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Zn isotopic heterogeneity in the mantle: A melting control?

Luc S. Doucet^{a,*}, Nadine Mattielli^a, Dmitri A. Ionov^b, Wendy Debouge^a, Alexander V. Golovin^{c,d}^a Laboratoire G-Time, DGES, Université Libre de Bruxelles, ULB, CP 160/02, 1050 Brussels, Belgium^b Géosciences Montpellier, UM & UMR-CNRS 5243, 34095 Montpellier, France^c Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk 630090, Russia^d Novosibirsk State University, Novosibirsk 630090, Russia

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ABSTRACT

We present new Zn elemental and isotope data on seventeen fertile and refractory mantle peridotite xenoliths. Eleven fertile peridotites are garnet and spinel lherzolites from Vitim and Tariat (Siberia and Mongolia) and represent some of the most pristine fertile peridotites available. Six refractory peridotites are spinel harzburgites from the Udachnaya kimberlite (Siberian craton) that are nearly pristine residues of high-degree polybaric melting at high pressure (7–4 GPa). Geochemical data suggest that Zn isotopic compositions in the peridotites have not been affected by post-melting processes such as metasomatism, contamination by the host-magmas or alteration. The fertile peridotites have uniform Zn concentrations (59 ± 2 ppm) and Zn isotopic compositions with $\delta^{66}\text{Zn}$ (relative to JMC-Lyon-03-07491) $= +0.30 \pm 0.03\text{‰}$ consistent with the Bulk Silicate Earth estimates of $\delta^{66}\text{Zn} = +0.28 \pm 0.05\text{‰}$ (Chen et al., 2013). The refractory peridotites have Zn concentrations ranging from 30 to 48 ppm and $\delta^{66}\text{Zn}$ from $+0.10 \pm 0.01\text{‰}$ to $+0.18 \pm 0.01\text{‰}$ with an average of $+0.14 \pm 0.03\text{‰}$. Our data suggest that the lithospheric mantle has a heterogeneous Zn isotopic composition. Modeling of Zn isotope partitioning during partial melting of fertile mantle suggests that high degrees of melt extraction ($>30\%$) may significantly fractionate Zn isotopes (up to 0.16‰) and that during mantle melting, Zn concentrations and isotopic compositions are mainly controlled by the stability of clinopyroxene and garnet within the melting residue. Because the stability of clinopyroxene and garnet is mainly pressure dependent we suggest that both the depth and the degrees of melt extraction may control Zn isotope fractionation during mantle melting.

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1. Introduction

It has been recently demonstrated that stable isotope ratios of iron, the most abundant 1st group transition metal, show significant variability in mantle rocks that can be attributed to melt extraction, fractional crystallization and oxidation state (Dauphas et al., 2009; Foden et al., 2015; Nebel et al., 2015; Schuessler et al., 2009; Weyer and Ionov, 2007; Williams et al., 2009). Nevertheless, the range and relative contributions of individual factors to the isotopic fractionation for different transition elements remain to be quantified.

Zinc (Zn) is a 1st group transition metal; it is lithophile at high temperatures (Mann et al., 2009) and is present in trace amounts in peridotite minerals, mainly in olivine (Adam and Green, 2006). The single valence state of zinc (Zn^{2+}) makes it insensitive to oxy-

gen fugacity ($f\text{O}_2$) in contrast to some other transition metals like Fe, Cu or V. Hence, Zn has a great potential to provide a better insight into the factors that control the elemental and isotope fractionation of transition metals during mantle processes (i.e., partial melting, melt-rock reaction, metasomatism) independent of variation in oxygen fugacity (Albarède, 2004).

Published Zn isotopic data are scarce for mantle-derived rocks including mid-ocean ridge basalts (MORBs), ocean island basalts (OIBs), andesites, serpentinized orogenic peridotites and granitoids (Ben Othman et al., 2006; Chen et al., 2013; Herzog et al., 2009; Maréchal et al., 1999; Pons et al., 2011; Telus et al., 2012). The Zn isotope composition of magmas can be affected during their ascent, eruption, solidification and alteration. In particular serpentinization may change $\delta^{66}\text{Zn}$ by -0.5‰ (Pons et al., 2011). Chen et al. (2013) found that fractional crystallization causes only very limited ($\leq 0.1\text{‰}$) Zn isotopic fractionation between lavas and related cumulates. As a result, mantle-derived lavas from different tectonic settings (MORB, OIB, andesite), as well as serpentinized

* Corresponding author. Tel.: +32 (0)2 650 22 52.

E-mail address: ldoucet@ulb.ac.be (L.S. Doucet).

Table 1

Summary of petrological data on peridotite xenoliths in this study.

N°Sample	Locality	Rock		T°C	Oxides, LOI (wt.%), Mg#, Cr# in bulk rocks						Modal abundance (%)				
		type	facies		LOI	Mg#	Cr#	Al ₂ O ₃	FeO _t	CaO	ol	opx	cpx	spl	gar
Fertile mantle															
Garnet peridotites															
313-8	Vitim	Lhz	Gar-Spl	1004	−0.17	0.894	0.056	4.58	7.94	3.53	57.0	13.4	15.6	tr.	14.0
313-104	Vitim	Lhz	Gar-Spl	1037	0.35	0.892	0.054	4.43	8.11	3.49	53.9	19.7	14.2	tr.	12.2
313-112	Vitim	Lhz	Gar-Spl	1041	0.23	0.894	0.057	4.28	8.20	2.84	55.8	21.1	10.5	tr.	12.7
313-6	Vitim	Lhz	Gar	1023	−0.17	0.893	0.065	3.73	8.41	2.95	63.7	12.1	12.9	0.0	11.3
313-102	Vitim	Lhz	Gar	1053	0.08	0.890	0.055	4.76	8.16	3.43	49.9	23.0	13.6	0.0	13.5
Spinel peridotites															
314-58	Vitim	Lhz	Spl	874	0.25	0.893	0.064	3.76	8.23	3.04	62.3	18.8	15.7	3.2	
4500-26	Tariat	Lhz	Spl			0.893	0.061	3.82	8.16	3.24					
MOG 1	Tariat	Lhz	Spl	898	0.00	0.890	0.056	4.47	8.09	3.63	44.8	34.8	17.1	3.3	
MOG 5	Tariat	Lhz	Spl	919	0.33	0.893	0.062	4.35	7.88	3.40	48.2	32.4	16.3	3.1	
MHP 1	Tariat	Lhz	Spl	873		0.892	0.059	3.92	8.21	3.12	54.8	27.8	14.7	2.7	
4500 8	Tariat	Lhz	Spl	963	0.35	0.890	0.057	3.84	8.34	3.22	53.7	28.1	15.6	2.6	
Refractory mantle (spinel harzburgites)															
Uv-504/09	Udachnaya	Hzb	Spl	839	−0.51	0.919	0.310	0.16	7.48	0.82	86.9	9.7	3.3	0.1	
Uv-107/03	Udachnaya	Hzb	Spl	939	0.49	0.924	0.290	0.55	6.99	0.54	86.2	11.1	2.0	0.7	
Uv-105/03	Udachnaya	Hzb	Spl	881	−0.12	0.928	0.249	0.67	6.65	0.33	86.4	12.8	0.0	0.8	
Uv-KC-150(2)	Udachnaya	Hzb	Spl	904	0.49	0.923	0.343	0.36	7.21	0.44	87.6	12.0	0.0	0.4	
Uv-454/09	Udachnaya	Hzb	Spl	818	−0.73	0.926	0.181	1.22	6.57	0.47	75.2	22.2	1.6	1.0	
Uv-600/09	Udachnaya	Hzb	Spl	912	−1.21	0.927	0.288	0.57	6.73	0.63	86.2	10.5	2.5	0.8	

Lh, lherzolite; Hzb, harzburgite; Gar, garnet; Spl, spinel; LOI, loss on ignition (3 h at 1000 °C) in wt.% (positive values show weight gain owing to oxidation of FeO to Fe₂O₃ and near absence of secondary alteration). Mg#, Mg/(Mg/Fe)_{at}; Cr#, Cr/(Al + Cr)_{at}. Equilibration temperatures (T) were estimated using Ca-in-opx thermometer of Brey and Köhler (1990) assuming pressure of 2.5 GPa. Modal estimates were obtained by least-squares method from bulk-rocks and mineral analyses.

orogenic peridotites, have similar Zn isotopic compositions, suggesting a homogeneous mantle source. On the basis of their data set, these authors defined a Zn isotopic composition of the Bulk Silicate Earth at $\delta^{66}\text{Zn} = +0.28 \pm 0.05\text{‰}$ (2SD).

This study explores the range of Zn isotopic composition in the Earth's mantle, which is currently poorly known, based on analyses of both fertile and strongly melt-depleted mantle peridotites brought up to the surface as xenoliths by volcanic eruptions. We further aim to constrain the main factors that control the Zn isotope fractionation in the mantle and use Zn isotopes to better understand the behavior of transition group metals during mantle melting. We report Zn isotope data on 11 fresh *garnet* and *spinel lherzolites* in alkali basalts from Vitim (southern Siberia) and Tariat (Mongolia) that are considered as pristine fertile peridotites, a rare rock type in most xenolith suites (Ionov, 2002). The data on these fertile lherzolites are compared with those for 6 highly *refractory spinel harzburgites* from the Udachnaya kimberlite (Siberian craton). These harzburgites represent highly melt-depleted mantle rocks and are interpreted as residues of high-degree polybaric melting of fertile mantle at high pressures (7–4 GPa) (Doucet et al., 2012; Ionov et al., 2010). The peridotites in this study show little or no evidence for alteration or contamination during or after the eruption of host magmas, nor modal/cryptic metasomatism, and represent extreme end-members of the range of modal, major and trace element compositions for fertile vs. residual mantle peridotites.

2. Geological setting

The samples in this study were chosen from a suite of well-studied peridotite xenoliths from the Vitim basaltic field in Siberia (e.g. Ionov et al., 2005a) and the Tariat volcanic field in Mongolia (e.g. Ionov and Hofmann, 2007) (both off-craton) and the Udachnaya kimberlite pipe in the central Siberian craton (KML file) (Ionov et al., 2010). A summary of petrologic information available for these samples is reported in Table 1.

The Pliocene–Pleistocene Vitim basaltic field is located east of the Baikal Lake near the upper Vitim River (KML file) (see Ionov, 2002 for review). Xenoliths in this study are from a 15–18 My old

picrite tuff deposit in the eastern part of the Vitim field (Ionov et al., 2005a).

The Tariat volcanic field is situated on the northern slope of the Hangay Mountains in central Mongolia. The peridotite xenoliths were sampled in volcanic breccia at the 0.5 Ma old Shavaryn-Tsaram eruption center (elevation 2300 m), that is known for the abundance of mantle and lower crustal xenoliths (Ionov and Hofmann, 2007).

The Devonian Udachnaya kimberlite is located in central Siberia and is part of the Daldyn-Alakit kimberlite field. Xenoliths in this study were sampled in the 420–620 m depth range of the open-pit diamond mine, near the center of the Udachnaya-East pipe, in the remarkably well-preserved type-I kimberlite containing fresh xenoliths (Kamenetsky et al., 2012). Various petrophysical, petrologic and geochemical data on fresh peridotite xenoliths from Udachnaya, including all samples from this study, were recently published (e.g. Doucet et al., 2013, 2012, 2014; Ionov et al., 2010, 2015). These publications discuss the depth, degrees, fluid regime and age of melt extraction during the formation of the local cratonic lithosphere.

3. Sample selection and preparation

The chemical compositions of peridotites from Vitim and Tariat were studied in detail by Press et al. (1986), Ionov et al. (2005a, 2005b, 1998), Ionov (2007) and Ionov and Hofmann (2007). Those mantle xenoliths are fresh (LOI < 1%) garnet, garnet-spinel or spinel lherzolites with a narrow range of Mg# (0.890 to 0.894) and high Al₂O₃ (3.7–4.8%) and CaO contents. The modal abundances of olivine (45–64%) are relatively low whereas those of orthopyroxene (opx, 12 to 35%), clinopyroxene (cpx, 11–17%) and garnet (11–14%) are variable, but generally high. Spinel lherzolites contain 2.6 to 3.3% of spinel (Table 1 and Fig. 1). The lherzolites from Vitim and Tariat are pristine fertile peridotites with modal, major and trace element compositions close to the primitive mantle estimates (Ionov et al., 2005a; Ionov and Hofmann, 2007), and thus are suitable to examine the Zn isotope composition of fertile mantle, assumed to be the source of basaltic magmas and residual lithospheric peridotites. The term “fertile peridotites” is used below to refer to the Vitim and Tariat lherzolites.

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