University of Wollongong

Research Online

Faculty of Science, Medicine and Health -
Papers: part A

Faculty of Science, Medicine and Health

1-1-2012

The silicon isotope composition of granites

Paul S. Savage
University of Oxford

R Bastian Georg
Nottingham Trent University

Helen M. Williams
University of Durham

Simon P. Turner
Macquarie University

Alex N. Halliday
University of Oxford

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/smhpapers>

Recommended Citation

Savage, Paul S.; Georg, R Bastian; Williams, Helen M.; Turner, Simon P.; Halliday, Alex N.; and Chappell, Bruce W., "The silicon isotope composition of granites" (2012). *Faculty of Science, Medicine and Health - Papers: part A*. 45.
<https://ro.uow.edu.au/smhpapers/45>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

---

The silicon isotope composition of granites

Abstract

Because weathering results in preferential incorporation of the lighter Si isotopes into clay minerals, the Si in magmas derived from (meta)sedimentary lithologies enriched in such phases should also be isotopically light, relative to melts derived from igneous sources. With the advent of new high precision techniques it should therefore be possible to resolve such differences. Hence, Si isotopes have to potential to distinguish between, and characterise, different magmatic source regions.

To explore this, here we report the Si isotopic compositions of a suite of Phanerozoic I-, S- and A-type granites and mineral separates, as well as samples of associated country rock. The whole-rock data fall between $\delta^{30}\text{Si} = -0.40$ and $-0.11 \pm 0.04\text{‰}$ (95% s.e.). This range is more limited than that defined by previous low precision measurements of granites, but is significantly broader than that displayed by more recent, high precision, measurements of high-Si extrusive igneous rocks. As predicted, S-type granites are, on average, isotopically lighter than I- and A-type samples, and negative correlations with alumina saturation index (ASI) values and initial $^{87}\text{Sr}/^{86}\text{Sr}$ provide evidence that Si isotope variations in granites can be explained by variable incorporation of an enriched sedimentary component. However, the relatively small isotopic perturbations and apparent degree of overlap between granite affinities suggest that Si isotopes are not as sensitive to sedimentary input, relative to more established proxies such as, for example, O isotopes. The average Si isotope value of all granites analysed in this study is $\delta^{30}\text{Si} = -0.23 \pm 0.15\text{‰}$ (2 s.d.), which is entirely consistent with a recently published estimate for the continental crust, based on an andesitic bulk composition and the well defined relationship between Si isotopes and magmatic fractionation.

Keywords

silicon, isotope, granites, composition

Publication Details

Savage, P. S., Georg, R. Bastian., Williams, H. M., Turner, S. P., Halliday, A. N. & Chappell, B. W. (2012). The silicon isotope composition of granites. *Geochimica Et Cosmochimica Acta*, 92 (N/A), 184-202.

Authors

Paul S. Savage, R Bastian Georg, Helen M. Williams, Simon P. Turner, Alex N. Halliday, and Bruce W. Chappell

The silicon isotope composition of granites

Paul S. Savage^{a,*}, R. Bastian Georg^b, Helen M. Williams^c, Simon Turner^d,
Alex N. Halliday^a, Bruce W. Chappell^{e,1}

^a Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, United Kingdom

^b Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, Ont., Canada K9J 7B8

^c Department of Earth Sciences, Durham University, Science Labs, Durham DH1 3LE, United Kingdom

^d Department of Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia

^e School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW 2522, Australia

Received 10 January 2012; accepted in revised form 19 June 2012; available online 2 July 2012

Abstract

Because weathering results in preferential incorporation of the lighter Si isotopes into clay minerals, the Si in magmas derived from (meta)sedimentary lithologies enriched in such phases should also be isotopically light, relative to melts derived from igneous sources. With the advent of new high precision techniques it should therefore be possible to resolve such differences. Hence, Si isotopes have the potential to distinguish between, and characterise, different magmatic source regions.

To explore this, here we report the Si isotopic compositions of a suite of Phanerozoic I-, S- and A-type granites and mineral separates, as well as samples of associated country rock. The whole-rock data fall between $\delta^{30}\text{Si} = -0.40$ and $-0.11 \pm 0.04\%$ (95% s.e.). This range is more limited than that defined by previous low precision measurements of granites, but is significantly broader than that displayed by more recent, high precision, measurements of high-Si extrusive igneous rocks. As predicted, S-type granites are, on average, isotopically lighter than I- and A-type samples, and negative correlations with alumina saturation index (ASI) values and initial $^{87}\text{Sr}/^{86}\text{Sr}$ provide evidence that Si isotope variations in granites can be explained by variable incorporation of an enriched sedimentary component. However, the relatively small isotopic perturbations and apparent degree of overlap between granite affinities suggest that Si isotopes are not as sensitive to sedimentary input, relative to more established proxies such as, for example, O isotopes. The average Si isotope value of all granites analysed in this study is $\delta^{30}\text{Si} = -0.23 \pm 0.15\%$ (2 s.d.), which is entirely consistent with a recently published estimate for the continental crust, based on an andesitic bulk composition and the well defined relationship between Si isotopes and magmatic fractionation.

© 2012 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Granites, in the broadest sense, constitute ~50% of the mass of the upper continental crust (Wedepohl, 1995) but are too Si-rich to be in equilibrium with the mantle (e.g. Rudnick, 1995) – that is, much of the continental crust cannot

have formed through simple mantle melting events. Therefore, some other process or combination of processes must occur to form such evolved melts. The array of likely processes includes the following:

- (i) fractional crystallisation of primitive mantle melts;

* Corresponding author. Present address: Department of Earth and Planetary Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130-4899, USA. Tel.: +1 314 935 7525; fax: +1 314 935 7361.

E-mail address: savage@levee.wustl.edu (P.S. Savage).

¹ Sadly, Bruce Chappell passed away on April 22nd, 2012. Bruce Chappell transformed our understanding of granite geochemistry and petrogenesis by defining clear and systematic relationships between magma and source compositions. He will be sorely missed by many in the field.

- (ii) partial melting of basaltic crust;
- (iii) anatexis of crustal sediments;
- (iv) mixing of magmas of various provenances (derived from i–iii).

Processes involving fractional crystallisation ultimately drive the continental crust toward more Si-rich compositions by, for example, delamination of dense ultramafic cumulate material back into the mantle (e.g. Rudnick, 1995). Anatexis of crustal material that has already experienced supracrustal weathering can also impart a high-Si content, because weathering enriches the residue in relatively insoluble elements, such as Si and Al, resulting in a fluid phase that is rich in Mg, Ca etc. (which eventually enters the ocean; Albarède and Michard, 1986). Therefore, formation of granites can involve both primitive, mantle-derived components and/or evolved (supra-)crustal material. Identifying the provenance of such rock is important, because granites that are ultimately mantle-derived represent new volumes of continental crust.

The Si isotope system has the potential to differentiate between granites of mantle and sedimentary provenance, as follows. Silicon isotope fractionation is limited in the igneous realm, relative to that generated as a result of low-temperature, secondary or biogenic processes. The $\delta^{30}\text{Si}$ value (using NBS28 as the bracketing standard; see Section 3.2 for definition) of Bulk Silicate Earth (BSE) is $-0.29 \pm 0.08\text{‰}$ (Fig. 1; Savage et al., 2010) and studies show that mafic and ultramafic igneous rocks appear to show little variation from this value (e.g. Fitoussi et al., 2009; Zambardi et al., 2009; Savage et al., 2010; Armytage et al., 2011). Despite this, and in contrast to many stable isotope systems that show little resolvable isotope fractionation as a result of high-temperature igneous processes, i.e. Mg (Teng et al., 2007) or Li (Tomascak et al., 1999), there appears to be resolvable, equilibrium-controlled Si isotope fractionation during magmatic differentiation, whereby an increase in SiO_2 content is accompanied by a concentration

Fig. 1. Plot of $\delta^{30}\text{Si}$ vs. SiO_2 displaying the “igneous array” for Si isotopes (Savage et al., 2011) defined by analysis of a suite of cogenetic rocks from the volcano of Hekla, Iceland (diamond symbols) and various other volcanic igneous samples (triangle symbols). Magmatic differentiation enriches more silica-rich samples in the heavier isotopes. Also shown is the Si isotope value for Bulk Silicate Earth (BSE, square symbol, Savage et al., 2010).

of the heavier Si isotopes (Fig. 1; Savage et al., 2011). The magnitude of fractionation between the basaltic and rhyolitic end-members is $\Delta^{30}\text{Si} \sim 0.20\text{‰}$. Crucially, this enrichment appears to be a fundamental property of the Si isotope system, such that $\delta^{30}\text{Si}$ composition varies linearly with SiO_2 content and an ideal “igneous trend” for Si isotopes can be established. This means that, for a given SiO_2 content, an “igneous” $\delta^{30}\text{Si}$ composition can be calculated. It is hypothesised, therefore, that granites derived by melting or differentiation of igneous materials should have Si isotope compositions that lie on or close to this “igneous trend”, similar to the compositions of dacites and rhyolites ($\delta^{30}\text{Si} \sim -0.21$ to -0.12‰).

In contrast, granites derived from anatexis or assimilation of metasedimentary rocks are not expected to lie on the igneous trend. Studies show that formation of clay minerals and other secondary phases preferentially enriches the product in the lighter Si isotopes (Ziegler et al., 2005a,b; Georg et al., 2009) such that sedimentary rocks containing secondary phases have a lighter Si isotope composition than their unweathered protolith material (Fig. 2). This is corroborated by the current dataset for clastic sedimentary rocks, which have lighter and more diverse range of $\delta^{30}\text{Si}$ values than igneous rocks (Fig. 2; Douthitt, 1982; Ding et al., 1996). Although the amount of fractionation can be variable (predominantly as a function of weathering intensity, temperature and fluid composition) it is anticipated that granites formed via anatexis of sedimentary material should have lighter and more variable Si isotope compositions than granites formed by melting or differentiation of mantle-derived igneous materials.

The concept that Si isotopes may be used to differentiate between granites of different protoliths is not novel, and

Fig. 2. Selection of clay mineral and whole-rock data from various sources in the literature, showing that chemical weathering enriches the product in the lighter isotopes of Si. Sandstone protolith data are taken from Georg et al. (2009); granitic protolith data are taken from Ziegler et al. (2005b). Also shown are various Si isotope data for unrelated clastic sedimentary material analysed by Douthitt (1982) and Ding et al. (1996), as well as the I- and S-type granite analyses from Douthitt (1982); this work suggests that, although granites have a large range of isotope compositions, Si isotopes do not differentiate between the two types. The data from Fig. 1 is given for comparison.

was tested by Douthitt (1982) who analysed a suite of I- and S-type granites from the Lachlan Fold Belt (LFB), Australia. These results show that both granite types (see Section 2.1 for definitions of these “types”) have a large range of $\delta^{30}\text{Si}$ values (-0.8 to $+0.3\text{‰}$) and that there are no systematic isotopic variations between granites that have igneous or sedimentary affinities (Fig. 2). However, the method precision (up to $\pm 0.6\text{‰}$) associated with some of these measurements is insufficient to resolve the small isotopic variations typically associated with high temperature Si isotopic fractionation. As such, revisiting this problem using much improved and more precise analytical techniques, as well as a larger sample set, is timely.

Other non-traditional stable isotope systems have also been applied to granites, where isotope variations related to source heterogeneity might be expected, with mixed results. In their study of the Li isotope composition of the upper continental crust, Teng et al. (2004) show a limited range of $\delta^7\text{Li}$ values in I- and S-type granites from the LFB, with no distinction between granites of different affinities. Heavy Fe isotope compositions, relative to mantle values, have been measured in granites from various localities, but such variations have been related to either isotopic fractionation between melt and an exsolving magmatic fluid (Poitrasson and Freyrier, 2005), or igneous processes (Schoenberg and von Blanckenberg, 2006) rather than an effect of crustal anatexis (we note that the latter study does not rule out the possibility of crustal assimilation, but suggests that is unlikely, given the lack of a putative source enriched in heavy Fe isotopes). As with Li, Mg isotopes do not appear to distinguish between I- and S-type granites of the LFB (Li et al., 2010), with both groups showing little variation away from mantle values. However, Mg isotopes in granites from China (Li et al., 2010) and California (Shen et al., 2009) appear to reflect, in both cases, mixing between juvenile, mantle-derived material and an evolved (weathered) crustal source.

To investigate the Si isotopic systematics of granites, we have analysed a representative suite of samples including I-, S- and A-type granites, pegmatites and aplites from Australia and south-western England. We have also analysed a selection of country rock samples to assess source compositions, as well as a suite of typical granitic mineral phases to investigate isotopic fractionation as a result of fractional crystallisation. Our aims are to examine whether the large range of granite Si isotope data seen by Douthitt (1982) is real or an analytical artifact, assess whether Si isotopes distinguish between granites of various affinities and evaluate how Si isotopes behave during granite formation. As well as providing a framework for Si isotope systematics in granites, we also aim to provide an estimate for the igneous component of the upper continental crust.

2. SAMPLES

2.1. I- and S-type granites from SE Australia

The Lachlan Fold Belt (LFB) is an area of extensive granitic plutonism located in south-eastern Australia. Granite emplacement is related to the Lachlan orogen, a

palaeo-convergent margin along the eastern margin of Gondwanaland present during the early Ordovician to Devonian (Foster and Gray, 2000). The pioneering work of Chappell and White (1974, 2001) noted that, on the basis of mineralogical and major element analysis, most of the granites in the LFB could be divided into two contrasting types, which they termed I- and S-type.

I-type granites are metaluminous or weakly peraluminous, hornblende-bearing, and have ASI values < 1.1 (Alumina Saturation Index = molar $[\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})]$; Shand, 1927), high CaO contents and Ca/Na ratios. On the basis of this geochemical and further textural evidence, these rocks are inferred to have formed from melting of a predominantly igneous or metaigneous protolith that has not undergone major continental weathering, hence I-type (Igneous or Infracrustal).

S-type granites, by contrast, are always peraluminous (ASI > 1.0) (typically cordierite-bearing in the LFB) and depleted in soluble elements such as Na, Ca and Sr relative to I-type rocks. S-type rocks often contain metasedimentary enclaves, some of which are of a higher metamorphic grade than the country rock (Fleming, 1996; Maas et al., 1997). Therefore, S-type granites are assigned a Sedimentary, or Supracrustal, source that has a pelitic affinity.

Despite their discreet sources, granites from the LFB exhibit compositional overlap, which challenges the simple I- and S-type classification. Trace element patterns from both groups are very similar (e.g. Collins, 1998) and, most notably, plotted on an ε_{Nd} vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ diagram, I- and S-type granites appear to fall on a single hyperbolic array (McCulloch and Chappell, 1982). Some authors have suggested this indicates that, rather than I- and S-type granites forming from discrete protoliths, granite petrogenesis in the LFB is a result of large scale mixing between two or three isotopically distinct sources (e.g. Gray, 1984; Keay et al., 1997). The sources invoked are a primitive depleted mantle component (which is completely absent in the original model) and the ubiquitous Ordovician marine turbidite sequences present as country rock in the LFB (Wyborn and Chappell, 1983) – a sometimes posited third component is metaigneous Cambrian basement (Nelson et al., 1986). Further support for this model comes from coupled Hf–O isotopic analysis of zircons from the LFB, which show that both magmatic and enriched crustal sources are involved in I-type granite petrogenesis (Hawkesworth and Kemp, 2006).

The mixing models are particularly useful in explaining why some LFB I-type granites have enriched Sr, Nd and O isotope compositions, indicating a component of sedimentary protolith and, likewise, why S-type granites can display geochemical affinities closer to that of I-type material. However, despite the agreement with isotope data, simple mixing models cannot adequately replicate the bulk rock compositions of the LFB granites (e.g. Chappell, 1996). Hence, the topic of LFB granite petrogenesis can often be contentious (cf. Collins, 1998, and subsequent replies); application of a new isotope system such as Si may yield new insights into this problem.

We have analysed a number of I- and S-type granites from the LFB. All samples were collected away from weathering surfaces and are well characterised for major

and trace elements as well as isotopic studies (O'Neil and Chappell, 1977; McCulloch and Chappell, 1982; Chappell et al., 1990, 1991; Gray, 1990; McCulloch and Woodhead, 1993). The samples and localities are described in more detail below.

2.1.1. Bega and Moruya batholiths

Six I-type samples were analysed from the Bega (425–395 Ma) and Moruya (395–389 Ma) batholiths. These outcrop toward the eastern margin of the LFB, where the metasedimentary pile may be thin or absent (Collins, 1998) and, as such, the majority of the granites from these batholiths have I-type affinities. The samples are taken

from 6 of the 7 supersuites recognised in this area (Moruya, Cobargo, Glenbog, Tonghi, Candelo and Bemboka; Chappell et al., 1991) and display a range of SiO₂ contents (65–73 wt.%; Table 1). The samples also display a range of initial ϵ_{Nd} (+3.0 to –6.4) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.704–0.709), which may indicate the involvement of a non-juvenile source. Of all the LFB granites analysed in this study, the Moruya sample displays the most primitive radiogenic Sr and Nd isotope compositions.

2.1.2. Berridale batholith

Eight samples were analysed from the Berridale (436–413 Ma; Ickert and Williams, 2011) batholith. This

Table 1
External standard data.

Standard		SiO ₂ (wt.%)	$\delta^{30}\text{Si}$ (‰)	2 s.d.	95% s.e.	$\delta^{29}\text{Si}$ (‰)	2 s.d.	95% s.e.	n
Diatomite	1	100	1.26	0.11	0.04	0.64	0.06	0.02	11
	2		1.22	0.22	0.07	0.62	0.09	0.03	11
	3		1.27	0.15	0.05	0.69	0.15	0.05	11
	4		1.23	0.08	0.03	0.65	0.07	0.02	11
	5		1.22	0.09	0.03	0.62	0.08	0.03	11
	6		1.26	0.12	0.05	0.63	0.06	0.02	9
	7		1.23	0.10	0.04	0.63	0.07	0.02	11
	8		1.21	0.09	0.06	0.68	0.08	0.05	5
	9		1.27	0.12	0.04	0.68	0.12	0.04	11
Replicate	1		1.22	0.11	0.04	0.61	0.08	0.03	11
	2		1.20	0.10	0.03	0.60	0.06	0.02	11
	3		1.28	0.12	0.04	0.65	0.07	0.02	11
Average			1.24	0.11	0.01	0.64	0.10	0.01	124
Reynolds et al. (2007)			1.26	0.20		0.64	0.14		
Georg et al. (2009)			1.23	0.16		0.62	0.11		
Savage et al. (2011)			1.23	0.10		0.64	0.08		
BHVO-2	1	49.9	–0.28	0.11	0.04	–0.13	0.06	0.02	9
	2		–0.33	0.16	0.05	–0.18	0.1	0.04	11
	3		–0.28	0.10	0.04	–0.14	0.1	0.03	11
	4		–0.34	0.06	0.02	–0.16	0.11	0.04	11
	5		–0.31	0.08	0.03	–0.17	0.08	0.03	10
	6		–0.29	0.04	0.01	–0.17	0.07	0.02	11
	7		–0.31	0.10	0.03	–0.15	0.09	0.03	11
	8		–0.29	0.07	0.02	–0.16	0.06	0.02	11
	9		–0.31	0.12	0.04	–0.15	0.08	0.03	11
	10		–0.31	0.05	0.02	–0.15	0.05	0.02	11
	11		–0.26	0.12	0.04	–0.13	0.09	0.03	11
Average			–0.30	0.09	0.01	–0.15	0.09	0.01	118
Abraham et al. (2008)			–0.29	0.11		–0.17	0.04		
Zambardi and Poitrasson (2011)			–0.27	0.08		–0.14	0.05		
Savage et al. (2011)			–0.29	0.09		–0.15	0.08		
GSP-2	1	66.6	–0.16	0.11	0.04	–0.06	0.07	0.02	11
	2		–0.23	0.13	0.04	–0.10	0.05	0.02	11
Replicate	1		–0.22	0.11	0.04	–0.11	0.07	0.02	11
	2		–0.21	0.06	0.02	–0.11	0.02	0.01	11
Average			–0.20	0.11	0.02	–0.10	0.07	0.01	44

Silicon isotope data for external standards, as well as literature values for said standards. Numbers refer to repeat analysis of the same solution, “Replicate” refers to analyses made with a separate dissolution of the standard.

batholith is located toward the centre of the LFB, is comprised of approximately equal volumes of I- and S-type granites and straddles the so-called IS-line (White et al., 1976), east of which S-type granites are absent.

Five S-type granites were chosen for analysis from the Berridale batholith, which are representative of the three identified S-type suites (Cootralantra, Dalgety and Tingaringy; Chappell et al., 1991). These rocks have a limited range of SiO₂ contents (67–73 wt.%; Table 1) and display isotopically “enriched” compositions (initial $\epsilon_{\text{Nd}} = -8.4$ to -6.1 , initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$ – 0.712 , $\delta^{18}\text{O} = 9.2$ – 10.5‰) consistent with derivation from a sedimentary protolith.

I-type granites from the Berridale batholith form distinct intermediate and felsic plutons. As such, one intermediate (Tara, 68 wt.% SiO₂) and two felsic (Maffra and Buckley’s Lake; 77 and 71 wt.% SiO₂, respectively) samples were chosen for analysis. These samples have much more primitive radiogenic isotope compositions (initial $\epsilon_{\text{Nd}} = -3.2$ to $+0.0$, initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.705$ – 0.707) than their S-type counterparts, although they do still display elevated $\delta^{18}\text{O}$ values ($+7.9$ to $+9.3\text{‰}$) relative to mantle values ($\delta^{18}\text{O} \sim +5.5\text{‰}$, Matthey et al., 1994).

2.1.3. Wagga batholith

One S-type sample was analysed from the Wagga batholith (436–430 Ma; Ickert and Williams, 2011). This batholith is located further west in the LFB, where the metasedimentary pile may be thickest (e.g. Collins, 1998) and S-type granites dominate. The Wagga sample displays a strong S-type affinity, with high ASI (1.3) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.716) values.

2.1.4. Ordovician turbidites

Four samples of Ordovician turbidite material from the Snowy Mountains, south-eastern Australia have been analysed. These are described by Wyborn and Chappell (1983) and are cited by some workers to be the main sedimentary protolith for the S-type granites in the LFB (e.g. Keay et al., 1997), on the basis of their geochemistry and ubiquity in the region. The samples are fresh, having been collected during tunnelling work in the Snowy Mountains, and range from quartz-rich to clay-rich greywackes and shales, with some marine carbonate and chert bands. High quartz/feldspar ratios suggest that these samples have undergone at least two weathering cycles. The samples we have chosen span the compositional range from silica-rich (high proportions of detrital quartz) to silica-poor (clay-rich).

2.2. New England batholith

The New England batholith (NEB) is located north-east of, and is tectonically distinct from, the LFB, forming in the New England orogen that was a result of an ocean-continent convergent margin (Devonian to Triassic; Shaw and Flood, 1981). Five granite suites, two S-type and three I-type, have been identified on the basis of mineralogical and geochemical parameters (Shaw and Flood, 1981). Two samples were analysed from this batholith, one I-type and one S-type.

The I-type granite is taken from the Moonbi plutonic suite (250 Ma); this suite displays typical I-type characteristics with ASI < 1.0, high Sr and Na concentrations and low initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.704–0.705). The S-type sample from the NEB is taken from the Bundarra Plutonic suite (286 Ma); this suite displays many characteristics of S-type granites (high ASI values, cordierite mineralogy, heavy $\delta^{18}\text{O}$ values) but does not display the high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and negative initial ϵ_{Nd} values that often define such suites. In fact, all of the S-type granites from the NEB have relatively primitive initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.706–0.708; Flood and Shaw, 1977), similar to that of the I-type granites. This has led authors to suggest that the sedimentary protolith component was derived from juvenile volcanogenic sediments, associated with arc volcanism in the area (Hensel et al., 1985).

2.3. A-type granites from SE Australia

A-type granites were first defined by Loiselle and Wones (1979) and display elemental and isotopic characteristics that imply a petrogenetic history distinct to that of I- and S-type granites. They are characterised by high SiO₂, FeO_c (total) and alkali elements, low MgO, Al₂O₃, CaO and P, high incompatible/compatible trace element ratios, low H₂O and high F content (e.g. Whalen et al., 1987; Eby, 1990; Frost and Frost, 2011). Isotopically, they typically have low initial $^{87}\text{Sr}/^{86}\text{Sr}$ and high initial ϵ_{Nd} values (e.g. Eby, 1990). Such geochemical features tend to preclude the involvement of heavily altered or evolved (metagneous or sedimentary) crustal sources in the parental magma and imply instead that petrogenesis occurred either through extreme fractional crystallisation of a basaltic magma or partial melting of quartz- and feldspar-rich granites. Therefore, some A-type granites (those derived from extreme fractional crystallisation) may be representative of the “igneous” Si-isotopic end-member composition of the upper continental crust.

We have analysed three A-type granites from the Padthaway Ridge suite in south-eastern Australia (Turner et al., 1992). The samples are highly siliceous (SiO₂ > 74 wt.%), have low compatible trace element concentrations (Sr, Sc, Ni, Cr), high incompatible trace element concentrations (Rb, LREE, Nb), negative Eu anomalies as well as mantle-like initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.703–0.706) and ϵ_{Nd} values (-1.7 to -2.3). On the basis of this evidence, Turner et al. (1992) conclude that this suite evolved predominantly by fractional crystallisation of a basaltic magma, with limited involvement (<10%) of a crustal component.

2.4. Aplites and pegmatites from SW England

Igneous-derived pegmatites are hypabyssal lithologies, often associated with granitic bodies, that formed from volatile- and incompatible element-rich magma, and are commonly inferred to be representative of the residual melt at the final stages of crystallisation (London, 2005). Aplites are fine grained analogues of pegmatites, formed from similar material which has lost its volatile and flux content suddenly, resulting in a rapid quenching of the melt (London, 2005). Analysis of such lithologies may elucidate whether

processes such as volatile enrichment, volatile loss and/or extensive fractional crystallisation can affect the Si isotope composition of granites. As such, a selection of aplitic and pegmatitic samples from south-western England were chosen for analysis.

The Hercynian granitic plutons and associated lithologies of south-western England are components of a 250 km-long, sub-surface granitic body, the Cornubian batholith (Exley and Stone, 1982; Chappell and Hine, 2006). These plutons intruded a series of metamorphosed sediments and igneous lithologies of mid-Palaeozoic age, with emplacement commencing at the start of the Permian. Variable Rb–Sr and U–Pb ages from each of the plutons indicate that the granites formed between ~300–275 Ma (Darbyshire and Shepherd, 1985, 1994; Chesley et al., 1993), with some plutons forming via multiple stages of magmatism. In contrast to many other granitic terranes, the lithologies present are restricted; typically, granites are coarse grained, peraluminous leucogranites with a strong S-type affinity, derived from fractional crystallisation of a partial melt derived from feldspar-rich sedimentary lithologies (Exley and Stone, 1982; Chappell and Hine, 2006). The aplites and pegmatites display strong geochemical similarities, and have Rb–Sr ages concurrent, with their associated plutons, suggesting that aplite/pegmatite formation was magmatic (Darbyshire and Shepherd, 1985, 1987) and not metasomatic. The samples for this study were taken from the Meldon aplite and the “roof complex” of the Tregonning granite.

The Meldon aplite (279 ± 2 Ma) is geochemically similar to the Dartmoor granite pluton and displays some of the lowest ASI (~1.15) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.710) recorded from the Cornubian batholith (Darbyshire and Shepherd, 1985). Three aplite samples from the main body as well as one aplite vein were chosen for analysis. Mineral separates from a pegmatitic zone containing albite, K-feldspar and minor lepidolite were also picked for Si isotopic analysis.

The Tregonning granite (280 ± 4 Ma), in comparison to the Meldon aplite, has much higher ASI (~1.3) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.715). This indicates the involvement of a more evolved sedimentary component during petrogenesis (Darbyshire and Shepherd, 1987). The pluton is noted for its abundance of Li-rich micas, and at the upper contact between the granite and the country rock, a “roof complex” of banded aplites and pegmatites has formed (Exley and Stone, 1982). Two aplites and a pegmatite (picked for quartz, albite and tourmaline), as well as a lithionite granite from the Tregonning main intrusion (picked for quartz, albite and lepidolite) were chosen for analysis.

3. METHODS

All the Australian granite samples were received as powders and required no further processing before alkali fusion. The aplites and pegmatites were obtained from the British Geological Survey as whole-rock samples; aplites were crushed and powdered in an agate mill in-house; pegmatites were crushed and mineral separates were picked using a binocular microscope under ethanol, then powdered in an alumina pestle and mortar. The use of agate mills does not resolvably affect the Si isotope composition of samples,

as shown from tests made by Zambardi and Poitrasson (2011) and Savage et al. (2011).

3.1. Alkali fusion

All samples and standards were processed using the HF-free alkali fusion method as detailed in Georg et al. (2006). About 10 mg of sample powder was weighed into a silver crucible along with ~200 mg of the NaOH flux (analytical grade in pellet form). The crucible was then placed into a muffle furnace, preheated to 720 °C, for 12 min. After removal from the furnace, the crucible was allowed to cool slightly before placing it into 20 ml of MQ-e (18.2 M Ω) water. After 24 h, the fusion cake was agitated in an ultrasonic bath and heated to ~60 °C to ensure quantitative removal of the fusion material from the crucible. The solution was then transferred into pre-cleaned polypropylene bottles, diluted further with MQ-e water and acidified with triple-distilled concentrated HNO₃ (to 1% v/v). Sample concentrations and yields were checked after fusion using the “molybdenum-blue” method on a Hach Lange DR 2800 photospectrometer. The average yield of all samples processed for this study is $98 \pm 1\%$ (1 s.d.).

All samples and standards were purified before mass spectrometry using a single column pass, using BioRad (Hercules, CA, USA) Poly-prep 10 ml columns filled with 1.8 ml of DOWEX 50 W-X12 (200–400 mesh) cation exchange resin. Because at low pH Si exists in the non-ionic or anionic forms (Si(OH)₄ or H₃SiO₄[−]), it is not retained by the resin and so can be eluted immediately after loading, using MQ-e water. After purification, the samples were acidified to 1% v/v HNO₃ before analysis. This method ensures quantitative Si recovery and removes all major and trace cations from the eluate. This method does not, however, remove anionic species, and the effect that large concentrations of such species in the eluate may have on analysis was tested by Georg et al. (2006). No anomalous results were noted when samples doped with large concentrations of anionic species were analysed for Si isotopes. Also, the good reproducibility of external standards using this method (see Section 4.1) suggests that the presence of anionic species in the purified samples does not cause any matrix effects during analysis. Further tests and evidence for the robustness of this method are provided in Savage et al. (2010), Zambardi and Poitrasson (2011) and Armytage et al. (2011).

3.2. Mass spectrometry

Silicon isotope analyses were made using the Nu Plasma High-Resolution Multiple-Collector Inductively-Coupled-Plasma Mass Spectrometer (HR-ICP-MS, Nu Instruments, Wrexham, UK) at the Department of Earth Sciences, University of Oxford. Running conditions for Si isotope analyses are described in detail in Georg et al. (2006). Samples were ionised in a “dry” plasma; solutions were introduced using a 6 mm PFA concentric microflow nebuliser (Saville, MN, USA) with an uptake rate of ~50 $\mu\text{l min}^{-1}$ and desolvated using an Aridus II (Cetac, NE, USA).

To avoid polyatomic interferences on the Si beams, analyses were made at “medium” resolution (resolving

power $M/\Delta M \sim 3300$, where ΔM is defined at 5% and 95% of peak height; Weyer and Schwieters, 2003). This requires the ion beam to be physically narrowed, which results in a $\sim 85\%$ reduction of instrument sensitivity (at sample Si concentrations of 750 ppb, a total signal of 1×10^{-10} A was typical).

Isotopic analyses were made using a standard-sample bracketing protocol to correct for instrumental mass bias. The silica sand standard NBS28 (NIST RM8546) was used as the bracketing standard, and was processed through identical chemistry as for all samples. Each isotope datum consists of an average of ~ 11 values (5–6 sample analyses) – each analysis comprised 20 cycles and each cycle was integrated for 8 s. Instrumental background was checked before each measurement by deflecting the ESA for 20 s; a typical background signal of 2×10^{-13} A gives a signal to noise ratio of ~ 500 .

Variations in Si isotopes are represented by the delta notation as $\delta^{30}\text{Si}$ or $\delta^{29}\text{Si}$, defined as the deviation in per mil (‰) of a sample's ratio of $^{30}\text{Si}/^{28}\text{Si}$ from the standard (NBS28), as such:

$$\delta^{30}\text{Si} = [(^{30}\text{Si}/^{28}\text{Si}_{\text{sample}})/(^{30}\text{Si}/^{28}\text{Si}_{\text{standard}}) - 1] \times 1000;$$

$$\delta^{29}\text{Si} = [(^{29}\text{Si}/^{28}\text{Si}_{\text{sample}})/(^{29}\text{Si}/^{28}\text{Si}_{\text{standard}}) - 1] \times 1000.$$

We discuss our Si isotope data using $\delta^{30}\text{Si}$ values, which are approximately twice the magnitude of $\delta^{29}\text{Si}$ values. This is assuming mass dependence, which, for terrestrial samples, is a valid assumption – indeed, this relationship was used as a test for data quality and any data that did not display mass dependence were discarded.

4. RESULTS

4.1. External standards

Sample data accuracy was ensured by the repeat analysis of external standards during each data acquisition session. The standards used were Diatomite and BHVO-2. Diatomite is a natural, pure silica standard and BHVO-2 is a natural basaltic rock standard, distributed by the USGS. Both are widely available and have been extensively utilised as external standards for Si isotope studies and, as such, a large body of previous analyses are available in the literature for comparison (Reynolds et al., 2007; Abraham et al., 2008; Fitoussi et al., 2009; Georg et al., 2009; van den Boorn et al., 2009; Ziegler et al., 2010; Chakrabarti and Jacobsen, 2010; Zambardi and Poitrasson, 2011; Armytage et al., 2011). We have also repeatedly analysed two separate dilutions of the USGS granodiorite standard GSP-2 during the course of this study, in an attempt to characterise a natural, Si-rich external standard.

External standard data are given in Table 1. Our values of $\delta^{30}\text{Si} = -0.30 \pm 0.09\text{‰}$ (2 s.d., $n = 118$) for BHVO-2 and $\delta^{30}\text{Si} = 1.24 \pm 0.11\text{‰}$ (2 s.d., $n = 124$) for Diatomite agree well with the literature data and exemplify the good levels of precision and reproducibility that can be achieved with our methods and instrumentation. The errors associated with the data are a combination of the “chemical” and “mass spectrometric” reproducibility, as all standards and samples

were processed through identical chemistry prior to analysis. Analysis of a replicate dilution of Diatomite gives identical isotope values, suggesting our sample processing techniques are robust. Repeated analysis of GSP-2 gives a value of $\delta^{30}\text{Si} = -0.20 \pm 0.11\text{‰}$ (2 s.d., $n = 44$); the precision and reproducibility are identical to those associated with our other external standards, and isotopic analysis of two separate dilutions shows no sample heterogeneity.

4.2. Whole-rock sample data

All sample Si isotope data are given in Tables 2 and 3. Analytical uncertainties are represented using both the $2 \times$ standard deviation (2 s.d.) and the standard error of the mean at the 95% confidence level ($95\% \text{ s.e.} = t \times \text{s.d.}/(n)^{1/2}$, where t = inverse survival function of the Student's t -test at the 95% significance level and $n - 1$ degrees of freedom). The average 2 s.d. value for all samples analysed in this study is $\pm 0.10\text{‰}$, which is very close to that given by external standards. At an average population of $n = 11$, this gives an overall 95% s.e. of $\pm 0.034\text{‰}$, which we take to be our representative precision.

4.2.1. Lachlan Fold Belt

Whole-rock $\delta^{30}\text{Si}$ data for granites from the LFB range from -0.40 to -0.14‰ (Fig. 3). I-type granites range from $\delta^{30}\text{Si} = -0.25$ to -0.14‰ with an average value of $\delta^{30}\text{Si} = -0.19 \pm 0.07\text{‰}$ (2 s.d.), whereas S-types have a broader and lighter isotopic range (viz. $\delta^{30}\text{Si} = -0.40$ to -0.25‰) with an average of $\delta^{30}\text{Si} = -0.28 \pm 0.14\text{‰}$ (2 s.d.). There are no strong correlations between $\delta^{30}\text{Si}$ and proxies for magmatic differentiation (e.g. SiO_2 , MgO). The isotopic ranges of both I- and S-type granites from the LFB analysed here ($\sim 0.25\text{‰}$) are more limited than that displayed by the data of Douthitt (1982, $>1.0\text{‰}$; Fig. 2). The reasons for this are unclear but the lower precision associated with their methods would naturally lead to a statistical increase in spread of the data.

Even though the range of data is small, the isotopic variations are larger than would be expected from solely igneous differentiation, given the limited variation in SiO_2 contents (65–77 wt.%; cf. rhyolitic material from Afar and Hekla, see Section 1). For instance, samples MG58 and VB140 have almost identical SiO_2 contents but, whereas MG58 has a strong I-type affinity and an “igneous” Si isotope composition ($\delta^{30}\text{Si} = -0.14\text{‰}$), sample VB140 is strongly S-type and has a more negative $\delta^{30}\text{Si}$ value (-0.40‰). There is, however, significant overlap between the isotope compositions of I- and S-type granites (Fig. 3), the possible reasons for which will be discussed below.

Silicon isotope data for a selection of Ordovician turbidites from the LFB define a narrow range ($\delta^{30}\text{Si} = -0.24$ to -0.18‰), much smaller than the isotopic ranges for the S-type granites. This is unexpected, especially given the compositional and mineralogical variation of the samples analysed.

4.2.2. New England batholith

The Si isotope composition of the I-type granite from the NEB (sample G38; $\delta^{30}\text{Si} = -0.14\text{‰}$) falls within the

Table 2
Whole-rock Si isotope data for Lachlan Fold Belt and other Australian granites.

Sample	Type	Locality	SiO ₂ (wt.%)	δ ³⁰ Si (‰)	2 s.d.	95% s.e.	δ ²⁹ Si (‰)	2 s.d.	95% s.e.	n	ASI	⁸⁷ Sr/ ⁸⁶ Sr _(i)	ε _{Nd(i)}	δ ¹⁸ O (‰)
<i>Lachlan Fold Belt</i>														
<i>Bega</i>														
AB006	I-type	Glenbog	67.2	−0.18	0.06	0.02	−0.11	0.07	0.03	9	0.95	0.70869	−6.4	8.80
AB082	I-type	Brogo	66.9	−0.21	0.10	0.04	−0.12	0.08	0.03	9	0.96	0.70456	−1.3	
AB102	I-type	Bemboka	72.2	−0.18	0.11	0.03	−0.12	0.08	0.02	22	1.03	0.70790	−6.0	
AB195	I-type	Yurammie	65.3	−0.19	0.07	0.03	−0.12	0.08	0.03	9	0.95	0.70544	−4.6	9.20
AB234	I-type	Tonghi	69.2	−0.24	0.10	0.03	−0.14	0.06	0.02	11	0.98	0.70869	−6.4	
MG58	I-type	Moruya	72.5	−0.14	0.09	0.03	−0.08	0.12	0.04	11	1.10	0.70410	3.0	8.10
<i>Berridale</i>														
BB10	I-type	Buckleys Lake	71.2	−0.18	0.04	0.01	−0.10	0.08	0.03	10	1.00	0.70673	−2.6	8.78
BB21	I-type	Maffra	76.6	−0.15	0.14	0.05	−0.08	0.08	0.03	11	1.05	0.70504	0.0	9.32
				−0.22	0.11	0.04	−0.13	0.04	0.01	11				
				−0.19	0.07	0.03	−0.07	0.07	0.02	11				
				−0.18	0.12	0.02	−0.09	0.08	0.01	33				
BB87	I-type	Tara	67.7	−0.25	0.14	0.05	−0.14	0.08	0.03	10	0.97	0.70628	−3.2	7.86
BB02	S-type	Numbla Vale	73.5	−0.23	0.14	0.05	−0.12	0.10	0.03	11	1.09	0.71076	−8.0	10.23
BB09	S-type	Dalgety	68.2	−0.26	0.04	0.01	−0.12	0.03	0.01	11	1.08	0.70986	−6.1	9.56
BB12	S-type	Dalgety	67.4	−0.25	0.15	0.03	−0.13	0.10	0.02	21	1.06	0.70991	−6.5	9.20
BB53	S-type	Tingaringy	67.8	−0.33	0.13	0.04	−0.18	0.08	0.02	16	1.13	0.71153	−7.5	10.53
BB83	S-type	Cootralantra	67.4	−0.22	0.07	0.03	−0.14	0.07	0.02	8	1.16	0.71206	−8.4	10.55
<i>Wagga</i>														
VB140	S-type	Granya	72.5	−0.37	0.16	0.06	−0.20	0.11	0.04	9	1.31	0.71580		
				−0.45	0.06	0.02	−0.25	0.05	0.02	11				
				−0.40	0.05	0.02	−0.19	0.06	0.02	11				
				−0.37	0.16	0.06	−0.21	0.13	0.04	10				
				−0.40	0.14	0.02	−0.21	0.10	0.02	43				
<i>Ordovician turbidites</i>														
OS31			63.4	−0.18	0.07	0.02	−0.10	0.04	0.01	11		0.71350	−12.0	
				−0.26	0.10	0.03	−0.14	0.03	0.01	11				
				−0.27	0.07	0.02	−0.14	0.10	0.03	11				
				−0.24	0.12	0.02	−0.12	0.07	0.01	33				
OS35			56.8	−0.22	0.12	0.04	−0.12	0.04	0.01	11		0.71650	−13.0	
				−0.14	0.08	0.03	−0.11	0.11	0.04	10				
				−0.18	0.12	0.03	−0.12	0.08	0.02	21				
OS37			89.9	−0.20	0.08	0.03	−0.08	0.03	0.01	11		0.71910	−14.0	
				−0.18	0.10	0.03	−0.09	0.08	0.03	11				
				−0.19	0.09	0.02	−0.09	0.06	0.01	22				

(continued on next page)

Table 2 (continued)

Sample	Type	Locality	SiO ₂ (wt.%)	δ ³⁰ Si (‰)	2 s.d.	95% s.e.	δ ²⁹ Si (‰)	2 s.d.	95% s.e.	<i>n</i>	ASI	⁸⁷ Sr/ ⁸⁶ Sr _(i)	ε _{Nd(i)}	δ ¹⁸ O (‰)
OS39			80.3	−0.24	0.09	0.03	−0.10	0.04	0.01	11		0.71950	−13.0	
				−0.18	0.12	0.04	−0.08	0.13	0.05	10				
				−0.21	0.12	0.03	−0.09	0.09	0.02	21				
Other SE Australian														
New England batholith														
NEB247	S-type	Bundarra	72.7	−0.11	0.16	0.04	−0.04	0.08	0.02	20	1.06	0.70500	−0.2	12.00
G38	I-type	Moonbi	68.0	−0.14	0.08	0.01	−0.07	0.07	0.01	33	0.96	0.70498	1.3	8.00
Padthaway														
2001	A-type	Mt. Monster	73.9	−0.13	0.10	0.03	−0.08	0.05	0.02	11	0.99	0.70402	−1.7	
PG-11	A-type	Marcollat	75.1	−0.15	0.06	0.02	−0.07	0.10	0.04	11	0.96	0.70257	−2.7	
2000	A-type	Seismograph	74.6	−0.19	0.09	0.03	−0.11	0.13	0.04	11	0.95	0.70630	−2.3	
				−0.18	0.15	0.07	−0.05	0.06	0.03	7				
				−0.18	0.05	0.02	−0.11	0.18	0.06	10				
				−0.18	0.09	0.02	−0.10	0.14	0.03	28				

Silicon isotope data of whole-rock analyses of Lachlan Fold Belt (and associated sediments), New England batholith and Padthaway suite granites made during this study. Data in grey boxes are long term averages of repeat analyses of the same sample solution. Other element and isotopic data are taken from the following sources: *LFB*: O'Neil and Chappell (1977), McCulloch and Chappell (1982), Wyborn and Chappell (1983), Gray (1990), Chappell et al. (1991), and McCulloch and Woodhead (1993), unpub. analyses; *NEB*: O'Neil and Chappell (1977), Shaw and Flood (1981), Hensel et al. (1985), Bryant et al. (2004), and Shaw and Flood (2009); *Padthaway*: Turner et al. (1992).

Data in italics are taken from a closely related sample from the same pluton or an average made from various analyses from the same locality – these are used only when data is not available for a specific sample. See Section 5.

Table 3
Silicon isotope data for aplite, pegmatite and host granite samples from SW England.

Sample	Type	Description	SiO ₂ (wt.%)	$\delta^{30}\text{Si}$ (‰)	2 s.d.	95% s.e.	$\delta^{29}\text{Si}$ (‰)	2 s.d.	95% s.e.	<i>n</i>	ASI	$^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$	$\epsilon_{\text{Nd}(i)}$	$\delta^{18}\text{O}$ (‰)
Meldon														
MEL01–10	S-type	Aplite vein	70.3	−0.23	0.14	0.03	−0.14	0.11	0.02	22	<i>1.15</i>	<i>0.70976</i>	<i>−4.7</i>	<i>10.8</i>
MEL02–10	K-feldspar	Pegmatitic aplite	69.0	−0.22	0.09	0.03	−0.11	0.07	0.02	11				
	Albite		68.0	−0.29	0.09	0.03	−0.16	0.09	0.03	11				
	Lepidolite		50.0	−0.31	0.16	0.05	−0.16	0.15	0.05	11				
	Modal average (0.12: 0.76: 0.12)			−0.28	0.11	0.04	−0.15	0.10	0.03					
MEL03–10	S-type	Aplite	62.0	−0.28	0.07	0.02	−0.16	0.04	0.01	11	<i>1.15</i>	<i>0.70976</i>	<i>−4.7</i>	<i>10.8</i>
MEL04–10	S-type	Fine grained aplite	68.9	−0.26	0.13	0.04	−0.13	0.06	0.02	11	<i>1.15</i>	<i>0.70976</i>	<i>−4.7</i>	<i>10.8</i>
MEL05–10	S-type	Fine grained aplite	69.3	−0.22	0.12	0.04	−0.11	0.09	0.03	11	<i>1.15</i>	<i>0.70976</i>	<i>−4.7</i>	<i>10.8</i>
Megaliggarr														
MEG01–10	Quartz	Pegmatite	100	−0.34	0.11	0.04	−0.16	0.14	0.05	11				
	Tourmaline		36.00	−0.22	0.07	0.02	−0.09	0.08	0.03	11				
	Albite		65.00	−0.48	0.14	0.05	−0.28	0.10	0.04	10				
	Modal average (0.45: 0.1: 0.45)			−0.39	0.11	0.04	−0.21	0.11	0.04					
MEG02–10	S-type	Aplite (top of sill)	69.10	−0.39	0.08	0.03	−0.19	0.04	0.01	11	<i>1.3</i>	<i>0.71498</i>	<i>−7.4</i>	<i>14.0</i>
MEG03–10	S-type	Aplogranite	69.50	−0.35	0.09	0.03	−0.16	0.08	0.03	11	<i>1.3</i>	<i>0.71498</i>	<i>−7.4</i>	<i>14.0</i>
MEG04–10	Quartz	Lithionite granite	100.00	−0.33	0.07	0.02	−0.16	0.08	0.03	11				
		Lepidolite	52.00	−0.40	0.12	0.04	−0.23	0.13	0.04	11				
		Albite	63.00	−0.43	0.08	0.03	−0.23	0.08	0.03	11				
	Modal average (0.45: 0.1: 0.45)			−0.38	0.09	0.03	−0.20	0.10	0.03					

Silicon isotope data of the whole-rock aplite and mineral separate pegmatite and granite analyses made during this study. Data in grey boxes represent modal bulk averages calculated from the mineral separate analyses (mineral proportions are given in the brackets). Silica contents were measured spectrophotometrically in-house. Other geochemical data (in italics) were not measured on these samples but are taken from analyses made from the same locality, from [Sheppard \(1977\)](#) and [Darbyshire and Shepherd \(1985, 1994\)](#).

Fig. 3. Silicon isotope data for the whole-rock granite samples taken from the Lachlan Fold Belt, New England batholith and Padthaway suites analysed in this work (error bars are 95% s.e.; see text for sample description and discussion). The box plots in the bottom half of the figure display the sample maxima and minima (the bars), the interquartile range (the box) and the sample median (vertical line in the box), and illustrate the much larger range of data defined by S-type granites.

range delineated by the I-type granites from the LFB. The S-type granite (NEB247) has a composition ($\delta^{30}\text{Si} = -0.11\text{‰}$) that is slightly *heavier* than (but within error of) sample G38 and is resolvable heavier than any of the S-type granites from the LFB (Fig. 3).

4.2.3. Padthaway (A-type) granites

The A-type granites samples from the Padthaway suite show the most limited range of Si isotope data ($\delta^{30}\text{Si} = -0.18$ to -0.13‰) and heaviest average ($\delta^{30}\text{Si} = -0.15 \pm 0.05\text{‰}$) of the three granite affinities analysed in this study. The isotopic range is similar to that seen in rhyolites from Hekla volcano and the Afar region (Savage et al., 2011), consistent with their derivation from a mantle source.

4.3. Aplites and pegmatite mineral separates

Whole-rock aplite $\delta^{30}\text{Si}$ data ranges from -0.39 to -0.22‰ (Table 3, Fig. 4). The range of data for the S-type aplites from the Cornubian batholith coincides with the range for the S-type granites from the LFB. As with those granites, the aplite data do not show any strong relationship with proxies for magmatic differentiation.

Silicon isotope data for the mineral separates for the Megaliggar pegmatite and host lithionite granite are as follows: pegmatite: $\delta^{30}\text{Si}_{\text{quartz}} = -0.34 \pm 0.04\text{‰}$, $\delta^{30}\text{Si}_{\text{albite}} = -0.48 \pm 0.05\text{‰}$ and $\delta^{30}\text{Si}_{\text{tourmaline}} = -0.22 \pm 0.02\text{‰}$; lithionite granite: $\delta^{30}\text{Si}_{\text{quartz}} = -0.33 \pm 0.02\text{‰}$, $\delta^{30}\text{Si}_{\text{albite}} = -0.43 \pm 0.03\text{‰}$ and $\delta^{30}\text{Si}_{\text{lithionite}} = -0.40 \pm 0.04\text{‰}$ (all errors 95% s.e.; Table 3, Fig. 4). The similarity of the $\delta^{30}\text{Si}$ values for quartz and albite samples from both pegmatite and granite is striking, as is the magnitude of fractionation

between the phases (viz. $\Delta^{30}\text{Si}_{\text{qtz-fspr}} = \sim 0.10\text{--}0.14\text{‰}$). The sense and magnitude of fractionation agree with both those observed by other empirical measurements (Georg, 2006) and calculated using Density Functional Theory (Méheut et al., 2009). They are also consistent with the theory that equilibrium fractionation between mineral phases will be predominantly controlled by degree of polymerisation, with the heavier isotopes favouring the phase(s) with the higher degree of polymerisation (Grant, 1954). However, as noted by Méheut et al. (2009), polymerisation degree is not the only discriminating factor, and other network-forming cations, such as Al, could affect bond strength and ultimately the degree of fractionation. This could explain why tourmaline, in which both Al and B can act as network-forming cations, displays a heavier $\delta^{30}\text{Si}$ value than quartz.

The Meldon pegmatite data are as follows: $\delta^{30}\text{Si}_{\text{K-feldspar}} = -0.22 \pm 0.03\text{‰}$, $\delta^{30}\text{Si}_{\text{albite}} = -0.29 \pm 0.03\text{‰}$ and $\delta^{30}\text{Si}_{\text{lepidolite}} = -0.31 \pm 0.05\text{‰}$ (all errors 95% s.e.; Table 3, Fig. 4). Although the absolute values for the mineral separates are distinct to those from Megaliggar, there are important similarities. In both the Megaliggar and Meldon samples, there is no fractionation between albite and lepidolite. This is in agreement with analyses made by Georg (2006) on granite mineral separates, whose data imply that feldspar and muscovite record similar Si isotope values. Also, in both Megaliggar and Meldon, albite seems to concentrate the lighter isotopes. In the Meldon pegmatite (where quartz is not present in appreciable quantities), K-feldspar displays a heavier $\delta^{30}\text{Si}$ value than albite, which is surprising, as it may be expected that both feldspars would have similar isotope compositions if they formed in equilibrium. However, there is some evidence that albite had already crystallised before pegmatite emplacement

Fig. 4. Whole-rock Si isotope data for the aplite samples, and mineral separate data for the pegmatite and granite samples from the Cornubian batholith (error bars are 95% s.e.; see text for sample descriptions and discussion).

(Chaudry, 1971), which may explain this discrepancy. Alternatively, coupled Al–Si substitution in the plagioclase and lack thereof in the K-feldspar will affect internal bond strengths and so may cause fractionation between the two phases (dependent on Ca content).

Bulk $\delta^{30}\text{Si}$ averages for the pegmatites and lithionite granite have been calculated using the modal abundance of each analysed phase (recast to 100%) and weighted by the relative SiO_2 content of each phase (Table 3). Bulk Si isotope estimates fall within the range of data for each locality.

For all the samples analysed in this study, although there are resolvable Si isotopic differences between different granite suites, within each locality there is surprisingly limited variation (Figs. 3 and 4). The scale of this provincial control is variable, however, as in the aplites and pegmatites it appears to exist on a pluton-scale, i.e. on a much smaller scale than seen in south-eastern Australia, where variation is limited within each *batolith*.

5. DISCUSSION

5.1. Silicon isotope variation in granites

A major hypothesis of this study is that granites derived from an igneous source (I- and A-type) should have Si isotope compositions similar to those of intraplate rhyolites and dacites, whereas granites with a sedimentary affinity (S-type) should display $\delta^{30}\text{Si}$ values that are much more variable and, on average, much lighter. This can be tested by plotting the $\delta^{30}\text{Si}$ data against SiO_2 content, along with the “igneous array” for Si isotopes (Fig. 5) as defined in Savage et al. (2011). Fig. 5a shows that the $\delta^{30}\text{Si}$ data for I- and A-type granites lie on or very close to the “igneous array” suggesting that the isotope compositions of both groups are predominantly controlled by magmatic processes, i.e. partial melting and fractional crystallisation.

Fig. 5b shows that S-type granites have a much larger range of $\delta^{30}\text{Si}$ values, many of which, as predicted, do not lie on the “igneous array”.

However, there are a number of issues relating to the data, which indicate that the behaviour of Si isotopes in granitoid material is not as simplistic as described in the preceding paragraph. Firstly, there is a significant amount of overlap between the Si isotopic ranges of S-types and other granites. Also, some S-type $\delta^{30}\text{Si}$ values lie on the igneous array whereas some I-type granites plot below the array. Lastly, both I- and S-type granites from the New England batholith appear to plot *above* (although within error of) the array. Because of this, it is pertinent to investigate what processes may be affecting Si isotopes during and post petrogenesis.

5.1.1. Secondary alteration processes

Secondary alteration processes can be ruled out, as all samples were taken from fresh surfaces with no evidence of alteration. The extremely comprehensive body of literature on the samples from the Lachlan Fold Belt and New England batholith provides ample evidence that these rocks represent fresh granitic material (see Section 2 for references and sample descriptions). The limited Mg isotope variation seen by Li et al. (2010) for the LFB precludes large-scale secondary alteration; as Mg is more fluid-mobile than Si, the affect on Si isotopes should be even smaller.

5.1.2. Kinetic isotope fractionation

There is increasing evidence that diffusion-related kinetic isotopic fractionation can affect the low-mass stable isotopes to a larger degree than equilibrium processes at high temperatures and pressures (see Richter et al., 2009a for a review). Although Si isotopes do not appear to be affected by chemical diffusion (Richter et al., 1999) there is some experimental (Richter et al., 2009b) and theoretical (Lundstrom, 2009) evidence that Soret (thermal) diffusion pro-

Fig. 5. Silicon isotope data for the Lachlan Fold Belt, New England batholith and Padthaway suite (a) I- and A-type and (b) S-type granites plotted against SiO_2 (symbols as in Fig. 3, error bars are 95% s.e.). Also plotted is the “igneous array” as in Fig. 1 (Savage et al., 2011). Whereas most of the I- and A-type granites plot on the array, many S-type samples do not. Symbols as for Fig. 3.

cesses can cause resolvable Si isotope effects, particularly if a temperature gradient is present for an extended period, for instance that associated with the cooling of a granitic pluton.

The problem is that thermal effects are extremely difficult to test in a natural setting unless a transect across the predicted thermal gradient is available (such as that studied by Lundstrom, 2009). Also, there are significant differences between laboratory experiments, which are typically made using chemically homogeneous samples, and granite batholiths, where chemical gradients and crystal settling may perturb such thermal diffusion profiles. However, we can use previous stable isotope studies of the LFB to quantify such processes, in particular, Mg isotopes. Magnesium isotopes appear to be fractionated readily by thermal diffusion; Richter et al. (2009b) showed, using experimental data, that the magnitude of Mg isotopic fractionation during thermal diffusion is approximately six times that of Si isotopes (see also Huang et al., 2010). Therefore, if Si isotopes were being affected by Soret diffusion in the LFB, we would expect to see large Mg isotope fractionation in the same system. In fact, the opposite is true: Mg isotope analyses of LFB granites do not appear to show any variation away from mantle values (Li et al., 2010). Unfortunately, no such data are available for the New England and Cornubian batholiths and so we cannot use this approach to quantify Soret effects, although the relationships between Si isotopes and other geochemical indices of source composition (see later) tend to preclude large kinetic isotope effects in these samples.

5.1.3. Volatile phase-related fractionation

Granitic magmas are often volatile-rich and, during crystallisation, the residual melt is enriched in the volatiles, as well as other elements that act as network-modifiers (such as B, P, F, Li). The role of network-modifying cations appears to have an important control over equilibrium Si isotope fractionation (e.g. Méheut et al., 2009) and so the volatile-rich phase may play a role in the Si isotopic systematics of granites, particularly as the residual melt phase will become increasingly Si-rich as crystallisation continues. Therefore, studying the Si isotope composition of zoned aplite and pegmatites, which are both representative of late stage granitic melt and whose petrogenesis has involved variable interaction with volatiles (see Section 2) may indicate whether these phases are important in affecting the Si isotope composition of granites.

In both aplite-pegmatite localities analysed in this study, we find no isotopic offset between the bulk $\delta^{30}\text{Si}$ composition of the pegmatites, aplites and host granite (Fig. 4, Table 3). This suggests that neither volatile enrichment nor subsequent volatile loss affects the bulk Si isotope composition of the granite or residual phases. What volatile enrichment appears to affect is the Si isotope composition of individual crystal phases. The magnitudes of offset between the isotope compositions of crystal phases from the bulk Megaliggar pegmatite are much larger than for the host granite, even though the sense of fractionation of common phases remains the same (Fig. 4). This phenomenon may be an effect of the increase in composition

of network-modifying cations in a volatile-rich melt (see Section 3).

5.1.4. Igneous processes

In an igneous rock that has evolved from a mantle-derived melt, the effect that fractional crystallisation (and/or partial melting) has on the Si isotope composition of such a rock defines the “igneous array” for Si isotopes (see above). Using this relationship, the range of SiO_2 contents represented by the granite samples analysed in this study (65–75 wt.%) predicts a limited variation in $\delta^{30}\text{Si}$, between -0.20 and $-0.15 \pm 0.05\text{‰}$. Therefore we infer that measured granite $\delta^{30}\text{Si}$ values that lie off this trend indicate that such samples have not evolved from a mantle source. However, this does not rule out the possibility that other igneous processes such as cumulate formation, whereby the final composition is not representative of an equilibrium melt assemblage, could also cause resolvable isotopic fractionation away from the predicted value, particularly if the degree of inter-mineral fractionation can be as large as that seen for the Megaliggar pegmatite.

By using the pegmatite and granite mineral separate data (Fig. 4), we can predict what effect removal and/or accumulation of certain phases would have on the Si isotope composition of a melt. Accumulation of albite or mica will drive the melt to a heavier Si isotope composition leaving an isotopically light cumulate (although we have not analysed biotite, this phase has already been shown to be isotopically lighter than both bulk rock composition and co-existing muscovite; Georg, 2006). However, the paucity of very light S-type granites from the LFB argues against this. Either, quartz, being relatively isotopically heavy, has accumulated which is highly unlikely, or the S-type granites show overlap with I-type granites because they have experienced preferential removal of such phases.

However, trace element ratios do not support this suggestion: most of the granites we have analysed have Rb/Sr ratios of <2 (removal of feldspar will deplete a melt in Sr relative to Rb; e.g. Halliday et al., 1991) suggesting that feldspar was not residual or removed from the melt. For comparison, Padthaway granites, which have experienced fractional crystallisation of feldspars, have Rb/Sr ratios of between 3 and 9. Of the LFB granites that do have Rb/Sr > 2 , VB140 has the largest value (~ 6), and also shows other geochemical characteristics compatible with fractional crystallisation, but this sample also displays the *lightest* $\delta^{30}\text{Si}$. Therefore, the Si isotope composition of the initial melt for this sample was even lighter ($< -0.40\text{‰}$).

If mica was a residual or fractionating phase, then it would drive the melt toward high Sr/Ba (more so for biotite than for muscovite e.g. Hanson, 1978) and, possibly, low Li concentrations. However, most Sr/Ba ratios are < 0.40 for the granites studied here, and Li concentrations are all much greater than mantle values (Bryant et al., 2004; Teng et al., 2004).

A final point to make is that it is very difficult to constrain the Si isotope composition of a magma that is formed via melting of a pelitic source, unless the sediment is completely melted. Specifically, the mineralogical components will not have formed in equilibrium, so the isotope compo-

sition of each phase is impossible to predict. Suppose that partial melting occurs via incongruent dehydration reactions (e.g. Thompson, 1982), whereby hydrous phases (e.g. mica) react with quartz to produce melt and a feldspar-rich residue; given that mica tends to be isotopically light and quartz relatively heavy, the resultant melt may be isotopically similar to the source. On the other hand, given that the residue is enriched in feldspar, which is also isotopically light, the melt phase may reflect an enrichment in the heavier isotopes. Given this, all we can confidently say is that partial anatexis of a pelitic sediment will result in a melt that has a Si isotope composition that is similar to, or slightly heavier than, the protolith.

5.2. Silicon isotope variations in granites as a function of source heterogeneity

Having ruled other processes, we conclude that source heterogeneity is the most likely cause of Si isotope variation (away from predicted values) in many of the granites analysed in this study. In Fig. 6, we have plotted Si isotopes against ASI value, $\delta^{18}\text{O}$, initial $^{87}\text{Sr}/^{86}\text{Sr}$ and initial ϵ_{Nd} , all of which have been used in the Lachlan Fold Belt to differentiate between granites of igneous or sedimentary affinities. In all the plots, a least-squared linear regression has been performed on the LFB data *only*, this is shown as well as the R^2 value for each regression. These relationships are discussed below.

Firstly, fairly strong correlations exist between Si isotopes and ASI values, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 6a and c). Weaker relationships between $\delta^{18}\text{O}$ and initial ϵ_{Nd} are present, but in all cases, the relationships are such that lighter Si isotope values appear to be related to a more weathered (high ASI and $\delta^{18}\text{O}$ values) and less mantle-like (radiogenic Sr, low initial ϵ_{Nd} values) source.

Secondly, (most) analyses for the New England batholith, Padthaway suite and Cornubian batholith aplites also plot on the arrays delineated by the LFB granites and, in all cases, recalculating the R^2 values using all granite data results in better regression statistics. There are some exceptions, for instance the NEB S-type sample in Fig. 6b, but in general Si isotope values of granites from unrelated sources display similar systematics, again suggesting that Si isotopic heterogeneity in granites is a result of variations in source components. However, as is noted above, the offset between the $\delta^{30}\text{Si}$ values of I- and S-type granites is not always as conclusive as with other elemental or isotopic proxies.

5.2.1. Composition of sedimentary source

An important caveat of the original hypothesis, that Si isotopes should distinguish between igneous- and sedimentary-derived granites, is that the sedimentary material from which the granites form should be isotopically distinct from the composition of igneous rocks. The large range of very negative $\delta^{30}\text{Si}$ displayed in Fig. 2 supports this assertion.

Fig. 6. Silicon isotope data for whole-rock granite and aplite samples plotted against (a) ASI values, (b) $\delta^{18}\text{O}$, (c) $^{87}\text{Sr}/^{86}\text{Sr}_{\text{(i)}}$ and (d) $\epsilon_{\text{Nd}(\text{i})}$ where such data was available (error bars are 95% s.e.; symbols as in Figs. 3 and 4; data references are given in the text and in Tables 2 and 3; subscript (i) denotes initial values). Least-squared linear regressions were performed in Gnumeric (<http://projects.gnome.org/gnumeric/>) using only the Lachlan Fold Belt data, R^2 values for these are provided. See Section 5.

It is also evident, however, that some sedimentary material has Si isotope compositions that overlap those of igneous rocks and this may be the case for the sedimentary component of many of the LFB granites. The data from the Ordovician turbidites define a remarkably limited Si isotopic range (much smaller than that measured in the granites), with the four samples, which are representative of the range of sedimentary compositions in this suite, having $\delta^{30}\text{Si}$ values between -0.24 and -0.18‰ (Table 2) and an average Ordovician turbidite value of $\delta^{30}\text{Si} = -0.20 \pm 0.05\text{‰}$ (2 s.d.).

If the Ordovician sediment is the enriched source of the LFB granites, as previous authors suggest (e.g. Keay et al., 1997; Collins, 1998; Kemp and Hawkesworth, 2003), then any amount of this material in the source of the granites would not result in any isotopic variation away from igneous values. Fig. 7 shows a simple mixing model (analogous to the mixing model of Keay et al., 1997) between various putative end-members for the LFB, in $\delta^{30}\text{Si}$ vs. initial $^{87}\text{Sr}/^{86}\text{Sr}$ space. Strontium isotopes were chosen because the correlation between these and Si isotopes is strongest in the LFB; also, Sr isotopes differentiate well between I- and S-type granites in the LFB and the Sr isotope dataset is also the most complete. The solid lines in Fig. 7 define a mixing envelope between (A) igneous material of rhyolitic composition (which could be derived from component B); (B) mantle-derived material of basaltic composition, and; (C) average Ordovician turbidite value for the LFB. A line joining end-member A to B is analogous to the “igneous array” (Fig. 1); isotopic variations along this line could be controlled by igneous processes or mixing. Component C was defined using the average Si isotope composition of the sedimentary samples given in the preceding paragraph (Table 2) and previous data (bulk chemical analyses given in Wyborn and Chappell, 1983; Sr isotope data from McCulloch and Woodhead, 1993). Silicon isotope data for the LFB granites are also plotted, and it is evident that most granite Si isotope compositions fall within the solid mixing envelope. This demonstrates that little variation outside of igneous $\delta^{30}\text{Si}$ values is predicted for both I- and S-type granites from the Lachlan Fold Belt, when mixing occurs with a sediment of composition C. That only two granite samples plot outside of this range supports this model.

Considering the data in terms of the “restite” model (e.g. Chappell, 1984) does not significantly affect the conclusions of the paper. Here, instead of a magma of intermediate composition between A and B assimilating component C, there is concomitant melting of a batch of fertile igneous and sedimentary material (e.g., a composition between B and C). Although we can predict confidently that melting of igneous material (component B) will result in a melt enriched in heavier isotopes, we cannot place as strong constraints upon what happens to the Si isotope composition of a pelitic sediment during partial melting (and removal of a restite phase; see Section 5.1.4). All we can confidently surmise is that the partial melt of a pelitic sediment will have a Si isotope composition equal to or heavier than the protolith; therefore, the restite model would predict Si isotope granite compositions that lie on or above the tie line

Fig. 7. Plot showing $\delta^{30}\text{Si}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}_i$ isotope mixing curves between two igneous and two sedimentary sources, representative of possible end-member components in the Lachlan Fold Belt. Component A represents a rhyolitic mantle-derived melt with $\text{SiO}_2 = 70$ wt.%, $\text{Sr} = 400$ ppm, $\delta^{30}\text{Si} = -0.12\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.703$; component B represents a basaltic mantle-derived melt with $\text{SiO}_2 = 48$ wt.%, $\text{Sr} = 300$ ppm, $\delta^{30}\text{Si} = -0.32\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.703$. A line from component B to A is analogous to the Si isotope “igneous array” as defined by Savage et al. (2011). Solid mixing lines define a mixing envelope between the end-members of the igneous array (A and B) and the average Ordovician sedimentary composition (component C), as calculated from analyses given in Table 2 and defined as $\text{SiO}_2 = 73$ wt.%, $\text{Sr} = 88$ ppm, $\delta^{30}\text{Si} = -0.20\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.717$. Dashed mixing lines define a mixing envelope between the igneous array and a sedimentary end-member (component D) with a more negative $\delta^{30}\text{Si}$ content ($\delta^{30}\text{Si} = -0.40\text{‰}$) but otherwise identical to component C. Tick marks represent 10% mixing graduations. Also plotted are the granite data for the Lachlan Fold Belt samples and the Ordovician sedimentary data (boxed cross symbols are the sediments, otherwise symbols as for Fig. 3, error bars are 95% s.e.). See Section 5.

joining components B and C, which describes most of the granite analyses presented here.

There are, however, two samples (BB53 from the Berriedale batholith and VB140 from the Wagga batholith) that plot outside the solid mixing envelope (or below the B–C mixing line). Both of these samples have strong S-type affinities suggesting that, with VB140 especially, these samples are derived almost completely from sedimentary protoliths. This then suggests that there is also present, in the LFB, a sedimentary source that is isotopically more negative than mantle-derived igneous rocks and also the Ordovician turbidites, as partial melting of a sediment is not predicted to result in a more negative isotope composition than its protolith (see above). The dashed lines in Fig. 7 describe a mixing envelope between the same two igneous end-members A and B and a putative sediment of composition D. This component is identical to component C apart from it having a much more negative Si isotope composition, as would be expected for a clay-rich sedimentary material (e.g. Ziegler et al., 2005a,b; Georg et al., 2009). If such a sediment as end-member D exists, then it does not appear to be a wide-spread source for S-type granites in the LFB, as only samples BB53 and VB140 plot close to it.

These two samples indicate that Si isotopes could be developed as a useful proxy with which to infer the presence and broad lithological association of sedimentary material during the petrogenesis of a granite. This of course depends on the composition of the sedimentary material itself but the difference between authigenic and clastic sedimentary material is significant (i.e. marine silica can be $\sim 1\text{--}3\text{‰}$ heavier than clastic sedimentary material; De La Rocha, 2003) and anatexis of such material could impart significant Si isotope variability onto a melt, as will be discussed in the Section 5.2.2.

5.2.2. The New England batholith

The relatively heavy Si isotope composition of the S-type granite from the New England batholith merits comment. This value is the heaviest $\delta^{30}\text{Si}$ value measured in this study, heavier than all I- and A-types. The sample is taken from the Bundarra supersuite, which displays many geochemical properties consistent with a sedimentary protolith such as high ASI values, cordierite mineralogy, heavy $\delta^{18}\text{O}$ and light $\delta^7\text{Li}$ (Flood and Shaw, 1977; Bryant et al., 2004). Unlike the S-type granites of the LFB, it has mantle-like Sr and Nd isotope values (Hensel et al., 1985), suggesting that the sedimentary source was derived from rapid reworking of volcanogenic arc-derived sediment. Rapid weathering may not have allowed for significant chemical alteration of the protolith, thereby limiting the amount of Si isotope fractionation that occurred in the sedimentary pile, resulting in an unfractionated sediment (relative to igneous rocks). However, it does not explain why the S-type is isotopically heavier than all I-type granites. One possibility is that the Si in the sedimentary source derived partially from biogenic silica, which can have much heavier $\delta^{30}\text{Si}$ values than igneous rocks (e.g. De la Rocha, 2003; Hendry et al., 2010). Incorporation of biogenic silica should not significantly affect the Li, Sr and Nd isotope compositions but would also result in heavy $\delta^{18}\text{O}$ values. However, on the basis of one sample, it is difficult to make any firm statements about the petrogenesis of NEB granites.

5.3. The Si isotope composition of the upper continental crust

Granites comprise $\sim 50\%$ of the upper continental crust, and are thought to occur in significant quantities in the middle and lower crust (Wedepohl, 1995; Rudnick and Fountain, 1995). Therefore, providing an average value for granitic crust is an important step toward defining the Si isotope composition of Earth's continental crust. The average value for all the granites (I-, S- and A-type) and the aplites (which we have established are unfractionated from their host granites) analysed in this study is $\delta^{30}\text{Si} = -0.23 \pm 0.15\text{‰}$ (2 s.d.). Although there is a significant amount of variation, this value is identical to the "igneous" composition of the continental crust of $\delta^{30}\text{Si} = -0.23 \pm 0.05\text{‰}$ (2 s.e. of the regression) calculated by Savage et al. (2011), using the "igneous array" equation defined by extrusive igneous material (Fig. 1) and Rudnick and Gao (2003) estimate of the SiO_2 content in the continental crust (60.6 wt.%). Such good agreement between these two values is somewhat surprising, given that granite

petrogenesis can involve multiple, geochemically evolved sources, but suggests that the Si isotope composition of the crystalline upper continental crust is predominantly controlled by igneous processes. This value is slightly heavier than the composition of Bulk Silicate Earth ($\delta^{30}\text{Si} = -0.29 \pm 0.08\text{‰}$; 2 s.d.; Savage et al., 2010), which is expected given that magmatic differentiation tends to enrich a melt in the heavier Si isotopes (Savage et al., 2011).

6. CONCLUSIONS

1. Analysis of granites from south-eastern Australia and south-western England indicate that significant Si isotope variations occur in granites. This range is greater than that displayed by other high-Si igneous rocks, such as rhyolites and dacites (e.g. Savage et al., 2011). We do not replicate the much larger range of Si isotope values that Douthitt (1982) reports for granites from the Lachlan Fold Belt, and we suggest that the large isotope variations presented in that study is most likely a result of larger analytical uncertainties.
2. Although there is a small amount of fractionation expected from varying degrees of magmatic differentiation, some S-type samples display much lighter $\delta^{30}\text{Si}$ values than would be predicted had they derived from a mantle source. Also, on average, S-type granites have lighter Si isotope compositions than I-type granites. This agrees with the hypothesis that S-type granites will have lighter Si isotope compositions if derived from pelitic sedimentary material (which is typically enriched in the lighter isotopes).
3. Correlations between Si isotopes and other proxies for source composition in granites (ASI value, $\delta^{18}\text{O}$, initial $^{87}\text{Sr}/^{86}\text{Sr}$ and initial ϵ_{Nd}) supports the above conclusion that the Si isotope variations recorded in granites are predominately related to source heterogeneity. However, such geochemical indices distinguish between granites of varying source affinity more conclusively than Si isotopes. Analysis of the proposed sedimentary source for many of the LFB granites reveals why this might be, as the sediments are isotopically unfractionated (with respect to Si) relative to igneous rocks. However, isotopically light S-type granites do exist in the LFB, suggesting that there may be sedimentary material with a correspondingly light Si isotope composition that has not yet been analysed.
4. The presence of a volatile-rich melt phase is typical during granite petrogenesis. However, aplite and pegmatite mineral separate data suggest that volatile-related processes do not affect the bulk Si isotope composition of granitic melts.
5. An important outcome of this study is the provision of a robust estimate for the Si isotope composition of the igneous component of upper continental crust. The average Si isotope value of the granites analysed in this study is $\delta^{30}\text{Si} = -0.23 \pm 0.15\text{‰}$ (2 s.d.). This is entirely consistent with the value calculated in Savage et al. (2011), of $\delta^{30}\text{Si} = -0.23 \pm 0.05\text{‰}$ (2 s.e. of the regression), based on an andesitic crustal composition, and indicates that

continental crust is somewhat enriched in isotopically heavy Si, compared to the mantle and oceanic crust. Such a value is fundamental for use as a terrestrial “baseline” in future studies concerning Si isotope variation as a result of continental weathering.

ACKNOWLEDGEMENTS

P.S. would like to thank Richard Scrivener for a comprehensive introduction to granite geology, especially in relation to the Cornubian batholith. The British Geological Survey kindly provided the Meldon and Megaliggar samples from this region. Many thanks go to Ros Armytage, Julie Prytulak and Kevin Burton for insightful suggestions and discussion throughout the project. The authors would like to extend their gratitude toward Klaus Mezger and two anonymous reviewers for their thorough and perceptive critical input, as well as Steven Shirey for his editorial help and comments. Lastly, this research was made possible due to the valuable technical assistance and support provided by Steve Wyatt, Teodor Krastev and Nick Belshaw. This work was funded by a NERC CASE studentship supported by Nu Instruments. Isotopic research at Oxford is funded by an ERC grant to A.H.

REFERENCES

- Abraham K., Opfergelt S., Fripiat F., Cavagna A., de Jong J. T. M., Foley S. F., André L. and Cardinal D. (2008) $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ determinations on USGS BHVO-1 and BHVO-2 reference materials with a new configuration on a Nu Plasma Multi-Collector ICP-MS. *Geostand. Geoanal. Res.* **32**, 193–202.
- Albarède F. and Michard A. (1986) Transfer of continental Mg, S, O and U to the mantle through hydrothermal alteration of the oceanic crust. *Chem. Geol.* **57**, 1–15.
- Armytage R. M. G., Georg R. B., Savage P. S., Williams H. M. and Halliday A. N. (2011) Silicon isotopes in meteorites and planetary core formation. *Geochim. Cosmochim. Acta* **75**, 3662–3676.
- Bryant C. J., Chappell B. W., Bennett V. C. and McCulloch M. T. (2004) Lithium isotopic compositions of the New England Batholith: Correlations with inferred source rock compositions. *Trans. Royal Soc. Edinburgh, Earth Sci.* **95**, 199–214.
- Chakrabarti R. and Jacobsen S. B. (2010) Silicon isotopes in the inner Solar System: Implications for core formation, solar nebular processes and partial melting. *Geochim. Cosmochim. Acta* **74**, 6921–6933.
- Chappell B. W. (1984) Source rocks of I- and S-type granites in the Lachlan fold belt, southeastern Australia. *Phil. Trans. Roy. Soc. London* **A310**, 693–707.
- Chappell B. W. (1996) Magma mixing and the production of compositional variation within granite suites: Evidence from the granites of southeastern Australia. *J. Petrol.* **37**, 449–470.
- Chappell B. W. and White A. J. R. (1974) Two contrasting granite types. *Pacific Geol.* **8**, 173–174.
- Chappell B. W. and White A. J. R. (2001) Two contrasting granite types: 25 years later. *Aust. J. Earth Sci.* **48**, 489–500.
- Chappell B. W. and Hine R. (2006) The Cornubian batholith: An example of magmatic fractionation on a crustal scale. *Res. Geol.* **56**(3), 203–244.
- Chappell B. W., Williams I. S., White A. J. R. and McCulloch M. T. (1990) Granites of the Lachlan Fold Belt. In *ICOG 7 Conference Field Guide*. Bureau of Mineral Resources, Geology and Geophysics, Australia.
- Chappell B. W., White A. J. R. and Williams L. S. (1991) A transverse section through granites of the Lachlan Fold Belt. In *Second Hutton Symposium on Granites and Related Rocks*.
- Chaudry M. N. (1971) Feldspars from the Meldon aplite, Devonshire, England. *Mineral. Mag.* **38**, 179–185.
- Chesley J. T., Halliday A. N., Snee L. W., Mezger K., Shepherd T. J. and Scrivener R. C. (1993) Thermochronology of the Cornubian batholith in southwest England: Implications for pluton emplacement and protracted hydrothermal mineralization. *Geochim. Cosmochim. Acta* **57**, 1817–1835.
- Collins W. J. (1998) Evaluation of petrogenetic models for Lachlan Fold Belt granitoids: Implications for crustal architecture and tectonic models. *Aust. J. Earth Sci.* **45**, 483–500.
- Darbyshire D. P. F. and Shepherd T. J. (1985) Chronology of granite magmatism and associated mineralization, SW England. *J. Geol. Soc.* **142**, 1159–1177.
- Darbyshire D. P. F. and Shepherd T. J. (1987) Chronology of magmatism in southwest England: The minor intrusions. *Proc. Ussher Soc.* **6**, 431–438.
- Darbyshire D. P. F. and Shepherd T. J. (1994) Nd and Sr isotope constraints on the origin of the Cornubian batholith, SW England. *J. Geol. Soc.* **151**, 795–802.
- De la Rocha C. L. (2003) Silicon isotope fractionation by marine sponges and the reconstruction of the silicon isotope composition of ancient deep water. *Geology* **31**, 423–426.
- Ding T., Jiang S., Wan D., Li Y., Li J., Song H., Liu Z. and Yao X. (1996) *Silicon Isotope Geochemistry*. Geological Publishing House, Beijing, China.
- Douthitt C. B. (1982) The geochemistry of the stable isotopes of silicon. *Geochim. Cosmochim. Acta* **46**, 1449–1458.
- Eby G. N. (1990) The A-type granitoids: A review of their occurrence and chemical characteristics and speculations on their petrogenesis. *Lithos* **26**, 115–134.
- Exley C. S. and Stone M. (1982) *Hercynian intrusive rocks in Igneous Rocks of the British Isles*. John Wiley & Sons, United Kingdom.
- Fitoussi C., Bourdon B., Kleine T., Oberli F. and Reynolds B. C. (2009) Si isotope systematics of meteorites and terrestrial peridotites: Implications for Mg/Si fractionation in the solar nebula and for Si in the Earth's core. *Earth Planet. Sci. Lett.* **287**, 77–85.
- Fleming P. D. (1996) Inherited deformation structures in metasedimentary enclaves in granites as “windows” into deeper levels of the crust. *Tectonophysics* **267**, 177–185.
- Flood R. H. and Shaw S. E. (1977) Two “S-type” granite suites with low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the New England Batholith. *Aust. Contrib. Mineral. Petrol.* **61**, 163–173.
- Foster D. A. and Gray D. R. (2000) Evolution and structure of the Lachlan Fold Belt (Orogen) of eastern Australia. *Annu. Rev. Earth Planet. Sci.* **28**, 47–80.
- Frost C. D. and Frost R. R. (2011) On ferroan (A-type) granitoids: Their compositional variability and modes of origin. *J. Petrol.* **52**(1), 39–53.
- Georg R. B. (2006) Geochemistry of stable silicon isotopes measured by High-Resolution Multi-Collector Inductively-Coupled Plasma Mass Spectrometry (HR-MC-ICP-MS). Ph. D. thesis, ETH Zurich, Switzerland.
- Georg R. B., Reynolds B. C., Frank M. and Halliday A. N. (2006) New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. *Chem. Geol.* **235**, 95–104.
- Georg R. B., Zhu C., Reynolds B. C. and Halliday A. N. (2009) Stable silicon isotopes of groundwater, feldspars, and clay coatings in the Navajo Sandstone aquifer, Black Mesa, Arizona, USA. *Geochim. Cosmochim. Acta* **73**, 2229–2241.

- Grant F. S. (1954) The geological significance of variations in the abundances of the isotopes of silicon in rocks. *Geochim. Cosmochim. Acta* **5**, 225–242.
- Gray C. M. (1984) An isotopic mixing model for the origin of granitic rocks in southeastern Australia. *Earth Planet. Sci. Lett.* **70**, 47–60.
- Gray C. M. (1990) A strontium isotopic traverse across the granitic rocks of southeastern Australia: Petrogenetic and tectonic implications. *Aust. J. Earth Sci.* **37**, 331–349.
- Halliday A. N., Davidson J. P., Hildreth W. and Holden P. (1991) Modelling the petrogenesis of high Rb/Sr silicic magmas. *Chem. Geol.* **92**, 107–114.
- Hanson G. N. (1978) The application of trace elements to the petrogenesis of igneous rocks of granitic composition. *Earth Planet. Sci. Lett.* **38**, 26–43.
- Hawkesworth C. J. and Kemp A. I. S. (2006) Using hafnium and oxygen isotopes in zircons to unravel the record of crustal evolution. *Chem. Geol.* **226**, 144–162.
- Hendry K. R., Georg R. B., Rickaby R. E. M., Robinson L. F. and Halliday A. N. (2010) Deep ocean nutrients during the Last Glacial Maximum deduced from sponge silicon isotopic compositions. *Earth Planet. Sci. Lett.* **292**, 290–300.
- Hensel H. D., McCulloch M. T. and Chappell B. W. (1985) The New England Batholith: Constraints on its derivation from Nd and Sr isotopic studies of granitoids and country rocks. *Geochim. Cosmochim. Acta* **49**, 369–384.
- Huang F., Chakraborty P., Lundstrom C. C., Holmden C., Glessner J. J. G., Kieffer S. W. and Leshner C. E. (2010) Isotope fractionation in silicate melts by thermal diffusion. *Nature* **464**, 396–400.
- Ickert R. B. and Williams I. S. (2011) U–Pb zircon geochronology of Silurian–Devonian granites in south-eastern Australia: Implications for the timing of the Benambran Orogeny and the I–S dichotomy. *Aust. J. Earth Sci.* **58**, 501–516.
- Keay S., Collins W. J. and McCulloch M. T. (1997) A three-component Sr–Nd isotopic mixing model for granitoid genesis, Lachlan fold belt, eastern Australia. *Geology* **25**, 307–310.
- Kemp A. I. S. and Hawkesworth C. J. (2003) Granitic perspectives on the generation and secular evolution of the continental crust. *Treatise Geochem.* **3**, 349–410.
- Li W.-Y., Teng F.-Z., Ke S., Rudnick R. L., Gao S., Wu F.-Y. and Chappell B. W. (2010) Heterogeneous magnesium isotopic composition of the upper continental crust. *Geochim. Cosmochim. Acta* **74**, 6867–6884.
- Loiselle M. C. and Wones D. R. (1979) Characteristics and origin of anorogenic granites. *Geol. Soc. Am. Abstr. Programs* **11**, 468.
- London D. (2005) Granitic pegmatites: An assessment of current concepts and directions for the future. *Lithos* **80**, 281–303.
- Lundstrom C. (2009) Hypothesis for the origin of convergent margin granitoids and Earth's continental crust by thermal migration zone refining. *Geochim. Cosmochim. Acta* **73**, 5709–5729.
- Maas R., Nicholls I. A. and Legg C. (1997) Igneous and metamorphic enclaves in the S-type Deddick Granodiorite, Lachlan fold belt, SE Australia: Petrographic, geochemical and Nd–Sr isotopic evidence for crustal melting and magma mixing. *J. Petrol.* **38**, 815–841.
- Mattey D., Lowry D. and Macpherson C. (1994) Oxygen isotope composition of mantle peridotite. *Earth Planet. Sci. Lett.* **128**, 231–241.
- McCulloch M. T. and Chappell B. W. (1982) Nd isotopic characteristics of S- and I-type granites. *Earth Planet. Sci. Lett.* **58**, 51–64.
- McCulloch M. T. and Woodhead J. D. (1993) Lead isotopic evidence for deep crustal-scale fluid transport during granite petrogenesis. *Geochim. Cosmochim. Acta* **57**, 659–674.
- Méheut M., Lazzeri M., Balan E. and Mauri F. (2009) Structural control over equilibrium silicon and oxygen isotopic fractionation: A first-principles density-functional theory study. *Chem. Geol.* **258**, 28–37.
- Nelson D. R., McCulloch M. T. and Sun S.-S. (1986) The origins of ultrapotassic rocks as inferred from Sr, Nd and Pb isotopes. *Geochim. Cosmochim. Acta* **50**, 231–245.
- O'Neil J. R. and Chappell B. W. (1977) Oxygen and hydrogen isotope relations in the Berridale batholith. *J. Geol. Soc.* **133**, 559–571.
- Poitras F. and Freydier R. (2005) Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. *Chem. Geol.* **222**, 132–147.
- Reynolds B. C., Aggarwal J., André L., Baxter D., Beucher C., Brzezinski M. A., Engström E., Georg R. B., Land M., Leng M. J., Opfergelt S., Rodushkin I., Sloane H. J., Van Den Boorn S. H. J. M., Vroon P. Z. and Cardinal D. (2007) An inter-laboratory comparison of Si isotope reference materials. *J. Anal. At. Spectrom.* **22**, 561–568.
- Richter F. M., Liang Y. and Davis A. M. (1999) Isotope fractionation by diffusion in molten oxides. *Geochim. Cosmochim. Acta* **63**, 2853–2861.
- Richter F. M., Dauphas N. and Teng F. Z. (2009a) Non-traditional fractionation of non-traditional isotopes: Evaporation, chemical diffusion and Soret diffusion. *Chem. Geol.* **258**, 92–103.
- Richter F. M., Watson E. B., Mendybaev R., Dauphas N., Georg B., Watkins J. and Valley J. (2009b) Isotopic fractionation of the major elements of molten basalt by chemical and thermal diffusion. *Geochim. Cosmochim. Acta* **73**, 4250–4263.
- Rudnick R. L. (1995) Making continental crust. *Nature* **378**, 571–578.
- Rudnick R. L. and Fountain D. M. (1995) Nature and composition of the continental crust: A lower crustal perspective. *Rev. Geophys.* **33**, 267–309.
- Rudnick R. L. and Gao S. (2003) Composition of the continental crust. *Treatise Geochem.* **3**, 1–64.
- Savage P. S., Georg R. B., Armytage R. M. G., Williams H. M. and Halliday A. N. (2010) Silicon isotope homogeneity in the mantle. *Earth Planet. Sci. Lett.* **295**, 139–146.
- Savage P. S., Georg R. B., Williams H. M., Burton K. W. and Halliday A. N. (2011) Silicon isotope fractionation during magmatic differentiation. *Geochim. Cosmochim. Acta* **75**, 6124–6139.
- Schoenberg R. and von Blanckenberg F. (2006) Modes of planetary-scale Fe isotope fractionation. *Earth Planet. Sci. Lett.* **252**, 342–359.
- Shand S. J. (1927) On the relations between silica, alumina, and the bases in eruptive rocks, considered as a means of classification. *Geol. Mag.* **64**, 446–449.
- Shaw S. E. and Flood R. H. (1981) The New England batholith, eastern Australia: Geochemical variations in time and space. *J. Geophys. Res.* **86**, 10530–10544.
- Shaw S. E. and Flood R. H. (2009) Zircon Hf isotopic evidence for mixing of crustal and silicic mantle-derived magmas in a zoned granite pluton, eastern Australia. *J. Petrol.* **50**, 147–168.
- Shen B., Jacobsen B., Lee C.-T. A., Yin Q. and Morton D. M. (2009) The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation. *Proc. Natl. Acad. Sci. U. S. A.* **106**, 20652–20657.
- Sheppard S. M. F. (1977) The Cornubian batholith, southwest England: D/H and ¹⁸O/¹⁶O studies of kaolinite and other alteration minerals. *J. Geol. Soc. London* **133**, 573–591.
- Teng F. Z., McDonough W. F., Rudnick R. L., Dalpé C., Tomascak P. B., Chappell B. W. and Gao S. (2004) Lithium isotopic composition and concentration of the upper continental crust. *Geochim. Cosmochim. Acta* **68**, 4167–4178.

- Teng F. Z., Wadhwa M. and Helz R. T. (2007) Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth Planet. Sci. Lett.* **261**, 84–92.
- Thompson A. B. (1982) Dehydration melting of pelitic rocks and the generation of H₂O-undersaturated granitic liquids. *Am. J. Sci.* **282**, 1567–1595.
- Tomaschak P. B., Tera F., Helz R. T. and Walker R. J. (1999) The absence of lithium isotope fractionation during basalt differentiation: New measurements by multicollector sector ICP-MS. *Geochim. Cosmochim. Acta* **63**, 907–910.
- Turner S. P., Foden J. D. and Morrison R. S. (1992) Derivation of some A-type magmas by fractionation of basaltic magma: An example from the Padthaway Ridge, South Australia. *Lithos* **28**, 151–179.
- Van Den Boorn S. H. J. M., Vroon P. Z. and Van Bergen M. J. (2009) Sulfur-induced offsets in MC-ICP-MS silicon-isotope measurements. *J. Anal. At. Spectrom.* **24**, 1111–1114.
- Wedepohl K. H. (1995) The composition of the continental crust. *Geochim. Cosmochim. Acta* **59**, 1217–1232.
- Weyer S. and Schwieters J. B. (2003) High precision Fe isotope measurements with high mass resolution MC-ICPMS. *Int. J. Mass Spectrom.* **226**, 355–368.
- Whalen J. B., Currie K. L. and Chappell B. W. (1987) A-type granites: Geochemical characteristics, discrimination and petrogenesis. *Contrib. Mineral. Petrol.* **95**, 407–419.
- White A. J. R., Williams I. S. and Chappell B. W. (1976) The Jindabyne thrust and its tectonic, physiographic and petrogenetic significance. *J. Geol. Soc. Aust.* **23**, 105–112.
- Wyborn L. A. I. and Chappell B. W. (1983) Chemistry of the Ordovician and Silurian greywackes of the Snowy Mountains, southeastern Australia: An example of chemical evolution of sediments with time. *Chem. Geol.* **39**, 81–92.
- Zambardi T. and Poitrasson F. (2011) Precise determination of silicon isotopes in silicate rock reference materials by MC-ICP-MS. *Geostand. Geoanal. Res.* **35**, 89–99.
- Zambardi T., Poitrasson F., Quitté G. and Anand M. (2009) Silicon isotope variations in the Earth and meteorites. *Geochim. Cosmochim. Acta* **73**, A1497.
- Ziegler K., Chadwick O. A., Brzezinski M. A. and Kelly E. F. (2005a) Natural variations of $\delta^{30}\text{Si}$ ratios during progressive basalt weathering, Hawaiian Islands. *Geochim. Cosmochim. Acta* **69**, 4597–4610.
- Ziegler K., Chadwick O. A., White A. F. and Brzezinski M. A. (2005b) $\delta^{30}\text{Si}$ systematics in a granitic saprolite, Puerto Rico. *Geology* **33**, 817–820.
- Ziegler K., Young E. D., Schauble E. A. and Wasson J. T. (2010) Metal-silicate silicon isotope fractionation in enstatite meteorites and constraints on Earth's core formation. *Earth Planet. Sci. Lett.* **295**, 487–496.

Associate editor: Steven B. Shirey