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Hafnium isotopic disequilibrium during sediment melting and assimilation

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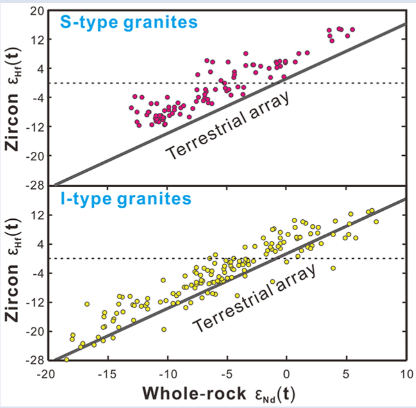
Abstract



Identification of juvenile and mature crustal sources in granite formation relies on radiogenic isotopic systems such as Sm-Nd and Lu-Hf and assumes isotope systems reach equilibrium between the melt and residual phases prior to melt extraction. However, we hypothesise disequilibrium melting and residual zircon result in preferential retention of ^{177}Hf in residues, generating partial melts with higher ^{176}Hf/^{177}Hf ratios. To test this hypothesis, we evaluate radiogenic isotopic signatures of strongly-peraluminous granites from the Chinese Altai. These granites show Nd-Hf isotopic decoupling and inherited zircons with negative $\varepsilon_{Hf}(t)$ values providing evidence for incomplete Hf release. This is consistent with the significant depletions in Zr and Hf. The Chinese data compilation shows that strongly-peraluminous and calcic to calc-alkalic, magnesian metaluminous or ferroan peraluminous (often respectively referred to as S- and I-type) granites show elevated $\varepsilon_{Hf}(t)$ relative to the terrestrial Hf-Nd isotopic array. Hf isotope disequilibrium marked by the preferential release of radiogenic Hf is likely ubiquitous during anatexis of zircon-rich protoliths.

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Introduction

Strongly-peraluminous granites (SPG) generally indicate that partial melting of metasedimentary crustal rocks has been occurring throughout Earth's history (Harris *et al.*, 2000; Appleby *et al.*, 2010; Bucholz and Spencer, 2019). Experimental and geodynamic modelling have been applied to understanding the chemistry and physics of partial melting processes (Sawyer *et al.*, 1991, 2011). It is assumed that crustal partial melts inherit the radiogenic isotope composition of their protoliths. Hafnium (Hf) is a geochemically important element in zircon because its isotopic composition is a sensitive tracer of crustal and mantle processes (Kemp *et al.*, 2006). Zircon retains the initial melt isotopic composition because of its low Lu/Hf ratio and refractory nature in sedimentary processes (Andersen *et al.*, 2002). However, studies of SPG have shown the Hf isotopic composition of partial melts may not match the inferred magma source (Belousova *et al.*, 2005; Villaros *et al.*, 2012; Iles *et al.*, 2019). Residual zircons, *i.e.* not dissolved during partial melting, may retain a significant amount of unradiogenic Hf (*i.e.* low ^{176}Hf/^{177}Hf) causing the derivative crustal melts to have higher ^{176}Hf/^{177}Hf ratios relative to the bulk source (Farina *et al.*, 2014). In such cases, source composition and melting conditions exert a first order control on Hf isotopic equilibrium during anatexis (Tang *et al.*, 2014). To test the residual zircon effect on Hf isotopes in granitic rocks, we carried out a Nd-Hf-O isotopic study of SPG in the Chinese Altai. We then evaluate the generality of residual zircon effect in granitic magmatism using a compiled Nd-Hf isotope database.

The Central Asian Orogenic Belt (CAOB) is Earth's largest Phanerozoic accretionary orogen (Kröner *et al.*, 2014). The Chinese Altai is located in the central CAOB (Fig. S-1a), with >40 % of the exposed rocks being granites (Zhang *et al.*, 2017). Previous studies dated CAOB plutons as Late Ordovician-Devonian (450 to 370 Ma) and Permian (280 to 270 Ma) and also report Nd-Hf isotopic decoupling in these granites (*e.g.*, Zhang *et al.*, 2017). This paper reports new U-Pb

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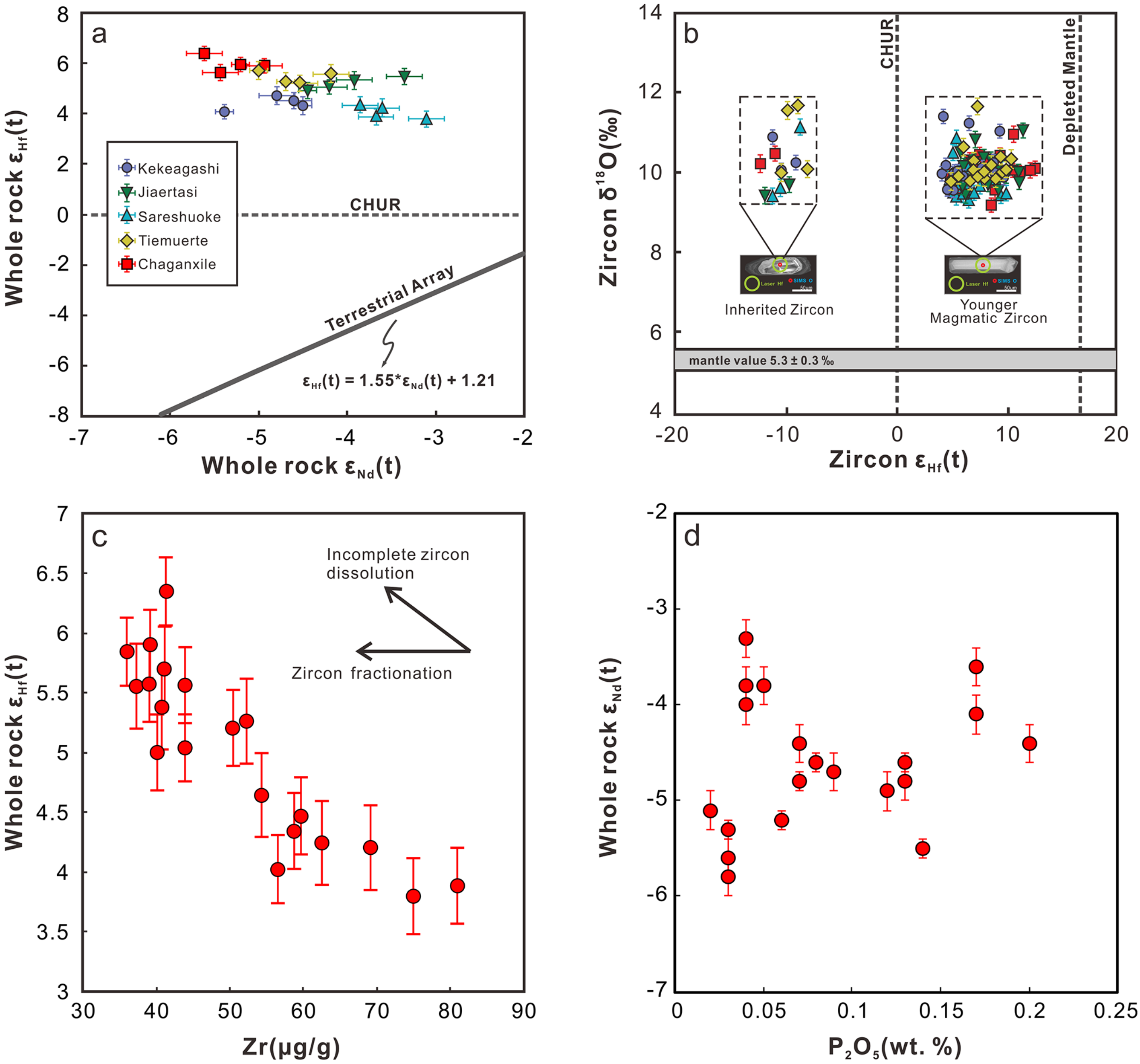

Figure 1 **(a)** $\varepsilon_{Hf}(t)$ *versus* $\varepsilon_{Nd}(t)$ for SPG in the Chinese Altai calculated based on U-Pb ages of the various plutons. Terrestrial array equations are from Vervoort *et al.* (2011). **(b)** Zircon $\varepsilon_{Hf}(t)$ *versus* zircon $\delta^{18}O$ for SPG in the Chinese Altai. Mantle values after Valley *et al.* (1998). Inherited zircons show $\varepsilon_{Hf}(t)$ and $\delta^{18}O$ values, indicating a metasedimentary source. Younger magmatic zircons show positive $\varepsilon_{Hf}(t)$ values and similarly high $\delta^{18}O$ values, CHUR-chondritic uniform reservoir. **(c)** $\varepsilon_{Hf}(t)$ *versus* Zr (μg/g). **(d)** $\varepsilon_{Nd}(t)$ *versus* P_2O_5 (wt. %). Uncertainties of all isotope measurements are internal 2σ.

ages, Nd-Hf-O isotopic compositions, major and trace element geochemistry, and Hf-O isotopes of inherited zircons within SPG samples from the Chinese Altai with the aim of providing insights into SPG melting processes and isotope systematics.

Methods and Results

Granite samples from the Kekeagashi, Tiemuerte, Jiaertasi, Chaganxile, and Sareshuoke plutons in the Chinese Altai (Fig. S-1b) were analysed. *In situ* zircon U-Pb analysis was performed using laser ablation inductively coupled plasma mass spectrometry (ICP-MS). Whole rock (WR) major/trace element compositions were analysed using X-ray fluorescence spectrometry and inductively coupled plasma mass spectrometry. Nd isotope measurements were conducted using a MAT-262 thermal ionisation mass spectrometer in static mode. Hf isotope measurements were analysed using Nu Plasma II ICP-MS. *In situ* zircon Hf isotope analyses were conducted using a Thermo Scientific Neptune ICP-MS coupled to a 193-nm laser. *In situ* zircon O isotope analyses were conducted using a Cameca IMS-1280HR secondary ion mass spectrometer. Details of analytical methods are provided in Supplementary Information.

Zircon U-Pb ages show granite crystallisation between 437 and 409 Ma (Fig. S-2). U-Pb dating of inherited zircon cores indicate that Palaeozoic zircon grains seeded on significantly older crystals, with ages ranging from 3506 to 1990 Ma (Fig. S-3). The WR $\varepsilon_{Nd}(t)$ and $\varepsilon_{Hf}(t)$ values range from −5.6 to −3.1 and +3.8 to +6.3, respectively. The $\delta^{18}O$ and $\varepsilon_{Hf}(t)$ values of the magmatic zircon rims spanned from +9.2 to +11.6 ‰ and +4.0 to +12.3, respectively. The $\delta^{18}O$ values of zircon cores range from +9.3 to +11.8 ‰ and $\varepsilon_{Hf}(t)$ values from −12.4 to −8.2. Data are available in Tables S-1 and S-2.

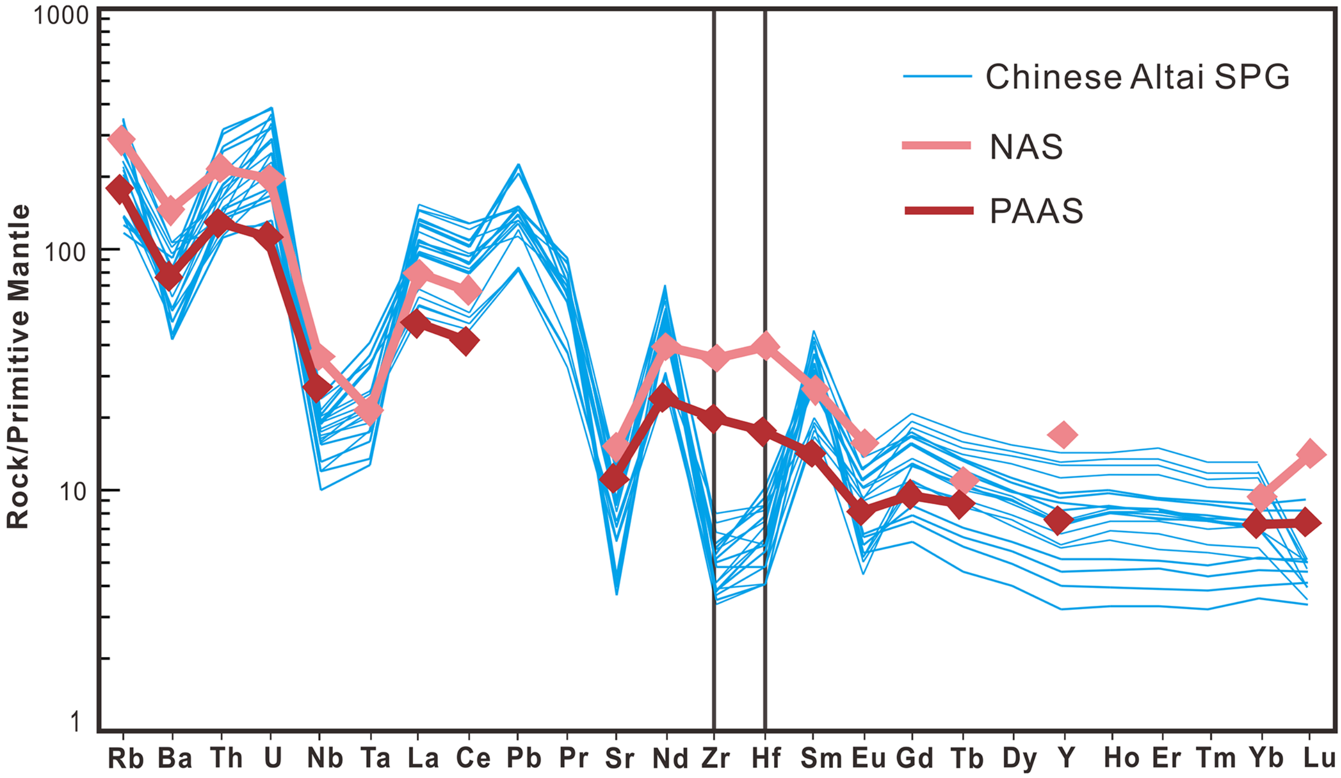

Figure 2 Primitive mantle-normalised trace element spider patterns of the studied granites, PAAS and NAS. Normalisation data from Sun and McDonough (1989). Note the Zr-Hf depletions of the SPG from this study. All the data are listed in Table S-4.

Discussion and Implications

High $\delta^{18}O$ values (+9.2 to +11.6 ‰), low $\varepsilon_{Nd}(t)$ values (−5.6 to −3.1), strongly-peraluminous character (A/CNK = 1.1-1.3), presence of aluminous minerals (*i.e.* garnet, sillimanite, cordierite, and muscovite; Fig. S-4), and low Fe, Mg, Ca, and Na contents are consistent with derivation of melted sediment (Chappell and White, 1974).

The highly radiogenic Hf isotopes of these SPG and Nd-Hf isotopic decoupling (Fig. 1a) give contradictory implications as to the contributions of isotopically depleted and enriched materials. It is feasible that Nd-Hf isotopic decoupling is either highlighting differential source signature or caused by crustal melting processes. Mineral sorting effects during sediment transport can concentrate zircon in coarse-grained sedimentary rocks while fine-grained, clay-rich rocks are nearly devoid of zircon (Carpentier *et al.*, 2009). Consequently, zircon-depleted sediments tend towards radiogenic Hf isotope signatures, while zircon-rich sediments generally have unradiogenic Hf isotope compositions. Melting of fine-grained, zircon-poor sedimentary rocks is likely to produce magmas with radiogenic Hf isotope compositions relative to their Nd isotope composition and account for a negative correlation between magma $\varepsilon_{Hf}(t)$ and Zr concentration (Fig. 1c). However, we suggest that this mechanism is unlikely to be responsible for isotopic decoupling in the investigated granites as; 1) the sedimentary rocks in the studied area are sandstones and mudstones that are enriched in zircon and have moderate to low Nd/Hf ratios (from 0.8 to 3.8, Long *et al.*, 2008); 2) fine-grained clastic sedimentary proxies (Post-Archean Australian Shales [PAAS] and North American Shales [NAS]), are not depleted in Zr and Hf while SPG of the Chinese Altai are depleted in Zr and Hf (Fig. 2); 3) inherited zircon cores are abundant in SPG, suggesting the source is not zircon-depleted. Thereby, we therefore conclude that radiogenic Hf isotopes are not source signatures nor is Nd-Hf isotopic decoupling due to melting of zircon-poor fine-grained sediments.

Nd-Hf isotopic decoupling may also be generated by disequilibrium melting with incomplete zircon dissolution (Fig. S-5; Zeng *et al.*, 2005; Farina *et al.*, 2014; Tang *et al.*, 2014; Iles *et al.*, 2018). Because Hf diffusion in zircon is slow under crustal melting conditions (Watson and Harrison, 1983), Hf isotope equilibrium during crustal anatexis is largely controlled by zircon dissolution. Inherited zircons in our samples are evidence of incomplete zircon dissolution during anatexis. Residual zircon in magma sources can retain unradiogenic Hf (*i.e.* low $^{176}Hf/^{177}Hf$) and may produce partial melts with elevated $\varepsilon_{Hf}(t)$ relative to the source. This model explains Hf isotope variability recorded by zircon crystallising during partial melting and inherited zircon dissolution. This may generate melt batches with variable Hf isotope compositions, even if melts come from a single source (Tang *et al.*, 2014). This single source melting scenario is supported by the zircon O isotopic compositions for the Chinese Altai granites. If the variation in zircon Hf isotopic composition is due to mixing between mantle-derived magmas and metasedimentary materials, negative correlations between zircon $\varepsilon_{Hf}(t)$ and zircon $\delta^{18}O$ (Kemp *et al.*, 2007) are expected. However, Chinese Altai granites show similar $\delta^{18}O$ (cores: +9.3 to +11.8 ‰; rims: +9.2 to +11.6 ‰) despite the large Hf isotopic variation (>20 epsilon units; Fig. 1b).

Disequilibrium melting with residual zircon can explain strong Zr and Hf depletions in the Chinese Altai granites (Fig. 2) as zircon hosts most Zr and Hf. More importantly, the WR and zircon $\varepsilon_{Hf}(t)$ values of SPG correlate negatively with Zr concentrations (Fig. 1c), which is expected if residual zircon controls Hf isotopes and Zr and Hf concentrations in partial melts. Zircon fractionation during magma differentiation may also cause Zr and Hf depletions, but would not produce negative correlations between Hf isotopic composition and Zr concentration.

Nd concentrations in the melt and residue are dominantly controlled by apatite and monazite (Zeng *et al.*, 2005). Nd isotopes may be affected by disequilibrium melting with

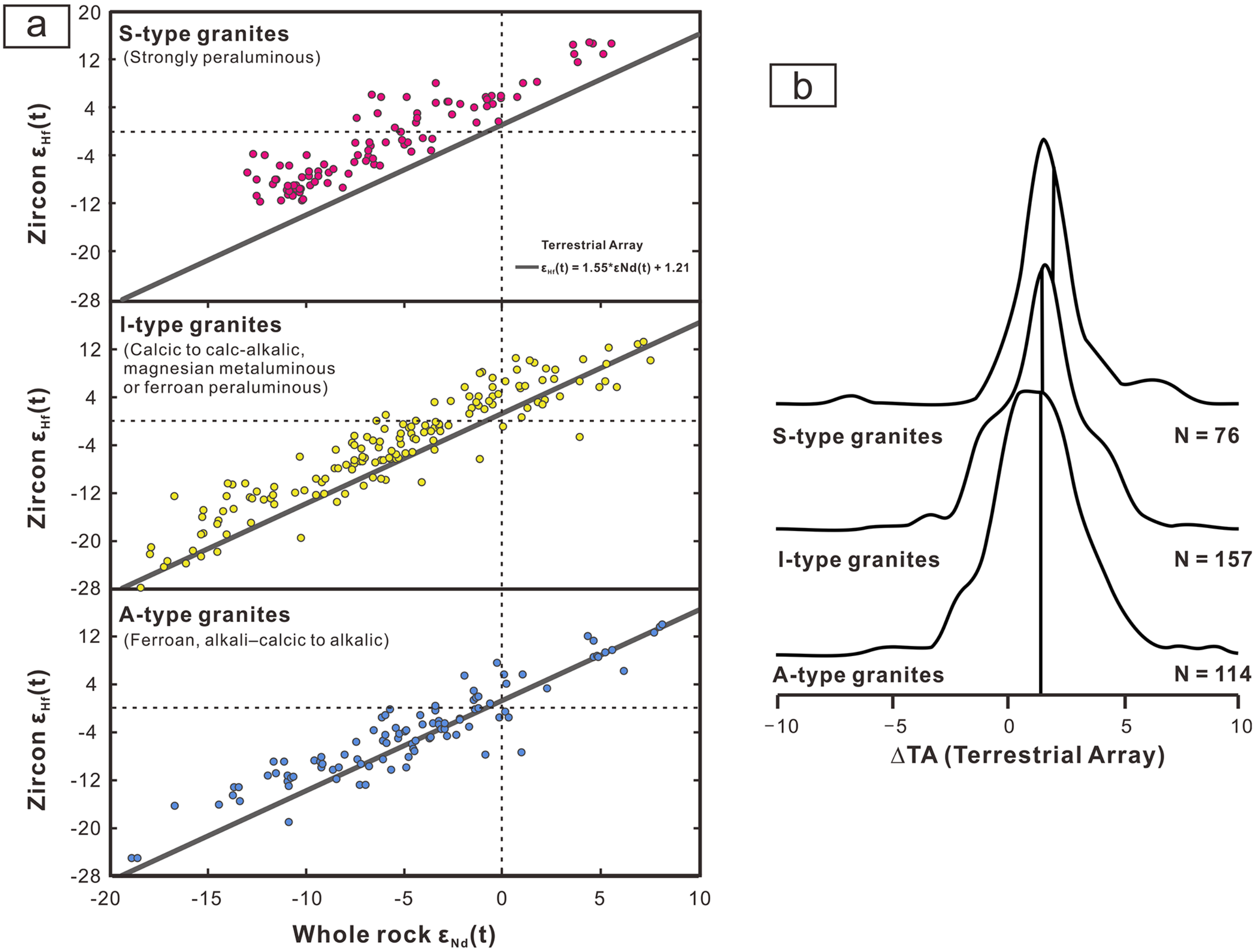

Figure 3 **(a)** Compilation of published neodymium and hafnium isotopic compositions of I-type, A-type, and S-type granites (as defined in the figure). Points represent average zircon values from single plutons. References listed in Table S-3. **(b)** Distance from the terrestrial array (TA) expressed as ΔTA calculated for the three granite groups. Vertical line represents the median of all of the samples and demonstrate an increasing shift towards greater Hf disequilibrium (above the TA) with increasing aluminousity.

residual apatite and monazite. However, zircon has extremely low Lu/Hf and thus strongly fractionates Hf from Lu while apatite and monazite only moderately fractionate Nd and Sm. Therefore, Hf isotopes are more sensitive to disequilibrium melting than Nd isotopes even if both zircon and P-bearing accessory minerals are present in the residues. This is supported by the observation that ε_{Hf}(t) strongly correlates with Zr concentration while ε_{Nd}(t) varies independently from P_2O_5 in our samples (Fig. 1d). We suggest that Nd-Hf decoupling of Altai SPG is caused by the Hf isotopic disequilibrium and incomplete zircon dissolution during sediment melting. Mineral sorting might have a minor contribution to isotopic decoupling in zircon-rich sources.

To evaluate the generality of residual zircon effects in granitic magmatism, we compiled a database of Chinese granite Nd-Hf isotope compositions. Nd-Hf isotopic decoupling is present in SPG with systematically elevated ε_{Hf}(t) relative to the terrestrial Nd-Hf isotope array (TA) and is also present to a lesser degree in I-type (calcic to calc-alkalic, magnesian metaluminous or ferroan peraluminous) granites (Fig. 3). This is in contrast to A-type (ferroan, alkali-calcic to alkalic) granites that overlap with the TA. We calculated minimum temperatures required to dissolve zircon completely in the source rocks (Fig. 4). We assume the melting degree to be ~30 % (Petford *et al.*, 2000). Our calculation shows that, for peraluminous melts (M > 1.1), complete zircon dissolution would require >950 °C if the source contains >200 µg/g Zr, which appears to be too high for most SPG systems. Considering that the average PAAS and NAS contains 210 and 200 µg/g Zr, respectively (Gromet *et al.*, 1984; Taylor and McLennan, 1985), residual zircon seems to be inevitable if the source rocks are detritus-rich sedimentary rocks. I-type granites also deviate from the TA to a lesser degree than SPG but greater than A-type granite implying sediment assimilation in typical arc settings (Fig. 3). We suggest that may also be explained by a residual zircon effect if zircon is present in the sources of I-type granites.

These findings raise questions to the utility of Hf isotopes in quantifying crustal recycling as disequilibrium melting and residual zircon may lead to radiogenic Hf isotopes in the partial melts that falsely indicate juvenile sources. Therefore, Hf isotopes of SPG and I-type granites may not faithfully reflect the protoliths. Hf isotopes biased by residual zircon may lead to erroneous conclusions in detrital zircon studies as petrogenetic context is missing. Rates of crustal reworking can be significantly underestimated if only Hf isotopes are applied. Therefore, caution is needed when using detrital zircon Hf isotopes to reconstruct the net growth of the continental crust.

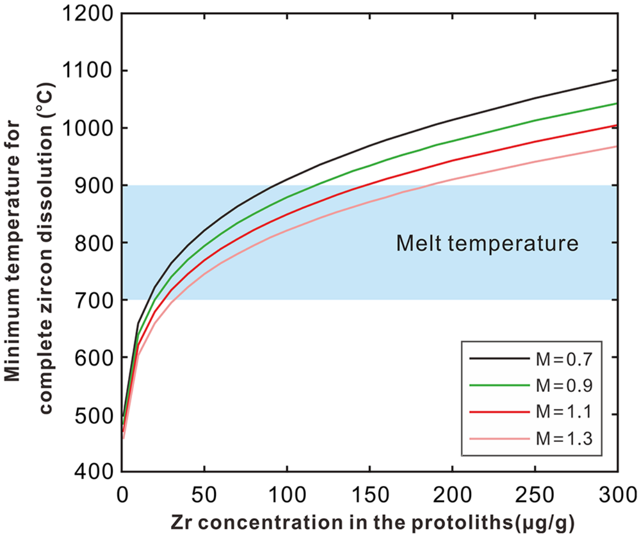

Figure 4 Calculated minimum melt temperature for zircon dissolution as a function of Zr concentration in the protoliths and M value (cation ratio). SPG have M values > 1.1 while I-type granites typically have M values < 1.0. Melt Zr concentration at zircon saturation using the zircon saturation model of Boehnke *et al.* (2013).

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Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article2001.

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