

## **Appendix 1. Analytical methods.**

### **High precision oxygen isotope analyses ( $^{18}\text{O}/^{16}\text{O}$ )**

In order to achieve sub-‰ precision and accuracy for in-situ oxygen isotope ( $^{18}\text{O}/^{16}\text{O}$ ) analyses in zircon, we have used the CAMECA IMS-1280 ion microprobe at the University of Wisconsin, Madison (Wisc-SIMS). Improvements on precision and analysis time are due to: (1) 10  $\mu\text{m}$  diameter primary  $\text{Cs}^+$  beam ( $\sim 3\text{ nA}$ ); (2) homogeneous electron beam alignment for charge compensation; (3) automated X-Y and manual Z focusing before individual spot analyses; (4) optimized ion optics for high transmission ( $>70\%$ ) using transfer optics magnification of  $\times 200$ ; (5) simultaneous acquisition of two oxygen isotopes using multi-collector Faraday Cups (FC); (6) fast automated analyses (3.5 min) per spot; and (7) highly stable magnetic field regulation using a nuclear magnetic resonance (NMR) probe ( $<10\text{ ppm}$  for 10 hours) without making a mass calibration for each analyses (Kita et al. 2009; Page et al. 2007a). A summary of the detailed analytical conditions is listed in the table below. We obtained high secondary ion count rates of  $3 \times 10^9$  cps (count per second) on  $^{16}\text{O}$  and  $6 \times 10^6$  cps on  $^{18}\text{O}$ , which reduced internal precision to 0.1‰ (1 sd), while keeping the small primary beam size ( $\sim 10\text{ }\mu\text{m}$ ) required for many geology applications. The homogeneous e-gun beam and fine re-tuning of secondary ions at each spot improved reproducibility of the analyses. For each spot analysis of zircon, there is no resolvable drift of oxygen isotope ratios with sputtering depth. The internal error of each analysis ( $\sim 0.1\%$ ) is consistent with statistical error expected from the thermal drift of the H1 FC detector ( $\sim 2000$  cps for 4 s integrations). Standard analyses are performed frequently to bracket sample analyses, so that any small sub-‰ instrumental changes could be monitored and corrected. The NMR probe was applied to analyses after December 2005 and was not available at the time of the analyses of ODP zircons in this study (Oct. 22-25, 2005). For this reason, we calibrated the magnetic field every few hours by Hall probe and confirmed that the drift of the magnetic field was insignificant compared to the flatness of the oxygen peaks.

Samples are prepared as 1 inch diameter epoxy mounts or thin sections with standard minerals (KIM-5 zircon,  $\delta^{18}\text{O} = 5.09 \pm 0.12$ , 2 sd, Valley 2003) and gold (or carbon) coated (30-60 nm). The secondary ions are accelerated by a uniform electric field ( $-10\text{ kV}$ ) applied to the sample surface. Significant topography on the sample surface would distort the uniformity of the field and may cause instrumental bias between  $^{16}\text{O}$  and  $^{18}\text{O}$  (Kita et al. 2009). Similar distortion of the field may occur near the edge of the holder because  $-10\text{ kV}$  is applied to the entire 12 mm thick metal holder. Therefore, samples and standards are mounted within a 10-15 mm diameter of the center and polished flat without creating significant relief.

Detailed analytical conditions for oxygen isotope ( $^{18}\text{O}/^{16}\text{O}$ ) analyses using CAMECA IMS-1280.

Primary ions	Focused $^{133}\text{Cs}^+$ / 3 nA/ 10 $\mu\text{m}$ /+10 kV
Electron-gun	-10 kV, homogeneous across 60 $\mu\text{m}$ ×100 $\mu\text{m}$ oval area
Secondary HV	-10 kV on sample surface
Transfer optics	Magnification of ×200 from sample to Field Aperture
Slits and apertures	Entrance slits=120 $\mu\text{m}$ Contrast Aperture=400 $\mu\text{m}$ Field aperture =4 mm×4 mm Energy slits =40 eV Exit slits 500 $\mu\text{m}$ (Multi-collectors)
Mass Resolution Power	~2,200 (10% height)
Secondary ion intensities	$^{16}\text{O} = 3 \times 10^9 \text{ cps}$ , $^{18}\text{O} = 6 \times 10^6 \text{ cps}$
Detectors (Multi-collectors)	$^{16}\text{O}$ : L2' (10 $^{10}$ ohm), $^{18}\text{O}$ : H1 (10 $^{11}$ ohm)
Detector noise and drift	≤ 1000 cps
Useful yield	≥70% (full transmission is defined as apertures and slit fully opened)
Magnetic field control	Hall probe control with stability ≤15 ppm for a few hours or NMR probe with stability ≤5 ppm for 10 hours.
Centering of secondary ions	Manual Z-focusing and automatic adjustment of secondary deflectors
Integration time	80 s (4 s, 20 cycles)
Total analysis time per spot	3.5 min
Internal precision	0.1-0.15‰ (1SE)
External precision	<0.3‰, 2 sd, within central 10 mm diameter, spot-to-spot

**Trace element analyses using CAMECA IMS-1280 at the University of Wisconsin, Madison.**

A CAMECA IMS-1280 was also used to obtain trace element abundances in zircon grains. We apply both energy filtering (40 eV offset) and high mass resolution mode (MRP=4500) in order to fully resolve molecular interferences including LREE oxide on HREE atomic ions. Primary ion beam of  $\text{O}^+$  (4 nA, 25  $\mu\text{m}$  diameter) was used and positive secondary ions of  $^{30}\text{Si}$ ,  $^{49}\text{Ti}$ , Y, REE, and Hf were detected using mono-collection electron multiplier pulse counting system with magnetic peak scan. See full description of analytical details in (Page et al. 2007b). Uncertainties are as follows: Ti (4%, 1 $\sigma$ ), all other trace elements (5%, 1 $\sigma$ ). NIST SRM 610 glass standard and 91500 zircon standard (Wiedenbeck et al. 2004) were also measured in the same session to calibrate sensitivity factors for REE against Si.

### **Oxygen isotope analysis for $\delta^{18}\text{O}$ (serpentinite) whole-rock by laser fluorination.**

Analyses for  $\delta^{18}\text{O}$  of ~2 mg aliquots of serpentinite whole-rock powders were made at the University of Wisconsin by gas source mass spectrometry using  $\text{BrF}_5$  and a 32 W  $\text{CO}_2$  laser and an airlock sample chamber that prevented pre-fluorination of samples (Spicuzza et al. 1998). Samples were corrected for accuracy with UWG-2 garnet ( $\delta^{18}\text{O} = 5.8\text{‰}$ ) (Valley et al. 1995), analyzed multiple times at the beginning of each run. The reproducibility of UWG-2 for the two analytical sessions was 0.06‰ and 0.14‰ (2 sd).

### **References cited**

- Kita, N.T., Ushikubo, T., Fu, B., and Valley, J.W. (2009) High precision SIMS oxygen isotope analyses and the effect of sample topography. *Chemical Geology*, in press.
- Page, F.Z., Fu, B., Kita, N.T., Fournelle, J., Spicuzza, M.J., Schulze, D.J., Viljoen, V., Basei, M.A.S., and Valley, J.W. (2007b) Zircons from kimberlites: New insights from oxygen isotopes, trace elements, and Ti in zircon thermometry. *Geochimica et Cosmochimica Acta*, 71, 3887–3903.
- Page, F.Z., Ushikubo, T., Kita, N.T., Riciputi, L.R., and Valley, J.W. (2007a) High precision oxygen isotope analysis of picogram samples reveals 2- $\mu\text{m}$  gradients and slow diffusion in zircon. *American Mineralogist*, 92, 1772–1775.
- Spicuzza, M.J., Valley, J.W., and McConnell, V.S. (1998) Oxygen isotope analysis of whole rock via laser fluorination: An air-lock approach. *GSA Abstracts with Programs*, 30, A80.
- Valley, J.W. (2003) Oxygen isotopes in zircon. In J.M. Hanchar and P.W.O. Hoskin, Eds., *Zircon*, 53, p. 343–385. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Chantilly, Virginia.
- Valley, J.W., Kitchen, N., Kohn, M., Niendorf, C.R., and Spicuzza, M.J. (1995) UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heating. *Geochimica et Cosmochimica Acta*, 59, 5223–5231.
- Wiedenbeck, M., Hanchar, J.M., Peck, W.H., Sylvester, P., Valley, J., Whitehouse, M., Kronz, A., Morishita, Y., Nasdala, L., Fiebig, J., Franchi, I., Girard, J.-P., Greenwood, R.C., Hinton, R., Kita, N., Mason, P.R.D., Norman, M., Ogasawara, M., Piccoli, P.M., Rhede, D., Satoh, H., Schulz-Dobrick, B., Skar, O., Spicuzza, M.J., Terada, K., Tindle, A., Togashi, S., Vennemann, T., Xie, Q., and Zheng, Y.-F. (2004) Further characterization of the 91500 zircon crystal. *Geostandards and Geoanalytical Research*, 28, 9–39.