cu- and Ag-(Au-)rich rims in MSDs from intra-oceanic arc systems like Brothers volcano align with a late-stage iss-dominated sulphide saturation, using mss-dominated remnants as nucleation sites. Abbreviation: iss = intermediate solid solution, mss = monosulphide solid solution, po = pyrrhotite.