

Oxygen and neodymium isotope evidence for recycling of juvenile crust in northeast China

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ABSTRACT

It has been long recognized from Nd and Sr isotopes that depleted mantle sources consist of recycled oceanic materials, but difficulty was encountered in identifying this signature by means of oxygen isotopes because of significant postemplacement hydrothermal alteration. Zircon is expected to preserve this signature because it is resistant to high-temperature hydrothermal alteration. This effect is illustrated by a combined Sm-Nd and oxygen isotope study of whole-rock and mineral samples from a Mesozoic A-type granite at Nianzishan in northeastern China. The Sm-Nd isotope results show positive $\epsilon_{Nd}(t)$ values of +0.86 to +4.27 with young Nd model ages of 569–846 Ma, manifesting a significant input of newly mantle derived material. The zircon $\delta^{18}O$ values of 3.12‰–4.19‰ are significantly lower than the $\delta^{18}O$ value of 5.3‰ \pm 0.3‰ for the normal mantle zircon and thus appear to require remelting of hydrothermally altered oceanic crust. The combined Nd-O isotope studies not only provide compelling evidence for geochemical recycling of young juvenile crust by plate subduction, but also demonstrate that the granitic magmas can result from partial melting of mantle-derived rocks that were subjected to seawater-hydrothermal alteration before magma generation. Disequilibrium oxygen isotope fractionations are observed between common rock-forming minerals with significantly lower $\delta^{18}O$ values for alkali feldspar than seawater, corresponding to meteoric-hydrothermal alteration after magma crystallization.

Keywords: oxygen isotopes, neodymium isotopes, zircon, hydrothermal alteration, A-type granite, China.

INTRODUCTION

The time and process of crust-mantle differentiation and continental crustal growth can be accessed by the Nd isotope composition of granites. Most granites show negative $\epsilon_{Nd}(t)$ values and old Nd model ages, suggesting that these granites were generated by recycling of preexisting continental crust with a minor proportion of ancient mantle-derived materials (e.g., Allègre and Ben Othman, 1980; McCulloch and Chappell, 1982; Farmer and DePaolo, 1983; Chen and Jahn, 1998). However, Phanerozoic granites from the Central Asian orogenic belt are commonly characterized by the Nd isotope signature of depleted mantle with positive $\epsilon_{Nd}(t)$ values and Nd model ages younger than 1.0 Ga (Kwon et al., 1989; Han et al., 1997; Chen et al., 2000; Wu et al., 2000), indicating that newly mantle derived materials may play a predominant role in their petrogenesis.

While the Nd isotope study of granites reveals the input of newly mantle derived materials, the O isotope analysis of constituent minerals can clearly define premagmatic and postmagmatic hydrothermal alterations in the granite. Postmagmatic, subsolidus interaction with meteoric water is very common for granites intruding into upper crustal levels. Geo-

chemically, this interaction is characterized by $\delta^{18}O$ values considerably lower than the normal mantle value of 5.7‰ \pm 0.5‰ (Mattey et al., 1994; Harmon and Hoefs, 1995; Eiler et al., 1997; Valley et al., 1998) and by disequilibrium oxygen isotope fractionations between quartz and feldspar (Taylor, 1971, 1977). A few low- $\delta^{18}O$ silicic magmas were reported for volcanic rocks (Friedman et al., 1974; Hildreth et al., 1984; Taylor and Shepard, 1986; Bacon et al., 1989; Balsley and Gregory, 1998; Bindeman and Valley, 2001) and felsic intrusive rocks (Gilliam and Valley, 1997; Monani and Valley, 2001), but difficulties were encountered in identifying the presence of low- $\delta^{18}O$ magma for hydrothermally altered granites. Because zircon is resistant to hydrothermal alteration even at high temperatures (Valley et al., 1994; Watson and Cherniak, 1997; Zheng and Fu, 1998), its isotope record can provide an unambiguous identification of ^{18}O depletion in magmas (Valley et al., 1994; Gilliam and Valley, 1997; King et al., 1998; Monani and Valley, 2001). With this robust technique, it is possible to distinguish an ^{18}O -depleted granitic magma from an ^{18}O -depleted granite that underwent meteoric-hydrothermal alteration. This paper presents a case study of a Mesozoic A-type granite pluton in northeast-

ern China; combined Nd-O isotope studies reveal that this intrusion was formed from oceanic crust that was previously altered by seawater at high temperature.

GEOLOGICAL SETTING

The Nianzishan A-type granite is located northwest of Haerbin city, northeastern China (Fig. 1). It is one of the representative Mesozoic A-type granites within extensional settings along the continental margin of eastern China (Wang et al., 1995). Tectonically, the Nianzishan A-type granite occurs in the southeastern part of the Central Asian orogenic belt, close to the northeastern part of the Sino-Korean craton and in the vicinity of the western margin of the Mesozoic Pacific plate (Hilde et al., 1977; Ma, 1988). The granitic pluton

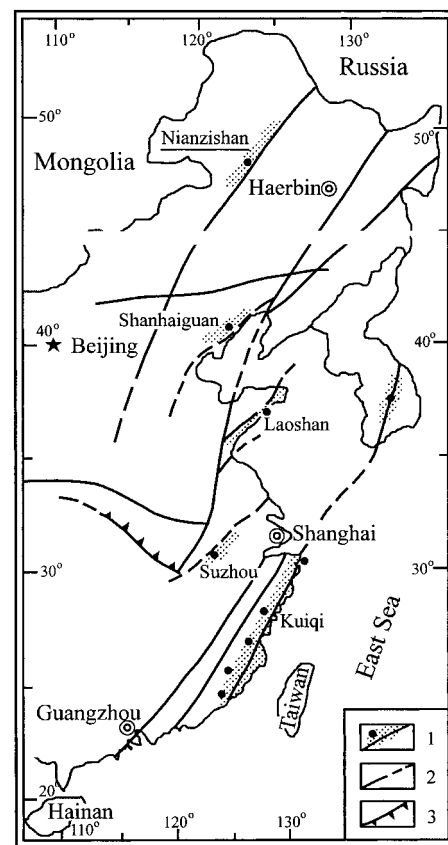


Figure 1. Map of Mesozoic A-type granite plutons distributed in eastern China (modified after Wang et al., 1995). Symbols: 1—tectonic belts related to A-type granites, 2—major faults, 3—boundary between Sino-Korean and Yangtze cratons.

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was intruded into high levels in the upper crust, as evidenced by mirolitic cavities. The pluton crops out over an area of ~15 km² and is surrounded by andesitic country rocks.

The mineral assemblages of the Nianzishan A-type granite are mainly composed of quartz, alkali feldspar, Na-rich amphibole, pyroxene, and minor amounts of accessory minerals such as magnetite and zircon (Wang et al., 1995; Wei et al., 2000). The granite has SiO₂ contents of 69.5 wt%–76.7 wt%, and K₂O + Na₂O > 8 wt% with (K₂O + Na₂O)/Al₂O₃ ≥ 1 (atomic ratio). Significant water-rock interaction during magma emplacement has been recognized for the granite pluton by the H and O isotope analyses of common rock-forming minerals (Li et al., 1991; Wei et al., 2000), but it is unclear whether the protolith of the granite was depleted in ¹⁸O before magma generation.

ANALYTICAL METHODS

Sm-Nd isotope analysis was carried out for whole-rock samples from the Nianzishan A-type granite. The samples were dissolved by acid (HNO₃ + HF) in a sealed Savillex beaker on a hot plate (80 °C). Separation of Sm and Nd was done by a routine two-column ion-exchange technique (Li et al., 1988; Wang et al., 1988). The Nd isotope ratio was measured on a Finnigan MAT-262 thermal ionization mass spectrometer at the University of Science and Technology of China. The ¹⁴³Nd/¹⁴⁴Nd ratios were normalized against ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. During the period of data acquisition, the Ames internal Nd standard gave ¹⁴³Nd/¹⁴⁴Nd ratios of 0.511967 ± 0.000002 (2σ), which is equivalent to the La Jolla value of 0.511865.

O isotope analysis was performed for mineral separates and whole rock. The minerals were separated by conventional magnetism and heavy-liquid techniques, and then hand-picked under a binocular microscope to purity generally better than 99%. Chlorite and clay minerals were not observed in the studied samples. Only transparent zircon was used for O isotope analysis. The ¹⁸O/¹⁶O ratio of zircon was analyzed at the University of Wisconsin—Madison by laser fluorination technique (Valley et al., 1995). Isotope ratios are expressed in conventional δ¹⁸O notation in per mil relative to standard mean ocean water. In the course of analysis, the average δ¹⁸O value of UWG-2 garnet standard was 5.74‰ ± 0.06‰ from four measurements, consistent with the accepted value of 5.80‰.

The ¹⁸O/¹⁶O ratios of whole-rock and common rock-forming minerals were analyzed at the University of Science and Technology of China by the conventional BrF₅ method with a reproducibility better than ±0.2‰ for ¹⁸O (Zheng et al., 1998). The ¹⁸O/¹⁶O ratio was measured on a Delta+ gas-source mass spec-

trometer at Hefei. Three different quartz standards were used: δ¹⁸O = 11.12‰ for the National Standard of China GBW04409, δ¹⁸O = -1.72‰ for the National Standard of China GBW04410, and δ¹⁸O = 9.64‰ for the International Standard NBS-28.

RESULTS

As listed in Table 1¹, the Sm-Nd isotope analyses of 10 whole-rock samples from the Nianzishan A-type granite show small variations in both ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd ratios (0.0984–0.1220 and 0.512603–0.512784, respectively). In terms of the whole-rock Rb-Sr isochron age of 123 Ma for the granite (Li and Yu, 1993), the initial ¹⁴³Nd/¹⁴⁴Nd ratio was calculated to yield positive ε_{Nd}(t) values of +0.86 to +4.27. Nd model ages were calculated by using a one-stage model relative to the depleted mantle (DePaolo, 1988) and a two-stage model (Liew and Hofmann, 1988) relative to the averaged continental crust (Jahn and Condie, 1995). In either case, Nd model ages younger than 1.0 Ga are obtained with T_{DM} of 520–788 Ma and T_{DM2} of 569–846 Ma. Both positive ε_{Nd}(t) values and young Nd model ages clearly point to a predominant contribution from newly mantle derived material in the Neoproterozoic, derived from either the oceanic crust or a mixed older crustal source with a juvenile source (DePaolo, 1988; Liew and Hofmann, 1988).

As shown in Table 2 (see footnote 1), the δ¹⁸O values of six zircon samples from the Nianzishan A-type granite are from 3.12‰ to 4.19‰, and the analytical precision of the four repeated samples is very good (1σ = 0.01‰–0.04‰). In contrast, there are large δ¹⁸O variations in the other phases: -1.6‰–2.0‰ for whole rock, 0.9‰–5.8‰ for quartz, -3.3‰–0.1‰ for alkali feldspar, and -7.0‰ to -1.5‰ for magnetite (Table 3; see footnote 1). Obviously, the δ¹⁸O values of the Nianzishan zircon are significantly lower than the δ¹⁸O values of the normal mantle (Mattey et al., 1994; Harmon and Hoefs, 1995; Eiler et al., 1997; Valley et al., 1998), and also of common A-type granites (Javoy and Weis, 1987), suggesting the input of a crustal component, particularly the surface fluid (Hoefs, 1997).

O isotope fractionations vary from -2.62‰ to 1.92‰ between quartz and zircon, -7.32‰ to -3.96‰ between alkali feldspar and zircon, 5.04‰ to 10.52‰ between zircon and magnetite, and 2.9‰ to 9.1‰ between quartz and alkali feldspar. Disequilibrium fractionations are very evident between these mineral

¹GSA Data Repository item 2002037, Nd, δ¹⁸O, and whole-rock analytical data from Nianzishan, northeast China, is available upon request from Documents Secretary, GSA, P.O. Box 9140, Boulder, Colorado 80301-9140, editing@geosociety.org, or at www.geosociety.org/pub/fit2002.htm.

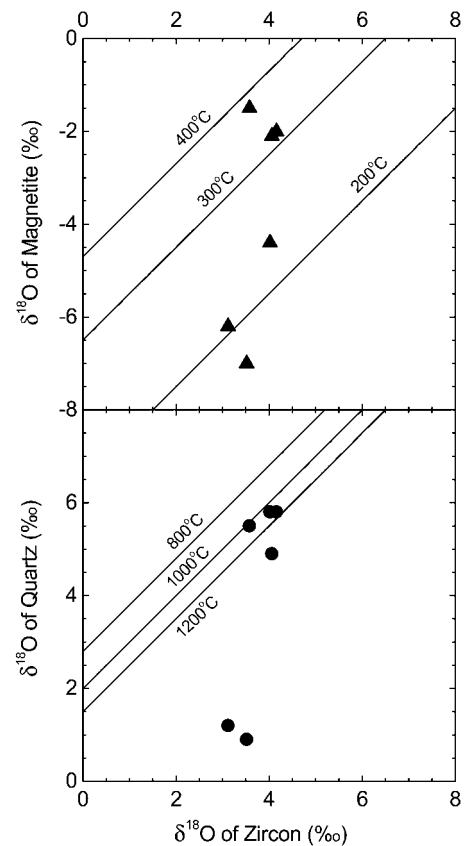


Figure 2. O isotope fractionations between quartz and zircon and between magnetite and zircon from Nianzishan A-type granite. Isotherms are calculated after Zheng (1993a, 1995).

pairs when compared with experimentally, empirically, and theoretically determined values for equilibrium fractionations (Clayton et al., 1989; Chiba et al., 1989; Zheng, 1993a, 1995), pointing to postmagmatic water-rock interaction under subsolidus conditions. A relatively steep pattern of δ¹⁸O distribution is observed not only among quartz, magnetite, and zircon (Fig. 2), but also between quartz and alkali feldspar (Fig. 3), suggesting short-lived kinetic effects of water-rock interaction in the postmagmatic stage (Criss et al., 1987; Gregory et al., 1989). Therefore, the disequilibrium fractionations are secondary, resulting from hydrothermal alteration after magma crystallization, and thus do not represent the δ¹⁸O values of original magma.

DISCUSSION

The statistical mean value of the 11 zircon δ¹⁸O analyses for the Nianzishan A-type granite is 3.85‰ ± 0.33‰ (1 S.D.), which is significantly lower than the δ¹⁸O range of 5.3‰ ± 0.3‰ for zircon in high-temperature equilibrium with the normal mantle (Valley et al., 1998). It could be proposed that high-temperature water-rock interaction in the postmagmatic stage reset zircon to lower δ¹⁸O values. If so, the δ¹⁸O value of altered zircons would

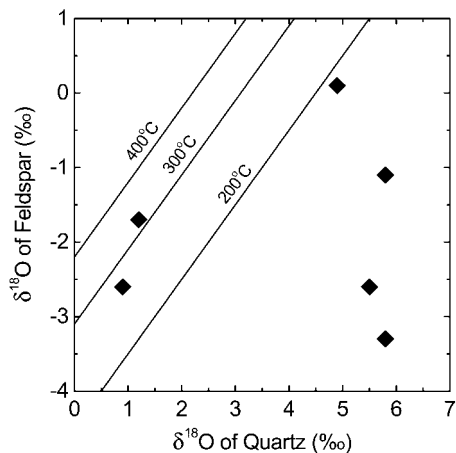


Figure 3. O isotope fractionation between quartz and alkali feldspar from Nianzishan A-type granite. Isotherms are calculated after Zheng (1993a).

be more variable than observed because the temperature, time scale, and water/rock ratio would not be constant during postmagmatic water-rock interaction.

The zircon $\delta^{18}\text{O}$ values measured for the Nianzishan A-type granite are relatively uniform and highly clustered at $3.85\text{‰} \pm 0.33\text{‰}$. Furthermore, zircon is very resistant to hydrothermal alteration because of the sluggish rate of oxygen diffusion of zircon (Valley et al., 1994; Watson and Cherniak, 1997; Zheng and Fu, 1998). In addition, nonmetamict, low-magnetism zircons typically retain their magmatic $\delta^{18}\text{O}$ values even through high-grade metamorphic events and thus are resistant to later hydrothermal activities (Valley et al., 1994; Gilliam and Valley, 1997; King et al., 1998; Monani and Valley, 2001). These lines of evidence argue against the possibility that the low $\delta^{18}\text{O}$ values for zircon from the Nianzishan A-type granite are due to the hydrothermal alteration in the postmagmatic stage. Instead, the low $\delta^{18}\text{O}$ values result from partial melting of crustal material that was subjected to hydrothermal alteration by an ^{18}O -depleted surface fluid at high temperature. In other words, the source material of the Nianzishan A-type granite was depleted in ^{18}O before magma generation.

It is well known that significant fractionation of oxygen isotopes occurs only at the surface of Earth and is temperature dependent (Hoefs, 1997). Normal mantle-derived magmas and their derivatives have well-defined $\delta^{18}\text{O}$ values of $5.7\text{‰} \pm 0.5\text{‰}$ (Mattey et al., 1994; Harmon and Hoefs, 1995; Eiler et al., 1997), and mantle zircons have $\delta^{18}\text{O}$ values of $5.3\text{‰} \pm 0.3\text{‰}$ (Valley et al., 1998). In contrast, altered basaltic and gabbroic rocks of the oceanic crust vary systematically in $\delta^{18}\text{O}$ from those $>9\text{‰}$ in pillow basalt-sheeted dike complexes to those $<4\text{‰}$ in deep gabbroic sections (Muehlenbachs, 1986). This differ-

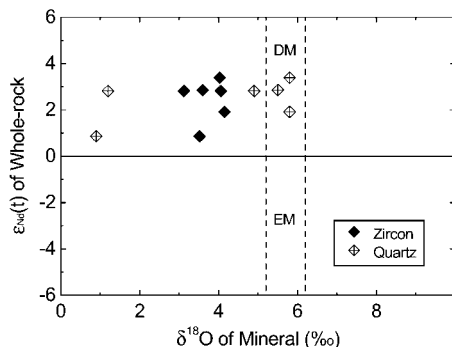


Figure 4. Nd and O isotope relationship for Nianzishan A-type granite. DM and EM denote depleted and enriched mantles, respectively.

ence in $\delta^{18}\text{O}$ as a function of depth within the oceanic crust is a direct result of increasing temperature of seawater-hydrothermal alteration, from $<150\text{ }^\circ\text{C}$ for the pillow-basalt section to $>300\text{ }^\circ\text{C}$ for the gabbroic section (Hoefs, 1997). Consequently, the O isotope composition of a mantle-derived mineral or melt is a sensitive indicator of recycled crustal materials as its protolith or in its source. Therefore, both low zircon $\delta^{18}\text{O}$ values of $3.85\text{‰} \pm 0.33\text{‰}$ and positive whole-rock $\epsilon_{\text{Nd}}(t)$ values of $+0.86$ to $+4.27$ for the Nianzishan A-type granite (Fig. 4) reflect the high-temperature seawater-hydrothermal alteration to its gabbroic protolith of the oceanic crust before partial melting. In particular, the positive $\delta^{18}\text{O}$ zircon values argue against meteoric-hydrothermal alteration to the source rock, although both meteoric water and seawater are large reservoirs of the ^{18}O -depleted surface fluid.

It is expected that there is O isotope fractionation between zircon and melt when the zircon crystallizes from the ^{18}O -depleted magma. According to the theoretical calculations of Zheng (1991, 1993a, 1993b) and the model abundance of gabbro minerals, equilibrium O isotope fractionations between gabbroic melt and zircon are $\sim 0.78\text{‰}$ – 0.58‰ at 1000 – $1200\text{ }^\circ\text{C}$. In terms of the zircon $\delta^{18}\text{O}$ values of 3.12‰ – 4.19‰ for the Nianzishan A-type granite (Table 2; see footnote 1), the gabbroic melt is calculated to have $\delta^{18}\text{O}$ values of 3.70‰ – 4.97‰ , still considerably lower than the $\delta^{18}\text{O}$ values of $5.7\text{‰} \pm 0.5\text{‰}$ for the normal mantle. The low $\delta^{18}\text{O}$ magma is best explained by partial melting of the oceanic crust during subduction that previously exchanged with heated seawater.

The significant ^{18}O depletion and variability in quartz, alkali feldspar, and magnetite from the Nianzishan A-type granite (Figs. 2 and 3) indicates O isotope exchange with a low $\delta^{18}\text{O}$ fluid under subsolidus conditions. The meteoric water is assumed to be the ^{18}O -depleted fluid for the following reasons: (1) the alkali

feldspar samples with $\delta^{18}\text{O} < 0\text{‰}$ are observed in the granite (Table 3; see footnote 1), which cannot result from isotopic exchange with seawater ($\delta^{18}\text{O} = 0\text{‰} \pm 1\text{‰}$); (2) extreme D depletion ($\delta\text{D} = -126\text{‰} \pm 13\text{‰}$) is found in whole-rock samples throughout the pluton (Wei et al., 2000); and (3) the extensional tectonic setting for the emplacement of the Nianzishan A-type granite has been a terrestrial environment since the Mesozoic (Hilde et al., 1977; Ma, 1988), and thus there was no seawater available to exchange with the Nianzishan pluton after magma crystallization.

Quartz in granitoids is usually considered resistant to O isotope exchange by hydrothermal alteration relative to feldspar and mica. As shown in Figure 4, however, quartz from the Nianzishan A-type granite shows a larger $\delta^{18}\text{O}$ range, 0.9‰ – 5.8‰ , than that of the coexisting zircon, 3.12‰ – 4.08‰ . This suggests that quartz exchanges O isotopes more easily than zircon at hydrothermal conditions, consistent with the remarkable difference in O diffusivity between zircon and quartz (Valley et al., 1994; Watson and Cherniak, 1997; Zheng and Fu, 1998). The timing and fluid source for the hydrothermal alteration of quartz differ from those of zircon in the Nianzishan granite. The comprehensive oxygen isotope study of zircon and common rock-forming minerals reveals distinct processes of water-rock interaction in the history of the Nianzishan A-type granite.

CONCLUSIONS

The low $\delta^{18}\text{O}$ values of zircon from the Nianzishan A-type granite manifest the presence of a low $\delta^{18}\text{O}$ granitic magma, and its positive $\epsilon_{\text{Nd}}(t)$ values and young Nd model ages demonstrate magma derivation from partial melting of newly mantle derived material that underwent surface-fluid hydrothermal alteration before magma generation. The combined O and Nd isotopic study argues for seawater hydration and recycling of oceanic crust into continental crust. This provides geochemical evidence for the recycling of juvenile crust by subduction and thus has important implications for understanding the formation and evolution of granitoids and young continental crust. Furthermore, oxygen isotope analyses of zircon and the common rock-forming minerals reveal that the Nianzishan A-type granite underwent premagmatic and postmagmatic water-rock interactions during its formation and evolution. The results demonstrate the potential of combined O and Nd isotope studies in tracking magma sources and evolution in granite petrogenesis. It is also clear from this study how important it is to know zircon oxygen isotope compositions for igneous rocks that frequently underwent a secondary alteration.

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