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Systematic variations in magmatic sulphide chemistry from mid-ocean ridges, back-arc basins and island arcs

Manuel Keith [a,*], Karsten M. Haase [b], Reiner Klemd [b], Ulrich Schwarz-Schampera [c], Henrike Franke [c]

[a] *Department of Geology, University of Leicester, Leicester LE1 7RH, UK*
[b] *GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Erlangen D-91054, Germany*
[c] *Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover D-30655, Germany*

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ABSTRACT

Immiscible sulphide liquids preserved as magmatic sulphide globules are hosted in igneous rocks of highly variable composition formed during magmatic processes at different tectonic settings. Here we report on compositional in situ data of magmatic sulphides from mid-ocean ridge, back-arc and island arc magmatic systems. Iron-Ni-rich monosulphide solid solutions (mss) that mainly consist of pyrrhotite and pentlandite are the dominant phases in magmatic sulphide globules. In subduction-related magmas mss are most abundant in relatively evolved melts and characterised by low Ni and high Fe contents, as well as low Ni/Cu ratios (<1). In contrast, mss from mid-ocean ridges and back-arcs without subduction input occur in mafic rocks and have high Ni/Cu ratios (>1). Thus, mss chemistry varies systematically in lavas from the different tectonic settings in terms of their Fe-Ni distribution and Ni/Cu ratio. The observed mineralogical and chemical variations between mss from the different settings reflect early S saturation accompanied by olivine fractionation along mid-ocean ridges compared to later stage S saturation in arc systems associated with Fe-Ti oxide fractionation. These systematics are probably related to the relatively oxidised character of subduction zone magmas opposed to more reduced mid-ocean ridge melts. Large Ni/Cu variations in mss from the same locality and in individual samples suggest that S saturation is a multistage or continuous process leading to inclusions of magmatic sulphides that represent different fractionation stages in the ascending magma.

1. Introduction

The formation of immiscible sulphide liquids is a common process observed in many magmatic systems of different tectonic settings (Francis, 1990; Barnes et al., 2006; Jenner et al., 2010; Patten et al., 2012). Sulphur saturation in silicate melts causing immiscible sulphide liquid segregation is mainly controlled by temperature, pressure, oxygen fugacity (fO_2), the degree of fractional crystallisation, the initial S and Fe content of the magma (Distler et al., 1983; Mavrogenes and O'Neill, 1999; Ackermand et al., 2007; Yang et al., 2014) and contamination-related processes such as country-rock sulphur assimilation (Li et al., 2002; Ripley et al., 2003). Sulphur solubility in silicate melts generally decreases with proceeding fractional crystallisation, increasing pressure and decreasing temperature and fO_2 (Distler et al., 1983; Wallace and Carmichael, 1992; Mavrogenes and O'Neill, 1999; Ackermand et al., 2007; Yang et al., 2014). However, several studies suggested that fO_2 is by far the most important parameter controlling S saturation due to the significantly higher solubility of sulphate compared to sulphide in silicate melts (Jugo et al., 2005, 2010; Jugo, 2009; Jenner et al., 2010). Hence, relatively oxidised subduction zone magmas are enriched in S compared to their reduced mid-ocean ridge counterparts (Wallace and Carmichael, 1992; Wallace, 2005; Jenner et al., 2010; Kelley and Cottrell, 2012).

In the oceanic crust, sulphide liquids are preserved as sulphide globules hosted in magmatic rocks and volcanic glass of variable composition (Francis, 1990; Ackermand et al., 2007; Patten et al., 2013). Sulphide globules mainly consist of monosulphide solid solutions (mss) representing the first phase that crystallises between 1000 and 1100 °C from a Fe-Ni-Cu-rich sulphide liquid, while intermediate solid solutions (iss) crystallise at temperatures between 800 and 850 °C from the remaining Cu-Fe-rich sulphide melt. Finally, at temperatures below 650 °C and during proceeding sulphide melt crystallisation mss recrystallise to pyrrhotite and pentlandite followed by chalcopyrite and cubanite representing the exsolution products of iss (Naldrett, 2004; Holwell and McDonald, 2010; Patten et al., 2012). Sulphide liquids extract significant amounts of chalcophile elements, such as Co, Ni, Cu, Se, Te, Au and Bi from the parental silicate magma (Mungall et al., 2005; Barnes et al., 2006; Holwell and McDonald, 2010; Patten et al., 2013) indicating that magmatic sulphide globules are a principal component of the crustal metal cycle. Consequently, magmatic

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* Corresponding author at: Department of Geology, University of Leicester, University Road, Leicester LE1 7RH, UK.
E-mail address: mk528@le.ac.uk (M. Keith).

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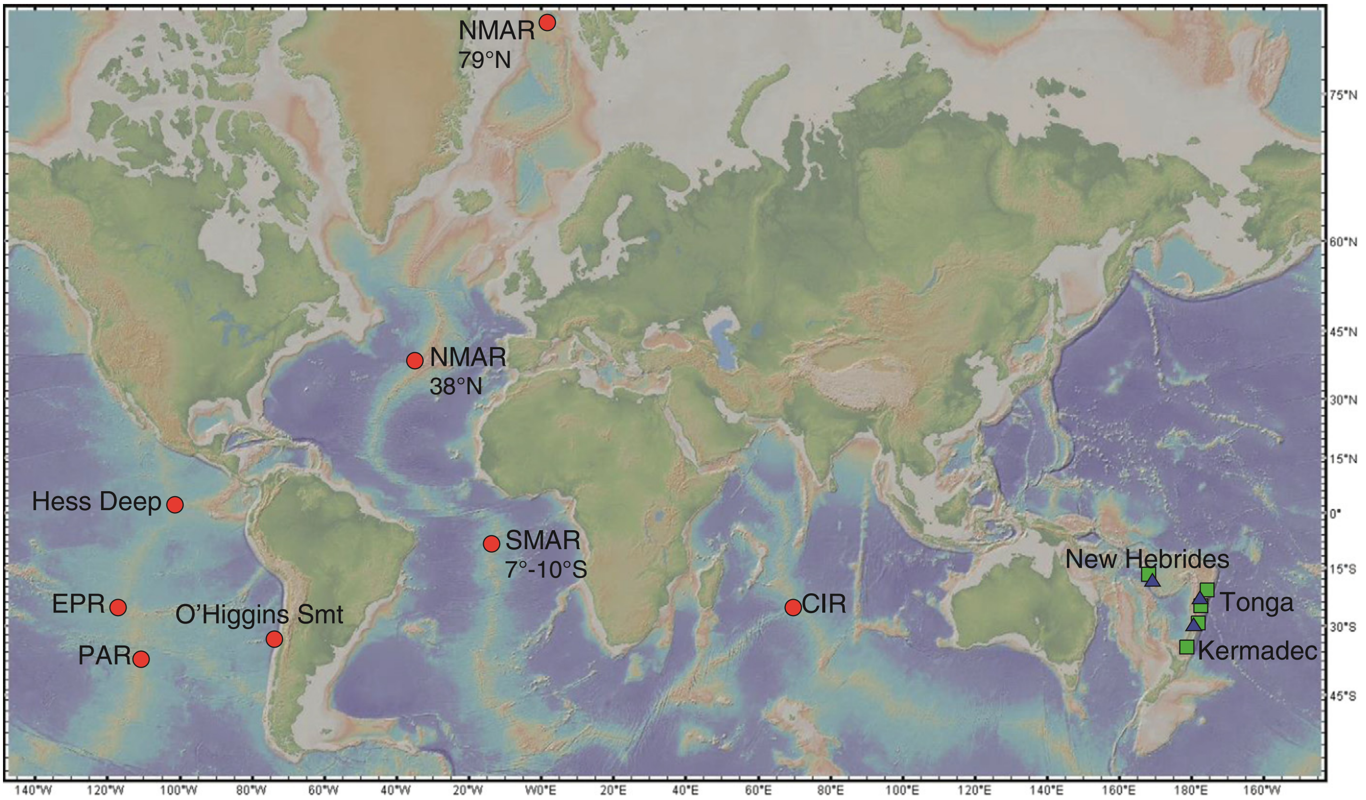

Fig. 1. Global distribution of the sample localities processed in this study. Circles represent the studied mid-ocean ridge sites, squares and triangles refer to island arc and back-arc systems, respectively. Seafloor map generated using GeoMapApp (http://www.geomapapp.org). Abbreviations: EPR = East Pacific Rise, PAR = Pacific-Antarctic Ridge, Smt = seamount, NMAR = northern Mid-Atlantic Ridge, SMAR = southern Mid-Atlantic Ridge, CIR = Central Indian Ridge.

sulphides represent a potential metal source for hydrothermal systems and their associated sulphide precipitates (Alt, 1995; Patten et al., 2016a), such as modern black smoker systems (Keith et al., 2014, 2016a; Wohlgemuth-Ueberwasser et al., 2015) or fossil VHMS deposits (Keays, 1987; Jowitt et al., 2012; Keith et al., 2016b; Patten et al., 2016b). However, most investigations that studied the formation of immiscible sulphide liquids in the oceanic crust focused on mid-ocean ridge systems (e.g., Francis, 1990; Peach et al., 1990; Patten et al., 2012) and our knowledge about the behaviour of chalcophile elements in subduction zone-related systems is limited to a few studies (Sun et al., 2004; Jenner et al., 2010, 2012, 2015; Li et al., 2016).

Here we report major and minor elements of magmatic sulphide globules hosted in igneous rocks and volcanic glass of highly variable composition from divergent and convergent plate margins. This study, for the first time, investigates the mineralogical and chemical composition of magmatic sulphides from a global perspective including back-arc and island arc magmatic systems.

2. Geological setting and sample localities

The samples presented here are of global distribution and representative for the oceanic crust metal cycle in the Atlantic, Pacific and Indian Ocean including mid-ocean ridges, back-arcs and island arcs (Fig. 1, Tables 1–3). Further details about the sampling techniques and the different locations can be found in the references cited in this chapter and listed in Tables 1 to 3.

2.1. Mid-ocean ridges

On- and off-axis samples from mid-ocean ridges in the Atlantic, Pacific and Indian Ocean were investigated in this study (Fig. 1, Table 1). Magmatic sulphides hosted in lavas and in associated glass rims of basaltic composition (Table 1) were studied from the southern Mid-Atlantic Ridge (SMAR) recovered a long a transect from 7°S to 10°S, from the Central Indian Ridge (CIR), the East Pacific Rise (EPR) and the Pacific-Antarctic Ridge (PAR, Fig. 1). Samples from the northern Mid-Atlantic Ridge (NMAR, Fig. 1) were studied to investigate the process of sulphide liquid immiscibility in gabbros and pyroxenites of the lower oceanic crust (Table 1). In addition, one magmatic sulphide-bearing abyssal peridotite specimen from Hess Deep has been analysed (Fig. 1, Table 1).

2.2. Back-arc basins

Back-arc basin lavas range from mid-ocean ridge to arc-like compositions due to variable contributions of the subducted slab increasing with proximity to the corresponding volcanic arc (Pearce et al., 1995; Haase et al., 2002, 2009). Samples from three different back-arc systems of the SW Pacific Ocean were studied (Fig. 1, Table 2).

The southward propagating Valu Fa ridge represents the southern extension of the Lau back-arc spreading centre located to the west of the Tonga arc (Fig. 1). In contrast to the mid-ocean ridge-like lavas of the Lau basin, those of the Valu Fa ridge are of arc-like composition suggesting a transition of spreading in the north to back-arc rifting in the south (Hergt and Farley, 1994; Fretzdorff et al., 2006; Haase et al., 2009). Samples of andesitic composition hosting magmatic sulphides from the southern Valu Fa ridge (Hine Hina, 22°32′S/176°43′W) were examined in this study (Table 2). The Havre Trough with the Raoul back-arc system separates the active Kermadec volcanic arc to the east and the remnant Colville ridge to the west. The lavas of the Havre Trough range from mid-ocean ridge to arc-like compositions due to variable degrees of slab contribution. Pacific mid-ocean ridge-like basaltic lavas containing magmatic sulphides occur in the northern Havre Trough between 24°S and 29°S close to the island of Raoul (Table 2, Haase et al., 2002). The Nifonea volcanic ridge is located east of the