Earth and Planetary Science Letters 427 (2015) 95–103

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Copper isotopic composition of the silicate Earth

Sheng-Ao Liu[a,*], Jian Huang[b], Jingao Liu[c], Gerhard Wörner[d], Wei Yang[e], Yan-Jie Tang[e], Yi Chen[e], Limei Tang[f], Jianping Zheng[g], Shuguang Li[a,b]

[a] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China
[b] CAS Key Laboratory of Crust–Mantle Materials and Environments, University of Science and Technology of China, Hefei, Anhui 230026, China
[c] Department of Earth and Atmospheric Sciences, University of Alberta, 1-26 Earth Sciences Building, Edmonton, Alberta T6G 2E3, Canada
[d] Geowissenschaftliches Zentrum Gotingen, Abt. Geochemie, Goldschmidtstr. 1, 37077 Gotingen, Germany
[e] State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 10029, China
[f] The Second Institute of Oceanography, SOA, China
[g] State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form 27 June 2015
Accepted 29 June 2015
Available online 16 July 2015
Editor: D. Vance

Keywords:
copper isotopes
isotope fractionation
peridotite
basalt
silicate Earth

ABSTRACT

Copper isotopes have been successfully applied to many fields in geochemistry, and in particular, as a strongly chalcophile element, the isotope systematics of Cu can be potentially applied as a proxy for crust–mantle and core–mantle differentiation processes. However, to date, the Cu isotopic composition of distinct silicate reservoirs in the Earth, as well as the behaviour of Cu isotopes during igneous processes and slab dehydration are not well constrained. To address these issues, here we report high-precision (±0.05‰; 2SD) Cu isotope data for 132 terrestrial samples including 28 cratonic peridotites, 19 orogenic peridotites, 70 basalts (MORBs, OIBs, arc basalts and continental basalts) and 15 subduction-related andesites/dacites sourced worldwide. The peridotites are classified into metasomatized and non-metasomatized groups, based upon their rare earth element (REE) patterns and the presence or lack of minerals diagnostic of metasomatism (e.g., phlogopite). The metasomatized peridotites span a wide range of δ^{65}Cu values from −0.64 to +1.82‰, in sharp contrast to the non-metasomatized peridotites that exhibit a narrow range of δ^{65}Cu from −0.15 to +0.18‰ with an average of $+0.03 \pm 0.24$‰ (2SD). Comparison between these two groups of peridotites demonstrates that metasomatism significantly fractionates Cu isotopes with sulfide breakdown and precipitation potentially shifting Cu isotopes towards light and heavy values, respectively. MORBs and OIBs have homogeneous Cu isotopic compositions ($+0.09 \pm 0.13$‰; 2SD), which are indistinguishable from those of the non-metasomatized peridotites within uncertainty. This suggests that Cu isotope fractionation during mantle partial melting is limited, even if sulfides are a residual phase. Compared with MORBs and OIBs, arc and continental basalts are more heterogeneous in Cu isotopic composition. In particular, basalts that were collected from a traverse across the Kamchatka arc over a distance of 200 to 400 km from the trench show a large range of δ^{65}Cu from −0.19 to +0.47‰, and samples with higher Ba/Nb ratios tend to be isotopically more heterogeneous. The large Cu isotopic variations in arc and continental basalts most probably reflect the involvement of recycling crustal materials in their sources.

Collectively, the dataset obtained in this study suggests that the bulk silicate Earth (BSE) has an average δ^{65}Cu value of $+0.06 \pm 0.20$‰ (2SD).

1. Introduction

Copper has two stable isotopes of ^{63}Cu and ^{65}Cu. As an important ore-forming metal, the stable isotopic systematics of Cu (δ^{65}Cu relative to NIST 976) has been widely applied as a tool for tracking fluid pathways and fingerprinting sources of copper in porphyry systems (e.g., Mathur et al., 2009; Li et al., 2010). For example, Mathur et al. (2009) showed that different zones in porphyry copper deposits can be distinguished using Cu isotopes. Li et al. (2010) observed a systematic Cu isotopic variation from the core to outwards of the porphyry Cu–Au deposit at Northparkes, Australia and concluded that Cu isotopes can be applied to fingerprint hydrothermal processes. Apart from application to low-temperature

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[*] Corresponding author.
E-mail address: lsa@cugb.edu.cn (S.-A. Liu).

http://dx.doi.org/10.1016/j.epsl.2015.06.061

fluid pathways, another important application of Cu isotopes is to trace the metal sources of copper deposits. Given that Cu in most porphyry deposits mainly originates from magmas, this application needs the knowledge of Cu isotopic compositions of silicate Earth reservoirs and possible Cu isotopic variations generated during magmatic processes.

On a more general level, as a strongly chalcophile element, Cu systematics in arc magmas has been used to constrain fluid enrichment and crust–mantle differentiation processes involved in the silicate Earth (Lee et al., 2012). The stable isotope system of Cu may hold the potential to constrain the crust–mantle differentiation and mantle-core differentiation processes that involve Cu partitioning between sulfides and silicates (Savage et al., 2015). For these applications the Cu isotopic compositions of the silicate Earth's reservoirs and possible Cu isotope fractionation during mantle partial melting, slab fluid enrichment and magmatic differentiation need to be constrained.

Li et al. (2009) showed that granitic rocks from SE Australia, representing the upper continental crust, generally have δ^{65}Cu values that cluster around zero, with average values of $+0.03 \pm 0.15$‰ for I-type granites and -0.03 ± 0.42‰ for S-type granites. However, the copper isotopic composition of the upper mantle and thus the bulk silicate Earth (BSE) is not well constrained yet. To date, Cu isotope data have rarely been reported for mantle peridotites, with only two conference abstracts, which reported that δ^{65}Cu values of peridotites or ultramafic igneous rocks scatter around zero (Ben Othman et al., 2006; Savage et al., 2013). However, mantle peridotites are commonly subjected to metasomatism and therefore caution must be exercised when using them to estimate the BSE. In addition to peridotites, analyzing mantle-derived basalts is another approach to estimate the Cu isotopic composition of the BSE if partial melting does not produce isotopic effects for Cu. To date, there is also no systematic investigation on Cu isotopic compositions of various types of basalts (continental basalts, arc basalts, MORBs and OIBs). The limited data from international geostandards (BIR-1, BCR-2, BHVO-2, etc.) show that δ^{65}Cu values of basaltic rocks range from -0.01 to $+0.39$‰ (e.g., Archer and Vance, 2004; Bigalke et al., 2010; Moeller et al., 2012; Liu et al., 2014a, 2014b; Sossi et al., 2015).

During partial melting of the Earth's upper mantle, Cu behaves moderately incompatibly, as basaltic magmas show Cu concentrations three to five times their mantle source (Fellows and Canil, 2012). Because Cu in mantle rocks is mainly hosted in sulfides, it remains unclear whether or not Cu isotopes could be fractionated during partial melting of the mantle when sulfides are a residual phase. It has been shown that iron isotopes could be significantly fractionated during partial mantle melting (Weyer and Ionov, 2007). Therefore, whether or not Cu isotopes are fractionated during partial melting and whether the Cu-isotopic composition of basalts could represent their mantle source needs to be clarified.

To address these questions, we report a systematic study of Cu isotopes on (a) metasomatized and non-metasomatized peridotites from both cratonic regions and orogenic belts, (b) various types of basalts including mid-ocean ridge basalts (MORBs), oceanic island basalts (OIBs), arc basalts and continental basalts, and (c) subduction-related andesites and dacites from a variety of locations worldwide. The comprehensive dataset allows us to systematically investigate Cu isotope fractionation during mantle metasomatism and partial melting and to characterize Cu isotopic compositions of distinct silicate reservoirs in the Earth and, ultimately, the BSE on average.

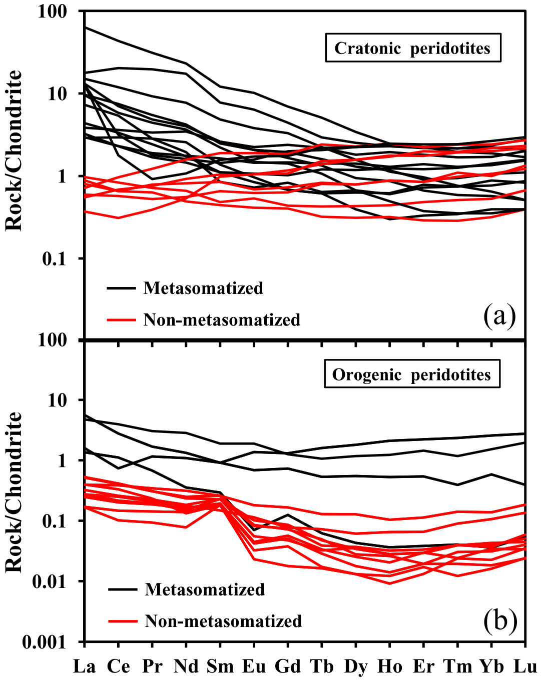

Fig. 1. The chondrite-normalized rare earth element (REE) patterns for cratonic peridotites (a) and orogenic peridotites (b) analyzed in this study. In each type, metasomatized and non-metasomatized peridotites are classified and plotted with different colors. The normalized values are after Sun and McDonough (1989).

2. Samples

2.1. Peridotites

The studied mantle peridotites include two types: cratonic and orogenic peridotites. The cratonic peridotites occur as xenoliths entrained by Cenozoic alkali basalts from three locations (Yangyuan, Fansi and Hannuoba) on the North China Craton (NCC). Petrography and chemical compositions of the xenoliths have been previously characterized (Rudnick et al., 2004; Liu et al., 2011). The samples comprise of spinel lherzolites, harzburgites and rare dunites, representing samples of the sub-continental lithospheric mantle. They span a wide range from typical refractory cratonic peridotites to fertile peridotites similar to the primitive upper mantle (Rudnick et al., 2004; Liu et al., 2011). The pattern of light rare earth elements (LREEs) is used here to evaluate the effect of metasomatism; those with $(\mathrm{La/Sm})_N > 1$ are classified into metasomatized peridotites, where N represents chondrite normalization. Many of the studied cratonic peridotites have enriched LREEs and high $(\mathrm{La/Sm})_N$, indicating significant metasomatism, whereas others have depleted LREEs and are not metasomatized (Fig. 1).

Orogenic peridotites are from two famous orogenic belts: the Alps and Dabie-Sulu. The Alpe Arami garnet peridotite from the Alpine collision zone (Switzerland) is composed of mainly olivine, two pyroxenes and up to 15% pyrope-rich garnet. This rock has an LREE-depleted pattern and represents a fragment of mantle rocks that was rapidly exhumed from mantle depths approaching or even exceeding 200 km (Olker et al., 2003). The Dabie-Sulu orogenic peridotites are from Raobazhai, Zhimafang and Xugou, including mainly dunite and harzburgite. All of these peridotites are mantle-derived and occur as blocks or lenses within exhumed gneiss (Zhang et al., 2000). Most of peridotites from Zhimafang and Xugou are phlogopite-bearing (Fig. S1) and have LREE-enriched patterns (Fig. 1), indicating that they have been metasomatized (Zheng et al., 2005, 2008), whereas those from Raobazhai are almost non-metasomatized.