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Origin of selective enrichment of Cu and Au in sulfide deposits formed at immature back-arc ridges: Examples from the Lau and Manus basins



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ABSTRACT

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It has long been recognized that magmatic fluids exsolved from the arc-like submarine magmas of immature back-arc basins can directly contribute metals such as Cu and Au to seafloor hydrothermal systems. The extent of this magmatic contribution, however, varies from basin to basin. In order to explain this variation, we make a comparative study of the behavior of Cu during magma differentiation in two immature back-arc ridges: Eastern Ridge (ER) of the Manus Basin and Valu Fa Ridge (VFR) of the Lau Basin. We investigate some of the factors that affect Cu behavior, including oxygen fugacity (fO_2), water content, and crystallization pressure, by means of a geochemical model. Cu abundances show a continuous decreasing trend with magma evolution in the VFR lavas, whereas in the ER lavas Cu increases during the early stage of magma evolution, followed by a rapid decrease. The contrasting Cu behavior for the two lava suites is controlled on the first order by the fO_2 of their primary magmas. The fO_2 values of the primary ER magmas were modeled to be FMQ + 1.2 to FMQ + 1.8, which is sufficiently high to avoid the early sulfide saturation that typically accompanies Cu removal. By comparison, the fO_2 values of the primary VFR magmas range from FMQ to FMQ + 1, falling within the range of mid-ocean ridge basalts. We attribute this difference in fO_2 values between the primary ER and VFR magmas to variable input of sediment melt to their mantle sources. In addition, we show for the first time that Cu content does not increase significantly until the onset of plagioclase crystallization. This finding suggests that both high water contents and high pressure, which suppress plagioclase crystallization, are unfavorable for Cu enrichment in evolved oxidized magmas. We argue that back-arc ridges that develop shallow submarine magma chambers and have a large input of subducted sediment, have a strong potential to support ore-bearing magmatic-hydrothermal systems.

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1. Introduction

It has long been recognized that the metal contents, especially Cu and Au, of hydrothermal sulfide deposits formed at back-arc ridges are commonly higher than those formed at mid-ocean ridges (Hannington et al., 2005, and references therein). The enhanced Cu and Au contents in sulfide deposits in back-arc settings have been attributed to the direct contribution of metals from magmatic fluids, in addition to those normally leached from the oceanic crust (e.g., Yang and Scott, 1996, 2002; Moss et al., 2001; Kamenetsky et al., 2001; Sun et al., 2004; de Ronde et al., 2011, 2014; Gruen et al., 2014). In fact, this input from magmatic fluids always occurs at immature back-arc ridges, beneath which arc-like magmas that are hydrous and enriched in volatiles are generated due to the strong influence of subduction (Martinez and Taylor, 2002, 2003). However, not all sulfide deposits hosted by arc-like volcanic rocks are associated with Cu and Au enrichment. For example, the Au contents in sulfide deposits from the Southern Lau Basin are within the range of East Pacific Rise (EPR) sulfide deposits, but an order of magnitude lower than those from the Eastern Manus Basin and Izu–Bonin Arc (Fig. 1a, b). Similarly, sulfide deposits of the Eastern Manus Basin are much more enriched in Cu than those of the Southern Lau Basin (Fig. 1c). The reasons behind these differences remain poorly understood.

Immature back-arc basins are typically floored by lavas that have experienced variable extents of magma differentiation (Tatsumi and Eggins, 1995). During magma differentiation, volatiles such as H₂O, CO₂, HCl, and SO₂ are exsolved once they reach saturation, and are then extracted from the magma as vapor fluid during magma degassing (e.g., Kamenetsky et al., 2002). Several lines of evidence show that magmatic fluids can enter the overlying hydrothermal convection system (Yang and Scott, 1996, 2002), including the anomalously low pH values of hydrothermal fluids (Gamo et al., 1997) and the anomalous H–O–S isotopic compositions of hydrothermal sulfides (Herzig et al., 1998; Roberts et al., 2003; Kim et al., 2004; Hou et al., 2005). Higher metal contents in evolved magmas should mean more efficient formation of metal-rich magmatic fluids. The pre-enrichment of metals in magma

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Fig. 1. Compilation of existing data of Au (a, b) and Cu (c) abundances in sulfide deposits from the East Pacific Rise (EPR), Southern Lau Basin, Eastern Manus Basin, and Izu–Bonin Arc. The data are from the database of the International Seabed Authority (http://www.isa.org.jm). The complete source references are not given here because of space constraints.

before large-scale pre-eruptive degassing is thus a crucial step in the generation of an ore-bearing magmatic-hydrothermal system (e.g., Sun et al., 2004; Candela and Piccoli, 2005; Jenner et al., 2010; Richards, 2011).

Previous studies have suggested that the abundance of chalcophile elements, such as Cu and Au, in magma depends mainly on the sulfur content and speciation (Jugo et al., 2005, 2010; Jugo, 2009). These

metals behave incompatibly when sulfate is the dominant sulfur species in an oxidized magma, and become compatible after the conversion of S^{6+} to S^{2-} due to magma reduction (e.g., Sun et al., 2004, 2011, 2012, 2013, 2015; Liang et al., 2006, 2009; Jenner et al., 2010). However, the most favorable oxygen fugacity (fO_2) for Cu–Au enrichment remains unclear. In addition, the influence of other factors (e.g., water content and crystallization pressure) on the behavior of Cu and Au has received little attention.

We base our study on a dataset compiled from the literature, and restrict our investigation to Cu, which behaves similarly to Au during magma evolution (Moss et al., 2001; Sun et al., 2004), because precise Au data for volcanic rocks are rare. We investigate several of the factors influencing Cu behavior, including fO2, water content, and crystallization pressure (P), by constructing a geochemical model using the Petrolog3 software package (Danyushevsky and Plechov, 2011). The aims of this study are (1) to investigate how these controlling factors (fO_2-H_2O-P) affect Cu behavior, (2) to determine the conditions favorable for Cu enrichment during magma evolution, and (3) to shed light on the origin of selective enrichment of Cu and Au in hydrothermal sulfide deposits that form at immature back-arc ridges in general. Two immature back-arc ridges in the Manus and Lau basins, were selected for this purpose, because they both possess a complete magmatic suite with a variable extent of differentiation (Jenner et al., 1987; Pearce et al., 1994; Sinton et al., 2003), and active hydrothermal venting as well as sulfide deposits occur at the ridge axes (Fouquet et al., 1991, 1993; Binns and Scott, 1993).

2. Geological background

The Manus Basin was formed by the extension of pre-existing crust (the Bismark Plate) associated with the subduction of the Solomon Sea Plate at the New Britain Trench (Fig. 2a). Two linked spreading segments formed between the Willaumez (WIT) and Djaul (DT) Transforms: the Manus Spreading Center (MSC) in the east and the Extensional Transform Zone (ETZ) in the west. To the east of the MSC, there is broadly distributed irregular strike-slip motion and extension, including in the Southern Rift (SR) and en echelon Eastern Ridge (ER; Martinez and Taylor, 1996). The ER is a shallow pull-apart basin with dispersed and irregularly distributed volcanism, but enhanced magmatism due to a strong subduction influence (Martinez and Taylor, 1996). The lavas range in composition from basalt to highly evolved rhyodacite (Sinton et al., 2003). Three active hydrothermal fields occur at the ER: PACMANUS, Susu Knolls, and Desmos. The former two are associated with extensive sulfide mineralization and are hosted exclusively by felsic rocks such as dacite and rhyodacite (Binns and Scott, 1993).

The Lau Basin, located between the Tonga Ridge (an active arc) and the Lau Ridge (an inactive arc), is a triangular back-arc basin with a maximum width of 500 km in the north (Fig. 2b). It consists of attenuated original island arc crust and crust formed at propagating spreading centers (Hawkins, 1995). The Eastern Lau Spreading Center (ELSC) started opening at 17°S at 6 Ma and progressively propagated southward to produce the Valu Fa Ridge (VFR). The Central Lau Spreading Center (CLSC) formed later by ridge jump of the northern ELSC, forming a 'relay' called the intermediate Lau Spreading Center (ILSC), located between the two (Hawkins, 1995). The northern end of the CLSC links the Lau Extensional Transform Zone and the Peggy Ridge (PR), which is located in the most northwestern part of the basin. From the CLSC and ELSC to the VFR, the lavas change in composition from normal mid-ocean ridge basalt (N-MORB)-type to arc-type, as the subduction zone is approached (Pearce et al., 1994; Martinez and Taylor, 2002). Notably, the VFR lavas are the most vesicular, fractionated, and enriched in slab-derived components (Jenner et al., 1987; Escrig et al., 2009; Li et al., 2015). In addition, widespread hydrothermal activity occurs at this most inflated ridge (e.g., Baker et al., 2006), and three major sulfide deposits



Fig. 2. Simplified tectonic setting of the Manus Basin (a) and Lau Basin (b), modified from Martinez and Taylor (2003). Thick lines are spreading segments, thin lines are transform faults. Triangles symbolize volcanoes. (a) MSC, Manus Spreading Center; ETZ, Extensional Transform Zone; SR, Southern Rift; ER, Eastern Ridge; WIT, Willaumez Transform; DT, Djaul Transform; WT, Weitin Transform. (b) CLSC, Central Lau Spreading Center; ILSC, Intermediate Lau Spreading Center; ELSC, East Lau Spreading Center; VFR, Valu Fa Ridge; LETZ, Lau Extensional Transform Zone; PR, Peggy Ridge.

(Hine Hina, Vai Lili, and White Church) occur in parts of the ridge floored by highly differentiated volcanic rocks (Fouquet et al., 1993; Fretzdorff et al., 2006).

3. Methods and data

The oxidation state of iron in oceanic basaltic lavas can effectively record mantle oxygen fugacity (fO_2) because the Fe³⁺/ Σ Fe ratio $[Fe^{3+}/(Fe^{2+} + Fe^{3+})]$ is independent of the extent of mantle melting (Bézos and Humler, 2005; Cottrell and Kelley, 2011), and does not vary significantly during ascent of primitive mantle melts to nearsurface magma chambers (Kelley and Cottrell, 2012). However, there is a broad, although slight, increase in ${\rm Fe^{3\,+}}/{\sum}{\rm Fe}$ during the factional crystallization of Fe²⁺-bearing olivine and clinopyroxene and Fe-poor plagioclase, because Fe^{2+} is compatible, whereas Fe^{3+} is incompatible in the first two minerals (Bézos and Humler, 2005; Cottrell and Kelley, 2011). Furthermore, magnetite crystallization and sulfur degassing lead to variable degrees of magma reduction (e.g., Sun et al., 2004; Burgisser and Scaillet, 2007; Jenner et al., 2010; Kelley and Cottrell, 2012). fO₂ fluctuations in the evolving magma thus make it difficult to determine the fO_2 of the primary melt by means of Fe^{3+}/\sum Fe data measured from evolved glasses. To constrain the fO_2 of the primary melt of both the ER and VFR, we use the method of inverse modeling, by reconciling the modeling differentiation path with the natural petrochemical trend (e.g., Almeev et al., 2013). In addition, other parameters such as water content and crystallization pressure can be collectively modeled using this method.

3.1. Petrolog3 modeling

We use the Petrolog3 software package (Danyushevsky and Plechov, 2011) for computer simulation of the magma differentiation path. This software incorporates multiple published mineral–melt equilibrium models for individual minerals, including those suitable for both anhydrous and hydrous systems (but not suitable for the very high water contents in arc settings), under polybaric or isobaric conditions. In this section, we give a brief introduction to the theory on which the forward modeling is based.

Initial fO_2 , water content, and pressure are the dominant factors that affect magma differentiation paths (e.g., Sisson and Grove, 1993; Berndt et al., 2005; Zimmer et al., 2010; Almeev et al., 2013). Oxygen fugacity determines the Fe³⁺/ \sum Fe composition of the magma and controls

the timing of Fe-oxide crystallization (Berndt et al., 2005). High fO_2 leads to early magnetite saturation and crystallization, resulting in a decrease in both the total Fe content (FeOt) and Fe³⁺/ \sum Fe during the early stages of magma evolution. For example, Petrolog3 predicts that magnetite would be forced to appear on the liquidus as early as at MgO >8% if the initial fO_2 value was assigned to be FMQ + 3.5 (FMQ is the fayalite–magnetite–quartz oxygen buffer; see Fig. 3). In contrast, at low fO_2 the onset of magnetite crystallization would be very late. For example, magnetite would not become saturated until a low MgO content (less than 4%) is reached at a fO_2 of FMQ (Fig. 3).



Fig. 3. Example of forward modeling results for total iron (FeOt) using the Petrolog3 software package (Danyushevsky and Plechov, 2011). Multiphase fractionation of olivine (ol) + plagioclase (plg) + clinopyroxene (cpx) + magnetite (mgt) was modeled at variable *f*O₂, water content, and crystallization pressure. The colored dotted curves represent magma differentiation paths calculated in steps of 0.01% in a series of parameter groups. The mineral–melt equilibrium models of Weaver and Langmuir (1990) were used for olivine, plagioclase, and clinopyroxene crystallization in an anhydrous system. The model of Danyushevsky (2001) was used for plagioclase crystallization in a hydrous system. In addition, the magnetite equilibrium model of Ariskin and Barmina (1999) was used for both the anhydrous and hydrous systems, and the model of Kress and Carmichael (1988) was used for the *f*O₂ calculation. FMQ here refers to the fayalite-magnetite-quartz oxygen buffer. Lavas of the East Pacific Rise (EPR) are from spreading segments over 5^{*}-24^oS. The data are from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp).

The effect of water content is to decrease the liquidus temperature of plagioclase relative to olivine and clinopyroxene, thus strongly suppressing plagioclase crystallization (Danyushevsky, 2001). Since plagioclase does not incorporate Fe, the fractional crystallization of plagioclase would increase the FeOt content of the remaining melt. The EPR MORBs mainly plot between the modeled lines of 0–0.2% water content (Fig. 3), consistent with the fact that MORBs contain a small amount of water (Michael, 1995). Because back-arc magmas typically contain more H₂O than MORB magmas, less FeOt enrichment would be expected for the back-arc magmatic suite than for MORB (Fig. 3). The other effects of water in the magma are to stabilize amphibole and suppress all silicates relative to magnetite (Sisson and Grove, 1993; Zimmer et al., 2010). However, these effects only occur in an arc setting with extremely high water content (>4% H₂O), and are not considered in our model.

Like mid-ocean ridge magmas, back-arc magmas mainly experience low-pressure factional crystallization at crustal depths (e.g., Langmuir et al., 2006). We therefore simulate the magma differentiation path at a relatively low pressure (<2 kbar). The effect of pressure is mainly to increase the liquidus temperature of clinopyroxene relative to plagioclase and olivine (Langmuir et al., 1992; Danyushevsky et al., 1996). For example, a greater rate of FeOt increase and higher FeOt content can be achieved by reducing the pressure from 1 kbar to 0.1 kbar (Fig. 3), because of lower volume of crystallized clinopyroxene at lower pressure. In addition, a well-known effect of pressure is to control the solubility of H_2O in the magma. Water becomes supersaturated in magma when it is forced beyond its solubility in response to pressure release (Newman and Lowenstern, 2002).

3.2. Data

The volcanic rock data for the ER and the VFR used in this study are exclusively from the published literature. ER data are from Moss et al. (2001); Kamenetsky et al. (2001); Sinton et al. (2003); Sun et al. (2007); Park et al. (2010), and Jenner et al. (2010); VFR data are from Hawkins (1977), Jenner et al. (1987); Boespflug et al. (1990); Frenzel et al. (1990); Vallier et al. (1991); Peate et al. (2001); Fretzdorff et al. (2006); Pearce et al. (2007); Escrig et al. (2009), and Yan et al. (2012). The dataset includes bulk-rock and glass analyses of volcanic rocks with variable degrees of differentiation. Since Cu is extremely incompatible in silicate minerals (Patten et al., 2013), the presence of phenocrysts in the rock has a negligible effect on its Cu content. Thus, both whole-rock and glass data were used to examine the variations in Cu content during magma evolution. In contrast, phenocrysts have a significant effect on the chemical composition of major elements. It follows that only the chemical composition of aphyric glasses can represent a real liquid line of descent (Zimmer et al., 2010). Because the ER lavas typically contain a large amount of phenocrysts (Yang and Scott, 2002; Sinton et al., 2003), we exclude all the bulk-rock data and only make use of the glass data. However, the limited basaltic glass data for the VFR lavas are insufficient to record a complete evolutionary trend, which reduces the credibility and accuracy of the inverse modeling results. To overcome this problem, the glass data plus a few bulk-rock data were used for the VFR. These phyric lavas are fine-grained and contain small numbers of microlites and microphenocrysts (Pearce et al., 1994; Yan et al., 2012) that have only a minor effect on the liquid line of descent. The dataset used in our modeling can be found in the Supplementary Material.

4. Results

4.1. Variations in Cu content during magma differentiation

Cu behaves compatibly during the magmatic evolution of mid-ocean ridge basalt (Doe, 1994; Doe, 1995). Fig. 4 shows that Cu contents in the EPR MORBs decrease with decreasing MgO or increasing SiO₂. In the VFR lavas, Cu contents decrease uniformly with magma differentiation

so that Cu is quite depleted in the most evolved lavas (Fig. 4a, b). In addition, Cu content in the most basaltic VFR lavas is much higher than that of EPR MORB, indicating a higher initial Cu content in the primary VFR melts than in those of the EPR MORB.

In contrast, Cu behaves in a more complicated way during differentiation of the ER magmas, and dual incompatible and compatible behavior can be identified. Cu content initially increases with increasing SiO₂ and reaches a maximum of more than 500 ppm at SiO₂ = 58%. This is followed by an abrupt Cu decrease that occurs over a narrow range of SiO₂ (Fig. 4c). This significant feature was first reported by Moss et al. (2001) and Sun et al. (2004), and has been confirmed in recent studies (Jenner et al., 2010; Park et al., 2013a). It is noteworthy that the variation in Cu content with respect to MgO is slightly different to that with respect to SiO₂. Fig. 4d shows that Cu does not show an initial increase relative to MgO but remains constant over a large interval before its rapid increase. The significance of the differences between these two diagrams for Cu behavior during magma differentiation will be discussed in the following section.

4.2. Modeling results for crystallization conditions (fO_2-H_2O-P)

In Section 3.1, we briefly introduced the theory on how the factors of fO₂, water content, and pressure affect magma differentiation paths-the basis of our forward modeling. Here, we explain how we reconcile our forward modeling results with the natural ER and VFR lava data. Firstly, for the modeling we choose elements that are relatively sensitive to changes in the mineral assemblage that crystallizes from the magma. The best candidate is FeOt-Fig. 5 shows that FeOt contents respond abruptly to changes in the mineral assemblage. To strengthen the validity of our modeling results, we also model SiO₂ and K₂O. Secondly, the most basaltic samples (MgO < 10%) of the ER and VFR were chosen as a reference to define the starting composition. Lastly, we follow the principle that low-FeOt magmas have higher SiO₂ and water contents than high-FeOt magmas, because low-FeOt magmas were generated in shallower and more hydrous mantle than high-FeOt magmas (e.g., Langmuir et al., 2006). The starting compositions used here are therefore slightly different to those of the reference samples (Table 1).

The modeled fO_2 values for the primary VFR magmas range from FMQ to FMQ + 1, and therefore fall within the MORB field, although they are slightly higher than average global MORB (Fig. 6). In contrast, the modeled fO_2 values for the primary ER magmas are within the range from FMQ + 1.2 to FMQ + 1.8, which is close to the results (~FMQ +2) calculated from the Fe³⁺/ Σ Fe ratio in the evolved ER lavas (Sun et al., 2004). This range falls within the upper limit of back-arc basin basalt (BABB) and the lower limit of island arc basalt (IAB; Fig. 6), and is much higher than that of the VFR magmas.

The modeled water contents for the primary VFR magmas ranges from ~0.05% to ~0.5%, and are considerably lower than those for the ER magmas, which ranges from ~0.2% to ~0.8% (Fig. 5). However, overall these water contents are lower than those measured in basaltic lavas, which are always more than 1% (e.g., Danyushevsky et al., 1993; Kent et al., 2002; Kamenetsky et al., 2001; Yang and Scott, 2005). In addition, the modeled crystallization pressure for the VFR magmas is ~1 kbar, which is in agreement with the depths of the low-velocity zone (2.34–2.82 km below the sea floor) constrained by seismic imaging (Turner et al., 1999; Jacobs et al., 2007). In contrast, the modeled crystallization pressure for the ER magmas is unrealistically low (~0.1 kbar), which is inconsistent with the magma chamber depth of ~2 km constrained by geochemical modeling (Sun et al., 2007).

5. Discussion

5.1. Validity of the modeling results

One of the most important advantages of the Petrolog3 software package is that it incorporates multiple published mineral-melt



Fig. 4. Variations in Cu content with magma differentiation for the Valu Fa Ridge (VFR) of the Lau Basin (a, b) and the Eastern Ridge (ER) of the Manus Basin (c, d). Data sources for the ER and VFR lavas can be found in the Supplementary Material. Data sources for the East Pacific Rise (EPR) lavas are the same as in Fig. 3.

equilibrium models by many workers. Inverse modeling using different models, however, may give slightly different results. To obtain the fO_2 of the primary melt, we used the mineral–melt equilibrium models of Ariskin and Barmina (1999) for magnetite crystallization, and the model of Kress and Carmichael (1988) for the fO_2 calculation. These models have been widely used and are considered to be a valid representation of melt processes.

As noted in Section 3.1, the dominant effect of water is to suppress plagioclase crystallization relative to olivine and clinopyroxene (Danyushevsky, 2001). To obtain the water content of the primary melt, we used the mineral-melt equilibrium model of Danyushevsky (2001) for plagioclase crystallization. Overall, the modeled water contents are less than those measured in basaltic glass (e.g., Danyushevsky et al., 1993; Kent et al., 2002), which could be partially due to the incompatible behavior of water during fractional crystallization (Michael, 1995). However, the modeled results are also lower than those

measured from melt inclusions trapped in olivine (Kamenetsky et al., 2001; Yang and Scott, 2005). We therefore argue that the model of Danyushevsky (2001) may slightly overestimate the ability of water to suppress plagioclase crystallization.

The results of the pressure modeling are problematic, as the calculated crystallization pressure of the ER magmas is only 0.1 kbar. As noted in Section 3.1, higher pressure should increase the volume of crystallized clinopyroxene relative to plagioclase (Langmuir et al., 1992; Danyushevsky et al., 1996). Fig. 5 shows that the highly evolved ER lavas have much higher K₂O and SiO₂ than the evolved VFR lavas, indicating that a larger volume of plagioclase was crystallized from the ER magmas than from the VFR magmas during the late stage of magma evolution (after magnetite crystallization). However, the ER magmas contain much more water than the VFR magmas (Fig. 5), which means that a greater degree of plagioclase suppression should occur at a given pressure. Hence, the only way to resolve this discrepancy is to



Fig. 5. Results of inverse modeling for the crystallization conditions (fO_2 -H₂O-P) of the primary VFR (a) and ER (b) magmas. The mineral-melt equilibrium models used here are the same as in Fig. 3. Note that all the minerals were modeled by pure fractional crystallization (solids completely removed from contact with the melt) in addition to magnetite crystallization (80%–90% removal). The mineral abbreviations are the same as in Fig. 3. The dotted vertical lines mark changes in the mineral assemblage.

decrease the crystallization pressure of the ER magmas. The most appropriate pressure to fit the natural geochemical data is as low as 0.1 kbar, which is unrealistic for a submarine magma chamber (the water depth of a back-arc basin can be as deep as 2000 m). We therefore suggest that the algorithm for pressure used by the Petrolog3 program yields unrealistic results.

In summary, among the modeled parameters the modeled fO_2 values are the most realistic. Although the modeled water content may be slightly underestimated, this is not a problem for a comparative study of magma differentiation paths. The modeled pressure may have

little quantitative significance; however, it provides useful information for a qualitative comparison of magma chamber depths.

5.2. Origin of the contrasting Cu behavior between the VFR and ER lavas

Cu partitions strongly into magmatic sulfides, up to several orders of magnitude higher than the partitioning into silicate or oxide minerals ($D_{Cu} = 1334 \pm 201$; Patten et al., 2013). Hence, the behavior of Cu during magma differentiation is determined mainly by changes in sulfur speciation. Cu behaves incompatibly when sulfate is the dominant

 Table 1

 The starting compositions used in the geochemical modeling

Location	ER	ER	ER	Reference sample	VFR	VFR	VFR	Reference sample
SiO ₂ (wt.%)	50.68	51.36	52.20	51.96	49.06	50.98	52.31	52.40
TiO ₂	0.38	0.38	0.38	0.38	0.65	0.70	0.70	0.70
Al_2O_3	15.87	15.46	14.37	12.99	16.77	15.99	15.47	15.77
Fe ₂ O ₃	1.83	1.97	2.17		1.37	1.61	1.81	
FeO	5.44	4.96	4.54		7.90	7.30	6.37	
FeOt	7.27	6.93	6.71	6.67	9.27	8.91	8.18	8.07
MgO	9.17	9.17	9.17	9.19	8.02	7.99	8.00	7.78
MnO	0.13	0.13	0.13	0.13	0.15	0.16	0.16	0.16
CaO	14.35	14.34	14.34	14.37	13.98	12.99	12.60	12.50
Na ₂ O	1.59	1.59	1.59	1.59	1.73	1.80	1.80	1.79
K ₂ O	0.28	0.25	0.22	0.25	0.19	0.20	0.20	0.20
P_2O_5	0.09	0.09	0.09	0.09	0.08	0.08	0.08	0.08
H ₂ O	0.20	0.30	0.80		0.05	0.20	0.50	
Oxygen	FMQ	FMQ	FMQ		FMQ	FMQ	FMQ	
fugacity	+1.2	+1.5	+1.8			+0.5	+1	

Note: $FeOt = FeO + Fe_2O_3$.

sulfur species, but becomes strongly compatible with the onset of sulfide saturation (Sun et al., 2015, and references therein). Experimental studies have suggested that the speciation of sulfur is primarily a function of fO_2 and that the $S^{6+}/\sum S$ ratio $[S^{6+}/(S^{2-} + S^{6+})]$ increases exponentially with increasing fO_2 (Jugo et al., 2010; Fig. 6).

The compatible behavior of Cu has been viewed as a natural consequence of MORB evolution (Doe, 1994, 1995; Fig. 4), and has been attributed to early sulfide saturation in reduced magmas (e.g., Yi et al., 2000). Fig. 6 shows that the fO_2 of the primary VFR magmas falls in the range of MORB and the lower limit of global BABB. The calculated $S^{6+}/\sum S$ ratios for the primary VFR magmas using the S speciation curve of Jugo et al. (2010) are no more than 0.42 (Fig. 6), indicating that sulfide is the dominant species in the melt. We therefore attribute the progressive Cu depletion in the VFR lavas to continuous sulfide removal from the differentiating magma.



Fig. 6. Projection of oxygen fugacity (fO_2) for the primary ER and VFR magmas in the $S^{6+}/\sum S$ vs. fO_2 diagram of Jugo et al. (2010). The height of each of the two colored boxes was defined by the intersection of the speciation curve with the modeled fO_2 range shown in Fig. 5. The fO_2 ranges for mid-ocean ridge basalts (MORB), back-arc basin basalts (BABB), oceanic island basalts (OIB), island arc basalts (IAB), and mantle wedge are all from Jugo et al. (2010). Δ FMQ refers to the log unit deviation from the FMQ buffer.

In contrast, the fO_2 of the primary ER magmas lies at the upper limit of BABB and in the field of IAB (Fig. 6). The results calculated from the speciation curve show that 65%–98% sulfur is in the form of sulfate in the primary ER magmas. In this case, the required S content for sulfide saturation calculated by the function of Jugo et al. (2010) is 0.4%–1.2%, which is unrealistically high for subduction zone magmas (de Hoog et al., 2001). The lack of early sulfide saturation explains why the Cu in the ER lavas does not show an initially decreasing trend, but behaves incompatibly (Fig. 4c). The subsequent abrupt Cu decrease, however, has been attributed either to pre-eruptive degassing (Moss et al., 2001; Sun et al., 2004) or to late sulfide saturation (Jenner et al., 2010; Park et al., 2013a). Despite this discrepancy in proposed models, these authors all agree that sulfate reduction triggered by magnetite crystallization plays an essential role in the drastic Cu loss.

As mentioned above, Cu does not increase immediately but remains constant during the early stages of ER magma differentiation, as observed in the MgO vs. Cu diagram (Fig. 4d). However, this effect is obscured in the SiO₂ vs. Cu diagram (Fig. 4c) because SiO₂ does not increase significantly until the onset of magnetite crystallization, as shown by the modeling results in Fig. 5. Furthermore, it is significant that the rapid Cu increase shown in Figs. 4d and 5 coincides with the sharp increase in FeOt that marks the onset of plagioclase crystallization. This means that the enrichment of Cu in the magma is probably associated with the crystallization of plagioclase rather than olivine and clinopyroxene, although Cu is reasonably incompatible in these minerals (Lee et al., 2012).

To test this hypothesis, we examined the variations in Cu/V during the early stage of magma evolution. Fig. 7 shows that the EPR MORB displays a progressively decreasing Cu/V trend with decreasing MgO. This feature can be attributed to Cu depletion due to sulfide saturation, and to V enrichment due to its incompatible behavior in olivine, clinopyroxene, and plagioclase. Although the VFR lavas display a wide range of Cu/V, which probably resulted from variable Cu contents in the primary VFR melts, an overall decreasing Cu/V trend is observed. In contrast, the ER lavas show a nearly constant Cu/V, which means that Cu behaves similarly to V during the early stage of magma evolution (before magnetite crystallization). Because V behaves similarly to FeOt, the constant Cu/V recorded in the ER lavas also indicates that a Cu increase is synchronous with plagioclase crystallization.

In fact, the phenomenon mentioned above is not a unique case, but is common in island arc settings. For example, in the Izu–Bonin and Kermadec arc magmatic suites, Cu and FeOt do not increase significantly



Fig. 7. Variations in Cu/V with MgO during the early stages of magma evolution (before magnetite saturation). The data used here are the same as in Fig. 4.



Fig. 8. Example of coupled FeOt-Cu variations during magma evolution in an arc setting. Data for the Hachijojima volcanic lavas of the Izu-Bonin Arc and Raoul volcanic lavas of the Kermadec Arc are from the GEOROC database.

until MgO \approx 5% is reached (Fig. 8). During the early stages of magma evolution (MgO > 5%), Cu and FeOt contents in these lavas remain relatively constant, although their primary melts have much more variable Cu contents than FeOt. We argue that plagioclase crystallization is an important index for the enrichment of Cu during magma evolution, although the reasons behind this are not clear and need to be investigated further.

5.3. Favorable fO₂ conditions for Cu enrichment

The fO_2 of the primary VFR magma (FMQ to FMQ + 1) is too low to avoid early sulfide saturation, whereas it is sufficiently high for the ER magma (FMQ + 1.2 to FMQ + 1.8) to avoid Cu depletion at the beginning of magma differentiation. This demonstrates that contrasting Cu behavior can occur over a narrow fO_2 range of no more than 0.2 log units, supposing that the primary ER and VFR melts have similar sulfur contents. Although the threshold fO_2 value to avoid early sulfide saturation cannot be determined, it is reasonable to constrain the range within FMQ + 1 to FMQ + 1.2, which is somewhat lower than the threshold value (FMQ + 2) for porphyry Cu formation (Mungall, 2002).

Although highly oxidized magmas (FMQ +2 to FMQ +4) are required for porphyry Cu formation (Mungall, 2002; Sun et al., 2013, 2015), this does not mean that the higher the fO_2 , the more Cu is concentrated in the evolved magma. This is because high- fO_2 conditions could lead to earlier magnetite saturation, which subsequently controls sulfide saturation due to the formation of S²⁻ through the reaction 12FeO + SO₄²⁻ = 4Fe₃O₄ + S²⁻ (Sun et al., 2015). Evidence for this process is provided by the occurrence of sulfide minerals such as chalcopyrite in association with Fe-oxide (magnetite?), which trapped at the margin of clinopyroxene in gabbro (Park et al., 2013b).

Petrolog3 predicts that at a fO_2 of FMQ + 3.5 the onset of magnetite saturation can occur as early as at MgO >8%, and this is reflected in the initial FeOt depletion trend (Fig. 3) that is common in high- fO_2 adakitic suites (Sun et al., 2011). In fact, the formation of sulfide cumulates from high- fO_2 magmas is not unusual, and has even been considered a critical step in porphyry Cu formation (e.g., Lee et al., 2012; Wilkinson, 2013). The early sulfide phase can be cannibalized by newly injected high- fO_2 magmas, or dissolved by magmatic fluids exsolved from the magma (Stavast et al., 2006; Nadeau et al., 2010; Wilkinson, 2013; Sun et al., 2015). In other words, metals in sulfides accumulated in the deep crust can be remobilized and then transferred into the upper root zone. This mechanism of Cu enrichment that occurs in thick continental crust, however, cannot be applied to the back-arc setting, where the crust is thin and does not develop a series of magma chambers (Lee et al., 2014). We therefore argue that at back-arc or even island-arc settings, the most favorable fO_2 for Cu enrichment is within a range slightly higher than the threshold value (FMQ + 1.2 to FMQ + 2).

5.4. Favorable H₂O–P conditions for Cu enrichment

Water content and pressure play a subordinate role relative to fO_2 for Cu enrichment. The main effect of H₂O is to affect the timing of plagioclase crystallization (Danyushevsky, 2001). Fig. 3 shows that if the water content of the magma changes from 0.2% to 1%, the peak FeOt content will decrease from 14.86% to 10.94%, equivalent to 25.6% suppression of plagioclase crystallization. If our previous inference that plagioclase crystallization marks the onset of Cu enrichment is valid, high water content would shorten the interval of Cu enrichment at a given fO_2 . For example, the lavas of Susu Knolls and Desmos (green crosses in Fig. 4) show less Cu enrichment than the Paul Ridge lavas (Fig. 4), probably because the former has a higher water content than the latter due to a greater subduction influence (Park et al., 2010). Similarly, the arc lavas of Kermadec and Izu–Bonin show less Cu enrichment than the ER lavas probably as a result of later plagioclase crystallization (Fig. 8).

The argument that lower water content in magma is favorable for Cu enrichment seems surprising because high- fO_2 magmas are typically associated with hydrous magmas (Kelley and Cottrell, 2009). One explanation is that the magma differentiation pressure is decreased, so that the maximum water content is limited. In addition, reducing the pressure can also increase the relative volume of crystallized plagioclase by suppressing the fractional crystallization of clinopyroxene (Langmuir et al., 1992; Danyushevsky et al., 1996), as seen in Fig. 3, where iron contents increase at a greater rate at lower pressure. Hence, shallow magma chambers with lower magma water contents are more favorable for Cu enrichment than deeper magma chambers.

5.5. Possible cause of the difference in fO_2 between the ER and VFR magmas

It is widely accepted that hydrous magmas generated at subduction zones inherently have higher fO_2 than MORB because of the metasomatism of the mantle source by oxidized materials from the subducted slab (e.g., Parkinson and Arculus, 1999; Kelley and Cottrell, 2009, 2012; Evans and Tomkins, 2011; Evans et al., 2012), although secondary

oxidation of reduced mantle-derived magma during crustal processes has also been proposed (Lee et al., 2005, 2010). In an intra-oceanic back-arc basin such as the Manus and Lau basins, the oxygen fugacity of primitive mantle melts changes very little as the melt ascends through the crust (Kelley and Cottrell, 2012). Thus, the contrast in fO_2 of the primary melts of the ER and VFR likely resulted from differences in the oxidation states of the mantle sources.

Kelley and Cottrell (2009) describe the quantitative relationship between Fe^{3+}/Σ Fe and water content in basaltic glasses. Their results show that the correlation of $Fe^{3+}/\sum Fe$ with H_2O is very good in MORB and BABB, but gets worse in IAB. This means that fO₂ increases with proximity to the subduction zone, but that the ability of H₂O to oxidize arc mantle (shown by dfO_2/dH_2O) varies from arc to arc (Kelley and Cottrell, 2009). The variation in dfO2/dH2O suggests that water itself is not an oxidation agent, and direct transport of Fe³⁺ or S⁶⁺ into the mantle source may be necessary, as suggested previously (Frost and Ballhaus, 1998; Parkinson and Arculus, 1999; Kelley and Cottrell, 2009; Evans and Tomkins, 2011). Evans et al. (2012) argued that the convergence rate of the subducted plate could affect the efficiency of transfer of Fe³⁺ and S⁶⁺ into the subarc mantle, and that faster convergence corresponds to higher transfer efficiency. However, the mantle beneath the VFR is much less oxidized than that beneath the ER, despite a much faster convergence for the Tonga subduction zone (>170 mm/y; Bevis et al., 1995) than the New Britain subduction zone (100 mm/y; Yoneshima et al., 2005).

There is consensus that hydrous melt is more efficient in transporting S^{6+} and especially Fe^{3+} into sub-arc mantle than aqueous fluid (e.g., Evans and Tomkins, 2011; Evans et al., 2012). Hence, the addition of sediment melts (Parkinson and Arculus, 1999) and partial melts of basaltic crust (Sun et al., 2011, 2013, 2015) can efficiently oxidize subarc mantle. The subducted plates at both the New Britain and Tonga trenches are too cold to undergo partial melting (e.g., Peacock et al., 1994); thus, the degree of sediment melt input should determine the differences in oxidation state of the sub-arc mantle. Fig. 9 shows that the ER lavas have a much higher Th/Nb (an index of hydrous melt input) than the VFR lavas at a given Ba/Nb (an index of total subduction input; see Pearce et al., 2005). This suggests a much higher sediment melt input at the New Britain subduction zone than at the Tonga subduction zone. This argument is in broad agreement with the fact that the sediment thickness in the New Britain trench (~950 m; Whitmore et al., 1999) is much greater than that in the Tonga trench (~200 m;



Fig. 9. Th/Nb vs. Ba/Nb diagram for the ER and VFR lavas. Th/Nb was used as a proxy for hydrous melt, and Ba/Nb was used as a proxy for the total subduction input (Pearce et al., 2005). The data used here are the same as in Fig. 4.

Plank and Langmuir, 1998). We therefore attribute the difference in initial fO_2 between the primary ER and VFR magmas mainly to variable inputs of sediment melt.

5.6. Implications for Cu–Au-rich sulfide deposit genesis at immature back-arc ridges

By studying melt inclusions in phenocrysts of submarine volcanic rocks that host hydrothermal sulfides in the Eastern Manus Basin, Yang and Scott (1996) presented the first evidence that vapor fluid exsolved from magmas can scavenge ore metals. The key requirement for forming metal-rich magmatic fluids, however, is a large amount of metals available to enter the exsolved vapor phase (e.g., Sun et al., 2004; Jenner et al., 2010). We argue that the lack of Cu–Au-rich sulfide deposits at the VFR results from the barrenness in metals of magmatic fluids released from a Cu–Au-depleted evolved magma, whereas at the ER, Cu–Au-rich magmas, which have a high potential to form metal-rich magmatic fluids, are responsible for the formation of Cu–Au-rich sulfide deposits.

High oxygen fugacity is the principal factor that favors Cu enrichment in evolved magma because of the avoidance of sulfide saturation. Since sediment melts are more efficient in transporting oxidized materials into the mantle than aqueous fluids released from altered oceanic crust (Parkinson and Arculus, 1999; Evans and Tomkins, 2011), subduction-related magmas generated in response to strong inputs of sediment melt should have high fO_2 . In fact, such magmas are always linked to the formation of Cu–Au-rich sulfide deposits. For example, Cu–Au-rich sulfide deposits are associated with the Eastern Manus Basin (Binns and Scott, 1993), the Izu–Ogasawara arc (Iizasa et al., 1999), and the southern Kermadec arc (de Ronde et al., 2011). These sulfide deposits are all close to land and in each case a thick sequence of terrigenous sediments has accumulated in the trench (Plank and Langmuir, 1998).

The subordinate factors that affect Cu enrichment are the combination of water content and crystallization pressure. Both high water content and high pressure suppress plagioclase crystallization, so are not favorable for Cu enrichment in evolved oxidized magmas because Cu increase is synchronous with plagioclase crystallization. Hence, a shallow magma chamber with low magma water content is more favorable for Cu enrichment than a deeper magma chamber. The depth of the magma chamber at a mid-ocean ridge is inversely correlated with spreading rate (Barth and Mutter, 1996). The depth of the magma lens at the VFR is inferred to be 2.34–2.82 km below the sea floor, much greater than its mid-ocean ridge counterpart that has a similar spreading rate (40–60 mm/y; Jacobs et al., 2007). The ER experienced a similar degree of subduction influence to the VFR, as shown by a similar total subduction input (Ba/Nb ratio; Fig. 9), but has a much higher spreading rate (>130 mm/y; Martinez and Taylor, 1996). This may explain why its magma chamber is shallower than that of the VFR.

6. Conclusions

Contrasting Cu behavior was identified during the differentiation of arc-like magmas from the VFR of the Lau Basin and the ER of the Manus Basin. In the ER magmas, Cu initially behaves incompatibly and its content increases to almost five times the initial amount, potentially resulting in Cu-rich magmatic fluids. In contrast, in the VFR magmas Cu behaves compatibly and decreases gradually, resulting in relatively Cu-barren magmatic fluids.

The modeled primary ER magmas are much more oxidized than the primary VFR magmas. This difference in oxygen fugacity (fO_2) between the primary ER and VFR magmas explains their contrasting Cu behavior. The sulfide phase is saturated very early during the differentiation of the relatively reduced VFR magmas (FMQ to FMQ + 1), while the relatively oxidized ER magmas (FMQ + 1.2 to FMQ + 1.8) do not experience the early sulfide saturation that accompanies Cu removal from the melt. The differences in oxygen fugacity between the primary magmas are most likely caused by variable inputs of sediment melt into their mantle sources.

In addition, we show for the first time that Cu content does not increase significantly until the onset of plagioclase crystallization. This finding suggests that both high water content and high pressure, which suppress plagioclase crystallization, are not favorable for Cu enrichment in evolved oxidized magmas. Because Cu and Au behave quite similarly during magma evolution, we propose that shallow submarine magma chambers with low magma water contents have a high potential to produce Cu–Au-enriched magmatic fluids, and therefore to form Cu–Au-rich sulfide deposits.

Conflict of interest

No conflict of interest exits in the submission of this manuscript, which is approved by all authors for publication.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.oregeorev.2015.11.010.

References

- Almeev, R.R., Ariskin, A.A., Kimura, J.I., Barmina, G.S., 2013. The role of polybaric crystallization in genesis of andesitic magmas: phase equilibria simulations of the Bezymianny volcanic subseries. J. Volcanol. Geotherm. Res. 263, 182–192.
- Ariskin, A.A., Barmina, G.S., 1999. An empirical model for the calculation of spinel-melt equilibria in mafic igneous systems at atmospheric pressure: 2. Fe–Ti oxides. Contrib. Mineral. Petrol. 134, 251–263.
- Baker, E.T., Resing, J.A., Walker, S.L., Martinez, F., Taylor, B., Nakamura, K.I., 2006. Abundant hydrothermal venting along melt-rich and melt-free ridge segments in the Lau back-arc basin. Geophys. Res. Lett. 33 (7), L07308.
- Barth, G.A., Mutter, J.C., 1996. Variability in oceanic crustal thickness and structure: multichannel seismic reflection results from the northern East Pacific Rise, J. Geophys. Res. 101 (B8), 17951–17975.
- Berndt, J., Koepke, J., Holtz, F., 2005. An experimental investigation of the influence of water and oxygen fugacity on differentiation of MORB at 200 MPa. J. Petrol. 46 (1), 135–167.
- Bevis, M., Taylor, F.W., Schutz, B.E., Recy, J., Isacks, B.L., Helu, S., Calmantli, S., 1995. Geodetic observations of very rapid convergence and back-arc extension at the Tonga arc. Nature 374 (6519), 249–251.Bézos, A., Humler, E., 2005. The Fe³⁺/∑Fe ratios of MORB glasses and their implications for
- Bézos, A., Humler, E., 2005. The Fe³⁺/∑Fe ratios of MORB glasses and their implications for mantle melting. Geochim. Cosmochim. Acta 69 (3), 711–725.
- Binns, R.A., Scott, S.D., 1993. Actively forming polymetallic sulfide deposits associated with felsic volcanic rocks in the eastern Manus back-arc basin, Papua New Guinea. Econ. Geol. 88 (8), 2226–2236.
- Boespflug, X., Dosso, L., Bougault, H., Joron, J.L., 1990. Trace element and isotope (Sr, Nd) geochemistry of volcanic rocks from the Lau Basin. Geol. Jahrb. 92, 503–516.
- Burgisser, A., Scaillet, B., 2007. Redox evolution of a degassing magma rising to the surface. Nature 445 (7124), 194–197.
- Candela, P.A., Piccoli, P.M., 2005. Magmatic processes in the development of porphyrytype ore systems. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P. (Eds.), Economic Geology 100th Anniversary Volume. Society of Economic Geologists, Littleton, CO, pp. 25–37.
- Cottrell, E., Kelley, K.A., 2011. The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. Earth Planet. Sci. Lett. 305 (3), 270–282.
- Danyushevsky, L.V., 2001. The effect of small amounts of H₂O on crystallisation of mid-ocean ridge and back-arc basin magmas. J. Volcanol. Geotherm. Res. 110 (3), 265–280.

- Danyushevsky, L.V., Plechov, P., 2011. Petrolog3: integrated software for modeling crystallization processes. Geochem. Geophys. Geosyst. 12 (7), Q07021.
- Danyushevsky, L.V., Falloon, T.J., Sobolev, A.V., Crawford, A.J., Carroll, M., Price, R.C., 1993. The water content of basalt glasses from southwest Pacific back-arc basins. Earth Planet, Sci. Lett, 117 (3), 347–362.
- Danyushevsky, L.V., Sobolevz, A.V., Dmitrievz, L.V., 1996. Estimation of the pressure of crystallization and water content of MORB and BABB glasses: calibration of an empirical technique. Mineral. Petrol. 57 (3–4), 185–204.
- Doe, B.R., 1994. Zinc, copper, and lead in mid-ocean ridge basalts and the source rock control on Zn/Pb in ocean-ridge hydrothermal deposits. Geochim. Cosmochim. Acta 58 (10), 2215–2223.
- Doe, B.R., 1995. Zinc, copper, and lead geochemistry of oceanic igneous rocks-ridges, islands, and arcs. Int. Geol. Rev. 37 (5), 379–420.
- Escrig, S., Bezos, A., Goldstein, S.L., Langmuir, C.H., Michael, P.J., 2009. Mantle source variations beneath the eastern Lau spreading center and the nature of subduction components in the Lau Basin–Tonga arc system. Geochem. Geophys. Geosyst. 10, Q04014.
- Evans, K.A., Tomkins, A.G., 2011. The relationship between subduction zone redox budget and arc magma fertility. Earth Planet. Sci. Lett. 308 (3), 401–409.
- Evans, K.A., Elburg, M.A., Kamenetsky, V.S., 2012. Oxidation state of subarc mantle. Geology 40 (9), 783–786.
- Fouquet, Y., von Stackelberg, U., Charlou, J.L., Donval, J.P., Foucher, J.P., Erzinger, J., Whitechurch, H., 1991. Hydrothermal activity in the Lau back-arc basin: sulfides and water chemistry. Geology 19 (4), 303–306.
- Fouquet, Y., Von Stackelberg, U., Charlou, J.L., Erzinger, J., Herzig, P.M., Mühe, R., Wiedicke, M., 1993. Metallogenesis in back-arc environments: the Lau basin example. Econ. Geol. 88, 2154–2181.
- Frenzel, G., Mu'he, R., Stoffers, P., 1990. Petrology of the volcanic rocks from the Lau Basin, southwest Pacific. Geol. Jahrb, Reihe D 92, 395–479.
- Fretzdorff, S., Schwarz-Schampera, U., Gibson, H.L., Garbe-Schönberg, C.D., Hauff, F., Stoffers, P., 2006. Hydrothermal activity and magma genesis along a propagating back-arc basin: Valu Fa ridge (southern Lau Basin). J. Geophys. Res. 111, B08205.
- Frost, B.R., Ballhaus, C., 1998. Constraints on the origin of the oxidation state of mantle overlying subduction zones: an example from Simcoe, Washington, USA. Geochim. Cosmochim. Acta 62, 329–331.
- Gamo, T., Okamura, K., Charlou, J.L., Urabe, T., Auzende, J.M., Ishibashi, J., Chiba, H., 1997. Acidic and sulfate-rich hydrothermal fluids from the Manus back-arc basin, Papua New Guinea. Geology 25 (2), 139–142.
- Gruen, G., Weis, P., Driesner, T., Heinrich, C.A., de Ronde, C.E., 2014. Hydrodynamic modeling of magmatic-hydrothermal activity at submarine arc volcanoes, with implications for ore formation. Earth Planet. Sci. Lett. 404, 307–318.
- Hannington, M.D., de Ronde, C.D., Petersen, S., 2005. Sea-floor tectonics and submarine hydrothermal systems. Economic Geology 100th Anniversary vol. 111–141.
- Hawkins, J.W., 1977. Petrologic and geochemical characteristics of marginal basin basalts. Island Arcs, Deep sea Trenches and Back-arc Basins, pp. 355–365.
- Hawkins, J.W., 1995. The geology of the Lau Basin. In: Taylor, B. (Ed.), Back-arc Basins: Tectonics and Magmatism. Plenum, New York, pp. 63–138.
- Herzig, P.M., Hannington, M.D., Arribas Jr., A., 1998. Sulfur isotopic composition of hydrothermal precipitates from the Lau back-arc: implications for magmatic contributions to seafloor hydrothermal systems. Mineral. Deposita 33 (3), 226–237.
- de Hoog, J.C.M., Mason, P.R.D., van Bergen, M.M., 2001. Sulfur and chalcophile elements in subduction zones: constraints from a laser ablation ICP-MS study of melt inclusions from Galunggung Volcano, Indonesia. Geochim. Cosmochim. Acta 65 (18), 3147–3164.
- Hou, Z.Q., Zaw, K., Li, Y.H., Zhang, Q.L., Zeng, Z.G., Urabe, T., 2005. Contribution of magmatic fluid to the active hydrothermal system in the JADE field, Okinawa trough: evidence from fluid inclusions, oxygen and helium isotopes. Int. Geol. Rev. 47 (4), 420–437.
- Iizasa, K., Fiske, R.S., Ishizuka, O., Yuasa, M., Hashimoto, J., Ishibashi, J., Naka, J., Horii, Y., Fujiwara, Y., Imai, A., Koyama, S., 1999. A Kuroko-type polymetallic sulfide deposit in a submarine silicic caldera. Science 283, 975–977.
- Jacobs, A.M., Harding, A.J., Kent, G.M., 2007. Axial crustal structure of the Lau back-arc basin from velocity modeling of multichannel seismic data. Earth Planet. Sci. Lett. 259 (3), 239–255.
- Jenner, G.A., Cawood, P.A., Rautenschlein, M., White, W.M., 1987. Composition of backarc basin volcanics, Valu Fa Ridge, Lau Basin: evidence for a slab-derived component in their mantle source. J. Volcanol. Geotherm. Res. 32, 209–222.
- Jenner, F.E., O'Neill, H.S.C., Arculus, R.J., Mavrogenes, J.A., 2010. The magnetite crisis in the evolution of arc-related magmas and the initial concentration of Au, Ag and Cu. J. Petrol. 51 (12), 2445–2464.
- Jugo, P.J., 2009. Sulfur content at sulfide saturation in oxidized magmas. Geology 37 (5), 415–418.
- Jugo, P.J., Luth, R.W., Richards, J.P., 2005. Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. Geochim. Cosmochim. Acta 69 (2), 497–503.
- Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: implications for S speciation and S content as function of oxygen fugacity. Geochim. Cosmochim. Acta 74 (20), 5926–5938.
- Kamenetsky, V.S., Binns, R.A., Gemmell, J.B., Crawford, A.J., Mernagh, T.P., Maas, R., Steele, D., 2001. Parental basaltic melts and fluids in eastern Manus backarc basin: implications for hydrothermal mineralization. Earth Planet. Sci. Lett. 184 (3), 685–702.
- Kamenetsky, V.S., Davidson, P., Mernagh, T.P., Crawford, A.J., Gemmell, J.B., Portnyagin, M.V., Shinjo, R., 2002. Fluid bubbles in melt inclusions and pillow-rim glasses: hightemperature precursors to hydrothermal fluids? Chem. Geol. 183 (1), 349–364.
- Kelley, K.A., Cottrell, E., 2009. Water and the oxidation state of subduction zone magmas. Science 325 (5940), 605–607.
- Kelley, K.A., Cottrell, E., 2012. The influence of magmatic differentiation on the oxidation state of Fe in a basaltic arc magma. Earth Planet. Sci. Lett. 329, 109–121.

Kent, A.J., Peate, D.W., Newman, S., Stolper, E.M., Pearce, J.A., 2002. Chlorine in submarine glasses from the Lau Basin: seawater contamination and constraints on the composition of slab-derived fluids. Earth Planet, Sci. Lett, 202 (2), 361–377.

Kim, J., Lee, I., Lee, K.Y., 2004. S, Sr, and Pb isotopic systematics of hydrothermal chimney precipitates from the Eastern Manus Basin, western Pacific: evaluation of magmatic contribution to hydrothermal system. J. Geophys. Res. 109 (B12), B12210.

Kress, V.C., Carmichael, I.S.E., 1988. Stoichiometry of the iron oxidation reaction in silicate melts. Am. Mineral. 73, 1267–1274.

Langmuir, C.H., Bézos, A., Escrig, S., Parman, S.W., 2006. Chemical systematics and hydrous melting of the mantle in back-arc basins. Back-arc Spreading Systems: Geological, Biological, Chemical, and Physical Interactions, pp. 87–146.

Langmuir, C.H., Klein, E.M., Plank, T., 1992. Petrological systematics of mid-ocean ridge basalts: constraints on melt generation beneath ocean ridges. In: Phipps Morgan, J., Blackman, D.K., Sinton, J.M. (Eds.), Mantle Flow and Melt Generation at Mid-ocean Ridges. American Geophysical Union Monograph 71, pp. 183–280.

Lee, C.-T.A., Lee, T.C., Wu, C.-T., 2014. Modeling the compositional evolution of recharging, evacuating, and fractionating (REFC) magma chambers: implications for differentiation of arc magmas. Geochim. Cosmochim. Acta 143, 8–22.

Lee, C.T.A., Leeman, W.P., Canil, D., Li, Z.X.A., 2005. Similar V/Sc systematics in MORB and arc basalts: implications for the oxygen fugacities of their mantle source regions. J. Petrol. 46 (11), 2313–2336.

Lee, C.T.A., Luffi, P., Chin, E.J., Bouchet, R., Dasgupta, R., Morton, D.M., Le Roux, V., Yin, Q.Z., Jin, D., 2012. Copper systematics in arc magmas and implications for crust–mantle differentiation. Science 336 (6077), 64–68.

Lee, C.T.A., Luffi, P., Le Roux, V., Dasgupta, R., Albarede, F., Leeman, W.P., 2010. The redox state of arc mantle using Zn/Fe systematics. Nature 468 (7324), 681–685.

Li, Z. G., Chu, F. Y., Dong, Y. H., Liu, J. Q., & Chen, L., 2015. Geochemical constraints on the contribution of Louisville seamount materials to magmagenesis in the Lau back-arc basin, SW Pacific. Int. Geol. Rev. 57(5–8): 978–997.

Liang, H.Y., Campbell, I.H., Allen, C., Sun, W.D., Liu, C.Q., Yu, H.X., Zhang, Y.Q., 2006. Zircon Ce⁴⁺/Ce³⁺ ratios and ages for Yulong ore-bearing porphyries in eastern Tibet. Mineral. Deposita 41 (2), 152–159.

Liang, H.Y., Sun, W.D., Su, W.C., Zartman, R.E., 2009. Porphyry copper–gold mineralization at Yulong, China, promoted by decreasing redox potential during magnetite alteration. Econ. Geol. 104 (4), 587–596.

Martinez, F., Taylor, B., 1996. Backarc spreading, rifting, and microplate rotation, between transform faults in the Manus Basin. Mar. Geophys. Res. 18 (2–4), 203–224.

Martinez, F., Taylor, B., 2002. Mantle wedge control on back-arc crustal accretion. Nature 416 (6879), 417–420.

Martinez, F., Taylor, B., 2003. Controls on back-arc crustal accretion: insights from the Lau, Manus and Mariana basins. J. Geol. Soc. Lond. 219 (1), 19–54.

Michael, P., 1995. Regionally distinctive sources of depleted MORB: evidence from trace elements and H₂O. Earth Planet. Sci. Lett. 131 (3), 301–320.

Moss, R., Scott, S.D., Binns, R.A., 2001. Gold content of eastern Manus basin volcanic rocks: implications for enrichment in associated hydrothermal precipitates. Econ. Geol. 96 (1), 91–107.

Mungall, J.E., 2002. Roasting the mantle: slab melting and the genesis of major Au and Au-rich Cu deposits. Geology 30 (10), 915–918.

Nadeau, O., Williams-Jones, A.E., Stix, J., 2010. Sulphide magma as a source of metals in arc-related magmatic hydrothermal ore fluids. Nat. Geosci. 3 (7), 501–505.

Newman, S., Lowenstern, J.B., 2002. VolatileCalc: a silicate melt–H₂O–CO₂ solution model written in Visual Basic for Excel. Comput. Geosci. 28 (5), 597–604.

Park, J.W., Campbell, I.H., Arculus, R.J., 2013a. Platinum-alloy and sulfur saturation in an arc-related basalt to rhyolite suite: evidence from the pual ridge lavas, the eastern Manus basin. Geochim. Cosmochim. Acta 101, 76–95.

Park, J.W., Campbell, I.H., Ickert, R.B., Allen, C.M., 2013b. Chalcophile element geochemistry of the Boggy Plain zoned pluton, southeastern Australia: a S-saturated barren compositionally diverse magmatic system. Contrib. Mineral. Petrol. 165 (2), 217–236.

Park, S.H., Lee, S.M., Kamenov, G.D., Kwon, S.T., Lee, K.Y., 2010. Tracing the origin of subduction components beneath the South East rift in the Manus Basin, Papua New Guinea. Chem. Geol. 269 (3), 339–349.

Parkinson, I.J., Arculus, R.J., 1999. The redox state of subduction zones: insights from arc peridotites. Chem. Geol. 160 (4), 409–423.

Patten, C., Barnes, S.J., Mathez, E.A., Jenner, F.E., 2013. Partition coefficients of chalcophile elements between sulfide and silicate melts and the early crystallization history of sulfide liquid: LA-ICP-MS analysis of MORB sulfide droplets. Chem. Geol. 358, 170–188.

Peacock, S.M., Rushmer, T., Thompson, A.B., 1994. Partial melting of subducting oceanic crust. Earth Planet. Sci. Lett. 121, 227–244.

Pearce, J.A., Ernewein, M., Bloomer, S.H., Parson, L.M., Murton, B.J., Johnson, L.E., 1994. Geochemistry of Lau Basin volcanic rocks: influence of ridge segmentation and arc proximity. In: Smellie, J.L. (Ed.), Volcanism Associated with Extension at Consuming Plate Margins. J. Geol. Soc. London 81, pp. 53–75.

Pearce, J.A., Kempton, P.D., Gill, J.B., 2007. Hf–Nd evidence for the origin and distribution of mantle domains in the SW Pacific. Earth Planet. Sci. Lett. 260, 98–114.

Pearce, J.A., Stern, R.J., Bloomer, S.H., Fryer, P., 2005. Geochemical mapping of the Mariana arc-basin system: implications for the nature and distribution of subduction components. Geochem. Geophys. Geosyst. 6 (7), 007006.

Peate, D.W., Kokfelt, T.F., Hawkesworth, C.J., van Calsteren, P.W.V., Hergt, J.M., Pearce, J.A., 2001. U-series isotope data on Lau basin glasses: the role of subduction-related fluids during melt generation in back-arc basins. J. Petrol. 42, 1449–1470. Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem. Geol. 145, 325–394.

Richards, J.P., 2011. Magmatic to hydrothermal metal fluxes in convergent and collided margins. Ore Geol. Rev. 40 (1), 1–26.

Roberts, S., Bach, W., Binns, R.A., Vanko, D.A., Yeats, C.J., Teagle, D.A.H., McDonald, B., 2003. Contrasting evolution of hydrothermal fluids in the PACMANUS system, Manus Basin: the Sr and S isotope evidence. Geology 31 (9), 805–808.

de Ronde, C.E., Massoth, G.J., Butterfield, D.A., Christenson, B.W., Ishibashi, J., Ditchburn, R.G., Takai, K., 2011. Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano, Kermadec Arc, New Zealand. Mineral. Deposita 46 (5–6), 541–584.

de Ronde, C.E.J., Walker, S.L., Ditchburn, R.G., Tontini, F.C., Hannington, M.D., Merle, S.G., ... Stoffers, P., 2014. The anatomy of a buried submarine hydrothermal system, Clark volcano, Kermadec arc, New Zealand. Econ. Geol. 109 (8), 2261–2292.

Sinton, J.M., Ford, L.L., Chappell, B., McCulloch, M.T., 2003. Magma genesis and mantle heterogeneity in the Manus back-arc basin, Papua New Guinea. J. Petrol. 44 (1), 159–195.

Sisson, T.W., Grove, T.L., 1993. Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism. Contrib. Mineral. Petrol. 113 (2), 143–166.

Stavast, W.J., Keith, J.D., Christiansen, E.H., Dorais, M.J., Tingey, D., Larocque, A., Evans, N., 2006. The fate of magmatic sulfides during intrusion or eruption, Bingham and Tintic districts. Utah. Econ. Geol. 101 (2), 329–345.

Sun, W.D., Arculus, R.J., Kamenetsky, V.S., Binns, R.A., 2004. Release of gold-bearing fluids in convergent margin magmas prompted by magnetite crystallization. Nature 431 (7011), 975–978.

Sun, W.D., Binns, R.A., Fan, A.C., Kamenetsky, V.S., Wysoczansk, R., Wei, G.J., Hu, Y.H., Arculus, R.J., 2007. Chlorine in submarine volcanic glasses from the eastern Manus basin. Geochim. Cosmochim. Acta 71, 1542–1552.

Sun, W., Huang, R.F., Li, H., Hu, Y.B., Zhang, C.C., Sun, S.J., Ling, M.X., 2015. Porphyry deposits and oxidized magmas. Ore Geol. Rev. 65, 97–131.

Sun, W.D., Liang, H.Y., Ling, M.X., Zhan, M.Z., Ding, X., Zhang, H., Yang, X.Y., Li, Y.L., Ireland, T.R., Wei, Q.R., Fan, W.M., 2013. The link between reduced porphyry copper deposits and oxidized magmas. Geochim. Cosmochim. Acta 103, 263–275.

Sun, W.D., Ling, M.X., Chung, S.L., Ding, X., Yang, X.Y., Liang, H.Y., Fan, W.M., Goldfarb, R., Yin, Q.Z., 2012. Geochemical constraints on adakites of different origins and copper mineralization. J. Geol. 120 (1), 105–120.

Sun, W.D., Zhang, H., Ling, M.X., Ding, X., Chung, S.L., Zhou, J.B., Yang, X.Y., Fan, W.M., 2011. The genetic association of adakites and Cu–Au ore deposits. Int. Geol. Rev. 53 (5–6), 691–703.

Tatsumi, Y., Eggins, S., 1995. Subduction Zone Magmatism. Blackwell Science, Cambridge.

Turner, I.M., Peirce, C., Sinha, M.C., 1999. Seismic imaging of the axial region of the Valu Fa Ridge, Lau Basin—the accretionary processes of an intermediate back-arc spreading ridge. Geophys. J. Int. 138 (2), 495–519.

Vallier, T.L., Jenner, G.A., Frey, F.A., Gill, J.B., Davis, A.S., Volpe, A.M., Hawkins, J.D., Morris, J.D., Cawood, P.A., Morton, J.L., Scholl, D.W., Rautenschlein, M., White, W.M., Williams, R.W., Stevenson, A.J., White, L.D., 1991. Subalkaline andesite from Valu Fa ridge, a back arc spreading center in southern Lau Basin: petrogenesis, comparative chemistry, and tectonic implications. Chem. Geol. 91, 227–256.

Weaver, J.S., Langmuir, C.H., 1990. Calculation of phase equilibrium in mineral-melt systems. Comput. Geosci. 16 (1), 1–19.

Whitmore, G.P., Crook, K.A.W., Johnson, D.P., 1999. Sedimentation in a complex convergent margin: the Papua New Guinea collision zone of the western Solomon Sea. Mar. Geol. 157 (1), 19–45.

Wilkinson, J.J., 2013. Triggers for the formation of porphyry ore deposits in magmatic arcs. Nat. Geosci. 6 (11), 917–925.

Yan, Q.S., Castillo, P.R., Shi, X.F., 2012. Geochemistry of basaltic lavas from the southern Lau Basin: input of compositionally variable subduction components. Int. Geol. Rev. 54, 1456–1474.

Yang, K., Scott, S.D., 1996. Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. Nature 383 (6599), 420–423.

Yang, K.H., Scott, S.D., 2002. Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific. Econ. Geol. 97, 1079–1100.

Yang, K., Scott, S.D., 2005. Vigorous exsolution of volatiles in the magma chamber beneath a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific: evidence from melt inclusions. Econ. Geol. 100 (6), 1085–1096.

Yi, W., Halliday, A.N., Alt, J.C., Lee, D.C., Rehkämper, M., Garcia, M.O., Su, Y., 2000. Cadmium, indium, tin, tellurium, and sulfur in oceanic basalts: implications for chalcophile element fractionation in the earth. J. Geophys. Res. 105 (B8), 18927–18948.

Yoneshima, S., Mochizuki, K., Araki, E., Hino, R., Shinohara, M., Suyehiro, K., 2005. Subduction of the Woodlark Basin at New Britain Trench, Solomon Islands region. Tectonophysics 397 (3), 225–239.

Zimmer, M.M., Plank, T., Hauri, E.H., Yogodzinski, G.M., Stelling, P., Larsen, J., Nye, C.J., 2010. The role of water in generating the calc-alkaline trend: new volatile data for Aleutian magmas and a new tholeiitic index. J. Petrol. 51 (12), 2411–2444.