



Constant Cu/Ag in upper mantle and oceanic crust: Implications for the role of cumulates during the formation of continental crust

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ABSTRACT

Delamination of dense, sulfide-bearing pyroxenitic cumulates was proposed to explain the low Cu content and the evolved major element composition of the continental crust, yet evidence for this hypothesis has been circumstantial. In this study, we present Cu and Ag contents of mantle pyroxenites and associated peridotites from the Balmuccia peridotite massif (Italian Alps) and mantle xenoliths from Hannuoba (North China Craton) to constrain the fractionation behavior of Cu and Ag during melt–peridotite reaction and magmatic accumulation in the mantle. Furthermore, we reexamine the behavior of these elements during arc magmatism and in other reservoirs to highlight the fractionation of Cu and Ag as an important tracer for processes that led to the formation of continental crust.

Melt–peridotite reaction and magmatic accumulation led to highly variable sulfide abundances, Cu and Ag contents in the mantle pyroxenites (e.g., Balmuccia, 87–484 $\mu\text{g/g}$ Cu; Hannuoba, 15–116 $\mu\text{g/g}$ Cu). The mean Cu/Ag of the pyroxenite suites (Balmuccia: 3800 ± 1100 ; Hannuoba: 3100 ± 900 , 1s) are indistinguishable from those of their host peridotites and other lherzolites (3500 ± 1200), MORBs (3600 ± 400), and Hawaiian basalts (3200 ± 100). These results reflect the limited fractionation of Cu from Ag during magmatic processes in the upper mantle and during the formation of oceanic crust, and indicate a similar mean Cu/Ag (3500 ± 1000 , 1s) in these reservoirs. Experimental data indicate that similar partitioning of Cu and Ag between sulfide melt and silicate melt is responsible for the limited variation of Cu/Ag.

Magmatic processes in the convecting mantle and in the oceanic crust, however, cannot explain the low Cu/Ag ratio of the continental crust (about 500). Experimental constraints on sulfide stability in oxidized mantle and data from back-arc magmatic series suggest that formation of primitive back-arc and island arc basalts inherit mantle-like Cu/Ag and thus also cannot explain the low Cu/Ag of the continental crust. In contrast, previous data on evolved back-arc magmas suggest that the low Cu/Ag coupled with a considerable depletion of Cu in the continental crust might be ascribed to the segregation of monosulfide solid solution (MSS) during fractional crystallization of evolving arc magmas. These results thus support the model that accumulation of sulfide-bearing mafic cumulates in the lower crust of magmatic arcs has been a critical process in defining some of the chemical characteristics of the continental crust.

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1. Introduction

The continental crust has a relatively SiO₂-rich bulk composition, similar to andesite (Rudnick and Gao, 2014). These compositional constraints are difficult to reconcile with the obser-

vation that the continental crust formed primarily by addition of mafic magmas from the upper mantle in magmatic arcs and in extensional tectonic settings. One compelling explanation for the imbalance of major elements such as Si, Mg and Fe in the continental crust compared with basic magmas is delamination and sinking of dense mafic lower crust into the convecting mantle (e.g., Bird, 1979; Lee and Anderson, 2015; Lee et al., 2006; Rudnick, 1995). For example, Lee and Anderson (2015) proposed that the basis of the lower crust underneath arcs mainly con-

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sists of dense pyroxenite cumulates and these cumulates can sink into the mantle. It has also been suggested that these pyroxenites may contain sulfides and the delamination of these sulfide-bearing cumulates would result in low contents of Cu and some other chalcophile elements in the continental crust (e.g., Lee et al., 2012; Li and Audetat, 2013; Jenner, 2017).

Copper and Ag behave similarly during the generation and differentiation of mid-ocean ridge basalts (MORBs), as indicated by the relatively constant Cu/Ag ratios in fertile lherzolites (3500 ± 1200 , 1s, Wang and Becker, 2015a), MORBs (3600 ± 400 , Jenner and O'Neill, 2012; Jenner et al., 2010) and sulfide droplets from MORBs (3000 ± 300 , Patten et al., 2013). The similar geochemical behavior of Cu and Ag during magmatic processes at mid-ocean ridges is supported by experimental studies that have yielded similar partition coefficients (D) of Cu and Ag between sulfide melt and silicate melts ($D_{\text{sulfide melt-silicate melt}}^{\text{Cu}} \approx D_{\text{sulfide melt-silicate melt}}^{\text{Ag}}$; Kiseeva and Wood, 2013, 2015; Li and Audétat, 2012, 2015). In contrast, geochemical studies of back-arc magma series have suggested that the segregation of crystalline monosulfide solid solution (MSS), rather than sulfide melt, may control chalcophile element inventories in arc magmas that have undergone advanced fractional crystallization (e.g., Li and Audetat, 2012, 2013; Jenner et al., 2010, 2015). Fractional crystallization of MSS in these back-arc magmas leads to a reduction of Cu/Ag in the derivative magmas from 3500 to 500. The latter value is similar to Cu/Ag in the continental crust. Therefore, the contrasting fractionation behavior of Cu and Ag during mid-ocean ridge magmatic processes and arc magmatism may be used as an important tool to constrain the fractionation processes that form the continental crust, particularly the hypothesis of the presence of Cu-enriched pyroxenitic cumulates at the base of the continental crust (Jenner, 2017; Lee et al., 2012).

The formation of sulfide-bearing pyroxenites is not only limited to in the lower crust of magmatic arcs. Sulfide-bearing pyroxenites also occur as a minor, but common lithology in the upper mantle and the deep oceanic crust (e.g., Dantas et al., 2007; Downes, 2007; Garrido and Bodinier, 1999; Liu et al., 2005; van Acken et al., 2008; Wang and Becker, 2015c). Sulfides in mantle pyroxenites typically occur interstitially between major silicate minerals and spinel, and were previously interpreted to have formed by exsolution of sulfide melt from sulfide-saturated silicate melts that migrate through the mantle (e.g., van Acken et al., 2010; Wang and Becker, 2015a, 2015c). In this context, it is important to note that different opinions exist on whether the fractionation of chalcophile elements in the upper mantle is predominantly controlled by sulfide melt–silicate melt partitioning or MSS–sulfide melt partitioning (e.g., Ballhaus et al., 2006; Bockrath et al., 2004; Brenan, 2015; Mungall and Brenan, 2014; Wang and Becker, 2015a, 2015b). The different partitioning behavior of Cu and Ag between MSS and sulfide melt would lead to different Cu/Ag in basalts and mantle pyroxenites compared to mantle peridotites. So far, no data sets of Cu and Ag contents on the same samples of mantle pyroxenites are available. Thus, it is unclear if Cu and Ag behave similarly or differently during the formation of pyroxenites in the upper mantle and in the lower crust of arcs.

Here, Cu and Ag contents in spinel pyroxenites (Balmuccia peridotite massif, Italian Alps) and in garnet pyroxenites and their reacted peridotite wall rocks (Hannuoba mantle xenoliths, North China Craton) were studied to constrain the fractionation behavior of Cu and Ag during melt–peridotite reaction and magmatic accumulation in the upper mantle. Based on these new results, the fractionation of Cu and Ag during magmatic processes in the upper mantle and oceanic crust is summarized. The new data in conjunction with the Cu and Ag data from primitive and differentiated members of arc volcanic series and from the continental crust are

used to explore the implications for the differentiation processes during the formation of the continental crust.

2. Samples and their geological setting

The mantle pyroxenites analyzed in this study are from two different geological settings, the orogenic Balmuccia peridotite massif, Italian Alps (Wang and Becker, 2015c) and mantle xenoliths enclosed in alkaline basalts of Hannuoba, North China Craton (Liu et al., 2005). The Balmuccia and Hannuoba pyroxenites are mainly products of melt–peridotite reaction and subsequent magmatic accumulation of pyroxenes, spinel or garnet and accessory phases (e.g., sulfides) in subcontinental lithospheric mantle.

2.1. Spinel pyroxenites in Balmuccia peridotite massif

The Ivrea–Verbano zone (IVZ), Italian Alps exposes rocks from the upper mantle (e.g., Balmuccia peridotite massif) and the lower and middle continental crust. The Balmuccia spinel peridotite massif is a fragment of subcontinental lithospheric mantle which has been emplaced into the lower crustal granulite facies metabasites of the IVZ and subsequently exposed to the surface during the course of the Mesozoic extension and Alpine compression (e.g., Handy et al., 2010; Mukasa and Shervais, 1999; Peressini et al., 2007; Shervais and Mukasa, 1991, also see geological maps therein). Geochronological data based on the Re–Os and Sm–Nd systems suggest that the peridotite massif records a history of melt infiltration during the Paleozoic and Mesozoic (Mukasa and Shervais, 1999; Wang et al., 2013; Wang and Becker, 2015c).

The pyroxenites mostly comprise Cr diopside-bearing websterites and spinel clinopyroxenites, which both show negligible low-temperature alteration. The rocks occur as veins, stretched shear folds or dikes of variable widths (up to 0.4 m) and commonly show sharp boundaries to the host peridotites (Mukasa and Shervais, 1999; Wang and Becker, 2015c). Some websterites, such as BM11–12 and BM11–14, also display reaction zones with the surrounding peridotites. Large pyroxene grains of up to 5 cm in size reflect magmatic mineral accumulation processes. Accessory sulfides have been identified in most samples and typically comprise intergrown aggregates of pentlandite, pyrrhotite and chalcopyrite. The early-formed websterites and later spinel clinopyroxenites were interpreted as cumulates which formed from sulfide-saturated magmas derived from the asthenosphere during multi-stage late Paleozoic and Mesozoic melt influx into thinned subcontinental lithospheric mantle of the IVZ (Mazzucchelli et al., 2010; Mukasa and Shervais, 1999; Rivalenti et al., 1995; Wang and Becker, 2015c; Wang et al., 2013). The parent magmas of the pyroxenites were modified to variable extents by reaction with peridotite host rock.

In this study, six websterites, eleven spinel clinopyroxenites and one orthopyroxenite from Balmuccia were analyzed. Detailed petrologic descriptions of these rocks and bulk rock major element, S, Se, Te, Re, platinum group elements (PGE) abundances have been reported before (Wang and Becker, 2015c). The clinopyroxenites display lower PGE and Te contents and stronger fractionation of Se/Te than websterites, probably indicating that parental magmas of clinopyroxenites had been affected by early-stage sulfide fractionation (Wang and Becker, 2015c). Therefore, websterites and clinopyroxenites from Balmuccia and their parent magmas reflect variable stages of sulfide fractionation and accumulation, which is useful for constraining the fractionation of Cu and Ag during magmatic accumulation of sulfides, silicates and oxides in the mantle.

2.2. Garnet pyroxenites and host peridotite xenoliths from Hannuoba

Many studies have unveiled that the lithospheric mantle under the North China craton has underwent large-scale thinning and re-

Table 1
Contents of Cu, Ag and selected other compositions of Balmuccia pyroxenites.

Samples	Rock types	Al ₂ O ₃ (wt.%)	MgO (wt.%)	FeO _T (wt.%)	S (μg/g)	Se (ng/g)	Cu (μg/g)	2s	Ag (ng/g)	2s	Cu/Ag	2s (%)
BM11-28A	Sp-cpx	14.0	18.8	6.6	1456	460	204	5	52.8	0.6	3862	3%
BM11-28B	Sp-cpx	6.0	23.7	6.3	1509	610	259	7	95.3	1.4	2720	3%
BM11-28C	Sp-cpx	6.0	23.0	6.1	1490	583	244	6	100.9	1.5	2413	3%
BM11-27	Sp-cpx	7.1	19.5	7.6	1559	609	253	7	76.6	1.1	3302	3%
BM11-15	Sp-cpx	11.6	18.0	5.2	1250	479	141	3	32.7	0.4	4296	2%
BM11-16A	Sp-cpx	10.4	17.8	5.2	1532	502	151	3	31.6	0.4	4780	2%
BM11-20	Sp-cpx	5.4	20.7	6.1	537	268	155	3	41.9	0.5	3705	2%
BM11-20	Replicate					166	5	5	42.7	0.4	3894	3%
BM11-22	Sp-cpx	8.1	18.0	6.3	523	241	150	3	23.5	0.3	6386	2%
BM11-23	Sp-cpx	11.0	17.9	7.2	1028	314	197	4	30.9	0.3	6397	3%
BM11-26	Sp-cpx	7.0	17.3	6.7	805	330	131	2	43.9	0.5	2981	2%
BM11-26	Replicate					144	4	4	42.9	0.4	3354	3%
BM11-29	Sp-cpx	6.6	17.3	4.8	323	164	98	4	27.5	0.3	3550	4%
BM11-25	Web	4.9	21.4	5.5	722	596	174	9	52.7	0.7	3297	5%
BM11-19	Web	5.1	21.8	6.0	611	270	132	6	24.5	0.3	5376	5%
BM11-21	Web	2.7	21.9	5.2	1745	921	484	51	155.7	3.2	3105	11%
BM11-12	Web	4.2	20.5	5.1	680	593	167	9	48.6	0.6	3447	5%
BM11-14	Web	5.0	26.1	6.6	468	278	90	3	24.6	0.3	3673	4%
BM11-14	Replicate					87	2	2	25.5	0.2	3421	2%
BM11-07B	Opx	5.4	30.6	7.8	1017	668	189	10	68.9	0.9	2749	6%
Mean											3835	
1s											1112	
Reference material												
UB-N	Peridotite						24.2	1.0	44.3	0.4	548	4%
UB-N	Peridotite						23.1	0.9	44.6	0.4	518	4%
Literature values							23	2	45	2	511	

Note: Sp-cpx: spinel clinopyroxenites; Web: websterites; and Opx: orthopyroxenite.

They are mainly veins/layers with sharp boundary with surrounding peridotites, but a few samples also show reactive zones. Major elements, S, Se, Te and HSE have been measured before (Wang and Becker, 2015c).

Literature data of UB-N is from Wang et al. (2015).

juvenation since the Mesozoic. During extension of the refractory cratonic lithospheric mantle, it was largely replaced by the thin, fertile lithospheric mantle that formed from cooling, upwelling asthenosphere (e.g., Chu et al., 2009; Zhu et al., 2012 and references therein). Abundant mantle xenoliths occur in Cenozoic alkaline basalts in the Hannuoba region, close to the northern margin of the North China Craton (e.g., Song et al., 1990). These xenoliths are dominated by spinel lherzolites and garnet, spinel and plagioclase pyroxenites (e.g., Liu et al., 2005).

The garnet pyroxenites generally occur as thin (a few centimeters wide) veins or layers in spinel lherzolites and in many cases, also show reaction zones with the host peridotites (Liu et al., 2005). The pyroxenites have been interpreted to form from melt-rock reaction between a silicic melt and ultramafic host rock (Liu et al., 2005). Here we focus on the garnet pyroxenites that display clear petrological and geochemical evidence for melt-peridotite reaction and transitional rocks from lherzolite to pyroxenite as indicated by gradual changes in olivine and orthopyroxene modal abundances (Liu et al., 2005). The abundances of sulfides, which occur as intergrown aggregates of pentlandite, chalcopyrite and pyrrhotite, are lower than in pyroxenites from Balmuccia. In this study, Cu and Ag contents of ten pairs of garnet pyroxenites and their reactive lherzolite wall rocks were analyzed to constrain the variations of Cu and Ag contents and Cu/Ag ratio during melt-peridotite reaction.

3. Analytical methods

Isotope dilution ICP-MS methods have been established at Freie Universität Berlin for analysis of Cu and Ag contents in the same sample aliquots in order to limit the effects of heterogeneous distribution of accessory sulfide phases. The methods have yielded precise data (<5%, 2s) for NIST SRM612 glass, different geolog-

ical reference materials, carbonaceous chondrites and peridotites (Wang and Becker, 2015a; Wang et al., 2015). The same methods were applied in the present work. Some replicates and the reference material UB-N were also measured to assess data reproducibility.

Because the analytical details have been described before (Wang and Becker, 2015a; Wang et al., 2015), only a brief outline of the method is given here. After addition of the mixed spike solution containing enriched ⁶⁵Cu and ¹⁰⁹Ag tracers, between 0.2 and 0.4 gram of sample powder was digested in a mixture of concentrated HF-HNO₃ in Parr digestion bombs at 190 °C for 2–3 days. The digestion solution was dried down and converted to chloride form for chromatographic separation (Wang et al., 2015). The Cu and Ag fractions were measured at Freie Universität Berlin on an Element XR sector field ICP-MS (Thermo Scientific) at medium mass resolution mode (M/ΔM = 4000) and low resolution (M/ΔM = 300), respectively. An Aridus-I desolvator was used to limit oxide formation (CeO⁺/Ce⁺ < 0.002). During the period of sample measurements, the total procedural blanks were 0.019 ± 0.09 ng Ag and 8 ± 3 ng Cu (2s, n = 8), which is negligible for samples of the present study (blank contribution <1%).

4. Results

Results for the samples from Balmuccia and Hannuoba are reported in Table 1 and Table 2, respectively, and their major element compositions are compiled in the Supplementary Table 1. The results for the reference material UB-N match literature values within uncertainty (Wang et al., 2015). Replicates of pyroxenites and peridotites were digested from different sample aliquots and they show repeatable Cu and Ag results within a few-percent uncertainty (Tables 1 and 2).

Table 2
Cu and Ag contents of the pairs of reactive peridotites and pyroxenites from Hannuoba xenoliths.

Pair number	Samples	Rock types	Al ₂ O ₃ (wt.%)	MgO (wt.%)	FeO _T (wt.%)	Cu (μg/g)	2s	Ag (ng/g)	2s	Cu/Ag	2s (%)
1	DMP448	Peridotite wall	4.6	36.9	9.1	13.4	0.2	6.8	0.1	1987	2%
	DMP448-v	Pyroxenite	8.3	26.6	7.0	89.4	2.5	41.3	1.0	2162	4%
2	DMP466	Peridotite wall	7.4	28.0	10.2	56.5	1.2	18.2	0.3	3107	3%
	DMP466 Replicate					52.5	2.5	18.3	0.1	2875	5%
3	DMP466-v	Pyroxenite	12.5	19.8	8.1	52.7	1.3	17.3	0.3	3040	3%
	DMP458	Peridotite wall	4.5	36.3	8.7	33.0	0.6	7.5	0.1	4379	2%
4	DMP458-v	Pyroxenite	11.3	19.8	5.5	84.4	2.3	25.1	0.5	3361	3%
	DMP460	Peridotite wall	2.8	38.4	8.5	117.1	3.8	38.4	0.8	3050	4%
5	DMP460 Replicate					106.0	7.7	38.1	0.3	2778	7%
	DMP460-v	Pyroxenite	9.3	21.1	5.7	116.2	4.4	43.1	1.1	2695	5%
6	DMP464	Peridotite wall	5.2	35.9	8.8	33.3	0.6	11.0	0.2	3027	2%
	DMP464-v	Pyroxenite	13.8	17.6	5.2	76.8	2.1	46.8	1.1	1640	4%
7	DMP314	Peridotite wall	1.2	44.2	9.2	4.6	0.1	1.6	0.1	2935	5%
	DMP314-v	Pyroxenite	4.0	26.8	5.2	14.5	0.2	5.4	0.1	2698	2%
8	DMP407	Peridotite wall	–	–	–	10.6	0.2	3.1	0.1	3409	3%
	DMP407-v	Pyroxenite	4.3	24.6	12.9	33.0	0.6	6.8	0.1	4851	2%
9	DMP441	Peridotite wall	4.3	35.3	8.4	54.4	1.1	12.4	0.2	4376	3%
	DMP441-v	Pyroxenite	11.7	21.5	6.2	88.5	2.1	23.3	0.4	3802	3%
10	DMP425	Peridotite wall	3.0	38.8	8.3	23.8	0.4	4.7	0.1	5013	2%
	DMP425-v	Pyroxenite	6.8	19.4	4.4	46.8	0.9	19.6	0.4	2392	3%
Mean 1s	DMP123	Peridotite wall	–	–	–	35.2	0.6	15.6	0.3	2257	2%
	DMP123-v	Pyroxenite	–	–	–	53.8	1.1	21.2	0.4	2542	3%
										3108	
										898	

Note: See the details of sample pairs and major element contents in Liu et al. (2005) and the compiled major element data are in the supplementary Table 1.

4.1. Balmuccia websterites and clinopyroxenites

Websterites and clinopyroxenites have Cu contents of 87–259 μg/g and Ag contents of 25–95 ng/g, with a sample BM11-21 showing significantly higher concentrations of 484 μg/g Cu and 156 ng/g Ag (Figs. 1 and 2). The Cu and Ag contents in most of these mantle pyroxenites overlap the concentration range of MORBs and primitive back-arc basalts, with a few pyroxenites showing higher contents. Melts in equilibrium with the Balmuccia pyroxenites have variable Cu and Ag contents which are lower than those of Balmuccia pyroxenites but typically are within the MORB range (Supplementary Table S2 and Fig. S1). The Cu contents are comparable to those in pyroxenite xenoliths from Hawaii (Fig. 2). Overall, the Cu and Ag contents in Balmuccia pyroxenites increase with increasing S contents. Sample BM11-21 with high Cu and Ag contents also has a high S content (1745 μg/g). The correlation between Cu, Ag, and S reflects the effect of modal abundance of sulfide phases in the bulk rock; high sulfide modal abundance leads to high contents of Cu and Ag (Fig. 2).

The Cu/S ratios in these pyroxenites vary from 0.1 to 0.3 and tend to be systematically higher than those in MORBs ($Cu/S_{MORB} = 0.05–0.15$, Fig. 2). Although the Cu and Ag contents are variable, Cu and Ag contents in both websterites and clinopyroxenites are linearly correlated, and show a Cu/Ag ratio ($Cu/Ag = 3800 \pm 1100$, 1s, $n = 20$) similar to those in fertile peridotites from Balmuccia and other localities, MORBs, and Hawaiian basalts (Fig. 3a and 4).

4.2. Pyroxenites and the lherzolite wall rocks from Hannuoba

Garnet pyroxenites from Hannuoba have Cu contents of 14.5–116 μg/g and Ag contents of 5.4–46.8 ng/g (Table 2, Fig. 3). These values tend to be lower than those of the pyroxenites from Balmuccia. Two pyroxenite–lherzolite wall rock pairs (DMP-466 and DMP460) display similar Cu and Ag contents in pyroxenite and lherzolite wall rock. Other pyroxenites show higher Cu and Ag contents than their lherzolite wall rocks (Table 2). Some of the reacted lherzolites have higher Cu and Ag contents than fertile lherzolites of other locations (Fig. 3).

Except for two samples, the pyroxenites and the associated lherzolites from Hannuoba show a positive correlation of Cu and Ag contents (Fig. 3). Six pairs of pyroxenite and lherzolite wall rock have very similar Cu/Ag ratios whereas other four pairs show no systematic variations (Fig. 3c). The mean Cu/Ag of 3100 ± 900 (1s, $n = 22$) is indistinguishable from other mantle rocks and MORBs (Fig. 4). Although the pyroxenites from Balmuccia and Hannuoba have different formation histories and show highly variable Cu and Ag contents (e.g., 14.5–484 μg/g for Cu), the Cu/Ag ratios display limited variations with most samples in the range of 2000–4500 (Figs. 3 and 4).

5. Discussion

5.1. Limited fractionation of Cu and Ag in the mantle and the oceanic crust

5.1.1. Influence of magmatic accumulation and melt–peridotite reaction on Cu/Ag in the mantle

The major element compositions of websterites and clinopyroxenites from the Balmuccia peridotite massif and their high S concentrations and preferred location of sulfide grains along grain boundaries suggests that the pyroxenites represent cumulates crystallized from sulfide-saturated mafic magmas (e.g., Sinigoi et al., 1983; Wang and Becker, 2015c). Some pyroxenites display orthopyroxenitic to websteritic reaction zones with host peridotites. The accumulation of sulfide led to variable, but typically enhanced contents of S, Se, Cu, Ag and some other chalcophile elements (e.g., Re, Pd), compared to peridotites (Figs. 1 and 2 and Wang and Becker, 2015c). Most websterites and clinopyroxenites from Balmuccia display a limited range of Cu/Ag ratios which are similar to values in lherzolites from Balmuccia and other locations (Fig. 4). The results indicate little fractionation of Cu from Ag during melt–peridotite reaction and subsequent accumulation of sulfide-bearing pyroxenites in the mantle. The clinopyroxenites display lower PGE and Te contents, but similar or higher S contents and higher Se/Te than websterites. Because the PGE and Te tend to be more chalcophile than S, Se, Cu and Ag (e.g., Mungall and Brenan, 2014; Brenan, 2015), this probably indicates that the parental mag-

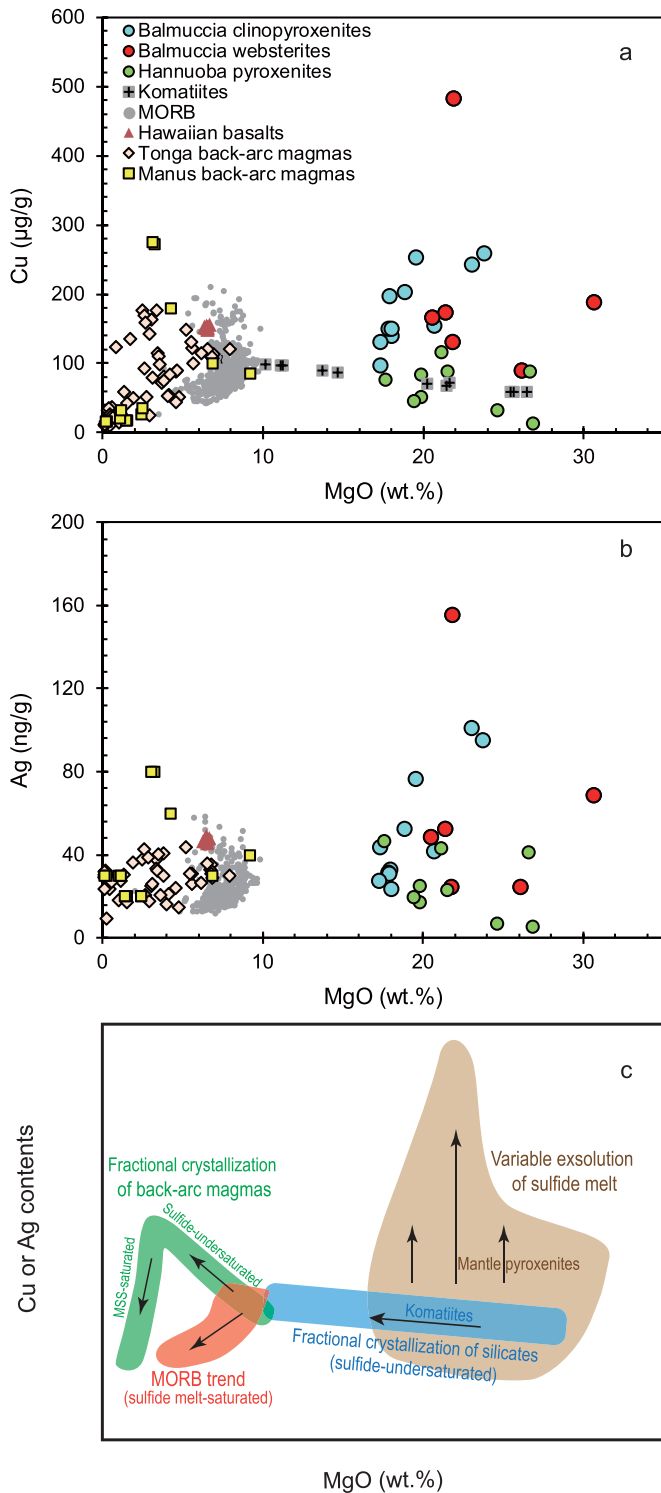


Fig. 1. Copper (a) and Ag contents (b) as a function of MgO contents in mantle pyroxenites from Balmuccia and Hannuoba, komatiites (Puchtel et al., 2016), Hawaiian basalts (Jenner et al., 2012), MORBs (Jenner et al., 2012; Jenner and O'Neill, 2012) and back-arc magmas (Jenner et al., 2010, 2015). c) schematically explains the main processes which affect the variations of Cu and Ag contents in magmatic rocks. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

mas of clinopyroxenites underwent early-stage sulfide saturation and segregation in the mantle (Wang and Becker, 2015c). We note that regardless of these different fractionation histories, the clinopyroxenites display Cu/Ag ratios similar to websterites. Because of the similar partitioning behavior of Cu and Ag during

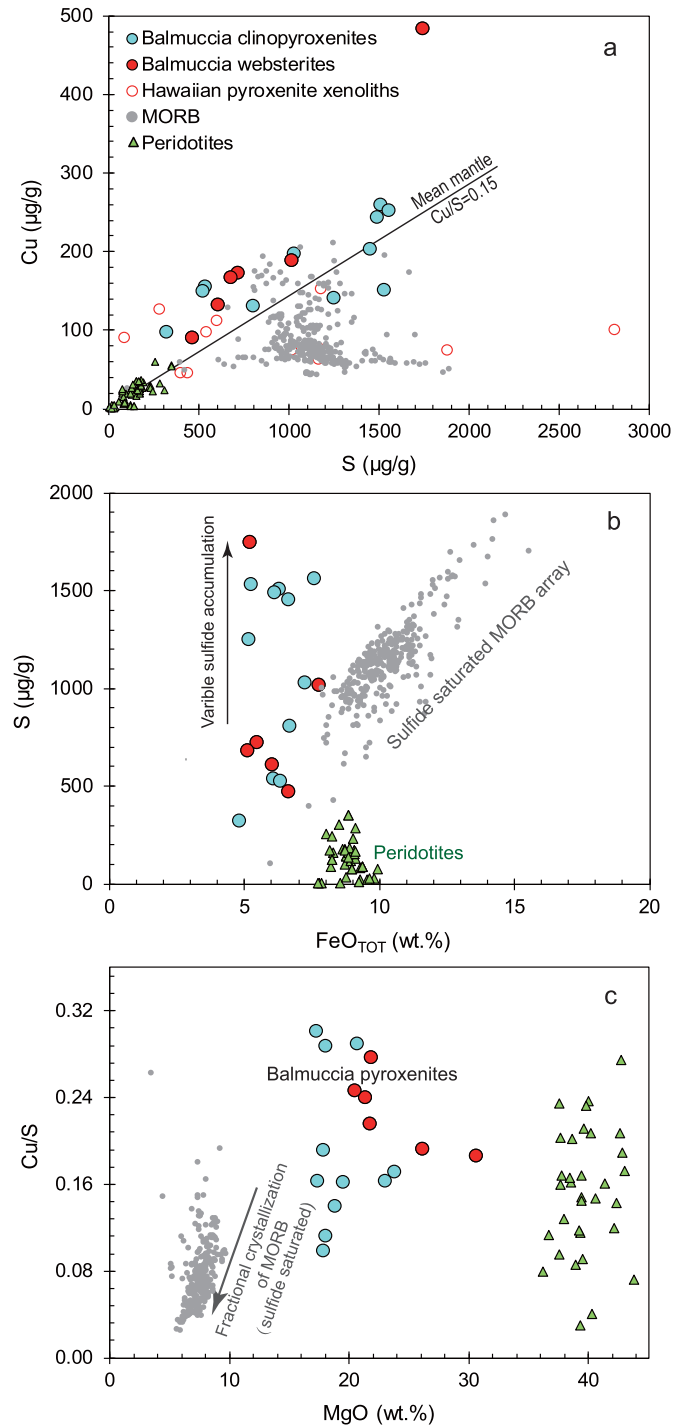


Fig. 2. Copper and S contents of Balmuccia pyroxenites. a) Cu contents in Balmuccia pyroxenites are similar to or higher than in pyroxenite xenoliths from Hawaii, and overlap with most MORB data. b) S contents of the Balmuccia pyroxenites vary independently of their FeO contents, indicating that sulfide in the pyroxenites were controlled by accumulation processes. The data of sulfide saturated MORBs are shown for comparison and reflect the increase in sulfur contents in MORBs with FeO contents. c) Most Balmuccia pyroxenites show higher Cu/S than MORBs, which reflects accumulation of sulfide melt in the pyroxenites and the higher sulfide melt-silicate melt partition coefficient of Cu relative to S (e.g., Mungall and Brenan, 2014; Patten et al., 2013). Cu/S ratios of MORBs decrease during fractional crystallization of silicates and co-precipitation of sulfide melt because Cu is more compatible than S (Jenner et al., 2010). The larger changes of Cu/S in the clinopyroxenites compared to the websterites may reflect changes in the sulfide saturation state of the different parent magma compositions. Literature sources: MORB (Jenner et al., 2012; Jenner and O'Neill, 2012); Hawaiian pyroxenite xenoliths (Sen et al., 2011) and peridotites (Wang and Becker, 2015a).

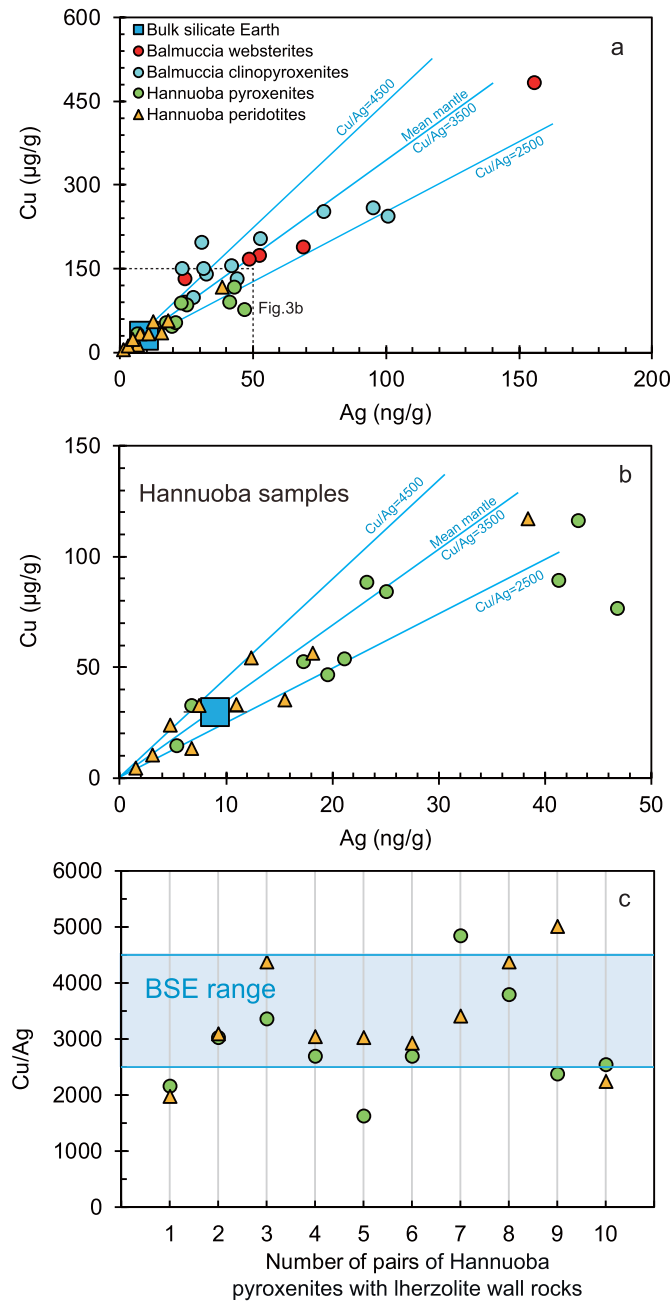


Fig. 3. Copper and Ag contents in pyroxenites and corresponding lherzolite wall rocks from Hannuoba xenoliths (North China Craton) and pyroxenites from Balmuccia. a) Copper and Ag contents of Hannuoba pyroxenites are variable and overall lower than those of Balmuccia pyroxenites, reflecting different proportions of sulfides in these samples. Although Cu and Ag contents show a large range in these samples, Cu/Ag display limited variation around the average mantle value of 3500 ± 1200 (1s, Wang and Becker, 2015a). b) highlights Cu and Ag contents in the pyroxenites and associated lherzolites from Hannuoba. Some Hannuoba lherzolites have higher Cu and Ag contents than the bulk silicate Earth (BSE), reflecting sulfide redistribution and enrichment during melt–peridotite reaction. c) With few exceptions, most pairs of Hannuoba pyroxenites and corresponding lherzolite wall rocks display very similar Cu/Ag within the range of the BSE, indicating limited fractionation of Cu from Ag during melt–peridotite reaction and redistribution of sulfide melt in these samples. The BSE values of Cu (30 ± 6 µg/g), Ag (9 ± 3 ng/g) and Cu/Ag (3500 ± 1200 , 1s) were estimated based on lherzolites from various locales (Wang and Becker, 2015a).

exsolution of sulfide melt from silicate melt, multiple episodes of sulfide melt segregation in the upper mantle result in limited changes of Cu/Ag ratios. Two clinopyroxenites (BM11-22 and BM11-23) show a relatively high Cu/Ag (about 6400). BM11-23

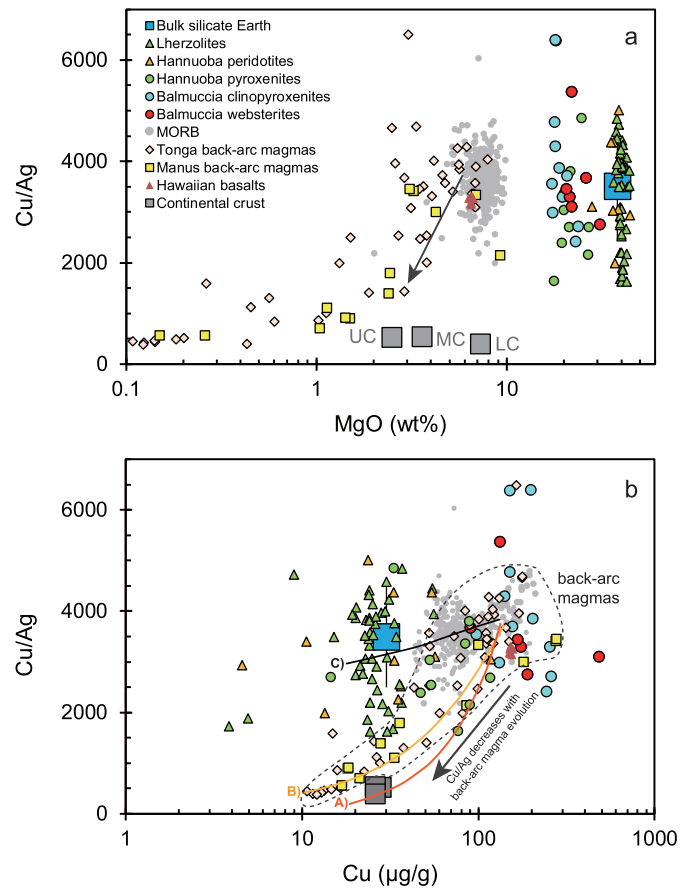


Fig. 4. Cu/Ag versus contents of MgO (a) and Cu (b) in rocks from the mantle, oceanic crust, arc magmas and in the continental crust. Rocks from the upper mantle such as fresh lherzolites and mantle pyroxenites, show limited variations in Cu/Ag ratios (mostly 2000 to 4500). These ratios are also indistinguishable from those of MORBs (Cu/Ag \approx 2500 to 4500, mean 3600 ± 400 , 1s, $n = 338$, Jenner et al., 2012; Jenner and O'Neill, 2012), MORB sulfide droplets (3000 ± 300 , 1s, $n = 7$, Patten et al., 2013) and Hawaiian basalts (Jenner et al., 2012). Notably, primitive back-arc magmas have initial Cu contents and Cu/Ag similar to MORBs with similar MgO. During fractional crystallization of these back-arc magmas (range with dashed line, Jenner et al., 2010, 2015), Cu contents and Cu/Ag decrease noticeably to a level similar to that of the continental crust. Upper, middle and lower continental crust (gray squares, UC, MC and LC, respectively) have similar Cu contents and Cu/Ag (Rudnick and Gao, 2014). These data indicate the contrasting fractionation behavior of Cu and Ag during fractional crystallization of back-arc magmas compared to magmatic processes in the upper mantle and during the formation and evolution of oceanic crust. The solid lines labeled with A, B, C show modeled fractionation trends of sulfide-saturated magmas. A): MSS–silicate melt with D_{Cu} of 400 and D_{Ag} of 40; B): MSS–silicate melt with D_{Cu} of 480 and D_{Ag} of 192 (equivalent to 80% MSS + 20% coexisting sulfide liquid); and C): sulfide melt–silicate melt with D_{Cu} of 900 and D_{Ag} of 800. The models follow the work of Li and Audétat (2012) and see details therein.

shows a very high Se/Te of 108, however, BM11-22 has a lower Se/Te of 45, similar to pyroxenites with 'normal' Cu/Ag ratios. Because Se is less chalcophile than Te (e.g., Hertogen et al., 1980; Brenan, 2015), the Se/Te ratio of magmatic rocks should monitor the extent of previous sulfide fractionation. Thus, occasionally higher Cu/Ag cannot always be related in a simple way to extensive sulfide fractionation (monitored by high Se/Te). Alternatively, because some clinopyroxenites from Balmuccia may have formed relatively shallow (e.g., Mukasa and Shervais, 1999; Wang and Becker, 2015c), the relatively high Cu/Ag of the above mentioned samples may have resulted from MSS–silicate melt partitioning during formation of these clinopyroxenites, because MSS preferentially retains Cu, relative to Ag (Li and Audétat, 2012, 2015; Zajacz et al., 2013).

The garnet pyroxenites and their spinel lherzolite wall rocks from Hannuoba show petrological and geochemical evidence of melt–peridotite reaction (Liu et al., 2005). Some of the lherzolites have higher Cu and Ag contents than the bulk silicate Earth model composition and fertile lherzolites of other locations, whereas the pyroxenites from Hannuoba mostly have lower Cu and Ag contents compared to the pyroxenites from Balmuccia. These observations indicate locally enhanced precipitation of sulfide melt in the lherzolite during silicate melt–peridotite reaction at Hannuoba (Fig. 3). The volume of parental magmas of pyroxenites from Hannuoba was likely very small, as reflected by thin pyroxenite veins of a few centimeters in width (note that the sizes of whole xenoliths of pyroxenites and associated peridotites were <8 cm in diameter, Liu et al., 2005). The inferred small volume of parental magmas (compared to Balmuccia) and redistribution of some sulfide melts during melt–peridotite reaction may be the main reasons for the low Cu and Ag contents in some Hannuoba pyroxenites. Although the garnet pyroxenites and reacted lherzolites from Hannuoba have different Cu and Ag contents, the Cu and Ag contents show a positive correlation, and Cu/Ag ratios of most pyroxenites are similar to those of the lherzolites. Most pairs of garnet pyroxenite and their lherzolite wall rock have similar Cu/Ag, indicating that the transport of dissolved sulfide from the parent melt of the garnet pyroxenites and precipitation of sulfide melt in the lherzolites during melt–peridotite reaction did not cause systematic changes of Cu/Ag (Fig. 3).

A few pairs of pyroxenites and associated lherzolites from Hannuoba display somewhat higher and lower Cu/Ag ratios (Fig. 3c). Cu/Ag ratios of pyroxenites and peridotites from Balmuccia and Hannuoba both display a similar range of 2000–4500 (Fig. 4). During sulfide melt–silicate melt partitioning, partition coefficients of Cu and Ag are similar at variable physicochemical conditions. However, the partition coefficients are not identical with $D_{\text{sulfide melt-silicate melt}}^{\text{Cu}}/D_{\text{sulfide melt-silicate melt}}^{\text{Ag}}$ ranging from 0.6 to 1.4 (Kiseeva and Wood, 2013, 2015; Li and Audétat, 2012, 2015). The small differences in sulfide melt–silicate melt partition coefficients can explain the variations of Cu/Ag in mantle rocks and in basalts (see line C in Fig. 4b). For instance, MORBs display a Cu/Ag range from 2000 to 4500 with a variation similar to mantle peridotites and pyroxenites. A similar range occurs in three different samples from the same clinopyroxenite vein in Balmuccia (BM11-28A, 28B and 28C) showing a Cu/Ag variation from 2400 to 3800 (Table 1). The Cu/Ag variation in Balmuccia and Hannuoba samples is limited and overall, these ratios remain within the range of mantle rocks and MORBs. Therefore, the data from Balmuccia and Hannuoba pyroxenites indicate that melt transport, melt–peridotite reaction and accumulation of sulfide melt in the upper mantle may lead to highly variable Cu and Ag contents (e.g., from 14.5 µg/g to 484 µg/g for Cu) but limited fractionation of Cu and Ag (within a factor of two).

5.1.2. Cu/Ag ratios in mantle rocks and in oceanic basalts and relevant partitioning processes

The Cu/Ag ratios of pyroxenites and lherzolites from Balmuccia and Hannuoba are within the range of the mantle (3500 ± 1000), which was estimated from post-Archean fertile lherzolites (Wang and Becker, 2015a). Furthermore, the Cu/Ag ratios of mantle lherzolites and pyroxenites are consistent with the mean Cu/Ag ratios of MORB glasses (Jenner and O'Neill, 2012; Jenner et al., 2010) and with sulfide droplets from MORBs (Patten et al., 2013). Oceanic island basalts from Hawaii also show similar Cu/Ag ratios as MORB and mantle rocks (Jenner et al., 2012, Fig. 4). The pyroxenites as magmatic products of migrating magmas bridge the gap between mantle peridotites and basaltic magmas derived from the convecting upper mantle. Although Cu and Ag contents may vary considerably in rocks from the mantle and in oceanic crust (Fig. 4),

their similar Cu/Ag ratios indicate the limited fractionation of Cu and Ag during magmatic processes in the upper mantle and in the oceanic crust.

The evolution of the chalcophile element composition of MORBs and their precursor magmas are likely controlled by sulfide melt–silicate melt partitioning (e.g., Jenner and O'Neill, 2012; Jenner et al., 2010; Patten et al., 2013; Wang and Becker, 2015b, 2015c). For example, MORBs show decreasing Cu/S and Cu/Se ratios with decreasing MgO (Jenner et al., 2010, 2015). The Cu/S ratios in cumulus pyroxenites from Balmuccia are higher than the range in oceanic floor basalts (Fig. 2). The changes of element ratios in pyroxenites and MORB are consistent with similar partitioning behavior of Cu and Ag, and more compatible behavior of Cu and Ag relative to S and Se during sulfide melt–silicate melt partitioning (Brenan, 2015; Jenner et al., 2010; Kiseeva and Wood, 2015; Li and Audétat, 2012).

The relative roles of MSS–sulfide melt or sulfide melt–silicate melt in the partitioning of chalcophile elements in the mantle has been a matter of debate. Previous experimental data on the P – T range of solidus and liquidus of mantle sulfide led to the suggestion that MSS might be stable over a large range of upper mantle P – T conditions (Bockrath et al., 2004). Thus MSS–sulfide melt partitioning was proposed to explain the depletion of Pt and Pd relative to compatible Os, Ir and Ru in depleted peridotites (Ballhaus et al., 2006; Bockrath et al., 2004). In a similar way, suprachondritic Se/Te ratios in some harzburgites were explained to result from partial melting, with residual MSS retaining these elements in mantle rocks (König et al., 2014). However, MSS–sulfide melt partitioning presents difficulties to explain the relative fractionation behavior of Pd, Au, Re, S, Se, Te and in particular Cu and Ag in mantle peridotites and pyroxenites (this work; Wang and Becker, 2015a, 2015b, 2015c; Becker and Dale, 2016). It has been argued that during low to moderate degrees of partial melting, reactive magma transport and fractional crystallization in the asthenospheric mantle, sulfide melt–silicate melt partitioning can account for the observed fractionations of chalcophile elements in lherzolites, pyroxenites and basic igneous rocks in the oceanic crust (Mungall and Brenan, 2014; Wang and Becker, 2015a, 2015b and references therein). The depletion of Pt and Pd relative to Os, Ir and Ru in harzburgites does not require MSS–sulfide melt partitioning. At high degrees of partial melting, quantitative dissolution of sulfide melt into silicate melt leads to a rapid decrease in f_{S_2} which triggers the formation of Os–Ir–Ru alloys (Fonseca et al., 2012). The combined effect of sulfide melt–silicate melt partitioning at low to moderate degrees of melting and retention of Os–Ir–Ru alloys at high degree of melting are consistent with the abundances and fractionation of PGE systematics in mantle peridotites, komatiites and primitive basalts (e.g., Mungall and Brenan, 2014).

Because the fractionation behavior of Cu and Ag differs significantly in MSS–sulfide melt and MSS–silicate melt partitioning ($D_{\text{Cu}}/D_{\text{Ag}} > 1$) compared to sulfide melt–silicate melt partitioning ($D_{\text{Cu}}/D_{\text{Ag}} \approx 1$ at $D_{\text{Cu}} \approx D_{\text{Ag}}$ in the range of 200–1200, Kiseeva and Wood, 2013, 2015; Li and Audétat, 2012, 2015; Zajacz et al., 2013), the fractionation of Cu and Ag (i.e. changes of Cu/Ag) in rocks and magmas from the upper mantle offers a tight constraint on the type of partitioning process involved. The similar Cu/Ag of mantle lherzolites (mean Cu/Ag = 3500 ± 1200 , Wang and Becker, 2015a), pyroxenites (mean Cu/Ag = 3500 ± 1100 , data from Tables 1 and 2) and MORBs (mean Cu/Ag = 3600 ± 400 , Jenner and O'Neill, 2012) clearly indicate that sulfide melt–silicate melt partitioning must be the main process relevant for changes in Cu and Ag, and thus also other chalcophile elements in the convecting upper mantle.

The mantle rocks at Balmuccia and Hannuoba represent sub-continental lithospheric mantle. The data on these samples indi-

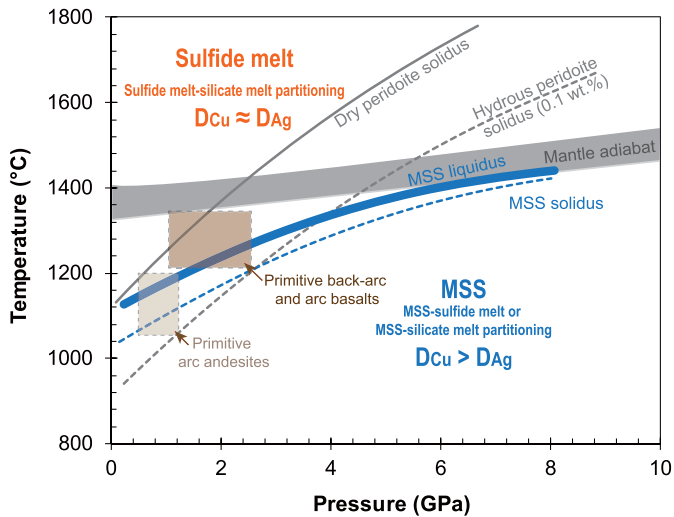


Fig. 5. Temperature–pressure dependence of sulfide melt and MSS stability and the effect on Cu–Ag fractionation. The MSS liquidus (solid blue curve) and solidus (dashed blue curve) are from recent experimental results (Zhang and Hirschmann, 2016). The co-existence of MSS and sulfide melt occurs in a narrow P – T range. At $P < 6$ GPa, the sulfide liquidus lies below the mantle adiabat (gray area, Katsura et al., 2010) and the solidus of dry peridotite (solid gray curve, Hirschmann, 2000), but intersects the solidus of hydrous peridotite (assuming 0.1 wt.% water, dashed gray line, Katz et al., 2003). The sulfide liquidus constrained by Zhang and Hirschmann (2016) represents an upper bound, indicating that sulfide melt is present in the convecting upper mantle at depths of <250 km. At P – T conditions above the sulfide liquidus (e.g., the convecting upper mantle and likely the hot part of the lithospheric mantle), sulfide melt–silicate melt partitioning controls the fractionation of chalcophile elements (i.e., Cu and Ag behave similarly and Cu/Ag does not change much). In contrast, at P – T conditions below the sulfide solidus (e.g., cold lithospheric mantle and in some cooling basic magmas), MSS–sulfide melt or MSS–silicate melt partitioning can fractionate Cu from Ag and decreases Cu/Ag in derivative magmas. Note that the P – T conditions (e.g., 1.0–2.5 GPa, 1220–1350 °C) to form primitive arc and back-arc basalts are mostly above the sulfide liquidus (Currie and Hyndman, 2006; Schmidt and Jagoutz, 2017). Fractionated magmas such as basaltic andesites and andesites form in the stability field of MSS.

cate that the chemical fractionations of Cu and Ag were either inherited from processes that occurred when these mantle rocks were part of the asthenosphere or that sulfide melt also controls chalcophile element partitioning in deep and hot parts of the litho-

spheric mantle. The limited variation of Cu/Ag in magmatic processes involving lherzolites, mantle pyroxenites and MORBs (Figs. 4 and 6) are consistent with recent experimental data (Fig. 5), which predict the predominant occurrence of molten sulfide rather than MSS in convecting upper mantle down to about 250 km depth (Zhang and Hirschmann, 2016). The data on peridotites and pyroxenites from Balmuccia, Hannuoba and from other locations indicate that sulfide melt–silicate melt partitioning also controls chalcophile elements when migrating magmas react with surrounding peridotites and precipitate sulfide–pyroxene assemblages. These processes may occur in the convecting and in deep lithospheric mantle, for instance during refertilization of depleted peridotites and the formation of pyroxenite layers. Because the clinopyroxenites from Balmuccia crystallized in the spinel pyroxenite stability field and plagioclase occurs as a subsolidus phase during cooling, it appears that even magma infiltration into shallow lithospheric mantle predominantly exsolves sulfide melt and not MSS. This can be understood if during the crystallization of the clinopyroxenites at 1–1.5 GPa, temperatures did not fall significantly below 1200 °C.

5.2. Implications for continental crust formation

5.2.1. Low Cu content and low Cu/Ag in the continental crust

The continental crust is chemically very heterogeneous, and the accuracy of estimates of its bulk composition depends on analyses of rocks and the correct weighting of the proportions of different rock types in the crust. Such compositional estimates are more difficult to assess for trace elements such as Cu and Ag, which are partly or mostly controlled by the distribution of accessory sulfide minerals. The Cu and Ag contents in the continental crust estimated by different studies are 25–75 $\mu\text{g/g}$ and 52–80 ng/g , respectively, indicating a low Cu/Ag of around 500 in the bulk continental crust (Rudnick and Gao, 2014 and references therein, Supplementary Table 3). According to the most recent estimate, the continental crust contains 27 $\mu\text{g/g}$ Cu and 56 ng/g Ag, respectively, with $\text{Cu/Ag} \approx 480$ (Rudnick and Gao, 2014). Lower, middle and upper continental crust display no obvious differences in Cu and Ag contents and Cu/Ag (Supplementary Table 3, Fig. 4). There is currently no evidence that would suggest that these estimates may be incorrect or biased.

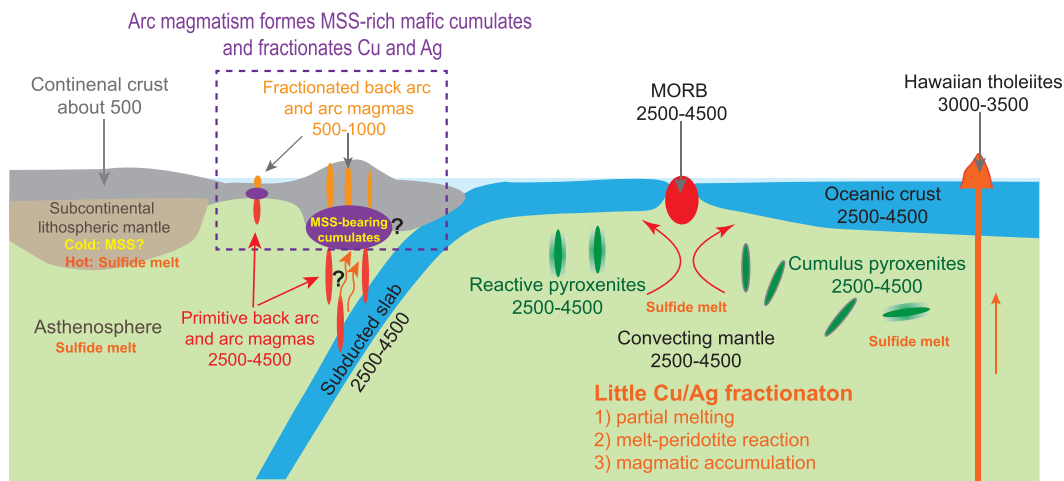


Fig. 6. Schematic illustration of Cu/Ag behavior in different magmatic environments and reservoirs. Magmatic processes in the convecting upper mantle and in the oceanic crust such as partial melting, silicate melt–peridotite reaction, accumulation of sulfide melt, and formation and evolution of oceanic crust result in limited fractionation of Cu from Ag (Cu/Ag varies within a factor of 2). Note that Cu/Ag ratios in primitive back-arc basalts and presumably also in primitive arc basalts inherit Cu/Ag of mantle sources and are similar in MORBs. In contrast, fractional crystallization during back-arc magmatism decreases Cu/Ag from MORB-like values in primitive magmas to 500–1000 in evolved magmas (Jenner et al., 2010, 2015), which is similar to values in the continental crust (about 500, Rudnick and Gao, 2014). The strong fractionation of Cu and Ag during the evolution of back-arc magmas is mainly ascribed to the formation of MSS in cumulates of the lower crust. Delamination of sulfide-bearing cumulates in the lower crust of magmatic arcs over Earth's history (e.g., Lee et al., 2012) may have led to an intermediate major element composition and a decrease in Cu content and Cu/Ag of the continental crust (details not shown).

Thus, the Cu/Ag ratio of the continental crust is about a factor of 7 lower than Cu/Ag of the oceanic crust and the mantle (3500 ± 1000). Because of the limited variation of Cu/Ag (within a factor of two) during the generation and fractional crystallization of MORB and magmatic processes in the convecting upper mantle (Section 5.1), the low Cu/Ag and low Cu content of the continental crust must reflect processes during continental crust formation. Arc magmatism is widely thought to play an important role in the formation of continental crust (e.g., Jagoutz and Kelemen, 2015). Sulfide segregation and accumulation in the lower crust of magmatic arcs was proposed to affect abundances of Cu and other chalcophile elements such as Ag, Au and the PGEs in the continental crust (Jenner, 2017; Lee et al., 2012; Li and Audétat, 2013). Thus, the different Cu/Ag ratio in the continental crust compared to the oceanic crust and the mantle probably provides an important hint to explore the role of sulfide segregation into the lower crust of arcs and the role of delamination of mafic cumulates in the formation of the continental crust (Jenner, 2017; Lee and Anderson, 2015; Lee et al., 2012).

5.2.2. Fractionation of Cu and Ag during the formation and evolution of arc magmas

The stability of different sulfide phases, MSS vs. sulfide melt, is critical to assess the fractionation of chalcophile elements during magmatic processes. As shown in Fig. 5, MSS may be stable in relatively cool lithospheric mantle at high pressures (Zhang and Hirschmann, 2016). Depending on magma temperatures and fO_2 , MSS may also be stabilized in the lower crust of magmatic arcs, and during cooling of basic magmas within the continental crust (e.g., as suggested for the formation and evolution of magmatic Cu–Ni sulfide deposits, Barnes et al., 2008). In these cases, MSS–sulfide melt or MSS–silicate melt partitioning may predominate and Cu becomes more compatible than Ag and thus fractionates from Ag when MSS is present (Li and Audétat, 2012, 2015; Zajacz et al., 2013).

Oxygen fugacities (fO_2) in arc magmas are generally higher than in basalts derived from normal convecting upper mantle (Richards, 2015). Experimental data obtained at both reduced and oxidized conditions (e.g., $\log fO_2$ ranging from $\Delta FMQ -2$ to $+3$, Li and Audétat, 2012, 2015; Zajacz et al., 2013) indicates that changing fO_2 does not change the MSS–silicate melt partitioning of Cu relative to Ag. High fO_2 arc magmas generated by oxidized, slab-derived fluids would dissolve more oxidized S (e.g., Jugo, 2009; Jégo and Dasgupta, 2014) and thus would destabilize sulfides in the mantle source of arc magmas, leading to the formation of sulfide-undersaturated primitive back-arc and island arc magmas. For example, experiments have indicated a range of sulfur content at sulfide saturation (SCSS) from 1500 $\mu\text{g/g}$ at $FMQ + 0.5$ to 7500 $\mu\text{g/g}$ at $FMQ + 2$ for back-arc basalts and as high as 1.4 wt% at $FMQ + 2.3$ for island arc basalts (Jugo, 2009).

The Cu/Ag ratios of primitive back-arc magmas reported so far (Jenner et al., 2010, 2012, 2015) are similar to those of the mantle peridotites and MORBs (Fig. 4), suggesting similar behavior of Cu and Ag in primitive back-arc basalts compared to MORBs and normal mantle rocks. Given the high fO_2 (e.g., as indicated by Fe^{3+}/Fe^{2+} of 0.25–0.3 for Pual Ridge basalts versus 0.15 for MORB, Jenner et al., 2010) and the high water content of the back-arc magmas, the fO_2 – temperature conditions at which the parent magmas formed likely led to complete exhaustion of sulfides in the mantle source (e.g., Jugo, 2009). In such a case, Cu, Ag and many other chalcophile elements are incompatible, and the complete budget of these elements in the mantle source would have been transferred into the magmas, leading to inheritance of the Cu/Ag ratio of the mantle source. Systematic changes in contents of Cu, Ag, S, Se and the PGE with fractional crystallization indices such as MgO indeed show that the most primitive back-arc magmas from

the Eastern Manus back-arc Basin and from numerous spreading centers and rifts of the Lau back-arc Basin (SW Pacific) were initially sulfide-undersaturated (Jenner et al., 2010, 2012, 2015; Park et al., 2013).

So far, limited abundance data on chalcophile elements exist for primitive island arc magmas. However, the increase of abundances of chalcophile elements such as Cu and PGE with decreasing MgO or Mg# in arc magmas from the Tonga arc, SW Pacific also indicate sulfide-undersaturation of the parental magmas (Dale et al., 2012; Jenner et al., 2015; Park et al., 2015). These data are consistent with the prediction of high SCSS in high- fO_2 arc magmas (Jugo, 2009). Assuming that the mantle sources of some arc magmas contained residual sulfide, the estimated P – T conditions (e.g., 1.0–2.5 GPa, 1220–1350 °C, Fig. 5) during the formation of primitive arc and back-arc basalts (Currie and Hyndman, 2006; Schmidt and Jagoutz, 2017) should be almost certainly above the sulfide liquidus. Under these conditions, arc magmas that equilibrate with residual sulfide melt should inherit source-like Cu/Ag via sulfide melt–silicate melt partitioning.

Fractional crystallization of primitive back-arc magmas from the Pual Ridge, Eastern Manus back-arc basin led to a decrease of Cu contents and a decrease of Cu/Ag from MORB-like values of 3500 to values of about 500 (Fig. 4, Jenner et al., 2010). These changes have been ascribed to the precipitation of Cu-rich solid sulfide (MSS) triggered by magnetite crystallization in oxidized arc magmas (Jenner et al., 2010; Li and Audétat, 2012). Similarly, the decrease of Cu contents and Cu/Ag from MORB-like values also occurs during fractional crystallization of magmas at spreading centers and rifts of the Lau back-arc basin in the SW Pacific (Fig. 4, Jenner et al., 2012, 2015). Therefore, the change of Cu/Ag ratios during late stages of crystal fractionation in back-arc systems is likely a common process. Based on the sulfide saturation constraints in oxidizing arc magmas and the likely role of magnetite crystallization in stabilizing MSS (e.g., Jenner et al., 2010), the decrease of Cu/Ag from primitive to more differentiated magmas is also expected to occur in arc magmas.

The difference in Cu/Ag between primitive and differentiated back-arc magmas is comparable to the difference in Cu/Ag between oceanic crust and the continental crust (Figs. 4 and 6). The low Cu/Ag and low contents of Cu, Sc, Ni, Cr, MgO and FeO in fractionated arc basalts compared to primitive back-arc/arc basalts and MORB require the presence of complementary sulfide-magnetite- (or garnet-) bearing pyroxenite cumulates in the lower crust of magmatic arcs (this work, Jenner, 2017; Lee and Anderson, 2015; Lee et al., 2012; Li and Audétat, 2013). A statistical assessment of Cu and major element contents of evolved volcanic rocks from arcs worldwide indicates that precipitation of Cu-rich sulfides also commences in arc basalts with about 8 wt.% MgO, typically near the base of thick (>30 km) arc segments (Chiaradia, 2014). Mass balance calculations indicate that 60–80% and 20–30% of the original Cu and S, respectively, in parental arc basalts are sequestered into such cumulates (Chiaradia, 2014; Lee et al., 2012). Due to low MSS–silicate melt partition coefficients of Ag relative to Cu (Li and Audétat, 2012, 2015; Zajacz et al., 2013), most of the Ag should remain in the magmas and thus in shallower parts of the continental crust.

Therefore, the shift of MORB-like Cu/Ag in primitive back-arc/arc magmas to the low Cu/Ag of the continental crust is caused by a decrease of Cu concentrations of oxidized magmas during fractional crystallization of MSS-bearing silicate assemblages in arc and back-arc magmas (e.g., Jenner et al., 2010, Jenner, 2017), rather than partial melting or other processes in the sub-arc mantle. Copper and Ag contents of sulfide-bearing cumulate rocks from the lower crust of magmatic arcs have not yet been studied or identified. Such rocks are predicted to have enhanced Cu concentrations and Cu/Ag significantly higher than the canonical mantle or MORB

value of 3500. Future work should explore the contents and fractionation of chalcophile elements in the sulfide-bearing mafic cumulates in the lowermost section of arcs (e.g., Chin et al., 2018; Jenner, 2017).

It has been suggested that delamination of Cu-rich sulfide bearing mafic cumulates in the lower crust of magmatic arcs over geological history may have been a critical process to explain the low Cu abundances and the peculiar major element composition of the continental crust (Lee and Anderson, 2015; Lee et al., 2012). Delamination of deep crustal pyroxenite cumulates involves sinking of this material back into the mantle. The current data on mantle rocks, including this study, offer no conclusive evidence for the occurrence of recycled lower crustal cumulates (as predicted by delamination models) in the mantle. Either such cumulates were efficiently mixed back into the convective mantle or they still reside in the roots of arcs and continents. The latter situation may be possible if bulk densities of cumulates yield seismic velocities similar to mantle rocks. If true, current estimates of the composition of the continental crust would have to be revised substantially.

6. Conclusions

Mantle pyroxenites and associated lherzolites from Balmuccia and Hannuoba indicate that melt–peridotite reaction and magmatic accumulation in the upper mantle led to highly variable Cu and Ag contents but limited fractionation of Cu and Ag. Combined with data from mantle peridotites, MORBs and OIBs, the new data show that diverse magmatic processes such as mantle melting, silicate melt–peridotite reaction and magmatic fractionation in the upper mantle and in the oceanic crust result in limited variability of Cu/Ag (3500 ± 1000 , 1s). The Cu/Ag data are consistent with experimental constraints indicating the predominant occurrence of sulfide melt in the convecting and in deep lithospheric mantle (Zhang and Hirschmann, 2016). It follows that sulfide melt–silicate melt partitioning predominantly controls chalcophile element systematics in these mantle and oceanic crust domains.

Because the Cu/Ag ratio of the continental crust (≈ 500) is a factor of 7 lower than Cu/Ag in the upper mantle and the oceanic crust, other partitioning processes must be involved in the generation of the continental crust composition. Primitive back-arc and island arc basalts likely inherit Cu/Ag from their mantle sources with values similar to MORBs. Therefore, the formation of primitive arc magmas cannot explain the low Cu/Ag of the continental crust. Experimental studies and data from differentiated back-arc magmas suggest that the segregation of monosulfide solid solution (MSS) during differentiation of evolving arc magmas should be the main reason for the low Cu/Ag coupled with a considerable depletion of Cu in the continental crust. If this hypothesis is correct, Cu-enriched pyroxenite cumulates with high Cu/Ag should occur in the lowermost crust of magmatic arcs, or should have been recycled into the convecting mantle, for instance by delamination of lower crust. These results thus support the idea that sulfide-bearing mafic cumulates in the lower crust of magmatic arcs could be compositionally complementary to the composition of continental crust (this study; Jenner, 2017; Lee et al., 2012; Li and Audétat, 2013).

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Appendix A. Supplementary material

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