

Zircon evidence of low $\delta^{18}\text{O}$ magma for A-type granites in eastern China

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Disagreement and debate exist for the origin of A-type granite, which usually occurs within extensional tectonic settings with alkaline and anhydrous imprints. In order to constrain the source of A-type granite, five well-documented late Mesozoic A-type granitic plutons (90 to 130Ma) in eastern China are studied. From north to south, they are Nianzishan, Shanhaiguan, Laoshan, Suzhou and Kuiqi plutons, respectively.

Systematic laser fluorination $\delta^{18}\text{O}$ analyses were carried out for zircon, quartz, and whole-rock. In total, 41 samples were separated and 109 analyses of $\delta^{18}\text{O}$ value from fresh zircon aliquots, 63 analyses of quartz and 57 analyses of whole-rock samples were measured. Compared to scattered $\delta^{18}\text{O}$ values of altered whole-rock (ranging 9.75‰ from -2.31‰ for Nianzishan pluton to 7.44‰ for Suzhou pluton), the overall $\delta^{18}\text{O}$ values of zircon from the A-type granites are uniformly low, which varies from 3.79±0.40‰ for Nianzishan pluton to 5.05±0.14‰ for Laoshan pluton.

Based on modeling and observed $\delta^{18}\text{O}$ values, the possibility of post-magmatic meteoric water-rock interaction and hydrothermally altered wallrock assimilation is ruled out as likely processes to lower the $\delta^{18}\text{O}$ value of zircons from these A-type granites. Low (less than "mantle zircon" $\delta^{18}\text{O}$ value of 5.3±0.3‰) and homogeneous zircon $\delta^{18}\text{O}$ values on the scale of hand specimen and pluton as well as equilibrium fractionation between quartz and zircon suggest these granites were derived from low $\delta^{18}\text{O}$ magma. As surface fluids of meteoric water and/or seawater are the known largest low $\delta^{18}\text{O}$ reservoir, we conclude that partial melting of crustal rock experiencing high-temperature alteration is the reasonable mechanism to produce the low $\delta^{18}\text{O}$ magma. This suggests that the origin of A-type granites in eastern China is primarily related to crustal reworking and/or recycling process. The crustal affinity of A-type granites in eastern China is not consistent with direct mantle-differentiation hypothesis. Combined Nd-Sr-Pb isotopic studies will further help to resolve intracrustal and/or interoceanic crust partial melting mechanism to generate A-type granites in eastern China.

Equilibrium Fe isotope fractionation between ferrous and ferric iron

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Equilibrium Fe isotope fractionation between aqueous ferrous and ferric species and the kinetics of isotope exchange were measured over a range of chloride concentrations (0, 11, 110 mM Cl⁻) and at two temperatures (0 and 22 °C). Results indicate that Fe isotope fractionation varies with temperature, but is independent of the extent of Fe(III)-Cl⁻ complexation over the range studied. Using ⁵⁷Fe-enriched tracer experiments the kinetics of isotopic exchange can be fit by a second-order rate equation, or a first-order equation with respect to both ferrous and ferric iron. The exchange is rapid at 22 °C, ~ 60-80 % complete within 5 seconds, whereas at 0 °C, exchange rates are about an order of magnitude slower.

The average measured equilibrium isotope fractionations, $\Delta_{\text{Fe(III)-Fe(II)}}$, in 0, 11, and 111 mM Cl⁻ solutions at 22 °C are identical within experimental error at +2.76±0.09, +2.87±0.22, and +2.76±0.06 ‰, respectively. This is very similar to the value measured by Johnson et al. (2002) in dilute (~ 20 mM) HCl solutions at pH ~ 2 and 5.5. At 0 °C, the average measured $\Delta_{\text{Fe(III)-Fe(II)}}$ fractionations are +3.25±0.38, +3.51±0.14 and +3.56±0.16 ‰ for 0, 11, and 111 mM Cl⁻ solutions. Assessment of the effects of partial re-equilibration on isotope fractionation during species separation suggests that the measured isotope fractionations are on average too low by ~ 0.20 ‰ and ~ 0.13 ‰ for the 22 °C and 0 °C experiments, respectively. Using corrected fractionation factors, we can define the temperature dependence of the isotope fractionation from 0 °C to 22 °C as:

$$10^3 \ln \alpha_{\text{Fe(III)-Fe(II)}} = A * 10^6 / T^2 + B$$

where A = 0.334±0.032 and B = -0.88±0.38.

These results confirm that the Fe(III)-Fe(II) fractionation is approximately half that predicted from spectroscopic data, and suggests that, at least in moderate Cl⁻ contents, the isotopic fractionation is relatively insensitive to Fe-Cl speciation.

References:

Johnson C.M., Skulan J.L., Beard B.L., Sun H., Neelson K.H. and Braterman P.S. (2002) *EPSL* **195**, 141-153.