Calcium Isotopic Fractionation and Compositions of Geochemical Reference Materials

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High-precision calcium isotopic compositions of a set of geological reference materials from the IAG (OU-6), ANRT (UB–N), MPI-DING, USGS and GSJ, relative to NIST SRM 915a, are reported here. Measurements were performed by thermal ionisation mass spectrometry (Triton instrument) using a ^{42}Ca–^{43}Ca double spike. $\delta^{44/40}Ca$ values of selected reference materials, mainly felsic rocks, are reported for the first time. Felsic rock values of $\delta^{44/40}Ca$ ranged from 0.13‰ to 1.17‰, probably implying Ca isotopic fractionation could occur during magma evolution. $\delta^{44/40}Ca$ values of ultramafic rocks, ranging from 0.74‰ to 1.51‰, were positively correlated with MgO and negatively with CaO contents, possibly owing to Ca isotopic fractionation during partial melting. $\delta^{44/40}Ca$ of intermediate-mafic rocks were around 0.78‰ and displayed limited variation, suggesting Ca isotopic fractionation is insignificant during magma evolution processes. As expected, $\delta^{44/40}Ca$ of sedimentary and metamorphic rocks varied widely due to complex geological processes.

Keywords: calcium isotopes, ^{42}Ca–^{43}Ca double spike, thermal ionisation mass spectrometry, isotopic fractionation, geological reference materials.

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Calcium is the most abundant alkaline earth element in the Earth's crust (McDonough and Sun 1995, Rudnick and Gao 2003). It has five stable nuclides, ^{40}Ca (96.941%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%) and one radioactive nuclide, ^{48}Ca (0.187%), which is treated as stable because of its long half-life (> 6×10^{18} years). $\delta^{44/40}Ca$ varies by *ca.* 6‰ in nature (e.g., DePaolo 2004, Heuser and Eisenhauer 2010, Fantle and Tipper 2014). In step with analytical advances, results of Ca isotope ratios have been used to better interpret research in Earth-surface processes (e.g., Hindshaw *et al.* 2011, Fantle *et al.* 2012, Jacobson *et al.* 2015), palaeoceanography (Farkaš *et al.* 2007a, b), cosmochemistry (e.g., Simon *et al.* 2009, Simon and DePaolo 2010), archaeology (e.g., Jochum *et al.* 2006, Reynard *et al.* 2008, 2010, 2011), biomedicine (e.g., Heuser and Eisenhauer 2010, Morgan *et al.* 2011, 2012) and mantle evolution (e.g., Huang *et al.* 2010, Kang *et al.* 2016).

High-precision and high-accuracy measurements are required for the use of Ca isotopes as a proxy based on the limited Ca isotopic fractionation in natural rocks. Up to now, nearly all Ca isotope ratio measurements have been carried out with thermal ionisation mass spectrometry (TIMS) (e.g., Russell *et al.* 1978, Skulan *et al.* 1997, Heuser *et al.* 2002, Fantle and DePaolo 2005, 2007, Amini *et al.* 2009, Simon and DePaolo 2010, Lehn *et al.* 2013, Feng *et al.* 2017) and multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) (e.g., Fietzke *et al.* 2004, Wieser *et al.* 2004, Schiller *et al.* 2012, Tacail *et al.* 2016). In a similar way to other isotopes, such as Li, Fe and Nd (Anbar *et al.* 2000, Pistiner and Henderson 2003, Wakaki and Tanaka 2012), large Ca isotopic fractionation could occur during chemical purification processes (possibly up to 4‰) and mass determination (e.g., Russell and Papanastassiou 1978, Zhu *et al.* 2016). To correct such fractionations, a double-spike technique is commonly adopted with TIMS. Russell *et al.* (1978) first published reliable measurements for Ca isotopes using TIMS with a ^{42}Ca–^{48}Ca double spike. After this, ^{43}Ca–^{48}Ca and ^{42}Ca–^{43}Ca double spikes were also developed in many different laboratories (e.g., Heuser *et al.* 2002, Hippler *et al.* 2003, Kasemann *et al.* 2005, Böhm *et al.* 2006, Farkaš *et al.*

2007a, b, Amini *et al.* 2008, 2009, Schmitt *et al.* 2009, Teichert *et al.* 2009, Holmden and Bélanger 2010, Huang *et al.* 2010, 2011, Cobert *et al.* 2011, Müller *et al.* 2011, Lehn *et al.* 2013, Zhu *et al.* 2016).

Calcium stable isotope ratios are commonly reported in conventional δ-notation relative to values for the reference material NIST SRM 915a. They can be reported as $\delta^{44/40}Ca$ or $\delta^{44/42}Ca$, while $\delta^{44/42}Ca$ can be transformed to $\delta^{44/40}Ca$ by multiplying by a factor of 2.099 (Fantle and Tipper 2014). $\delta^{44/40}Ca$ can be calculated (Eisenhauer *et al.* 2004, Coplen 2011) as:

$$\delta^{44/40}Ca = [(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{SRM\ 915a} - 1] \tag{1}$$

Previous studies have reported Ca isotopic compositions of many geological reference materials (e.g., Rehkämper and Hofmann 1997, Amini *et al.* 2009, Wombacher *et al.* 2009, Schiller *et al.* 2012, Magna *et al.* 2015, Feng *et al.* 2017, He *et al.* in press), but most focus on ultramafic and intermediate-mafic rocks. $\delta^{44/40}Ca$ values of felsic rocks have been infrequently reported (Valdes *et al.* 2014, He *et al.* in press), but such data could provide new insight into Ca isotopic fractionation during magma evolution. In this study, thirty-five reference materials with greatly varied compositions from different producers were analysed by TIMS using the $^{42}Ca–^{43}Ca$ double-spike technique. The reference materials analysed include the commonly used NIST SRM 915a and IAPSO seawater, OU-6 (Penrhyn slate from the IAG), serpentinite UB-N (from the Association Nationale de la Recherche Technique, ANRT) and MPI-DING glasses GOR128-G, GOR132-G, KL2-G, ML3B-G, T1-G, StHs6/80-G and ATHO-G. Other materials analysed, from the USGS and GSJ, include basalts (BIR-1, BCR-1, BCR-2, BHVO-2, JB-2), diabase (W-2), diorite (DNC-1), andesite (AGV-1, AGV-2, JA-2), rhyolite (RGM-1, JR-2), latite (QLO-1a), granodiorite (GSP-1, GSP-2, JG-1a), granite (G-2, JG-2), carbonatite (COQ-1), manganese nodule (NOD-A-1, NOD-P-1), shale (SGR-1), stream sediment (JSD-1) and mica schist (SDC-1). Our aim was to provide high-precision Ca isotopic compositions for a suite of geological reference materials, and enrich the existing knowledge of the behaviour of Ca isotopes in different geological processes.

Experimental procedure

All chemical experiments were carried out in a class 100 clean laboratory environment at the State Key Laboratory of Isotope Geochemistry (SKLaBIG), Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). Acids used in chemical procedure were double-distilled; AG

MP-50 (100–200 mesh) resin was carefully precleaned in 6 mol l^{-1} HCl and high-purity (18 MΩ cm resistivity) water repeatedly; Teflon® beakers and columns were heated in the presence of the following concentrated acids diluted in 1:1 ratios HNO$_3$, HCl and HNO$_3$, sequentially. For further experimental details see Liu *et al.* (2015) and Zhu *et al.* (2016).

Sample preparation and digestion

MPI-DING glass samples were firstly powdered to a grain size of < 0.075 mm in an agate mortar. For all silicate samples, 20–50 mg of rock powders were weighed into 7 ml PFA beakers (Savillex®). They were digested at 120 °C with 2 ml of a 3:1 mixture of HF (22 mol l^{-1}) and HNO$_3$ (15 mol l^{-1}) over a period of at least 1 week. Sample solutions were then evaporated to dryness at 100 °C. Following this, they were treated with concentrated HNO$_3$ once and 3 mol l^{-1} HCl several times to ensure that samples were totally dissolved. Finally, these samples were redissolved in 2 ml of 3 mol l^{-1} HCl.

About 5 mg of carbonatite COQ-1 was weighed into a 7 ml Savillex® beaker, and then dissolved in 2 ml of 3 mol l^{-1} HCl over 4 h at room temperature. This was then treated with concentrated HNO$_3$ and 3 mol l^{-1} HCl, and finally redissolved in 2 ml of 3 mol l^{-1} HCl.

Spiking

The $^{42}Ca–^{43}Ca$ double spike was made of ^{42}Ca and ^{43}Ca pure carbonates from the Isoflex Company with certificate compositions (Table 1). These two carbonates were carefully weighed to make a mixed $^{42}Ca/^{43}Ca$ ratio close to 5; they were then dissolved together with 10% *v/v* HNO$_3$. The composition of the double spike was calibrated by multiple measurements of the spiked and unspiked NIST SRM 915a and IAPSO seawater on a Triton thermal ionisation mass spectrometer. Detailed double-spike information is provided in Table 1.

An aliquot of each sample solution containing 50 μg Ca was mixed with an appropriate amount of $^{42}Ca–^{43}Ca$ double-spike solution. The optimal sample/spike ratio was calculated to $^{40}Ca_{sample}$:$^{42}Ca_{spike}$ = 7 (Liu *et al.* 2016), consistent with previous studies (Russell *et al.* 1978, Holmden and Bélanger 2010). The mixture solution was mixed well and refluxed in 3 mol l^{-1} HCl in capped beakers over 2 h before being evaporated to dryness and conditioned with concentrated HCl twice. Finally, the mixture was dissolved in 0.05 ml of 1.6 mol l^{-1} HCl for column chemistry.

Table 1.
Calcium spike compositions

	^{42}Ca single spike Abundance (%)	^{43}Ca single spike Abundance (%)		^{42}Ca –^{43}Ca double spike mol mol^{-1}
^{40}Ca	2.56	5.30	^{40}Ca/^{42}Ca	0.037014
^{42}Ca	96.8	0.18	^{42}Ca/^{42}Ca	1.000000
^{43}Ca	0.11	90.0	^{43}Ca/^{42}Ca	0.180745
^{44}Ca	0.51	4.44	^{44}Ca/^{42}Ca	0.014127
^{46}Ca	0.01	0.01	^{46}Ca/^{42}Ca	0.000012
^{48}Ca	0.02	0.08	^{48}Ca/^{42}Ca	0.000366

Chemical purification

Calcium purification was performed in Savillex® microcolumns (0.64 cm ID × 9 cm height, 30 ml reservoir) packed with 1 ml of Bio-Rad AG MP-50 cation resin. The chemical procedure is detailed in Table 2. Briefly, samples were loaded to preconditioned (with 5 ml of 1.6 mol l^{-1} HCl) resin, then matrices were eluted with 16.95 ml of 1.6 mol l^{-1} HCl, and Ca was collected with 27 ml of 1.6 mol l^{-1} HCl. After the Ca cut was evaporated to dryness, it was treated with concentrated HNO$_3$ several times and finally redissolved it with 10 μl 10% v/v HNO$_3$ for TIMS analysis. For quality control purposes, each batch of samples, at least one reference material (e.g., IAPSO seawater, BHVO-2, etc.) and one blank were processed simultaneously; sometimes, a sample duplicate was also added into the batch sequence. The precut and postcut solutions were collected and measured using ICP-AES to check the recovery (which was above 99%).

TIMS determination

Calcium isotope ratios were determined with a Triton TIMS instrument at SKLaBIG, GIG, CAS. About 1 μl solution containing 5 μg Ca was loaded carefully onto the centre of the out-degassed single Ta (99.995%) filament. To minimise the multi-reservoir effect (Hart and Zindler 1989, Fantle and Bullen 2009, Lehn and Jacobson 2015, Zhu *et al.* 2016), the sample spot on the filament should be as small as possible. After the sample was loaded, a droplet of 1 μl activator (10% v/v H$_3$PO$_4$) was carefully added to cover the sample spot.

Two measurement sequences of cup configuration were adopted because of the wide mass range of Ca isotopes (40–48). The first sequence was ^{40}Ca, ^{41}K, ^{42}Ca, ^{43}Ca and ^{44}Ca; the second was ^{43}Ca, ^{44}Ca and ^{48}Ca (Figure 1). The ^{41}K signal was monitored to correct isobaric interference of ^{40}K on ^{40}Ca using the ratio of intensities of ^{40}K/^{41}K such that it was equal to 1.7384×10^{-3}. Other elemental isobars (e.g., ^{48}Ti$^+$, ^{84}Sr^{2+}, ^{86}Sr^{2+}, ^{88}Sr^{2+}) and molecular isobars (e.g., ^{24}Mg^{16}O$^+$, ^{26}Mg^{18}O$^+$, ^{27}Al^{16}O$^+$, ^{28}Si^{16}O$^+$) were not detected in this study. Amplifier rotation was applied to minimise the effect of difference in amplifier gains. The intensity of ^{40}Ca was increased to 15 V, and each run contained sixteen blocks and thirteen cycles. The integration time of the first sequence was 4 s for each peak, while the second was 16 s due to the low intensities of ^{48}Ca. Instrument fractionation was corrected by the ^{42}Ca–^{43}Ca double-spike technique through an iterative algorithm with an exponential law adapted from Heuser *et al.* (2002). If a single measurement result deviated from the exponential law, which could be caused by the multi-

Table 2.
Calcium purification scheme

Step	Reagent	Volume (ml)	Comment
1. Cleaning	8 mol l^{-1} HNO$_3$	30	
	H$_2$O	5	
	6 mol l^{-1} HCl	60	
	H$_2$O	5	
2. Condition	1.6 mol l^{-1} HCl	5	
3. Load sample	1.6 mol l^{-1} HCl	0.05	Precut collection
4. Remove matrix	1.6 mol l^{-1} HCl	16.95	Precut collection
5. Collect Ca	1.6 mol l^{-1} HCl	27	
6. Cleaning	6 mol l^{-1} HCl	10	Postcut collection
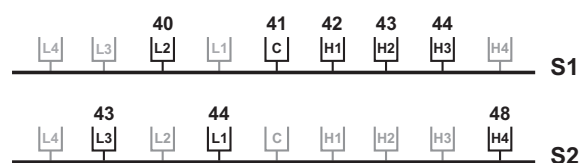
Figure 1. Cup configuration for Ca isotopic measurement. In the first sequence (S1), ^{40}Ca, ^{41}K, ^{42}Ca, ^{43}Ca and ^{44}Ca were collected. In the second sequence (S2), ^{43}Ca, ^{44}Ca and ^{48}Ca were collected.

reservoir mixing effect (Hart and Zindler 1989, Fantle and Bullen 2009, Zhu *et al.* 2016), then a data quality identification model was utilised to estimate the quality of data (Zhu *et al.* 2016).

Generally, the total procedural blanks were 20–70 ng, which were negligible compared with 50 µg Ca loaded into the column. The long-term mean and intermediate precision of independent measurements over a period of four years for $\delta^{44/40}$Ca of NIST SRM 915a and IAPSO seawater were 0.01 ± 0.06‰ (two standard deviations, 2*s*, *n* = 351) and 1.82 ± 0.12‰ (2*s*, *n* = 199), respectively (Figure 2).

Results

The $\delta^{44/40}$Ca values of geological reference materials and published data are listed in Table 3. Among these, ten of the thirty-five reference materials are reported for the first time for Ca isotopes. Overall, Ca isotopic compositions of most samples measured were in agreement with previous data (Table 3; Jochum *et al.* 2006, Amini *et al.* 2009, Wombacher *et al.* 2009, Schiller *et al.* 2012, Colla *et al.* 2013, Valdes *et al.* 2014, Feng *et al.* 2017, He *et al.* in press) except some MPI-DING glass samples (Table 3). Of the igneous rocks, $\delta^{44/40}$Ca values of ultramafic rocks ranged from 0.74 ± 0.13‰ (*n* = 3) to 1.59 ± 0.16‰ (*n* = 3), intermediate-mafic rocks showed a limited variation with an average value of 0.78 ± 0.14‰ (*n* = 47) and felsic rocks varied from 0.13 ± 0.11‰ (*n* = 5) to 1.17 ± 0.07‰ (*n* = 3) (Table 3). $\delta^{44/40}$Ca values of sedimentary rocks ranged from 0.47 ± 0.08‰ (*n* = 8) to 1.14 ± 0.11‰ (*n* = 3), and metamorphic rocks from 0.45 ± 0.07‰ (*n* = 3) to 0.93 ± 0.12‰ (*n* = 2).

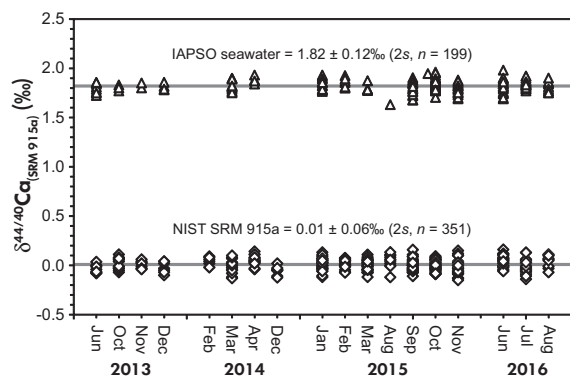**Figure 2. Long-term (> 4 years) $\delta^{44/40}$Ca measurements of NIST SRM 915a and IAPSO seawater. These two reference materials exhibited no drift.**

Discussion

No difference in $\delta^{44/40}$Ca with different double-spike pairs

Three double-spike pairs, namely ^{42}Ca–^{43}Ca, ^{42}Ca–^{48}Ca and ^{43}Ca–^{48}Ca, are commonly used for isotope ratio measurements with TIMS. Compared with ^{42}Ca–^{48}Ca and ^{43}Ca–^{48}Ca pairs, Gopalan *et al.* (2006) suggested that ^{42}Ca–^{43}Ca pair could minimise measurement uncertainties caused by rapid fluctuation of instrumental mass bias and produce more accurate mass bias correction. Lehn and Jacobson (2015) proposed that the ^{42}Ca–^{43}Ca pair provides the most precise analysis of $\delta^{44/40}$Ca because of the small average mass difference between ^{42}Ca/^{43}Ca and ^{40}Ca/^{44}Ca. However, within current measurement procedure and possible precision limits, our data and literature data show negligible difference with different double-spike pairs. For example, the seawater reference material, which has been widely analysed with different double-spike pairs in different laboratories, displayed limited variations (Table 4). Moreover, $\delta^{44/40}$Ca values of reference materials (such as BIR-1, BCR-2, BHVO-2, W-2, AGV-2, COQ-1 and SGR-1b) obtained with three different pairs also showed undetectable deviations (Table 3; Amini *et al.* 2009, Wombacher *et al.* 2009, Magna *et al.* 2015, Feng *et al.* 2017, He *et al.* in press).

The precision of the double-spike technique is mainly controlled by two factors, the composition of double spike and the proportion in which the double spike and sample are mixed. Rudge *et al.* (2009) provided MATLAB codes that can calculate the optimal double-spike compositions. Figure 3 illustrates the standard deviation of the mean (2SE) of $\delta^{44/40}$Ca with different double-spike pairs at the optimal composition (take ^{42}Ca–^{43}Ca double spike for example, the optimum composition is 50% ^{42}Ca and 50% ^{43}Ca). However, as indicated by Fantle and Bullen (2009), measurement precisions are not ultimately limited by double-spike pairs, but by the instrumentation. Typically, internal precision during measurement was better than the external precision. Theoretically, as shown in Figure 3, under proper sample/spike ratios, most of the precisions in $\delta^{44/40}$Ca obtained from all the three double-spike pairs are less than 0.06‰, which is close to the repeatability precision but lower than intermediate precisions (~ 0.12‰) of the measurement results obtained by TIMS or MC-ICP-MS. Hence, it is reasonable that no differences were detected within these three pairs. Therefore, different double-spike pairs should cause limited biases on the measurement of Ca isotopic compositions.

Table 3.
Calcium isotopic compositions of the geological reference materials

Sample	Lithology	Origin	δ⁴⁴/⁴⁰Ca (‰)	2sᵃ	nᵇ	CaO (% m/m)	MgO (% m/m)	K/Caᶜ
Commonly used RMs								
NIST SRM 915a	Calcium carbonate	This work	0.01	0.06	351	—	—	<10⁻⁶
IAPSO	Seawater	This work	1.82	0.12	199	—	—	0.993
Igneous rock								
DTS-1	Dunite	Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	1.44	0.27	15	0.17	49.5	0.007
		Huang *et al.* (2010), $^{43}Ca-^{48}Ca$	1.59	0.16	3			
		Feng *et al.* (2017), $^{42}Ca-^{48}Ca$	1.51	0.13	7			
DTS-2	Dunite	Feng *et al.* (2017), $^{42}Ca-^{48}Ca$	1.2	0.11	9	0.12	49.4	0.060
PCC-1	Peridotite	Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	1.15	0.09	13	0.54	42.9	0.015
JP-1	Peridotite	He *et al.* (in press), $^{43}Ca-^{48}Ca$	1.13	0.13	4	0.56	44.7	0.006
		Magna *et al.* (2015), $^{42}Ca-^{43}Ca$	1.15	0.07	4			
GOR128-G	Komatiite	This work	0.88	0.06	6	6.24	26	0.007
		Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	0.70	0.18	13			
		Jochum *et al.* (2006), $^{43}Ca-^{48}Ca$	0.66	0.15				
GOR132-G	Komatiite	This work	0.74	0.13	3	8.45	22.4	0.004
		Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	0.57	0.17	11			
		Jochum *et al.* (2006), $^{43}Ca-^{48}Ca$	0.49	0.15				
BM90/21-G	Peridotite	Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	1.01	0.28	16	2.1	34.3	0.002
		Jochum *et al.* (2006), $^{43}Ca-^{48}Ca$	1.29	0.15	7			
BIR-1	Basalt	This work	0.84	0.09	9	13.3	9.7	0.003
		Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	0.77	0.34	14			
		Wombacher *et al.* (2009); $^{43}Ca-^{48}Ca$	0.82	0.20	4			
		Schiller *et al.* (2012), SSB	0.80	0.06	4			
		Valdes *et al.* (2014), SSB	0.89	0.08	4			
		Feng *et al.* (2017), $^{42}Ca-^{48}Ca$	0.79	0.12	4			
BCR-1	Basalt	This work	0.82	0.09	3	6.98	3.50	0.295
		Colla *et al.* (2013), SSB	0.82	0.10	4			
BCR-2	Basalt	This work	0.82	0.09	12	7.12	3.6	0.296
		Amini *et al.* (2009), $^{43}Ca-^{48}Ca$	0.81	0.17	6			
		Wombacher *et al.* (2009), $^{43}Ca-^{48}Ca$	0.92	0.40	4			
		Schiller *et al.* (2012), SSB	0.89	0.08				
		Valdes *et al.* (2014), SSB	0.87	0.31	3			
		Feng *et al.* (2017), $^{42}Ca-^{48}Ca$	0.80	0.11	20			
		He *et al.* (2017), $^{43}Ca-^{48}Ca$	0.80	0.05	4			

Table 3 (continued).
Calcium isotopic compositions of the geological reference materials

Sample	Lithology	Origin	$\delta^{44/40}$Ca (‰)	2s[a]	n[b]	CaO (% m/m)	MgO (% m/m)	K/Ca[c]
BHVO-2	Basalt	This work	0.80	0.10	16	11.4	7.23	0.054
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.75	0.22	20			
		Schiller et al. (2012), SSB	0.80	0.08	10			
		Valdes et al. (2014), SSB	0.87	0.16	12			
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.77	0.10	7			
		He et al. (2017), ^{43}Ca–^{48}Ca	0.79	0.09	5			
		Magna et al. (2015), ^{42}Ca–^{43}Ca	0.90	0.11	5			
KL2-G	Tholeiite	This work	0.78	0.11	7	10.9	7.34	0.052
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.70	0.27	15			
		Jochum et al. (2006), ^{43}Ca–^{48}Ca	0.67	0.28	10			
ML3B-G	Tholeiite	This work	0.78	0.09	9	10.5	6.59	0.043
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.72	0.19	15			
		Jochum et al. (2006), ^{43}Ca–^{48}Ca	0.67	0.32	13			
JB-2	Basalt	This work	0.85	0.12	3	9.85	4.43	0.051
W-2	Diabase	This work	0.84	0.09	9	10.9	6.43	0.069
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.94	0.24	6			
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.70	0.08	3			
DNC-1	Dolerite	This work	0.83	0.06	5	11.49	10.13	0.024
		Schiller et al. (2012), SSB	0.80	0.06	9			
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.82	0.08	6			
T1-G	Quartz Diorite	This work	0.77	0.12	6	7.1	3.75	0.327
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.80	0.22	14			
		Jochum et al. (2006), ^{43}Ca–^{48}Ca	0.73	0.39	9			
AGV-1	Andesite	This work	0.72	0.06	3	4.89	1.51	0.716
		Colla et al. (2013), SSB	0.55					
AGV-2	Andesite	This work	0.71	0.11	8	5.15	1.8	0.671
		Valdes et al. (2014), SSB	0.77	0.17	3			
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.79	0.09	9			
		He et al. (2017), ^{43}Ca–^{48}Ca	0.75	0.12	3			
JA-2	andesite	This work	0.78	0.11	3	6.26	7.84	0.339
StHs6/80-G	Andesite ash	This work	0.69	0.06	4	5.28	1.97	0.291
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.75	0.20	16			
		Jochum et al. (2006), ^{43}Ca–^{48}Ca	0.74	0.24	9			
RGM-1	Rhyolite	This work	0.78	0.05	6	1.18	0.28	4.332
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.89	0.03	3			
ATHO-G	Rhyolite	This work	1.03	0.10	6	1.7	0.103	1.850
		Amini et al. (2009), ^{43}Ca–^{48}Ca	0.87	0.29	13			
		Jochum et al. (2006), ^{43}Ca–^{48}Ca	0.84	0.40	4			
JR-2	Rhyolite	This work	1.17	0.07	3	0.48	0.08	11.67
QLO-1a	Quartz latite	This work	0.80	0.12	3	3.17	1	1.353

Table 3 (continued).
Calcium isotopic compositions of the geological reference materials

Sample	Lithology	Origin	δ$^{44/40}$Ca (‰)	2s^a	n^b	CaO (% m/m)	MgO (% m/m)	K/Ca^c
GSP-1	Granodiorite	This work	0.13	0.11	5	2.04	1.09	3.212
GSP-2	Granodiorite	This work	0.25	0.07	9	2.1	0.96	3.052
		He et al. (2017), ^{43}Ca–^{48}Ca	0.30	0.03	3			
JG-1a	Granodiorite	This work	0.64	0.06	3	2.1	0.7	2.383
G-2	Granite	This work	0.59	0.10	3	1.91	0.75	2.807
		Valdes et al. (2014), SSB	0.57	0.12	3			
JG-2	Granite	This work	0.66	0.01	3	0.71	0.07	7.887
JG-2-R^d	Granite	This work	0.62	0.06	3	0.71	0.07	7.887
COQ-1	Carbonatite	This work	0.68	0.11	8	48.3	1.25	0.004
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.71	0.11	4			
		He et al. (2017), ^{43}Ca–^{48}Ca	0.66	0.12	4			
Sediments								
NOD-A-1	Manganese nodule	This work	1.14	0.11	3	15.4	4.76	0.046
		Feng et al. (2017), ^{42}Ca–^{48}Ca	1.00	0.14	9			
NOD-P-1	Manganese nodule	This work	0.74	0.10	13	3.1	3.3	0.461
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.74	0.08	8			
SGR-1b	Shale	This work	0.85	0.11	3	8.38	4.44	0.236
		Schiller et al. (2012), SSB	0.76	0.04	3			
		Wombacher et al. (2009), ^{43}Ca–^{48}Ca	0.86	0.25	3			
		Feng et al. (2017), ^{42}Ca–^{48}Ca	0.77	0.14	10			
JSD-1	Stream sediment	This work	0.69	0.02	3	3	2.1	0.879
SBC-1	Shale	Feng et al. (2017), ^{42}Ca–^{48}Ca	0.47	0.08	8	3.17	2.84	1.297
MAG-1	Marine mud	Wombacher et al. (2009), ^{43}Ca–^{48}Ca	0.71	0.32	4	1.37	3	3.087
Metamorphic rock								
OU-6	Penrhyn slate	This work	0.69	0.04	3	0.74	2.4	4.879
UB-N	Serpentinite	This work	0.93	0.12	2	1.25	37.8	0.019
		Wombacher et al. (2009), ^{43}Ca–^{48}Ca	0.91	0.36	4			
SDC-1	Mica schist	This work	0.45	0.07	3	1.4	1.69	2.791

SSB, sample-standard bracketing. δ$^{44/40}$Ca was transformed from δ$^{44/42}$Ca by multiplying by 2.099 (Fantle and Tipper 2014). The results were normalised to NIST SRM 915a as reference. The CaO and MgO contents were taken from the GeoReM database (http://georem.mpch-mainzgwdg.de). ^{a}2s, 2 standard deviation; ^{b}number of repeat analyses; ^{c}K/Ca atomic ratio; ^{d}duplicate sample.

Table 4.
$\delta^{44/40}$Ca of seawater obtained with different double-spike pairs in different laboratories

Laboratory	Reference	$\delta^{44/40}$Ca (‰)	Uncertainty	Type[a]	Double spike
IFM-GEOMAR	Amini *et al.* (2008)	1.86	0.04	2SE	^{43}Ca–^{48}Ca
IFM-GEOMAR	Amini *et al.* (2009)	1.82	0.03	2SE	^{43}Ca–^{48}Ca
IFM-GEOMAR	Böhm *et al.* (2006)	1.83	0.10	2SE	^{43}Ca–^{48}Ca
IFM-GEOMAR	Farkaš *et al.* (2007a)	1.86	0.15	2s	^{43}Ca–^{48}Ca
IFM-GEOMAR	Müller *et al.* (2011)	1.95	0.26	2s	^{43}Ca–^{48}Ca
IFM-GEOMAR	Teichert *et al.* (2009)	1.77	0.03	2SE	^{43}Ca–^{48}Ca
IFM-GEOMAR	Hippler *et al.* (2003)	1.82	0.13	2s	^{43}Ca–^{48}Ca
Harvard University	Huang *et al.* (2010)	1.90	0.12	2s	^{43}Ca–^{48}Ca
Harvard University	Huang *et al.* (2011)	1.90	0.03	2SE	^{43}Ca–^{48}Ca
Carleton University	Farkaš *et al.* (2007b)	1.86	0.20	2s	^{43}Ca–^{48}Ca
Bern	Hippler *et al.* (2003)	2.01	0.19	2SE	^{43}Ca–^{48}Ca
Strasbourg	Hippler *et al.* (2003)	1.89	0.17	2s	^{43}Ca–^{48}Ca
Bristol	Kasemann *et al.* (2005)	1.96	0.12	2s	^{43}Ca–^{48}Ca
Beijing, CUG	He *et al.* (in press)	1.89	0.18	2s	^{43}Ca–^{48}Ca
Berkeley	Skulan *et al.* (1997)	2.11	0.18	2s	^{42}Ca–^{48}Ca
Berkeley	Fantle and DePaolo (2005)	1.95	0.1	2s	^{42}Ca–^{48}Ca
Berkeley	Fantle and DePaolo (2007)	2.02	0.08	2s	^{42}Ca–^{48}Ca
Berkeley	Fantle and DePaolo (2007)	2.05	0.07	2s	^{42}Ca–^{48}Ca
Wuhan, CUG	Feng *et al.* (2017)	1.88	0.14	2s	^{42}Ca–^{48}Ca
Saskatchewan	Amini *et al.* (2009)	1.89	–	–	^{42}Ca–^{43}Ca
LHyGeS	Cobert *et al.* (2011)	1.91	0.10	2s	^{42}Ca–^{43}Ca
Saskatchewan	Holmden and Bélanger (2010)	1.86	0.05	2s	^{42}Ca–^{43}Ca
Saskatchewan	Schmitt *et al.* (2009)	1.80	0.20	2s	^{42}Ca–^{43}Ca
Northwestern University	Lehn *et al.* (2013)	1.87	0.04	2s	^{42}Ca–^{43}Ca
Guangzhou, SKLaBIG	This study	1.82	0.12	2s	^{42}Ca–^{43}Ca

All data were normalised to NIST SRM 915a as reference. [a]Statistical uncertainty reported as 2s (2 standard deviations) or 2SE (2 standard error).

MPI-DING reference glasses: homogeneous or heterogeneous?

Homogeneity is a fundamental requirement for reference materials (ISO Guide 34 2009). Previous studies demonstrate that MPI-DING glasses are homogeneous for most element and isotope systems (Jochum *et al.* 2000, 2006, Amini *et al.* 2009). To check whether Ca isotopes in MPI-DING glasses are homogeneously distributed, we analysed seven of these glasses. As illustrated in Figure 4, $\delta^{44/40}$Ca of four MPI-DING glasses, KL2-G, ML3B-G, T1-G and StHs6/80-G, were consistent with the results reported by Amini *et al.* (2009) and Jochum *et al.* (2006) within both 2s and (2SE = $2s/\sqrt{n}$). Based on 2s precisions, $\delta^{44/40}$Ca values of GOR128-G, GOR132-G and ATHO-G statistically overlap with published data (Figure 4a). However, under precisions expressed as 2SE, $\delta^{44/40}$Ca values of these measurement results are significantly higher than previous data (Figure 4b) (Jochum *et al.* 2006, Amini *et al.* 2009). Besides, $\delta^{44/40}$Ca of BM90/21-G (peridotite) reported by Amini *et al.* (2009) was lower than that reported by Jochum *et al.* (2006) (Figure 4b). This inconsistency might be attributed to measurement bias and/or sample heterogeneity.

The precision of the measurement results for Cr, Cu, Zn, Sn, Bi, (the noble metals) Ir, Pt, Au, and Li and Pb isotopes in MPI-DING glasses (Jochum *et al.* 2006) have lower precision values, which can be attributed to sample heterogeneity. For the two komatiites samples, GOR128-G and GOR132-G, a few fragments were observed due to quench crystallisation (Jochum *et al.* 2000, 2006). The quench crystallisation of the MPI-DING glasses is the probable cause of the discrepancy in the Ca isotope ratio measurement results. Therefore, we suggest that careful consideration should be taken when MPI-DING glasses are applied as laboratory reference materials for quality control for Ca isotopes.

Calcium isotopic fractionation of felsic, ultramafic and intermediate-mafic rocks

The igneous rocks demonstrated significant variability in Ca isotope compositions (Table 3, Figure 5), indicating that Ca isotopic fractionation could occur at high temperatures, as suggested by previous studies (Huang *et al.* 2010, Kang *et al.* 2016).

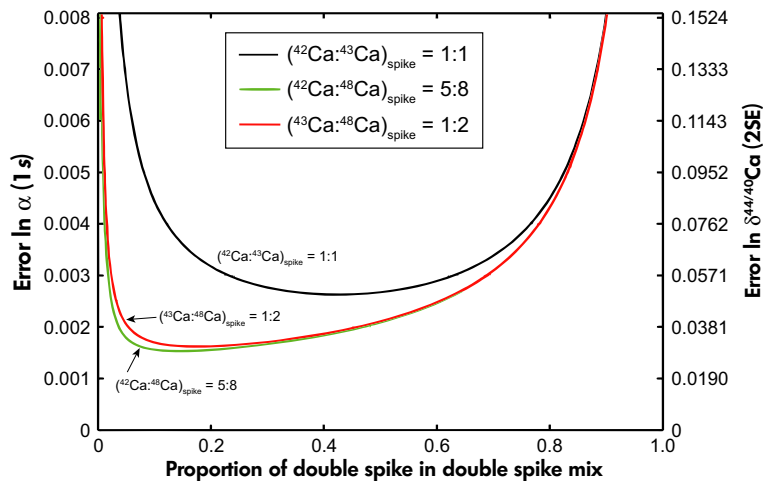Felsic rocks showed a wide variation in $\delta^{44/40}$Ca ranging from 0.13‰ to 1.17‰ (Table 3). Radiogenic

Figure 3. Plot of error in α (natural fractionation factor) and $\delta^{44/40}Ca$ against proportion of double spike in double-spike sample mixture with the optimal Ca double spikes. Precisions (2SE, standard deviation of the mean) in $\delta^{44/40}Ca$ are related to precisions (1s, standard deviation) in α by $\delta^{44/40}Ca = \alpha \times 1000 \times \ln(43.95549/39.96259) \times 2/\sqrt{100}$. The 2SE value was based on 100 measurement cycles with an integration time of 4 s. ^{42}Ca and ^{43}Ca spike composition is shown in Table 1, while the ^{48}Ca spike composition was $^{48}Ca = (2.10\%, 0.02\%, 0.01\%, 0.07\%, 0.01\%, 97.78\%)$ (data from Oak Ridge National Laboratory, USA). Inversion isotopes: ^{42}Ca–^{43}Ca double spike with a ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca inversion, ^{42}Ca–^{48}Ca double spike with a ^{40}Ca, ^{42}Ca, ^{44}Ca, ^{48}Ca inversion, and ^{43}Ca–^{48}Ca double spike with a ^{40}Ca, ^{43}Ca, ^{44}Ca, ^{48}Ca inversion.
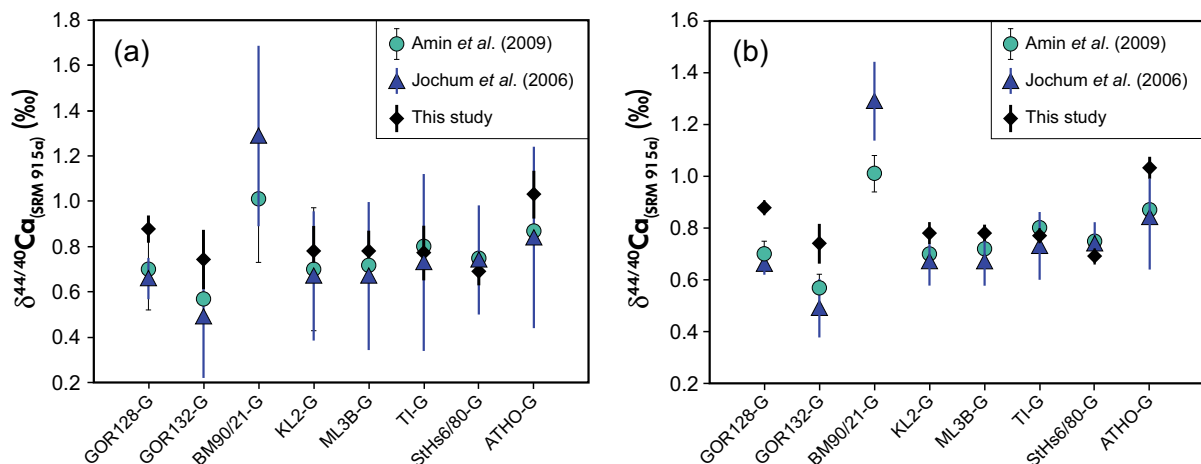
Figure 4. Calcium isotopic compositions of the MPI-DING reference glasses compared with published data. (a) Precisions shown as 2s; (b) Precisions shown as 2SE ($2SE = 2s/\sqrt{n}$).

^{40}Ca enrichment from ^{40}K decay probably has an important effect on the Ca isotopic composition. A nonlinear relationship was observed between $\delta^{44/40}Ca$ and K/Ca ratio (Figure 6), indicating that Ca isotopic fractionation was not simply controlled by the K/Ca value. The age of the rock is also important. Based on the calculation by Fantle and Tipper (2014), $\delta^{44/40}Ca$ could be lower by 0.3‰ for a rock aged 1 Ga with K/Ca = 5. When the K/Ca ratio increases to 10, $\delta^{44/40}Ca$ could decrease by 0.6‰. In the case of a rock aged > 1 Ga with K/Ca = 20, $\delta^{44/40}Ca$ could decrease by more than 1.0‰ (Fantle and Tipper 2014). So it seems that the K/Ca ratio and age of the rock could explain the large $\delta^{44/40}Ca$ difference (~ 1.04‰) in felsic rocks. However, among these felsic rocks, GSP-1 displayed the lowest $\delta^{44/40}Ca$ (0.13 ± 0.11‰, n = 6), with only a moderate K/Ca ratio of 3.21, which cannot be explained by radiogenic ^{40}Ca enrichment. Therefore, we suggest that Ca isotopic fractionation during magma evolution should not be ignored and more work needs to be carried out.
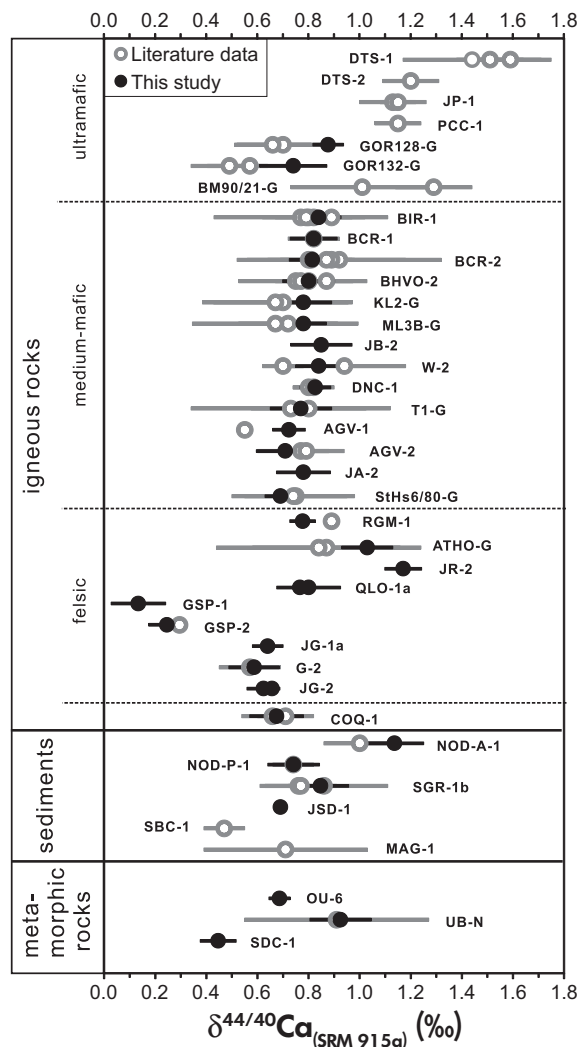
Figure 5. $\delta^{44/40}$Ca values for geological reference materials and comparison with literature data (normalised to NIST SRM 915a, $\delta^{44/40}$Ca = 2.099 × $\delta^{44/42}$Ca). Range bars represent 2s and are only shown when larger than the symbol.

$\delta^{44/40}$Ca values of ultramafic rocks varied from 0.74‰ to 1.59‰ (Table 3), implying that Ca isotopic fractionation occurred during magma evolution. As illustrated in Figure 7, CaO was negatively correlated with, while MgO was positively correlated with $\delta^{44/40}$Ca, consistent with previous results reported by Amini et al. (2009). Such relationships could be explained by partial melting of mantle peridotites. Experimental melting studies on anhydrous melting of peridotites indicate that CaO decreases and MgO increases with progressive melt extraction in the residue (Green 1973). Clinopyroxenes (cpx), orthopyroxenes (opx) and olivine (ol) are the main minerals of the ultramafic rocks. Previous studies demonstrate that heavier Ca isotopes prefer to enrich in ol and
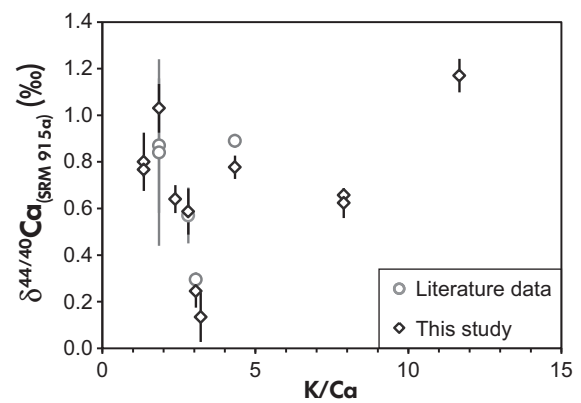
Figure 6. $\delta^{44/40}$Ca vs. K/Ca in felsic rocks. No correlation was displayed between them, indicating that ^{40}K decay is not the only factor that causes various Ca isotopic compositions.

opx rather than cpx because of the stronger Ca–O bonds in ol and opx (e.g., Huang et al. 2010, Kang et al. 2016). Moreover, cpx is consumed more rapidly than ol and opx in the residue during mantle melting (e.g., Green 1973, Jaques and Green 1980, Hirose and Kushiro 1993). Therefore, $\delta^{44/40}$Ca of the refractory residue should be correlated negatively with CaO and positively with MgO. This is in agreement with practical observations that dunite has the highest $\delta^{44/40}$Ca values (Table 3), which is the most refractory rock composed of ~ 90% olivine.

Unlike felsic and ultramafic rocks, intermediate-mafic rocks displayed limited variability in Ca isotopic compositions with an average $\delta^{44/40}$Ca of 0.78 ± 0.14‰, despite of wide ranges of CaO and MgO contents in these rocks (Figure 7). Variations of CaO and MgO contents are indicative of the breakdown and/or removal of Ca-bearing and Mg-bearing minerals during partial melting or fractional crystallisation. Limited Ca isotopic variation of intermediate-mafic rocks indicates insignificant isotopic fractionation during magma differentiation.

Calcium isotopic fractionation of sedimentary and metamorphic rocks

As shown in Table 3 and Figure 5, $\delta^{44/40}$Ca values of sedimentary and metamorphic rocks displayed large variations, indicating fractionation of Ca isotopes may also occur during low- temperature and metamorphic processes. Two manganese nodules, NOD-A-1 and NOD-P-1, displayed distinctive Ca isotopic compositions with 1.14 ± 0.11‰ (n = 3) and 0.74 ± 0.10‰ (n = 13),
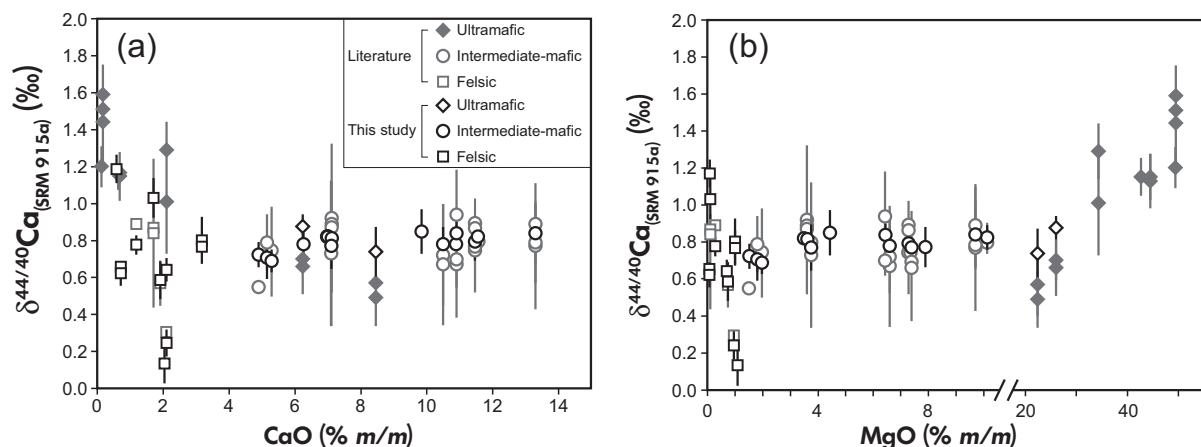
Figure 7. Calcium isotope ratios in igneous rocks as a function of CaO and MgO contents. $\delta^{44/40}$Ca values of ultramafic rocks were negatively correlated with CaO and positively with MgO, but no correlations were observed for intermediate-mafic and felsic rocks.

respectively, implying two different sedimentary environments. For the metamorphic rocks, $\delta^{44/40}$Ca of OU-6 (slate, 0.69 ± 0.04‰, n = 3) is higher than that of SDC-1 (mica schist, 0.45 ± 0.07‰, n = 3). As the metamorphic grade of schist is greater than that of slate, our data might imply that the $\delta^{44/40}$Ca value was lowered during metamorphism. UB-N (serpentinite) exhibited a $\delta^{44/40}$Ca value of 0.93 ± 0.12‰ (n = 2), slightly lower than the peridotite (~ 1.1‰, Table 3), indicating $\delta^{44/40}$Ca could decrease during serpentinisation, which is in line with the findings of John *et al.* (2012).

Conclusions

High-precision $\delta^{44/40}$Ca values obtained by thermal ionisation mass spectrometry (Triton instrument) are reported for thirty-five reference materials of various compositions, using a ^{42}Ca–^{43}Ca double spike. $\delta^{44/40}$Ca values for most reference materials were consistent with previously published data. Large variations in $\delta^{44/40}$Ca were observed in felsic and ultramafic rocks. Moreover, $\delta^{44/40}$Ca values of ultramafic rocks were correlated with Ca and Mg, possibly owing to the partial melting of mantle peridotites. On the other hand, $\delta^{44/40}$Ca of intermediate-mafic rocks showed limited variability. For sedimentary and metamorphic rocks, they also showed large Ca isotopic variations. It is also notable that no measurable $\delta^{44/40}$Ca deviations were observed when different double-spike pairs (^{42}Ca–^{48}Ca, ^{43}Ca–^{48}Ca and ^{42}Ca–^{43}Ca) were adopted for mass correction, suggesting that double-spike pairs should have little effect on the measurement of $\delta^{44/40}$Ca due to the limitation of the current analytical precisions.

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