



## The Cu isotopic signature of granites from the Lachlan Fold Belt, SE Australia

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### ABSTRACT

This contribution reports our preliminary work to determine Cu isotope ratios for various granite rocks and examine the Cu isotope systematics within granite suites. A chemical procedure, modified from Maréchal [Maréchal, C.N., Télouk, P. and Albarède, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, 156(1–4): 251–273.], was used to separate Cu from rock matrix. Quantitative recovery ( $100.6 \pm 1.6\%$ ), with a low total procedural blank ( $2.65 \pm 0.66$  ng) for Cu, has been achieved, allowing Cu isotopic measurements on samples with as little as 10 ppm Cu. The Cu isotope ratios ( $\delta^{65}\text{Cu}$  relative to NIST SRM 976) of 32 rock samples, ranging from mafic to felsic compositions, from 3 batholiths (2 I-type, 1 S-type) from the Lachlan Fold Belt in southeastern Australia, vary from  $-0.46\%$  to  $1.51\%$ . Most of them cluster around zero, with mean values for the I-type and S-type granites of  $0.03 \pm 0.15\%$  and  $-0.03 \pm 0.42\%$  (2 sigma) respectively. These data, together with Cu isotope ratios of two loess samples, provide preliminary evidence that the baseline Cu isotopic composition of the crystalline part of upper continental crust is close to zero. The tight clustering of Cu isotope ratios of rocks from the I-type suites suggests that high-temperature magmatic processes do not produce significant Cu isotope fractionation. However, two granites with abnormally heavy Cu isotope signatures (up to  $1.51\%$ ) appears to be the result of localized hydrothermal alteration. Measurable variation in Cu isotopic composition of the S-type granite may reflect isotopic heterogeneity in the sedimentary source region as a result of redox processes or may be due to hydrothermal overprinting. Thus, Cu isotope geochemistry may be a useful tracer for studying hydrothermal alteration and source heterogeneity of granitic rocks.

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### 1. Introduction

The advent of the revolutionary MC-ICP-MS has led to an explosion of research on the so called “non-traditional” stable isotopes; e.g., Fe, Cu, Zn, Mo, Li and Mg (e.g., Johnson et al., 2004). These novel isotope systems have been applied widely to the study of biogeochemical, cosmochemical, mineralising, surficial and magmatic processes.

Copper is an element that has received significant interest by isotopic geochemists. It is a multivalent element that is sensitive to the redox state of the environment; thus, Cu isotope fractionation should occur in response to oxidation–reduction processes. On the other hand, Cu is a mobile trace element in most rocks; thus kinetic Cu isotope fractionation might record Rayleigh-type fractionation processes. Therefore, there is potential to measure Cu isotope fractionation that is geologically meaningful. Additionally, as Cu is a typical sulfo-chalcophile element, its isotopes may provide new insights into the geochemical behavior of this group of elements.

The usefulness of isotopic signatures of multivalent elements and mobile trace elements has been manifested by studies on a number of elements such as Fe and Li. Despite continuous debate (Beard and Johnson, 2006; Poitrasson, 2006; Poitrasson, 2007; Weyer et al., 2007), it has been

gradually realized that significant Fe isotope variation exists in both mantle and crustal rocks, which could be induced by mineral–mineral (Zhu et al., 2002), mineral–melt (Weyer and Ionov, 2007), and mineral–fluid (Poitrasson and Freyrier, 2005) isotopic fractionations, as well as varying oxygen fugacities (Williams et al., 2004). Iron isotopes provide insights into the redox states and processes, such as partial melting and metasomatism that occurred during Earth's evolution. For Li isotopes, the potential for fingerprinting the sources and/or processes involved in subduction zones (Magna et al., 2006), mantle plumes (Kobayashi et al., 2004) and the crust (Teng et al., 2006) has been recognized. However, applications of Cu isotopes to understanding geological processes have not been investigated as intensively as for Fe and Li.

The main area of application of Cu isotopes to date has been the study of ore-forming systems (Jiang et al., 2002; Larson et al., 2003; Graham et al., 2004; Mason et al., 2005; Mathur et al., 2005; Markl et al., 2006; Maher and Larson, 2007). This is because Cu isotope signatures may provide the most direct evidence of the source of metals and fluid pathways in mineralizing systems. However, a major impediment to the interpretation of Cu isotope data is that baseline values of ratios for different geological reservoirs have not been well constrained. A bulk Earth Cu isotope ratio ( $\delta^{65}\text{Cu} = 0$ ,  $\delta^{65}\text{Cu}_{\text{sample}} = 1000 \cdot (R_{\text{sample}}/R_{\text{NIST976}} - 1)$ ,  $R = {}^{65}\text{Cu}/{}^{63}\text{Cu}$ ) was proposed based on measurements of basalts (Luck et al., 2003) and mantle peridotite (Ben Othman et al., 2006). The Cu isotope signature of seawater was found to be significantly heavier

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( $\delta^{65}\text{Cu} \approx 1\%$ ) (Bermin et al., 2006). To our knowledge, there has been no systematic measurement of the Cu isotope ratios of granites.

In this study, well characterized I-type and S-type granites from the Lachlan Fold Belt (LFB) in southeastern Australia were selected for Cu isotope measurement, with the following objectives: (1) to ascertain whether the Cu isotope signature reflects the source of the granite; (2) to investigate whether Cu isotopes fractionate during the processes associated with evolution of granite magma; (3) to constrain the baseline signature of Cu isotopes in granites, and thereby to increase the usefulness of Cu isotopes in petrologic and granite-related mineral deposit studies. I- and S-type granites are considered representative of the crystalline upper continental crust, so their Cu isotope signatures would provide an estimate for this reservoir. Two loess samples were also included in this study to provide a better estimate of the Cu isotope composition of the continental crust as loess is representative of average upper continental crust.

## 2. Samples

In this study, two suites of I-type granite (Yeoval Batholith and Marulan Batholith) and one suite of S-type granite (Wagga Batholith) from the LFB were chosen to investigate the role of source and magmatic processes on Cu isotope fractionation. The sampling location and

geological setting of the I- and S-type granites are shown in Fig. 1. Samples from all the three suites were selected on the basis of whole-rock major element chemistry to represent the range of compositions.

The I- and S-type granite subdivision was proposed by Chappell and White (1974, 1992) to explain the distinctive characteristics of granite suites from the LFB. The parent magmas of I-type granites are partial melts of mantle-derived igneous source material. The parent magmas of S-type granites are produced by partial melting of sedimentary source material that has undergone weathering at the Earth's surface. This concept, albeit oversimplified, has proven very useful and is widely accepted.

### 2.1. I-type rocks

The Yeoval Batholith of the Bogy Plain Supersuite is located in the north-central part of the Lachlan Fold Belt of SE Australia (Fig. 1) and has an early Devonian age ( $400 \pm 10$  Ma) (Wyborn et al., 1987). The batholith is concentrically zoned, corresponding to a sequence of cumulate rocks crystallized at the boundary between melt and previously crystallized material (Wyborn et al., 1987). The Yeoval Batholith is classified as a high-temperature I-type granite suite (Chappell et al., 1998) and provides an excellent example of fractional crystallization in magma evolution. Fractional crystallization processes produced a continuum of compositions from mafic to felsic (Wyborn et al., 1987). For example, as

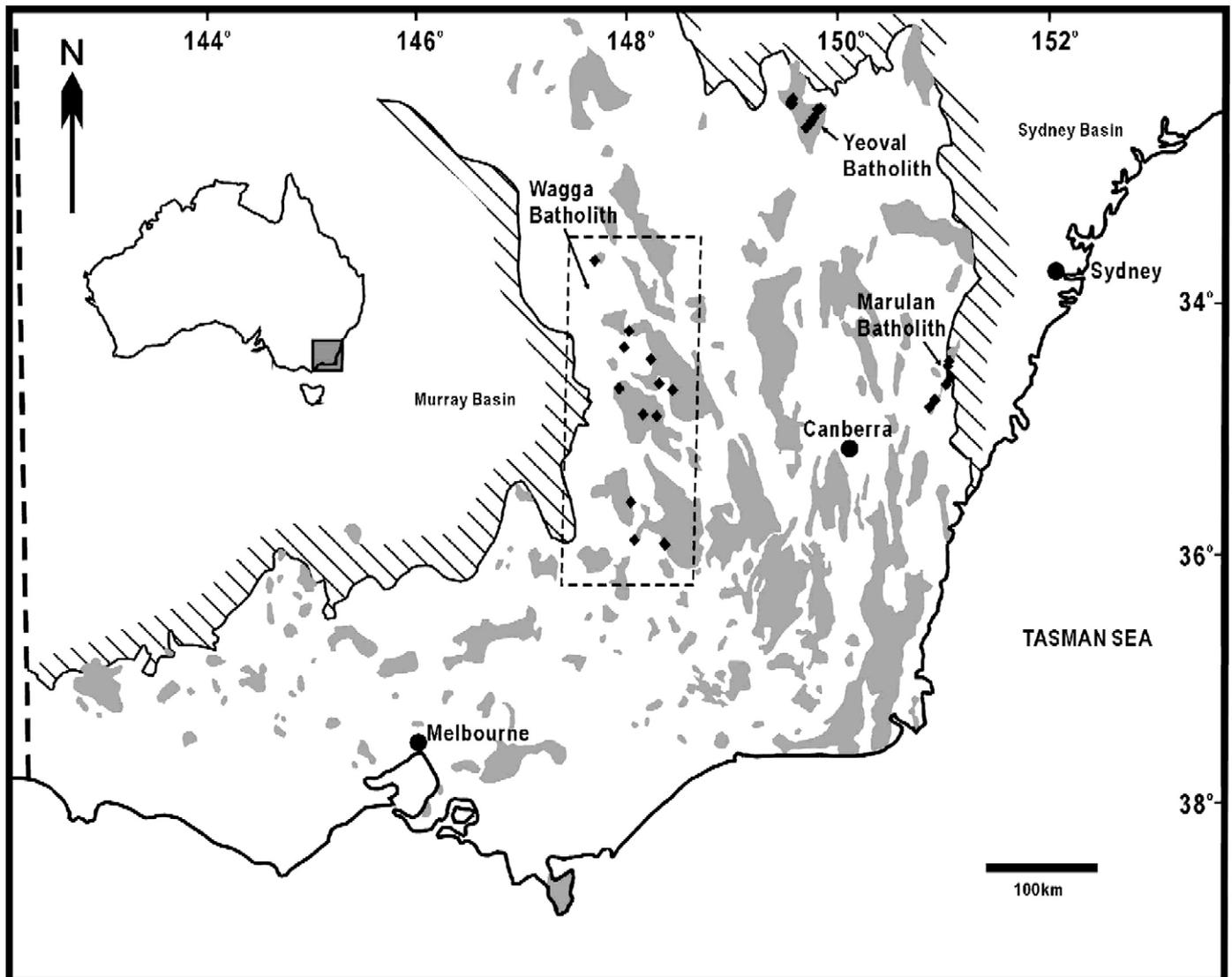


Fig. 1. Map showing the distribution of granites in the Lachlan Fold Belt and the sampling locations of granites analyzed in this study. Map is modified from Chappell et al. (1988) and Chappell et al. (2000).

the magma evolves to the high-SiO<sub>2</sub> end member, the concentration of Rb and Ba increase, while Cr decreases (Fig. 2). The Cu content of the samples from the Yeoval batholith is high and variable relative to the other two batholiths investigated in this study, with values varying between 23 and 115 ppm. Blevin and Chappell (1992) observed a trend of increasing Cu concentration from SiO<sub>2</sub>=45% to SiO<sub>2</sub>=55% followed by a decrease for higher SiO<sub>2</sub> contents.

The Marulan Batholith is located at the western edge of the Sydney Basin in the eastern part of the Lachlan Fold Belt, some 300 km to the south-east of the Bogy Plains Supersuite. This allows the effects of potentially different source material on Cu isotope signatures to be evaluated. The Marulan batholith is made up of 14 separate lithological units with a total area of 220 km<sup>2</sup>. The age of the Marulan Batholith, constrained by K–Ar and Rb–Sr dating of mica, is 400 Ma (Flood et al., 1982). It is also a high-temperature I-type granite suite (Chappell et al., 2000) with a continuous and uniform distribution of compositions from 55 to 73% SiO<sub>2</sub> within the batholith (Chappell et al., 1988). The trace element systematics of samples from the Marulan Batholith are generally similar to those of the Yeoval Batholith (Chappell et al., 2000), suggesting a similar fractional crystallization process (Fig. 2). However, with Cu concentrations between 14 and 24 ppm, the seven samples from the Marulan Batholith have a much lower and less variable Cu content than the samples from the Yeoval Batholith and there is no significant trend between contents of Cu and SiO<sub>2</sub> (Fig. 2).

## 2.2. S-type rocks

The Wagga Batholith comprises a diverse group of granites occurring as small, isolated exposures (128 lithological units) from Brewarrina to Nymagee in central New South Wales and continuing in

a broad belt southward through northeast Victoria, with a total area of 138,000 km<sup>2</sup> (Chappell et al., 1988). S-type granites are dominant in the Wagga Batholith. The batholith was emplaced during early Silurian magmatism around 430 Ma (Collins and Hobbs, 2001). The granites from the Wagga Batholith show evidence of fractional crystallization, such as increasing Rb, Nb and Cs concentrations and decreasing Sr and Ba concentrations as the rocks evolve to high silica end members (Chappell et al., 1988). Chromium also shows a decreasing trend as SiO<sub>2</sub> increases (Fig. 2), which is similar to that of the I-type granites; however, there is an offset between the I- and S-type trends. Copper contents of the S-type granites vary between 19 ppm and 10 ppm and decrease as SiO<sub>2</sub> increases (Fig. 2).

## 2.3. Chinese loess

Loess is formed by deposition of dust mechanically abraded from a large area; therefore, its elemental and isotopic signatures could represent those of the average crust. The Chinese Loess Plateau, located in the central northern part of China, represents the largest area of loess deposition in the world. The climate in this area is arid to semi-arid. Loess deposited during the last glacial–interglacial cycle (within the past 130,000 years) was used in this study. Detailed geographic and chemical information of the loess samples is provided by Gao and Ding (2008).

## 3. Methods

Below we report our chemical procedure to purify Cu from silicate rock samples. All chemical procedures were performed in laminar flow hoods (Class 100) in a clean room (Class 1000) with filtered air.

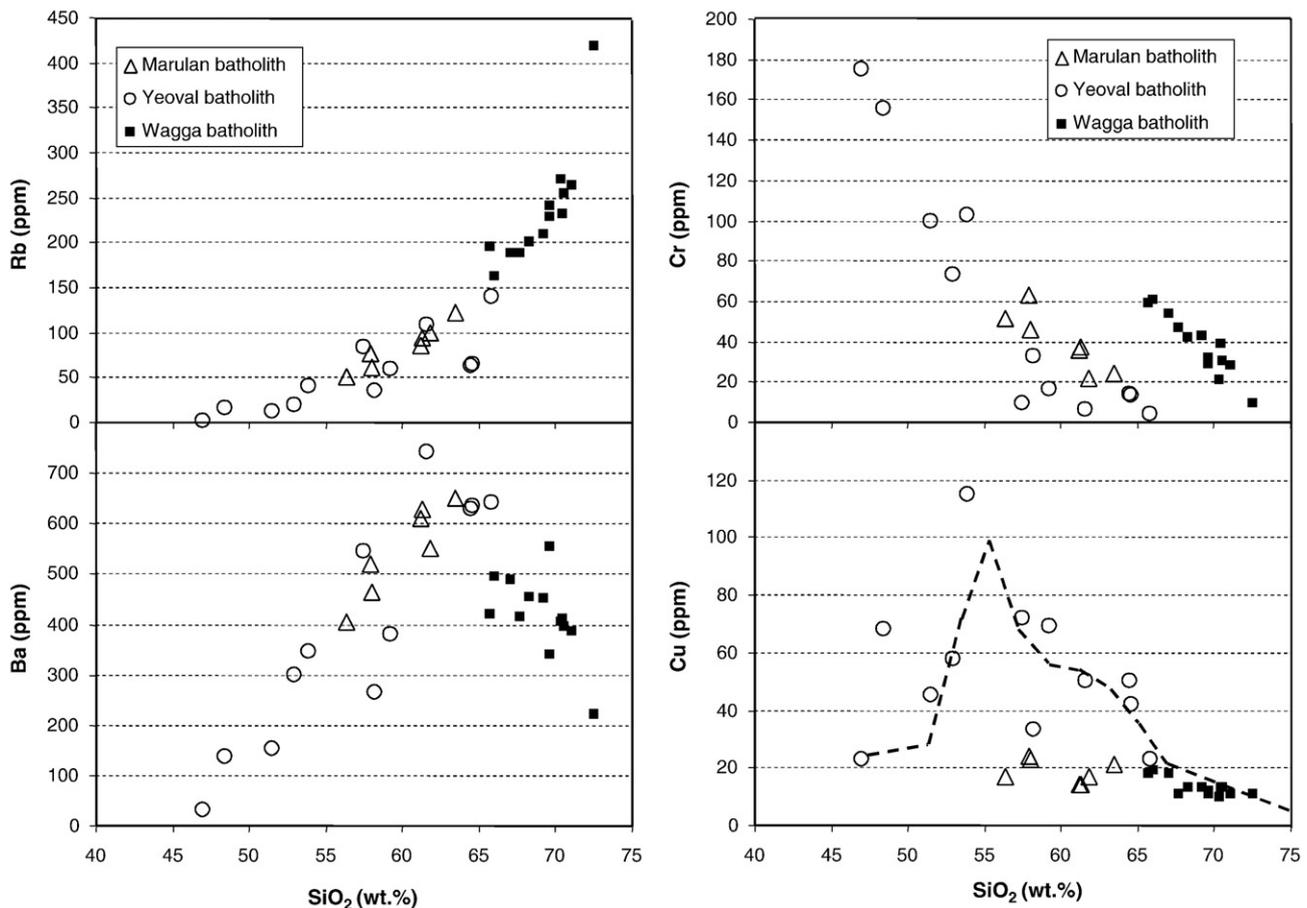


Fig. 2. Diagrams of Rb, Ba, Cr and Cu versus SiO<sub>2</sub> of rock samples from the Marulan, Yeoval and Wagga batholiths in SE Australia. The thick dashed line in the Cu diagram represents the mean Cu abundance calculated over 2% intervals of whole-rock SiO<sub>2</sub> from the Yeoval batholith (after Blevin and Chappell, 1992).

All beakers were PTFE (Savillex®). Double distilled reagents and >18.2 MΩ MQ water were used.

### 3.1. Dissolution

For each sample, 100 mg of powder was digested in 4 ml 1:1 mixture of HF:HNO<sub>3</sub> in a closed screw-top Savillex® teflon beaker on a hotplate at 130–140 °C for 2 days. After drying down, 2 ml 1:1 mixture of HF:HNO<sub>3</sub> was added and the closed Savillex beaker was heated for 1 day. Then the sample was heated at 130 °C overnight to dryness. Sometimes, there was some white residue left. This residue (Mg–Ca–F compounds, e.g., Yokoyama et al., 1999) was effectively decomposed by adding 3–5 drops of concentrated HClO<sub>4</sub> and heating at 170–180 °C to dryness (Croudace, 1980). 1 ml of 7 N HCl was then added to the beaker, and the sample was heated at 130 °C to dryness to expel the fluorine. This process was repeated 3 times to ensure that all cations were converted to chloride species. The final material was dissolved in 5 ml 7 N HCl and was ready for ion exchange chromatography.

### 3.2. Ion exchange chromatography

To minimize spectral and non-spectral effects of matrix elements (e.g., Albarède and Beard, 2004), which can severely affect the measured Cu isotope ratio, Cu must be separated from the matrix.

There are different techniques for separating transition metals from other elements, such as liquid extraction, precipitation (Bermin et al., 2006) and ion exchange chromatography (Maréchal et al., 1999; Archer and Vance, 2004; Chapman et al., 2006; Markl et al., 2006). Based on a study on Fe isotopes, (Schoenberg and von Blanckenburg, 2005) concluded that ion exchange chromatography is the most reliable in terms of yield, purity and low blank. Maréchal et al. (1999) published a protocol for separating Cu, Fe and Zn from geological samples with chlorine-based anion ion exchange resin (AG-MP1), which has been widely adopted by following researchers (Jiang et al., 2002; Zhu et al., 2002; Luck et al., 2003; Pichat et al., 2003; Mason et al., 2005; Pokrovsky et al., 2005). This protocol was modified by Archer and Vance (2004), Chapman et al. (2006) and Borrok et al. (2007). Another ion exchange method using a HBr-based anion resin (Dowex 1\*8) has also been reported (Markl et al., 2006).

In this study, we followed the methods of Maréchal et al. (1999) and Chapman et al. (2006). The protocol is summarized in Table 1. In each elution process, two 2 ml cuts before and after the main Cu cut were collected and analyzed on an Agilent 7500cs ICP-MS to ensure that matrix elements were separated from Cu and that there was no premature elution of Cu or tailing of the Cu peak.

Quantitative recovery of Cu was achieved (100.6±1.6%, 2σ, n=8), thus precluding Cu isotope fractionation during ion exchange chromatography (Maréchal and Albarède, 2002; Zhu et al., 2002). The total procedural blank for Cu was 2.65±0.66 ng (2σ, n=6), which is comparable with previous studies: 35±8 ng (Chapman et al., 2006), 5 ng (Maréchal et al., 1999), 2.2±1.2 ng (Bermin et al., 2006), and 0.2 ng (Markl et al., 2006).

Although the ion exchange procedure gave quantitative recovery of Cu and a low blank, the effectiveness of the method was checked by

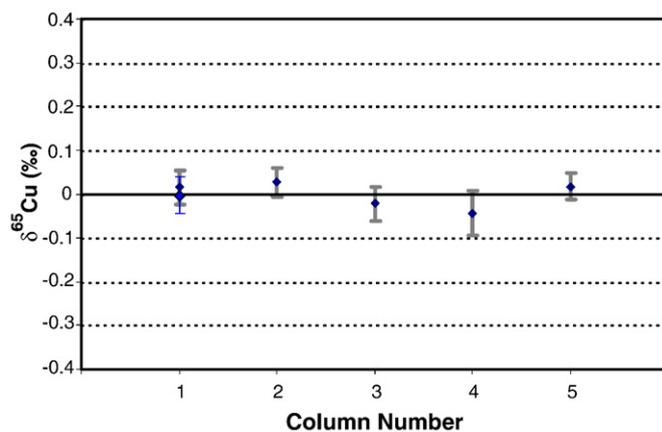
**Table 1**

Protocol for Cu purification by anion exchange

Eluent	ml	
7 N HCl+0.001% H <sub>2</sub> O <sub>2</sub>	1	Sample loading on the resin
7 N HCl+0.001% H <sub>2</sub> O <sub>2</sub>	9	Elution of the bulk sample matrix
7 N HCl+0.001% H <sub>2</sub> O <sub>2</sub>	2	"Left shoulder"
2 N HCl+0.001% H <sub>2</sub> O <sub>2</sub>	29	Cu eluted
2 N HCl+0.001% H <sub>2</sub> O <sub>2</sub>	2	"Right shoulder"
0.5 N HNO <sub>3</sub>	30	Rinse

Resin type: AG-MP-1, 100–200 mesh.

Column: Savillex Teflon, internal diameter: 6 mm.



**Fig. 3.** Plot of Cu isotope ratios of column-treated spiked "synthetic granite" relative to original in-house Cu standard. Error bars denote 2 standard deviations. Each aliquot of "synthetic granite" simulates a 10 mg load of dissolved granite with 50 ppm Cu, which contains: 800 μg Al, 150 μg Ca, 50 μg Mg, 200 μg Na, 400 μg K, 10 μg P, 300 μg Fe and 0.5 μg Cu (in-house Cu standard).

measuring the accuracy of Cu isotope ratios for two samples. Firstly, an in-house Cu standard solution was mixed with a solution of matrix elements made up in the approximate proportions of granite. This

**Table 2**

Cu isotope ratios of geological samples

Sample	Location (latitude, longitude)	Si (wt.%)	Cu (ppm)	δ <sup>65</sup> Cu (‰)	2σ (‰)	n
<i>I-type granites from Marulan batholith</i>						
NB003	34.908S,149.904E	63.47	21	0.114	0.053	5
NB006	34.848S,149.946E	56.38	17	-0.028	0.137	9
NB008	34.832S,149.953E	61.83	17	0.015	0.135	7
NB021	34.714S,150.041E	61.35	14	0.052	0.096	4
NB027	34.552S,150.055E	58.02	23	-0.042	0.042	6
NB029	34.652S,150.078E	61.16	14	0.125	0.052	6
NB033	34.518S,150.064E	57.90	24	0.092	0.074	6
<i>I-type granites from Yeoval batholith</i>						
ZB002	32.768S,148.635E	57.48	72	0.074	0.173	3
ZB003	32.794S,148.603E	61.59	50	0.004	0.130	3
ZB004	Not available	65.80	23	-0.045	0.231	3
ZB007	32.731S,148.656E	64.49	50	0.083	0.043	3
ZB008	32.710S,148.668E	64.63	42	0.137	0.078	4
ZB009	32.633S,148.724E	59.21	69	0.053	0.100	3
ZB015	32.637S,148.707E	53.94	115	0.947	0.065	6
ZB016	32.636S,148.702E	46.99	23	1.509	0.090	10
ZB129	32.591S,148.457E	58.23	33	-0.146	0.019	3
ZB132	32.614S,148.462E	53.01	58	0.060	0.118	3
ZB135	32.558S,148.475E	51.52	45	-0.003	0.061	3
ZB136	32.601S,148.472E	48.49	68	0.026	0.080	3
<i>S-type granites from Wagga batholith</i>						
VB001	35.093S,147.470E	68.35	13	-0.059	0.105	5
VB003	34.848S,147.514E	70.44	13	0.052	0.038	4
VB017	33.849S,146.856E	70.39	10	-0.040	0.121	3
VB030	34.886S,147.120E	66.06	19	0.105	0.082	10
VB032	34.878S,147.594E	69.60	12	0.205	0.072	7
VB037	34.635S,147.397E	69.19	13	0.101	0.065	3
VB038	34.547S,147.153E	65.78	18	-0.030	0.087	7
VB039	34.412S,147.190E	67.05	18	-0.070	0.158	6
VB065	35.086S,147.350E	67.71	11	0.149	0.293	5
VB099	35.812S,147.275E	69.63	11	-0.453	0.305	4
VB140	36.177S,147.577E	72.48	11	-0.463	0.100	3
VB143	36.171S,147.576E	70.55	13	0.091	0.245	5
VB160	36.281S,147.622E	71.07	11	0.043	0.305	6
<i>Chinese loess</i>						
Loess51YA	36.65N,109.18E			0.030	0.129	5
Loess23YIC	36.12N,110.23E			-0.017	0.059	4
<i>International rock standard</i>						
BIR				-0.018	0.096	31

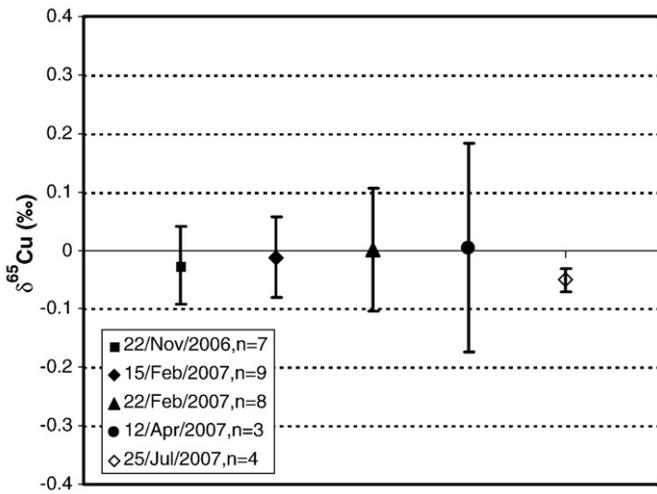


Fig. 4. Plot of  $\delta^{65}\text{Cu}$  for BIR-1 in different chemical and analytical sessions, the results are all consistent with the reported value ( $-0.03\%$ ) (Luck et al., 2003). Error bars denote 2 standard deviations.

“synthetic granite” was processed through ion exchange chromatography to separate Cu. As shown in Fig. 3, the column-treated Cu was isotopically identical to the original Cu solution. Secondly, an international rock powder standard, USGS basaltic reference material “BIR-1”, was processed along with every batch of samples analyzed in this study. Thirty-one measurements over 5 sessions gave a  $\delta^{65}\text{Cu}$  value of  $-0.02 \pm 0.10(2\sigma)\%$  (Table 2; Fig. 4), which is in agreement with the results from a previous study ( $-0.03\%$ , Luck et al., 2003).

### 3.2.1. Elution curves of different types of rocks

A series of elution experiments was carried out to check the influence of different bulk composition on the elution of Cu in ion exchange chromatography. In the elution experiments, the volume of resin was increased to 3 ml to better resolve the elution characteristics of the elements. Fig. 5 shows the elution curves for granodiorite (GSP-2), basalt (BCR-2) and peridotite (JP-1).

The peak shapes for Cu are all symmetrical, with no premature elution or tailing effect, which is in accord with the plate theory that successfully describes the elution of elements with ion exchange chromatography (Robards et al., 1994). The peak position of Cu in the three elution experiments is almost the same, suggesting that elution of Cu is not

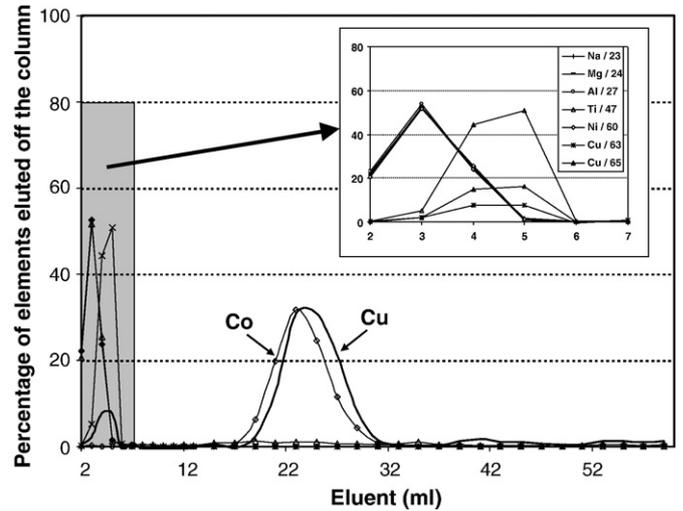


Fig. 6. Elution curve of basalt (BCR-2) with 2 ml resin (AG-MP-1).

affected by the chemical composition of the rock matrix. Therefore, this ion exchange chromatographic method is sufficiently robust for the separation of Cu from different types of rocks for isotopic measurement.

For the granite samples, the load of resin was reduced to 2 ml because it achieves near-perfect separation between Cu and the matrix (Fig. 6), and it reduces the amount of acid for elution by bringing forward the appearance, and reducing the broadening, of the Cu peak relative to that for the 3 ml load of resin.

### 3.2.2. Elution of Cu and influence of Co on isotopic measurement of Cu

It is shown in Figs. 5 and 6 that the majority (>99%) of the matrix elements (e.g., Mg, Ca, Na, K, Al) was eluted off the column in the first 6 ml of 7 N HCl. Nickel was also quantitatively eluted off in the first 6 ml of eluent because it has no affinity for the anion exchange resin (Kraus and Moore, 1953; Korkisch, 1989). Therefore, any Ni in the rock sample will not influence the measured isotopic ratio of Ni added to the Cu solution for mass bias correction.

Cobalt, however, cannot be separated from Cu with this technique (see Fig. 6) because the distribution coefficients for Co and Cu between the anion exchange resin and the 7 N HCl eluent are almost the same (Kraus and Moore, 1953). Because our rocks were pulverized using a tungsten carbide mill, which is well-known to introduce contamination of W, Ta, and Co (Hickson and Juras, 1986), there was a significant

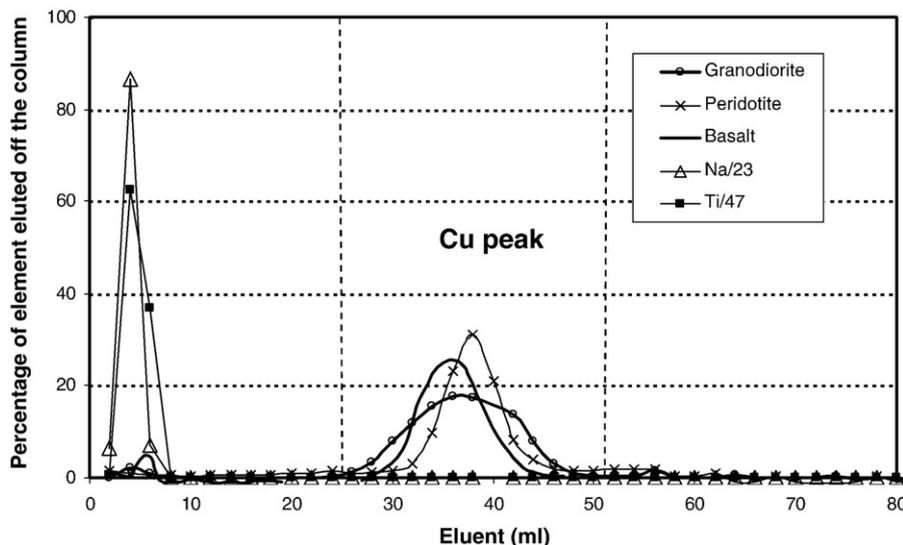


Fig. 5. Elution curves for peridotite (JP-1), basalt (BCR-2) and granodiorite (GSP-1). (Eluent is 7N HCl, load of resin is 3 ml AG-MP-1).

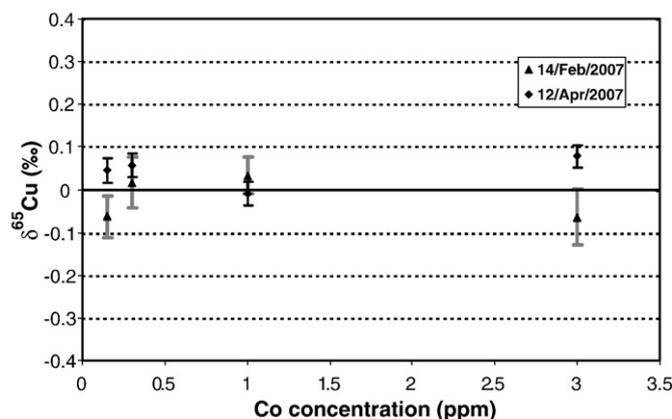


Fig. 7. Plot of Cu isotope ratios of Co-doped Cu solutions relative to original in-house Cu standard. Cu concentration is 300 ppb, error bars denote 2SE.

amount of Co remaining in the purified Cu cuts, with Co/Cu ratio ranging from 1.3 to 13. (Note that contamination of Cu from the tungsten carbide grinding device is negligible<sup>1</sup>).

Experiments were, therefore, performed using solutions of Cu doped with Co to assess the influence of Co on Cu isotope measurement (Fig. 7). The difference between measured Cu isotopic compositions of the doped and undoped Cu solutions varies from session to session, but the differences are all within the long-term reproducibility of the method, even at high Co concentration (Co/Cu = 10).

### 3.2.3. Potential interferences on Cu isotopes

The elution curves show the existence of peaks on the copper masses in the matrix cuts and the unnatural Cu ratio (mass65/mass63 near 1) indicates that these are due to polyatomic interferences.

There are a number of polyatomic interferences sharing the same mass number with the two isotopes of Cu, for example, <sup>23</sup>Na<sup>40</sup>Ar on mass 63. However, the strong correlation between the peak shapes of the elution curves for Ti and “Cu” (Fig. 6) implies that Ti is the major contributor to the polyatomic interferences on Cu. Titanium has five isotopes, from amu 46–50, which can combine with isotopes of O and H (most importantly <sup>16</sup>O and <sup>1</sup>H) to produce a variety of polyatomic oxide and hydroxide ion interferences on the two isotopes of Cu. The major polyatomic species, the oxides, of <sup>47</sup>Ti (7.44%) and <sup>49</sup>Ti (5.41%) would produce a <sup>49</sup>Ti<sup>16</sup>O/<sup>47</sup>Ti<sup>16</sup>O ratio of 0.73, which, while much closer to the measured ratio of mass65/mass63 (ca. 1) than the natural <sup>65</sup>Cu/<sup>63</sup>Cu ratio (0.45), suggests that there must be additional contributions of interfering polyatomic ions, particularly at mass 65. These are attributed to hydroxide (<sup>16</sup>O<sup>1</sup>H) of <sup>46</sup>Ti (8.25%) and <sup>48</sup>Ti (73.72%), which would produce a mass65/mass63 ratio of 8.94. Our observations are consistent with the viewpoint of Archer and Vance (2004), who stressed the influence of Ti and Fe on the measurement of Cu isotope ratios.

Based on the raw signal data of these Cu artifacts, the extent of the polyatomic interference of Ti on Cu isotopic ratio measurement can be estimated. Assuming that the <sup>63</sup>Cu signal at “4 ml” in Fig. 6 is caused solely by an oxide interference of <sup>47</sup>Ti, the ratio cps(<sup>63</sup>Cu)/cps(<sup>47</sup>Ti) represents the proportion of Ti atoms forming an interference on <sup>63</sup>Cu. A ratio of 0.00148 ± 0.00021 (*n* = 4) is obtained. Calculation using this ratio indicates that if the concentration of Ti in the solution is comparable with that of Cu, there will be about a 0.1% increase in the measured Cu isotopic ratio (δ<sup>65</sup>Cu). If hydroxide interferences are also taken into consideration, the measured isotopic offset for Cu will be 0.2%.

### 3.2.4. Column load and “limit of quantification”

The “limit of quantification” is defined as the lowest Cu concentration in rocks for which the Cu isotope ratio can be measured accurately and precisely using the methodology in this study.

If the Cu isotopic composition of the blank is similar to that of a sample, then the blank contribution will not offset the measured Cu isotopic composition for the sample. However, if the Cu isotopic composition of the blank is distinctively different from that of a sample, the measured isotopic composition will be changed by the blank contribution. The range of Cu isotope fractionation in natural systems is about 10‰ (e.g., Maréchal et al., 1999). Assuming that the isotopic compositions of a sample and blank are not different by more than this amount, the concentration of Cu in the sample should be 200 times more than the total procedural blank in order to ensure that the blank-induced isotopic offset is less than 0.05‰, roughly the internal precision of each measurement. For a chemical procedure with a total procedural blank of about 3 ng, 600 ng is the minimum quantity of Cu to guarantee the integrity of the isotopic measurement.

On the other hand, the amount of digested rock that can be loaded onto the column is limited. Chapman et al. (2006) suggested that column loading should be lower than 20% of the theoretical capacity of the resin. In 7 N HCl, the anions to be retained by AG-MP1 resin are FeCl<sub>4</sub><sup>-</sup>, CuCl<sub>3</sub><sup>-</sup>, CoCl<sub>3</sub><sup>-</sup>, ZnCl<sub>4</sub><sup>2-</sup> and ZnCl<sub>3</sub><sup>-</sup> (Kraus and Moore, 1953; Borrok et al., 2007). As Fe is by far the most abundant transition element in granite, the column loading can be estimated reasonably from the concentration of Fe in the rocks. The theoretical capacity for AG-MP1 resin is 1 meq/ml, and 2 ml resin has 2 × 10<sup>-3</sup> mol ion exchange capacity. Therefore, 0.4 × 10<sup>-3</sup> mol (22.4 mg) Fe is the upper limit for safe loading. Most rocks have less than 10 wt.% Fe, so 224 mg can be set as the maximum quantity of rock powder that can be loaded onto the resin for Cu isotope measurement.

The “limit of quantification” of the Cu isotope methodology described is, therefore, about 3 ppm Cu in the rock (600 ng/224 mg). Although this value is calculated in a conservative way, it should still be treated with great caution, because the true capacity of resin may, in practice, be lower than the theoretical value (Chapman et al., 2006). Careful calibration of the elution curve and monitoring of the “shoulder cuts” (Table 1) are vital when processing low Cu rock samples.

A lower “limit of quantification” can be achieved by decreasing the total procedural blank and increasing the loading capacity of the column. However, it is unlikely that the “limit of quantification” will be decreased significantly by using less resin. This is because, although using less resin will decrease the total procedural blank (Archer and Vance, 2004), it will also decrease the ion exchange capacity of the column.

### 3.3. MC-ICP-MS isotope ratio measurement

Sample and standard solutions were diluted to 300 ppb Cu in 2% HNO<sub>3</sub>, doped with 1.2 ppm Ni (NIST SRM 986). The use of Ni for external mass bias correction has been reported by previous researchers (Ehrlich et al., 2004; Markl et al., 2006). Copper and Ni isotopes (mass number from 60 to 66) were measured on a Nu Plasma HR-MC-ICP-MS at the GEMOC National Key Centre, Macquarie University. The instrument was operated in the “wet-plasma” mode using a Glass Expansion Micromist<sup>®</sup> nebulizer with an uptake rate of about 100 μl min<sup>-1</sup> and a Peltier-cooled cyclonic spray chamber. Other operating conditions of the instrument were similar to those described by Graham et al. (2004). Although the “wet-plasma” mode has lower sensitivity than the “dry-plasma” mode attained using a desolvating nebulisation system, it produced more accurate and reproducible results. Our data support the suggestion that desolvation systems may produce isotopic fractionation during sample introduction (Archer and Vance, 2004; Kamenov et al., 2004; Bermin et al., 2006; Schonbachler et al., 2007).

<sup>1</sup> [http://www.ga.gov.au/minerals/research/methodology/geochem/grind\\_contam\\_test.jsp](http://www.ga.gov.au/minerals/research/methodology/geochem/grind_contam_test.jsp).

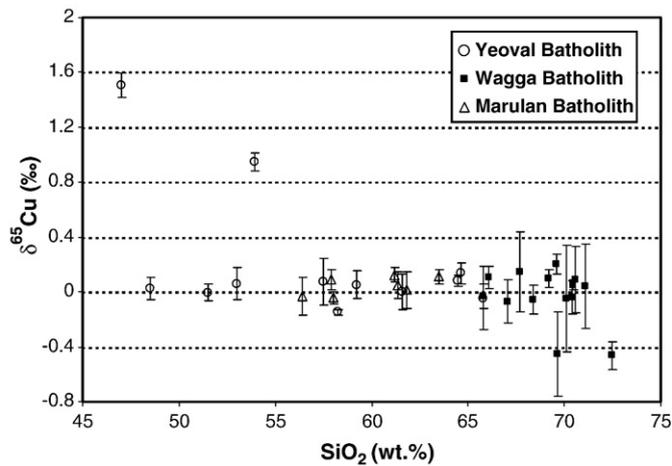


Fig. 8. Variation of  $\delta^{65}\text{Cu}$  against  $\text{SiO}_2$  content for rocks from the Lachlan Fold Belt. Error bar denote 2 standard deviations.

The total signal intensity for 300 ppb Cu varied from 3 V to 5 V in different analytical sessions. Each measurement included 20 s for measurement of on-peak acid background and  $30 \times 5$  second integrations for the sample. The total signal intensity of Cu for the acid background was below 10 mV. A combination of sample-standard bracketing (SSB) and empirical external normalization (EEN) was used for correcting instrumental mass fractionation. Mass fractionation was first corrected using the  $^{62}\text{Ni}/^{60}\text{Ni}$  ratio ( $^{62}\text{Ni}/^{60}\text{Ni}_{\text{true}} = 0.1386$ ) with the exponential mass bias function (Maréchal et al., 1999). The delta values were then calculated by calibrating the mass bias-corrected Cu isotope ratios against the mean of adjacent standards. Internal precision for each measurement was commonly better than  $\pm 0.05\%$  (2SE) for  $\delta^{65}\text{Cu}$ . The long-term external reproducibility over ten months, monitored by measuring the isotopic difference between our in-house Cu standard (dissolved Cu turnings) and the international Cu standard (NIST SRM 976 Cu), was  $0.09\%$  ( $2\sigma$ ,  $n = 105$ ). The in-house Cu standard has a  $\delta^{65}\text{Cu}$  value of  $0.06 \pm 0.09\%$  ( $2\sigma$ ,  $n = 105$ ).

Each sample was measured more than once and in different analytical sessions; duplicate or even triplicate analyses (including separate dissolution and column chemistry) were performed for the samples with abnormal values or with large analytical errors.

#### 4. Results

Copper isotope ratios are reported in Table 2 for the granites and loess (in per mil relative to NIST SRM 976). Major and trace element data for the granites measured by XRF are also reported. Most of the rocks show a limited variation in  $\delta^{65}\text{Cu}$  values with an overall range for the I-type and S-type granites from  $-0.46\%$  to  $1.51\%$ , and a median value of  $0.05\%$ . Excluding two outliers (ZB015 and ZB016), the rest of granite samples give mean  $\delta^{65}\text{Cu}$  values for the I-type and S-type granites of  $0.03 \pm 0.15\%$  ( $2\sigma$ ,  $n = 17$ ) and  $-0.03 \pm 0.42\%$  ( $2\sigma$ ,  $n = 13$ ) respectively. The  $\delta^{65}\text{Cu}$  values of the two loess samples from northern China are close to zero ( $0.03\%$  and  $-0.02\%$ ).

The seven I-type granite samples from the Marulan batholith show a limited variation of  $\delta^{65}\text{Cu}$ , from  $-0.04\%$  to  $0.13\%$ . These values almost overlap each other within analytical errors. The samples from the I-type Yeoval Batholith of the Boggy Plain Supersuite show very similar  $\delta^{65}\text{Cu}$  values. Despite the large variation in bulk rock chemical composition, the majority of samples show a tight distribution of  $\delta^{65}\text{Cu}$  values around zero (from  $-0.15\%$  to  $0.14\%$ ). Two mafic samples (ZB015 and ZB016) have significantly heavier Cu isotope signatures ( $0.95\%$  and  $1.51\%$ , respectively). Ignoring these two mafic samples, there is no discernible trend of  $\delta^{65}\text{Cu}$  with  $\text{SiO}_2$  content in the two I-type suites (Fig. 8).

The majority (11 out of 13) of the S-type granites have  $\delta^{65}\text{Cu}$  values in the range of  $-0.06\%$  to  $0.21\%$ , with samples VB099 and VB140 having lighter compositions of  $-0.45\%$  and  $-0.46\%$  in  $\delta^{65}\text{Cu}$ . VB140 is interpreted to be the most fractionated member of the batholith, and thus its low  $\delta^{65}\text{Cu}$  value may be a consequence of late stage magmatic processes. Otherwise as with the I-type granites, there is no correlation between  $\delta^{65}\text{Cu}$  and  $\text{SiO}_2$  in the S-type suite (Fig. 8).

#### 5. Discussion

##### 5.1. Cu isotope fractionation in high-temperature magmatic processes

The general consistency of Cu isotope signatures between MORB (Ben Othman et al., 2006), OIB (Luck et al., 2003), continental basalt (Archer and Vance, 2004), peridotite (Ben Othman et al., 2006) and granites (this study) implies a lack of Cu isotopic fractionation during Earth's differentiation. This is consistent with the viewpoint of Albarède (2004).

On a smaller scale, the absence of Cu isotope fractionation in magmatic processes is indicated by the samples from the three batholiths analyzed in this study. Previous work has established that the magmas from these batholiths underwent fractional crystallization, albeit the temperature of the magmas and fractionation processes were different (e.g., Chappell and White, 1992; Chappell et al., 1998). There is a lack of systematic change in Cu isotope ratio with evolution of the magma from mafic to felsic compositions in these batholiths (Figs. 8 and 9), strongly suggesting that there is no Cu isotope fractionation during magmatic processes, at least as a result of fractional crystallization.

The absence of Cu isotope fractionation in magmatic processes could be explained by the following possible scenarios: (1) there is no equilibrium Cu isotopic fractionation between different hosts of Cu in magmatic systems at high temperatures; (2) Cu only exists in one major phase in a magmatic system so there is no partitioning of isotopically different Cu between hosts of Cu in magmatic systems.

Copper isotope fractionation between different phases (or hosts) has been reported; for example, chalcopyrite–bornite (Larson et al., 2003; Maher and Larson, 2007) and pyroxenite–garnet (Ben Othman et al., 2006). However, Ben Othman et al. (2006) also suggested that the difference in Cu isotope ratio between olivine and pyroxene separated from peridotite and lherzolite is small.

The effect on the isotopic composition of Cu substituting into the lattice of a silicate mineral is poorly understood, both experimentally and theoretically. Nevertheless, equilibrium Cu isotopic fractionation between silicate minerals of a rock seems unimportant when

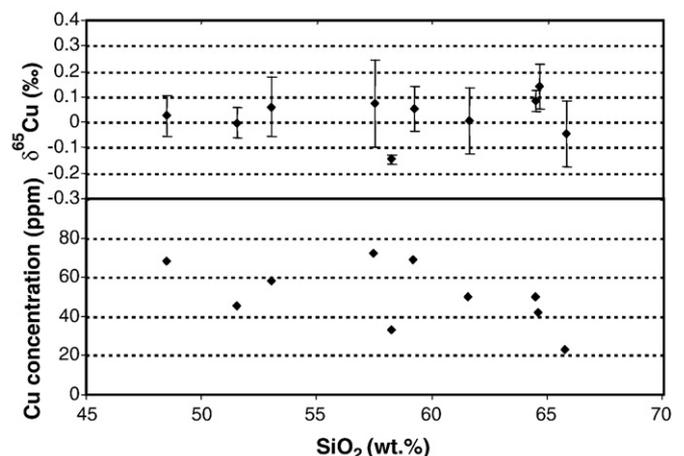


Fig. 9. Variations in  $\delta^{65}\text{Cu}$  and Cu concentration with  $\text{SiO}_2$  in the I-type Yeoval Batholith of the Lachlan Fold Belt, Australia. Two outliers (ZB015 and ZB016) are not included. Error bars denote 2 standard deviations.

considering the elemental budget of Cu in different hosts in rock. As a chalcophile element, Cu has a high partition coefficient between sulfide and silicate matrix for mafic rocks (Peach et al., 1990). Therefore, sulfide minerals (e.g., chalcopyrite, cupiferous pyrrhotite) are the dominant hosts of Cu in a rock (Candela and Davis, 2003). These Cu-rich sulfides exist in rocks either interstitially, or as inclusions in silicate minerals (Luguet et al., 2003); the latter may be the reason for the large scattering of Cu concentrations reported in silicate minerals (Zemann and Wedepohl, 1974).

The Cu concentration of a granite decreases as it evolves towards a felsic end member in a suite. One example is the Yeoval batholith, in which there is a general trend of decreasing Cu content accompanying the increasing SiO<sub>2</sub> content (Fig. 9). This has been explained by two mechanisms: (1) sulfide precipitation caused by a drop in S solubility as a magma becomes more felsic, which is almost self-evident because of the dominance of sulfide in Cu speciation in rocks; and (2) loss of Cu by the release of Cu-bearing fluid and gas during crystallization (Blevin and Chappell, 1992), as revealed by recent laser ablation analyses of fluid and melt inclusions in magma systems (Sun et al., 2004; Halter et al., 2005).

To summarize, there are three main hosts of Cu in magmatic systems: sulfides, silicate melts and fluid phases (gas and brine). This fact is not in agreement with assumption of scenario 2 (Cu only exists in one major phase in a magmatic system thus precluding partition of Cu between hosts of Cu in magmatic systems). Therefore, scenario 2 can be discarded as the explanation of the observed absence of Cu isotope fractionation. Scenario 1 (absence of significant equilibrium Cu isotopic fractionation between different hosts of Cu in magmatic systems) is preferred because, if there is any significant Cu isotopic fractionation between the reservoirs, Rayleigh processes during fractional crystallization will magnify it.

Seo et al. (2007) performed quantum chemical calculations of the isotopic fractionation of Cu between different species from 0 °C to 600 °C. Their work suggests that the isotopic composition of the vapour species of Cu (Cu<sub>3</sub>Cl<sub>3</sub>) is significantly heavier than other species, with equilibrium isotopic fractionation of Cu isotopes ( $\Delta^{65}\text{Cu}$ ) between Cu<sub>3</sub>Cl<sub>3</sub> and major Cu species (Cu(HS)<sub>2</sub> and CuCl<sub>2</sub>) in solution at 600 °C being as large as 0.45‰. The extent to which Cu can be removed as a vapour from a magma is illustrated by a study of melt inclusions from the Bajo de la Alumbrera porphyry deposit by Halter et al. (2005). They demonstrated that the original andesitic melt contained about 100 ppm Cu, which is four to five times the Cu content of the bulk rock. The authors suggested that the majority of the Cu has been lost during magma degassing upon eruption (Halter et al., 2005).

In summary, the theoretical consideration by Seo et al. (2007) suggests that there can be significant Cu isotope fractionation between Cu species, especially between solution species and some vapor species. Also, the investigation by Halter et al. (2005) suggests that Cu loss by degassing during magma evolution can be significant. In order to constrain the magnitude of possible Cu isotope fractionation by degassing during magmatic processes, we have constructed a simplified Rayleigh model. In this model, we assume: (1) there is no Cu isotope fractionation between Cu in melt and Cu in crystallized rocks, as Cu may exist in sulfide form in both of them; (2) during the whole fractional crystallization process, Cu concentrations of melt and crystallized rocks are the same; that is, we propose that any decrease in Cu concentration in the melt is caused solely by release of Cu during magma degassing, and this process is recorded in the crystallized rocks; (3) the degassing process is a Rayleigh process, and during this process, the factor of Cu isotope fractionation between the vapour and melt remains constant; (4) the Cu isotope ratio of the starting magma is 0.0‰.

Fig. 10 shows the influence of the degree of degassing and isotope fractionation factor on the isotope ratio of Cu remaining in the melt, which will be recorded according to assumption (2) in our model. Data from the Yeoval Batholith are plotted on the diagram. The initial Cu

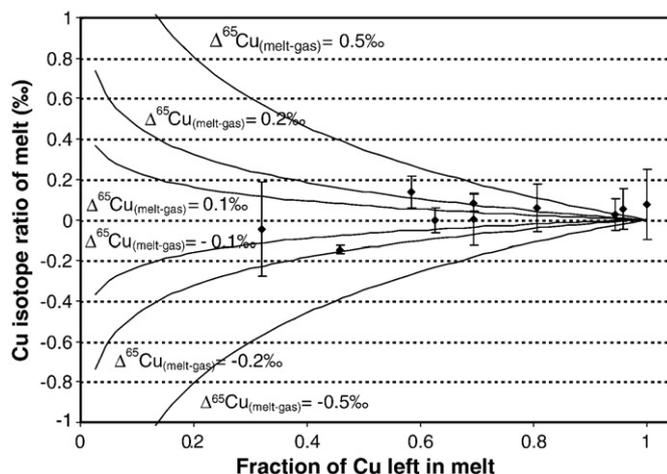


Fig. 10. Model for the release of Cu solely by Rayleigh degassing and the response of the Cu isotope signature of the melt to the Cu isotope fractionation factor and degree of Cu loss. Data points are from the Yeoval Batholith. Error bars denote 2 standard deviations.

concentration of the magma is arbitrarily set as 72 ppm, the second highest Cu concentration in the sample set. We did not use the Cu concentration of the sample with the highest Cu concentration, because this sample seems to have been altered (see next section). The data points do not show a clear trend on the diagram, which may be due to over-simplification of our model. The degassing process may be one end member of processes that produced the trend of Cu content versus silica content in the Yeoval Batholith. The real magmatic process is likely to have been more complex than the process we assumed. Nevertheless, the diagram provides the following constraint: that according to our simplified model, the Cu isotope fractionation between vapour and melt is restricted to within  $\pm 0.2\%$ .

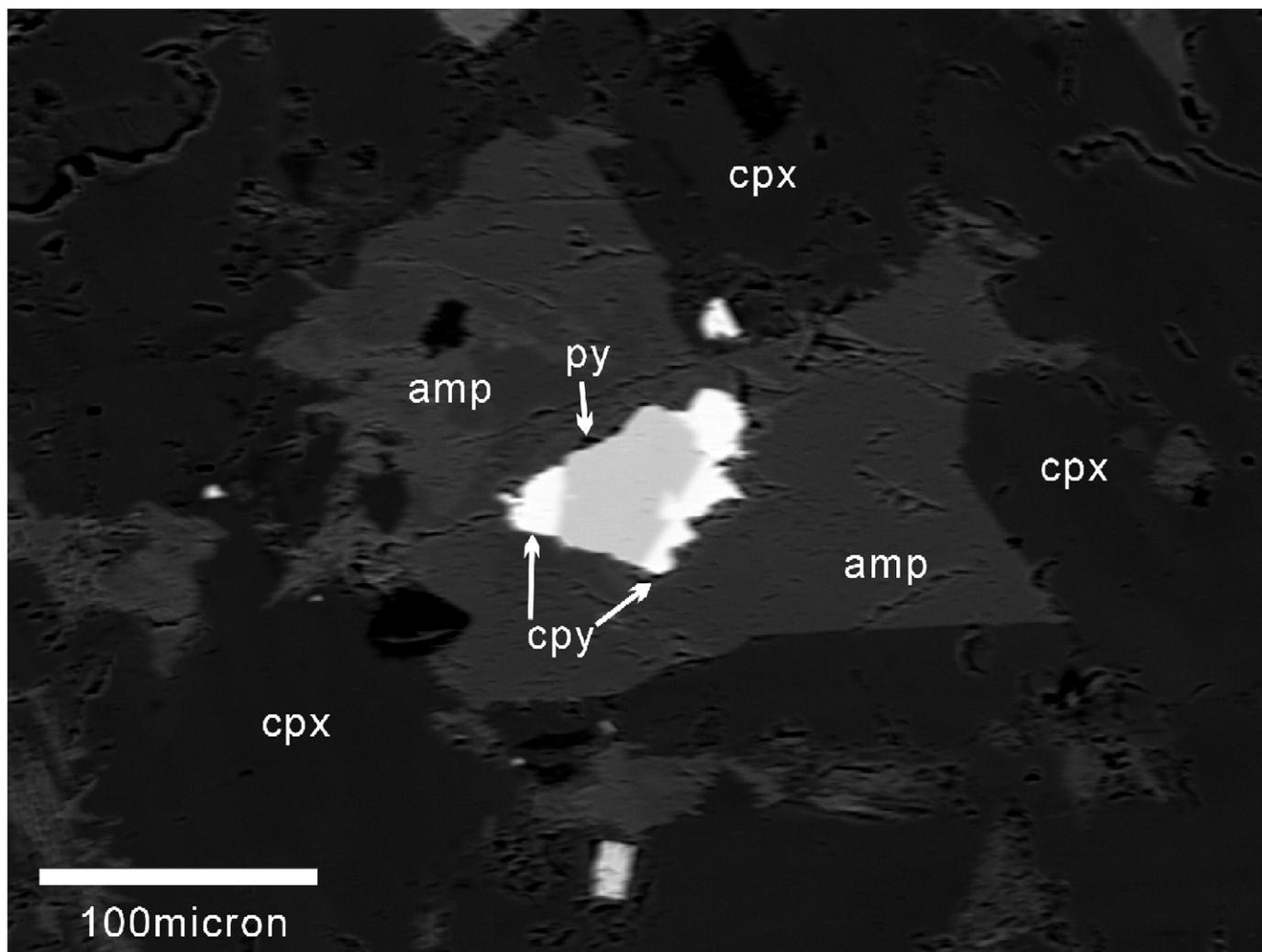
Extrapolation of the data by Seo et al. (2007) suggests that the Cu isotope fractionation between Cu<sub>3</sub>Cl<sub>3</sub> and major Cu species (Cu(HS)<sub>2</sub>) in solution is larger than 0.2‰, even at a temperature of 1200 °C. However, another vapour phase of Cu (CuCl(H<sub>2</sub>O)) has a lower fractionation factor than Cu<sub>3</sub>Cl<sub>3</sub>. Therefore, during magma degassing, Cu<sub>3</sub>Cl<sub>3</sub> cannot be the only species in the vapour.

## 5.2. Cu isotope heterogeneity and the processes recorded in rocks

Despite the general uniformity of Cu isotope ratios of the samples within each I-type suite, there are samples with anomalous Cu isotope signatures. The two samples (ZB015 and ZB016) with abnormally heavy Cu isotopic values from the Yeoval Batholith are located close to each other (about 700 m apart). In addition, the Cu concentration of one of the sample (ZB015) seems to be anomalously high (50% more Cu than samples with similar SiO<sub>2</sub> content within the suite).

The best explanation for the coincidence of these facts is that there has been a localized hydrothermal event in the area of the ZB015 and ZB016 sampling sites; i.e., isotopically heavier Cu from a hydrothermal fluid overprinted this area and caused Cu isotope anomalies. The  $\delta^{65}\text{Cu}$  value of ZB016 is higher than ZB015, suggesting that the proportion of the total Cu added by hydrothermal activity to ZB016 is higher. The evidence for hydrothermal alteration in ZB016 is provided by the replacement of clinopyroxene by amphibole. Additionally, electron microprobe analysis and BSE imaging of this sample have revealed the existence of chalcopyrite occurring interstitially to the amphibole and replacing pyrite in ZB016, providing direct evidence for hydrothermal activity (Fig. 11).

Copper is a trace element in rock, and interstitial sulfide is an important reservoir of Cu in rock. It is suggested that hydrothermal fluid may have infiltrated the rocks along crystal boundaries between the silicate minerals and, as sulfides are more reactive than most silicate



**Fig. 11.** BSE image of granite sample "ZB016". The major sulfide grain in the middle of the image occurs along a micro-crack that cuts through the hosting hornblende. The embayed outline of pyrite suggests that it has been replaced by chalcopyrite. The zigzag boundary between chalcopyrite and hornblende implies that the chalcopyrite was formed after the formation of the crack and is thus crack-filling. Cpx=clinopyroxene; amp=amphibole; py=pyrite; cpy=chalcopyrite.

minerals, overprinted the interstitial sulfides without disturbing the silicate minerals significantly. Thus, it is entirely possible that the Cu isotope signature was changed without obvious textural evidence for significant alteration or chemical evidence for metasomatism of the sample with mobile elements (e.g., Rb). We further conjecture that Cu isotope geochemistry may be a sensitive tool for detecting subtle secondary alteration processes in rocks, and that it may be a promising tool for prospecting for buried mineralizing systems.

The range of  $\delta^{65}\text{Cu}$  of rocks from the S-type Wagga Batholith is 0.7‰, which, despite the large analytical errors for some samples, represent analytically significant heterogeneity in the Cu isotopes within the batholith. The variation in the Cu isotope ratios seems to be regional, as the rocks with heavy and light Cu isotope signatures show spatial clustering. Granite samples located between the latitudes of 34.6°S and 35.1°S in the Wagga Batholith all have positive values ( $\delta^{65}\text{Cu} > 0$ ), while in the south and north part of the area, the granites generally show negative values ( $\delta^{65}\text{Cu} < 0$ ). As discussed in the previous section, magma fractionation processes do not produce Cu isotope fractionation. Therefore, this regional heterogeneity in Cu isotopes can be interpreted as an expression of source heterogeneity although secondary alteration after crystallization of the magmas cannot be ruled out.

Data both from field samples and laboratory experiments have demonstrated that the most significant Cu isotope fractionation in natural systems is produced by redox processes (Ehrlich et al., 2004;

Rouxel et al., 2004; Mathur et al., 2005; Asael et al., 2006; Markl et al., 2006; Asael et al., 2007). During redox reactions at low temperature (<100 °C), cupric Cu ( $\text{Cu}^{2+}$ ) is 2.5–3.5‰ isotopically heavier than cuprous Cu ( $\text{Cu}^+$ ) in  $\delta^{65}\text{Cu}$  (Asael et al., 2007). Therefore, the processes of weathering and diagenesis can potentially produce significant Cu isotope fractionation in weathered rocks (Rouxel et al., 2004) and sediments (Petit et al., 2006). When the weathering products of rocks are partially melted to produce an S-type granitic magma (Chappell and White, 1992), the magma will inherit the fractionated Cu isotope signature of the source material. Based on elemental geochemistry, Chappell and White (1992) argued that S-type granites are derived from more heterogeneous source materials than I-type granites. This conclusion is consistent with the variation of the Cu isotope ratios in the S-type granite revealed in this study although the possibility that the isotopic variations are related to secondary alteration of these rocks cannot be eliminated.

The exact reason(s) for the anomalous Cu isotope signatures of granitic rocks, and its potential for mineral exploration are interesting topics for future study.

### 5.3. Cu isotope baseline of upper continental crust

A number of studies have proposed a baseline Cu isotopic composition of bulk Earth. A  $\delta^{65}\text{Cu}$  value close to 0‰ has been

proposed based on the measurement of Cu isotope ratios in relatively primitive and undifferentiated igneous rocks (mantle peridotite and basalt). The  $\delta^{65}\text{Cu}$  value of basalts from Reunion Island and Iceland are  $-0.03\%$  and  $-0.10\%$ , respectively (Luck et al., 2003). The  $\delta^{65}\text{Cu}$  value for Columbia River basalt, BCR-1, is  $0.07 \pm 0.08\%$  (Archer and Vance, 2004), and the  $\delta^{65}\text{Cu}$  value of mantle peridotite generally varies between  $0.0\%$  and  $0.18\%$  (Ben Othman et al., 2006).

Baseline values of continental crust have also been estimated. In the pioneering study of Zhu et al. (2000), it was suggested that igneous rocks have homogeneous Cu isotope compositions, based upon measurements on chalcopyrite samples hosted in igneous rocks worldwide, which show similar  $\delta^{65}\text{Cu}$  values (1‰ of variation in  $\delta^{65}\text{Cu}$ , mostly within  $-0.23\%$  and  $+0.13\%$ ). This viewpoint was supported by Larson et al. (2003), who reported a range in  $\delta^{65}\text{Cu}$  of 1.5‰ for chalcopyrite samples from mafic intrusions with most values clustering between  $-0.10\%$  and  $-0.20\%$ . However, this approach to estimating the Cu isotopic composition of igneous rocks may be flawed as sulfide minerals in rocks may be produced by hydrothermal processes which can introduce large variations in Cu isotope signatures (e.g., Graham et al., 2004; Maher and Larson, 2007; this study).

This study is the first systematic measurement of the Cu isotope composition of granites from upper continental crust. These data are shown in Figs. 8 and 12. A comparison between the Cu isotope data of granites and those of other geological reservoirs is shown in Fig. 13. The mean Cu isotopic value of all granites is  $\delta^{65}\text{Cu} = 0.01 \pm 0.30\%$  ( $2\sigma$ ,  $n=30$ , ZB015 and ZB016 excluded). The granites come from an area of  $400 \times 300 \text{ km}^2$  and have a wide chemical composition ( $\text{SiO}_2$  from 48.49 wt.% to 72.48 wt.%; Fig. 8) and distinct source materials (Al saturation index from 0.71 to 1.35; Fig. 12). Therefore, this value can be viewed as the first estimation (albeit preliminary) of the Cu isotope ratio of the crystalline part of upper continental crust.

The Cu isotopic composition of the non-crystalline part of upper continental crust (sedimentary rocks) has not been determined in this study. Very few measurements have been made on sediments and scant data have shown that  $\delta^{65}\text{Cu}$  of sediments can be several per mil off 0‰ (Albarède, 2004). A much larger variation in  $\delta^{65}\text{Cu}$  values of sediments is expected because of redox reactions that happen in weathering and diagenetic processes. Redox processes are well-known to produce significant Cu isotopic fractionation (Zhu et al., 2002; Ehrlich et al., 2004; Rouxel et al., 2004; Mathur et al., 2005; Asael et al., 2006; Markl et al., 2006; Petit et al., 2006; Asael et al., 2007). Therefore, it is impossible to estimate the average Cu isotopic composition of upper crust by analyzing fine-grained clastic sediments such as shales. However, we propose that, despite the expected large variation of  $\delta^{65}\text{Cu}$  value of sediments, the weighted average  $\delta^{65}\text{Cu}$  value of all sediments on Earth is still close to 0‰. Because igneous rocks from mantle and crust all have  $\delta^{65}\text{Cu}$  values around 0‰

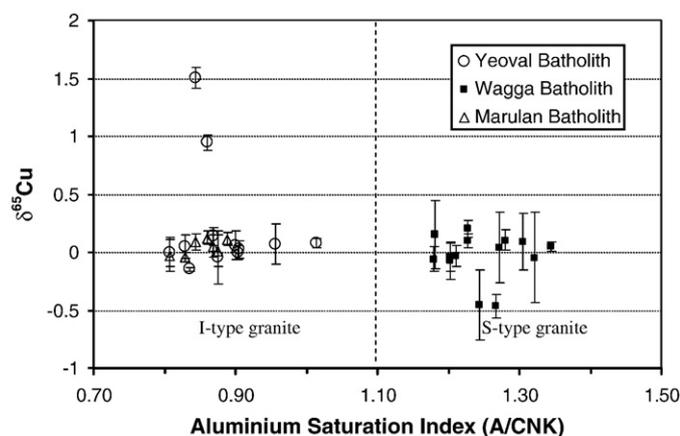


Fig. 12. Plot of  $\delta^{65}\text{Cu}$  for granitic rocks from Lachlan Fold Belt as a function of Aluminium Saturation Index. Error bar denotes 2 standard deviation.

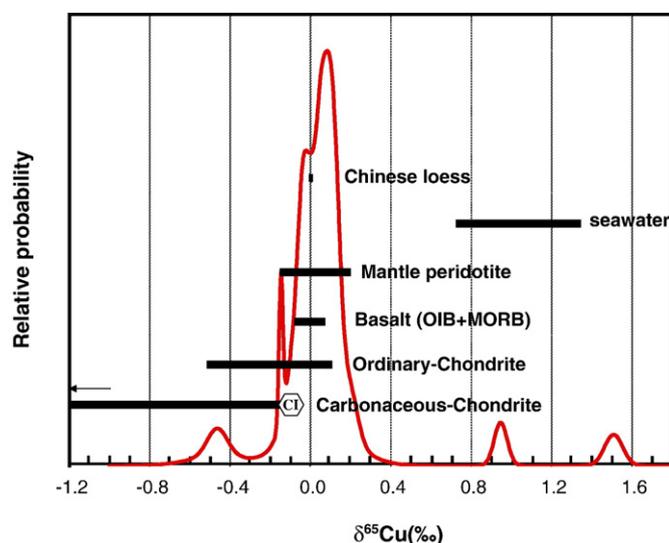


Fig. 13. Cumulative probability diagram of  $\delta^{65}\text{Cu}$  of granites from Lachlan Fold Belts and the range of  $\delta^{65}\text{Cu}$  of other geological reservoirs. The probability diagram is produced using Isoplot. Data source: chondrite (Luck et al., 2003), basalts (Luck et al., 2003; Archer and Vance, 2004), mantle peridotite (Ben Othman et al., 2006), seawater (Bermin et al., 2006), Chinese loess (this study).

(Luck et al., 2003; Archer and Vance, 2004; Ben Othman et al., 2006; and this study), and all sediments ultimately originate from igneous rocks, the mass balance in Cu isotopes constrains a  $\delta^{65}\text{Cu}$  value near 0‰ for the weighted average of all sediments. This estimate is partly confirmed by the average  $\delta^{65}\text{Cu}$  value of  $-0.03 \pm 0.42\%$  ( $2\sigma$ ,  $n=13$ ) for the S-type granite measured in this study, because S-type granite is produced by partial melting of sediments (Chappell and White, 1992).

Although sedimentary rock covers 75% of the Earth's surface, it only constitutes 5% of the volume of the crust (Pettijohn, 1975). Therefore, although the Cu isotopic composition of sediments may vary, it is unlikely to make a significant difference to an estimate of the Cu isotopic baseline for the bulk crust. The Cu isotopic signature of the crust can reasonably be represented by that of the crystalline part of upper continental crust, which is proposed in this study ( $\delta^{65}\text{Cu} = 0.01 \pm 0.30\%$ ,  $2\sigma$ ,  $n=30$ ).

An estimate of the Cu isotopic composition of upper continental crust can be derived from the analyses of the loess. Loess is an aeolian deposit that originated from desert regions and glacial outwash. During its formation, mechanical abrasion of large geographical areas occurred, while the effects of chemical weathering were limited (Gao and Ding, 2008). Thus, loess has been used for estimating the average chemical and isotopic composition of the upper continental crust (e.g., Taylor et al., 1983; Teng et al., 2004). The Cu isotope signatures of two Chinese loess samples are similar to those of the granites, confirming an upper crustal Cu isotope baseline value around 0.0‰.

Our contribution to establishing the baseline Cu isotopic composition of the continental crust is a first step based on limited data. A larger database is needed to establish a definitive value.

## 6. Concluding remarks

- (1) An effective and robust chemical procedure for Cu purification is vital for determination of Cu isotope ratio of rocks. The influence of Ti should receive more attention, especially for high-Ti rocks.
- (2) Although Co does not seem to produce a matrix effect in Cu isotope determination, we suggest avoiding using tungsten carbide for crushing rocks because one-step chromatography cannot effectively separate the Co contaminant from Cu.
- (3) A variation of 2‰ in Cu isotope ratios in granitic rocks has been discovered. The majority of this variation is attributed to secondary processes, which suggests that Cu isotope geochemistry may be a useful tool for detecting and studying hydrothermal alteration.

- (4) High-temperature magmatic processes produce negligible Cu isotope fractionation.
- (5) Unlike I-type granites, S-type granites show measurable Cu isotopic variation that may reflect Cu isotopic variability of the sedimentary protolith resulting from redox reactions during erosion/deposition/diagenesis. Thus Cu isotopes may be useful for studying source heterogeneity for granitic rocks.
- (6) The Cu isotopic baseline for granites, as estimated from the Cu isotope ratio of three I-type and S-type granites from the Lachlan Fold Belt, is  $\delta^{65}\text{Cu} = 0.01 \pm 0.30\%$  ( $2\sigma$ ,  $n = 30$ ).

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