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The molybdenum isotopic compositions of I-, S- and A-type granitic suites

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Abstract

This study reports Mo isotopic compositions for fifty-two Palaeozoic granitic rocks with contrasting source affinities (A-, I- and S-type) from the Lachlan Fold Belt (LFB) and the New England Batholith (NEB), both in SE Australia, and three compositionally zoned plutons (Loch Doon, Criffell, and Fleet) located in the Southern Uplands of Scotland. The results show relatively large variations in δ^{98}Mo for igneous rocks ranging from −1.73‰ to 0.59‰ with significant overlaps between different types. No relationships between δ^{98}Mo and δ^{18}O or ASI (Alumina Saturation Index) are observed, indicating that Mo isotopes do not clearly distinguish igneous vs. sedimentary source types. Instead, effects of igneous processes, source mixing, regional geology, as well as hydrothermal activity control the Mo isotope compositions in these granites. It is found that Mo is mainly accommodated in biotite and to a lesser extent in hornblende. Hornblende and Fe^{3+}-rich minerals may preferentially incorporate light isotopes, as reflected by negative correlations between δ^{98}Mo and K/Rb and [Fe_2O_3]. There is a positive correlation between initial ^{87}Sr/^{86}Sr and δ^{98}Mo in I-type granitic rocks, reflecting the admixing of material from isotopically distinct sources. Granitic rocks from Scotland and Australia display strikingly similar curvilinear trends in δ^{98}Mo vs. initial ^{87}Sr/^{86}Sr despite the differing regional geology. Localized hydrothermal effects can result in low δ^{98}Mo in granite, as seen in three samples from Loch Doon and Criffell which have anomalously light δ^{98}Mo of <-1‰. Based on this study, an estimate of $\delta^{98}\text{Mo} = 0.14 \pm 0.07$‰ (95% s.e.) for the Phanerozoic upper crust is proposed. This is slightly heavier than basalts indicating an isotopically light lower crust and/or a systematic change to the crust resulting from subduction of isotopically light dehydrated slab and/or pelagic sediment over time.

Keywords: Molybdenum isotopes; Granitic rock; Granite; A-type; I-type; S-type; Lachlan Fold Belt; Loch Doon; Criffell; Fleet; The upper crust

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1. INTRODUCTION

Stable molybdenum (Mo) isotopes in marine sediments have been widely used for paleo-redox reconstruction (e.g. Siebert et al., 2003; Planavsky et al., 2014) on the basis that significant isotopic fractionation occurs in low-temperature (low-T) settings, leading to isotopically distinct marine sediments depending on their redox conditions during formation (e.g. Barling et al., 2001; Siebert et al., 2003; Anbar, 2004; Tossell, 2005). Yet the continental baseline for Mo isotopes, which is essential to the application of this proxy, is still poorly constrained to date. The Mo isotopic

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composition (δ^{98}Mo) of the continental crust has long been uncertain. It was first approximated to be ~−0.25‰ (all δ^{98}Mo values in this study were (re-) normalised to NIST SRM3134, i.e. the δ^{98}Mo composition of NIST SRM 3134 is set to 0‰) based on few analyses of molybdenites (Barling et al., 2001) and igneous rocks (Siebert et al., 2003). This value was later revised to be ~0.4‰ heavier based on high-temperature molybdenites (Greber et al., 2014) and arc lavas (Voegelin et al., 2014). However, these estimates are still limited by the fact that 1) the lithologies used are not fully representative of the composition of the continental crust and 2) the number of samples is too limited to make a constrained assessment. High temperature materials investigated so far for Mo isotope fractionation are komatiites (Greber et al., 2015), arc lavas (Siebert et al., 2003; Voegelin et al., 2014; Freymuth et al., 2015, 2016; König et al., 2016), an Icelandic lava sequence (Yang et al., 2015), molybdenite deposits (e.g. Wieser and de Laeter, 2003; Hannah et al., 2007; Mathur et al., 2010; Greber et al., 2011, 2014; Shafiei et al., 2014) and a few silicic rocks (Siebert et al., 2003; Voegelin et al., 2012; Greber et al., 2014). The rather small database and relatively poor understanding of the behaviour of Mo isotopes in high-temperature conditions, is in stark contrast to knowledge of Mo isotope behaviour at low-temperatures, and hinders constraint of the Mo isotopic composition of the continental crust. Granitic rocks, used in the broadest sense here to include plutonic rocks of intermediate to felsic compositions including granite more strictly as well as trondjemite, tonalitie, granodiorite and diorite, are particularly poorly represented in the existing database but comprise a major part of the continental crust (Wedepohl, 1991). This work therefore focuses on granitic lithologies, and thus increases the database of continental Mo isotope data significantly.

Granitic magmas may in principle derive from one or more of the following processes:

(1) fractional crystallization of primary basaltic melts
(2) partial melting of subducted oceanic crust
(3) partial melting of mantle-derived protoliths in the crust
(4) anatexis of more evolved crustal lithologies including sediments

The significant Mo isotope fractionation under low-T conditions in the hydrosphere suggests that Mo isotopes in sediments must be significantly fractionated from igneous materials. A second objective of this study was therefore to test if the involvement of sediments in granite genesis can be traced using Mo isotopes. We test this possibility by investigating granitic rocks with a variety of known source affinities.

To constrain the budget and the behaviour of Mo isotopes in the continental crust, as well as to explore whether Mo isotopes can be a diagnostic indicator of granite provenance, we have investigated a large set of well-characterised granitiod samples derived from distinct sources, including A-, I- and S-type granitic rocks.

2. SAMPLES

Granitic rocks in the Australian Lachlan Fold Belt (LFB) are subdivided into I-type and S-type, based on the analysis of mineralogy and major element chemical composition (Chappell and White, 2001). I-type granites (igneous and intracrustal sources) are thought to be sourced from unexposed igneous precursors. They range in composition from felsic to intermediate, usually have high Na_2O and CaO contents and have ASI values <1.1 (Alumina Saturation Index = molar $[Al_2O_3/(CaO + Na_2O + K_2O)]$; Shand (1927)). S-type (sedimentary source) granites, derived by anatexis of sedimentary protoliths that have experienced at least one cycle of weathering, are mainly restricted to high SiO_2 compositions, and are characterised by relatively low concentrations of Na_2O and CaO, with high ASI values (>1.1). Due to the contrasting contents of aluminum and alkalis, I-types are commonly hornblende- and sphene-bearing, whereas S-types are hornblende-absent, and may contain monazite. Mica and apatite can be found in both I- and S-types. A-type (alkaline, anhydrous, or anorogenic) granites, first defined by Loiselle and Wones (1979) are thought to have formed through fractional crystallization of basaltic magmas or partial melting of intermediate crustal basement at high temperature (>850 °C). Relative to I- and S-types, A-type granites are characterised by high SiO_2, FeO (total), alkali and halogen elements, and low MgO, Al_2O_3, CaO, and H_2O contents (e.g. Whalen et al., 1987; Eby, 1990; Frost and Frost, 2010).

2.1. A-, I- and S-type granites, and sediments from SE Australia

Twenty plutonic and four sedimentary samples from well-characterised granitic outcrops of the LFB and New England Fold Belt (NEFB) in SE Australia were analysed in this study. The Lachlan and New England orogens are north–south trending deformed regions in SE Australia, which developed as parts of the eastern margin of Gondwanaland during the Cambrian-Devonian (Foster and Gray, 2000). Voluminous granitic plutons intruded into metasedimentary rocks in both the LFB and NEFB in response to convergent marginal tectonism during the Palaeozoic and early Mesozoic (Chappell and Simpson, 1984; Foster and Gray, 2000).

Although the LFB granites are divided into two contrasting categories (I-type and S-type) they display significant compositional overlap in their Nd and Sr isotopic compositions (e.g. McCulloch and Chappell, 1982; Keay et al., 1997) and trace element patterns (e.g. Collins, 1998). Therefore, rather than discrete sources, some authors have proposed models involving mixing of two or three distinct sources including a primitive depleted mantle component, Cambrian greenstones within the belt and the widespread Ordovician marine turbidites (Gray, 1984; Keay et al., 1997). The turbidites are also present as country rocks for the LFB intrusives (Wyborn and Chappell, 1983).