Oxygen Isotope Geochemistry of Zircon

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In situ analysis by SIMS and LA-ICP-MS allows correlation of multiple geochemical systems within single sub-domains as small as 1 μm^3 of a zircon crystal. Such data have provided detailed records of igneous, metamorphic and sedimentary events in the crust of Earth and elsewhere.

Igneous zircons with $\delta^{18}O$ values outside of the "mantle-equilibrated" range (5.3±0.6‰ 2sd) indicate crustal input to parent magma. These values are preserved by slow diffusion rate in non-radiation-damaged zircon even through granulite metamorphism and anatexis (1). Zircon growth zoning can thus record magma contamination or mixing during sucessive tectonic events. In contrast to radiogenic isotope systems that evolve with time and trace elements that fractionate due to different degrees of incompatibility, $\delta^{18}O$ fractionates largely in response to low temperature exchange with fluids. Each system contributes complimentary information.

High values of $\delta^{18}O$ in igneous zircons (>6‰) are not in equilibrium with primitive mantle and provide a clear indication of magmas that contain a significant crustal component. This crustal signature provides a means for sorting U-Pb age and εHf data, when correlated *in situ* for sub-domains in zircon, to distinguish quantities of recycled crust and identify mantle extraction events (2).

The range of $\delta^{18}O$ in igneous zircons has increased since the end of the Archean with maximum values of 7.5‰ throughout the Archean increaseing to ~12‰ in the Phanerozoic (3). This secular trend of $\delta^{18}O_{max}$ started at ~2.5 Ga due to increased recycling of high-$\delta^{18}O$ supracrustal material into melts. Clay-rich mudstones are the largest high-$\delta^{18}O$ reservoir on Earth today, but were less common in the Archean suggesting that zircons document increased continental weathering after 2.5 Ga due to expansion of continents and epeiric seas, and oxygenation of the atmosphere.

Low $\delta^{18}O$ igneous zircons (<4.5‰) are most common in young rocks, but this has been argued to result from poor preservation of near-surface environments (3). The absence of a secular trend in minimum values of $\delta^{18}O$(Zrc) is high-lighted by zircons with $\delta^{18}O$ as low as -26‰ at 2.4 Ga (4).

In contrast to the relatively restricted variability of $\delta^{18}O_{max}$ for igneous zircons, values of $\delta^{18}O$ for metamorphic zircons are generally more variable and range up to 25.5‰ in detrital (probably Tertiary) metamorphic zircons (5) and 10.4‰ at 2.6 Ga (1). Thus higher $\delta^{18}O$ metasediments existed *locally* throughout the rock record and the apparent absence (scarcity?) of such elevated $\delta^{18}O$ igneous zircons indicates homogenization of larger *regional* domains by magmatism. Metamorphic zircons thus preserve unique evidence of smaller-scale environments that may be key to understand the larger transitions on Earth.

(1) Bowman et al. (2011) Am J Sci **311**, in press. (2) Kemp et al. (2006) Nature **439**, 580-583.(3) Valley et al. (2005) Contr Min Pet **150**, 561-580. (4) Bindeman et al. (2010) Geology **38**, 631-634. (5) Cavosie et al. (2011) Contr Min Pet **162**, 961-974.

Tracing nanoparticle interactions within living systems and in the environment: a case for the use of stable isotope labelling

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Background

Nanotechnology has the potential to revolutionise modern life, but has also been linked with concerns about the potential toxicity of newly created materials. This is because on the nanoscale, common materials can take on entirely new chemical, physical and biological properties, offering new unique technological opportunities, but also leading to unpredictable and potentially harmful biological or environmental effects. A substantial body of research now exists on the potential toxicity of nanomaterials, but many of these studies have been limited by difficulties in detecting nanoparticles in biological or envioronmental media, at appropriate concentrations. Often, the concentrations that make an experiment environmentally relevant are so low that the identification of nanoparticles containing elements already present at elevated concentrations (e.g. of Cu or Zn) in the environment and/or biota is not feasible.

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Results and Conclusions

Here, we are reviewing the results from a number of very recent studies on isotopically modified CuO and ZnO [1,2,3] which have successfully demonstrated the application of this labelling method in *in vivo* experiments with environmental relevance. We are also considering the challenges in the synthesis of labelled particles and speculating about where the method of stable isotope modification has potential to go in the future, including in a life-cycle context. We are finally reviewing the importance of appropriately designed experiments, in which a thorough understanding of the behaviour of nanoparticles in experimental media can be established, specifically in terms of aggregation, dissolution and complexation and how labelling can also contribute to improvement of experimental designs.

References

[1] Misra *et al* (2012) *Environmental Science & Technology* **46**, 1216-1222. [2] Croteau *et al* (2011) *Nanotoxicology* **5,** 79-90. [3] Dybowska *et al* (2011) *Environmental Pollution* **159,** 266-273.