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Barium isotopic composition of the upper continental crust

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Abstract

The upper continental crust (UCC) is an important reservoir of Ba within the Earth. We report high precision ($\leq \pm 0.05$‰, 2SD) Ba isotopic data for 71 samples (including granites, granodiorites, loess, glacial diamictites, and river sediments) to constrain the Ba isotopic composition of the UCC. I-type granites from the Fogang batholith, Southeastern (SE) China, exhibit variable $\delta^{137/134}$Ba (−0.16‰ to 0.01‰), which may be due to isotopic fractionation during the latest stages of magmatic differentiation. The $\delta^{137/134}$Ba of S-type granites from Darongshan-Shiwandashan, SE China (−0.03‰ to 0.11‰) correlate with ε_{Nd} (t), likely reflecting mixing of heterogeneous crustal source materials. Five A-type granites with high SiO_2 contents (~76 wt%) from Nankunshan, SE China have remarkably low $\delta^{137/134}$Ba (−0.47‰ to −0.33‰), which possibly arose from magmatic differentiation or assimilation of crustal materials with light Ba isotopic compositions. Loess from northwestern China has homogeneous $\delta^{137/134}$Ba (−0.02‰ to 0.03‰) that shows no correlation with bulk compositions, sample locations, or degree of chemical weathering, suggesting that loess is representative of the average Ba isotopic composition of the UCC. Three river sediments from northern China have $\delta^{137/134}$Ba similar to that of loess. The $\delta^{137/134}$Ba of glacial diamictites vary with CIA values: those with high CIA ($\geq$60) have heterogeneous $\delta^{137/134}$Ba (−0.19‰ to 0.35‰), while those with low CIA (<60) have $\delta^{137/134}$Ba around 0‰, identical to the values of loess and river sediments, suggesting that Ba isotopes can be fractionated during chemical weathering. In all, samples from the UCC have highly heterogeneous $\delta^{137/134}$Ba, ranging from −0.47‰ to 0.35‰. Using the weighted average of samples in this study, the $\delta^{137/134}$Ba of the UCC is estimated to be 0.00 ± 0.03‰ ($2SD/\sqrt{n}$, $n = 71$), which is similar to the average Ba isotopic composition of the upper mantle, but significantly lower than $\delta^{137/134}$Ba of seawater.

Keywords: Barium isotopes; Granites; Loess; Glacial diamictites; River sediments

1. INTRODUCTION

Barium (Ba) is an alkaline earth metal and a large ion lithophile element (LILE) that is highly incompatible during mantle melting (Pilet et al., 2011). Because of its strong enrichment in the crust, especially the upper continental

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crust (UCC, ~630 ppm, Rudnick and Gao, 2014) relative to the mantle (~6.9 ppm, Sun and McDonough, 1989), Ba could be a sensitive tracer of crustal recycling. Moreover, because Ba is water soluble and also enriched in ocean floor sediments, it has been used to track contributions of subduction-related fluids to arc magmas (e.g., Hawkesworth and Norry, 1983) or recycled sediments to the mantle (Kuritani et al., 2011; Murphy et al., 2002). Particulate Ba or barite fluxes to the ocean and their accumulation rates in sediments have also been used to reconstruct the paleo-oceanic export productivity (e.g., Schmitz, 1987; Nürnberg et al., 1997; Paytan and Griffith, 2007).

Barium has seven stable isotopes: ^{130}Ba (0.11%), ^{132}Ba (0.10%), ^{134}Ba (2.42%), ^{135}Ba (6.59%), ^{136}Ba (7.85%), ^{137}Ba (11.23%), and ^{138}Ba (71.70%). Barium isotope data are usually expressed as $\delta^{13x/134}\text{Ba} = [(^{13x/134}\text{Ba}_{\text{sample}})/(^{13x/134}\text{Ba}_{\text{SRM3104a}}) - 1] \times 1000$ in permil (where $x = 7$ or 8, Horner et al., 2015; Nan et al., 2015). Significant Ba isotopic fractionation has been found in natural samples (Miyazaki et al., 2014; Horner et al., 2015; Moynier et al., 2015; Nan et al., 2015; Pretet et al., 2015; Bullen and Chadwick, 2016; Cao et al., 2016; van Zuilen et al., 2016a,b; Bates et al., 2017; Hsieh and Henderson 2017; Bridgestock et al., 2018). For example, $\delta^{137/134}$Ba of seawater varies greatly with depth (Horner et al., 2015; Cao et al., 2016; Bates et al., 2017; Hsieh and Henderson, 2017), and there are large Ba isotopic fractionations between modern seawater and corals ($\Delta^{137/134}\text{Ba}_{\text{coral-seawater}} \approx -0.26 \pm 0.14‰$, Pretet et al., 2015). Within the UCC, Ba isotopic fractionation has been observed in igneous rocks and in soil profiles (Miyazaki et al., 2014; Huang et al., 2015; Nan et al., 2015; Bullen and Chadwick, 2016; Gong et al., 2016; van Zuilen et al., 2016a,b). Experimental studies reveal significant Ba isotopic fractionation at low temperature, showing that $BaSO_4$, $BaCO_3$, and $BaMn(CO_3)_2$ preferentially incorporate lighter Ba isotopes relative to aqueous solutions during precipitation (von Allmen et al., 2010; Böttcher et al., 2012; Mavromatis et al., 2016). These studies indicate that Ba isotopes have the potential to track both high and low temperature geochemical processes.

In order to develop Ba isotopes as tracers of recycling, the compositions of Earth's reservoirs need to be evaluated. The UCC is an important reservoir of Ba in the Earth, containing ~15% of the budget of the bulk silicate Earth (calculated using the masses reported in Huang et al., 2013, Ba concentrations of UCC from Rudnick and Gao, 2014, and bulk silicate Earth from McDonough and Sun, 1995). However, the Ba isotopic composition of the UCC is still poorly known. There are only rare data for international rock standards that derive from the UCC reported in the literature (Miyazaki et al., 2014; Nan et al., 2015; van Zuilen et al., 2016a,b). Therefore, a comprehensive investigation of samples from the UCC is warranted.

Two methods have traditionally been used to constrain the composition of the UCC (Rudnick and Gao, 2014). One is to obtain the weighted averages of rocks exposed at the surface (e.g., Clarke, 1889; Clarke and Washington, 1924; Poldervaart, 1955; Shaw et al., 1967, 1976; Eade and Fahrig, 1973; Ronov and Yaroshevsky, 1976; Gao et al., 1992, 1998; Condie, 1993; Borodin, 1999; Hu and Gao, 2008), which is the main method by which major elements and a number of soluble trace element concentrations have been determined for the UCC. The other method is to analyze fine-grained clastic sedimentary rocks, loess, or the fine-grained matrix of glacial diamictites to determine the compositions of insoluble elements (e.g., Goldschmidt, 1933; Taylor and McLennan, 1985; Plank and Langmuir, 1998; Barth et al., 2000; McLennan, 2001; Hu and Gao, 2008; Gaschnig et al., 2016).

Here we present Ba isotopic data for a variety of upper crustal samples, including granites, granodiorites, loess, glacial diamictites, and river sediments, to estimate the average Ba isotopic composition of the UCC. First, we use the weighted average $\delta^{137/134}$Ba of granites (the most important Ba-rich igneous rock types in the UCC), to determine the Ba isotopic composition of the UCC. This method has been used to constrain the average metal stable isotope compositions of the UCC for Li, Mg, Si, Fe, Cu, Mo, and U (e.g., Teng et al., 2004; Li et al., 2009; Li et al., 2010; Savage et al., 2012; Foden et al., 2015; Tissot and Dauphas, 2015; Yang et al., 2017). Second, we determine the Ba isotopic composition of loess, glacial diamictites, and river sediments (see Rudnick and Gao, 2014) and references therein for an explanation of these various UCC proxies, and Gaschnig et al. (2016) for glacial diamictites). Our results reveal significant Ba isotope variations in upper crustal materials, which may reflect Ba isotopic fractionation during magmatic differentiation and chemical weathering. Based on the weighted average $\delta^{137/134}$Ba of the samples in this study, our estimate of Ba isotopic composition of the UCC is $0.00 \pm 0.03‰$ ($2SD/\sqrt{n}$, $n = 71$), which provides a benchmark for applications of Ba isotopes as geochemical tracers.

2. SAMPLES

The UCC is composed of granites, granodiorites, tonalities, gabbros, and metamorphic rocks (Verlag Wedepohl, 1995). The concentration of Ba in gabbros is low (~56 ppm, Field and Elliott, 1974), so the contribution of gabbro to Ba of the bulk UCC is negligible and is therefore not considered further in this study. (Meta)sediments are also important rocks for estimating the average composition of the UCC, with Ba contents ranging from <5 ppm to thousands of ppm (Foster, 1962; Binns, 1967). In particular, loess and diamictites are produced by natural wide-scale sampling, and have been used to derive an average composition of large areas of continental crust. Therefore, we focus our study on granites and sedimentary materials (loess, glacial diamictites and river sediments), which have higher Ba concentrations.

Granites investigated here include I-, S-, and A-type granites and granodiorites from SE China (Li et al., 2007; Qi et al., 2007; Chen et al., 2013). Clastic sediments include loess from northwestern China (Hao et al., 2012; Tsai et al., 2014), globally distributed Precambrian and Paleozoic glacial diamictites (Gaschnig et al., 2014), and sediments from northern China (the correlation plot of Ba and SiO_2 for all samples is provided in Fig. S1).