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Calcium isotopic fractionation between clinopyroxene and orthopyroxene from mantle peridotites

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ABSTRACT

We report the first observation of Ca isotopic fractionation between co-existing clinopyroxene and orthopyroxene from Kilbourne Hole and San Carlos mantle peridotites. The $^{44}Ca/^{40}Ca$ in orthopyroxenes is 0.36 to 0.75‰ heavier than that in the co-existing clinopyroxenes. Using these isotopic constraints and the relative proportions of major Ca-bearing minerals in the upper mantle, the estimated $^{44}Ca/^{40}Ca$ of the upper mantle is 1.05 ± 0.04‰ heavier relative to NIST SRM 915a. This is slightly higher than our average for basalts (0.97 ± 0.04‰ heavier relative to NIST SRM 915a). Combined with published $^{44}Ca/^{40}Ca$ data on low temperature Ca-bearing minerals (calcite, aragonite and barite), we infer that the inter-mineral fractionation of Ca isotopes at both low- and high temperatures is primarily controlled by the strength of Ca–O bond. Accordingly, the mineral with a shorter Ca–O bond and a smaller Ca coordination number (i.e., stronger Ca–O bond) yields a heavier Ca isotopic ratio (i.e., higher $^{44}Ca/^{40}Ca$). Since stable isotopes of major elements, such as Ca and Mg, exhibit small fractionations during igneous processes, the estimate of stable isotopic compositions of the bulk differentiated planetary bodies, including the Earth and the Moon, needs to take into account the relative proportions of major rock-forming minerals and their respective isotopic signatures.

1. Introduction

With the advancement of modern analytical techniques, non-traditional stable isotopes of Mg, Si, Ca and Fe, which were previously not believed to fractionate during magmatic processes, have become powerful tools in the fields of cosmochemistry (e.g., Georg et al., 2007; Fitoussi et al., 2008; Chakrabarti and Jacobsen, 2009) and high temperature geochemistry (e.g., Williams et al., 2004; Teng et al., 2008; Dauphas et al., 2009). As the fifth most abundant element in the Earth, Ca has six isotopes (^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca and ^{48}Ca), making it a geochemical and cosmochemical tracer with considerable potential (e.g., DePaolo, 2004). With the exception of H and He, Ca has the largest relative mass difference ($\Delta m/m = 20\%$) between the heaviest and the lightest isotopes. Thus, similar to stable isotopic studies of Si, Mg and Fe (e.g., Georg et al., 2007; Dauphas et al., 2009), the comparison of Ca isotopic ratios between the Earth and other planetary bodies, including the Moon, could yield important information regarding the early evolution of the Solar System and the origin of the Earth–Moon system (e.g., Simon and DePaolo, 2010). Knowledge of the Ca isotopic ratio in the Earth's mantle is also critical in investigating the chemical and isotopic evolution of seawater through geological time, as several lines of evidence suggest that the chemistry of the Archean and Paleoproterozoic oceans was strongly "mantle-buffered" due to massive circulation of seawater via oceanic crust and submarine hydrothermal systems (e.g., Veizer, 1982; Jacobsen and Kaufman, 1999).

Previous Ca isotopic studies have focused mostly on modern and ancient marine carbonates and sulphates, documenting large and systematic isotopic variations (e.g., DePaolo, 2004; Heuser et al., 2005; Kasemann et al., 2005; Farkaš et al., 2007; Griffith et al., 2008a), yet detailed work on igneous rocks is fairly limited (Russell et al., 1978; Skulan and DePaolo, 1999; DePaolo, 2004; Amini, 2007; Amini et al., 2009a, b). Russell et al. (1978) presented the first and the most extensive Ca isotopic study that covered a wide range of igneous rocks from the inner Solar System. More recently, DePaolo (2004) showed ~0.7‰ variation in $^{44}Ca/^{40}Ca$ in oceanic basalts (see his Fig. 5). Amini et al. (2009b) reported ~0.5‰ variation in $^{44}Ca/^{40}Ca$ in a series of silicate rocks, including both felsic and ultramafic rocks. Huang et al. (2009a) reported that Makapuu-stage Koolau lavas have slightly lower $^{44}Ca/^{40}Ca$ (by 0.2‰) than other Hawaiian tholeiitic lavas. The observed $^{44}Ca/^{40}Ca$ variation in basalts may be interpreted either as a result of recycling ancient carbonate into the mantle (Fig. 15 of DePaolo, 2004; Huang et al., 2009a), or due to the fractionation of stable Ca isotopes during igneous processes. In order to constrain the Ca isotopic composition of the Earth's mantle and to investigate the possible Ca isotopic fractionation during igneous process, we report $^{44}Ca/^{40}Ca$ measurements on a series of terrestrial igneous rocks, including two nephelinites from Oslo Rift (Norway), six Hawaiian shield stage tholeiites (USA), one dunite (DTS-1) from Twin Sisters (Washington, USA), and clinopyroxene and orthopyroxene separates

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Table 1
Ca isotopic ratios in selected mantle minerals and basalts.

	$\delta^{44/40}$Ca[a]	$2\sigma_{(m)}$[b]	$\delta^{42/40}$Ca[a]	$2\sigma_{(m)}$[b]	$\delta^{44/42}$Ca[a]	$2\sigma_{(m)}$[b]	Sample form	Acid leaching
Kilbourne Hole, New Mexico, USA								
Clinopyroxene								
	0.94		0.47		0.45		Crystals	Yes
	1.00		0.51		0.49		Crystals	Yes
	0.88		0.44		0.44		Crystals	Yes
	0.97		0.55		0.41		Crystals	Yes
	1.05		0.65		0.40		Crystals	Yes
	1.04		0.59		0.44		Crystals	Yes
	0.98		0.57		0.41		Crystals	Yes
Average	0.98	0.04	0.54	0.05	0.43	0.02		
Orthopyroxene								
	1.63		0.83		0.79		Crystals	Yes
	1.77		0.90		0.87		Crystals	Yes
	1.84		1.01		0.84		Crystals	Yes
	1.68		0.96		0.72		Crystals	Yes
Average	1.73	0.09	0.93	0.08	0.81	0.07		
San Carlos, Arizona, USA								
Clinopyroxene								
	1.11		0.58		0.53		Powdered crystals	Yes
	1.05		0.50		0.54		Powdered crystals	Yes
	1.02		0.58		0.43		Powdered crystals	Yes
	1.09		0.60		0.49		Powdered crystals	Yes
	1.03		0.51		0.52		Powdered crystals	No
	0.95		0.41		0.54		Powdered crystals	No
	1.01		0.62		0.39		Powdered crystals	No
Average	1.04	0.04	0.54	0.06	0.49	0.04		
Orthopyroxene								
	1.51		0.77		0.73		Powdered crystals	Yes
	1.41		0.82		0.59		Powdered crystals	Yes
	1.35		0.79		0.56		Powdered crystals	Yes
	1.30		0.66		0.66		Powdered crystals	Yes
	1.45		0.79		0.66		Powdered crystals	Yes
Average	1.40	0.07	0.77	0.06	0.64	0.06		
Orthopyroxene								
	1.16		0.56		0.60		Powdered crystals	No
	1.15		0.53		0.62		Powdered crystals	No
	1.31		0.70		0.61		Powdered crystals	No
Average	1.21	0.10	0.60	0.10	0.61	0.01		
Hawaii, USA								
Mauna Kea								
SR 687	0.88						Powder	No
	0.90		0.39	0.21	0.51	0.17	Powder	No
Average	0.89	0.13						
SR700	0.94		0.50		0.43		Powder	No
	0.89		0.40		0.48		Powder	No
	1.00		0.51		0.49		Powder	No
Average	0.94	0.06	0.47	0.07	0.47	0.04		
SR685	1.03		0.51		0.52		Powder	No
	0.90		0.49		0.41		Powder	No
Average	0.97	0.13	0.50	0.21	0.47	0.17		
Mahukona								
72-1	1.03	0.13	0.51	0.21	0.53	0.17	Powder	No
72-5	0.91	0.13	0.46	0.21	0.43	0.17	Powder	No
Kilauea								
BHVO-1	0.88						Powder	No
	1.04		0.51		0.53		Powder	No
	1.08		0.64		0.44		Powder	No
Average	1.00	0.12	0.58	0.21	0.49	0.17		
Nephelinites from Oslo Rift, Norway								
S36	0.94	0.13					Rock chip	No
S01	1.05		0.58		0.46		Rock chip	No
	1.07		0.60		0.47		Rock chip	No
Average	1.06	0.13	0.59	0.21	0.47	0.17		
All basalt average								
	0.97	0.04	0.51	0.04	0.48	0.02		
Twin Sisters Dunite								
DTS-1	1.57		0.76		0.81		Powder	No
	1.68		0.83		0.84		Powder	No
	1.53		0.77		0.76		Powder	No
Average	1.59	0.09	0.79	0.04	0.80	0.05		

[a] $\delta^{x/y}\text{Ca}=[(^{x}\text{Ca}/^{y}\text{Ca}_{\text{sample}}/^{x}\text{Ca}/^{y}\text{Ca}_{\text{SRM915a}})-1]*1000$; where $^{44}\text{Ca}/^{40}\text{Ca}_{\text{SRM915a}}=0.021549$, $^{44}\text{Ca}/^{42}\text{Ca}_{\text{SRM915a}}=3.2274$ and $^{42}\text{Ca}/^{40}\text{Ca}_{\text{SRM915a}}=0.006677$.

[b] If three or more analyses of one sample are available, the errors are 2 standard error of the mean. If only one or two analyses of one sample are available, the error is taken as 0.13 for $\delta^{44/40}$Ca, 0.21 for $\delta^{42/40}$Ca and 0.17 for $\delta^{44/42}$Ca. These reflect the external reproducibility of our analyses on SRM 915a and seawater (Table S3).