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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 μg/g Cu; Hannuoba, 15–116 μg/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.

1. Introduction

The continental crust has a relatively SiO_2-rich bulk composition, similar to andesite (Rudnick and Gao, 2014). These compositional constraints are difficult to reconcile with the observation 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 ($D^{Cu}_{\text{sulfide melt–silicate melt}} \approx D^{Ag}_{\text{sulfide melt–silicate melt}}$, 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-