

## Appendix

### Analytical Methods

#### Boron and trace element abundances

Approximately 50-60 mg of sample powder was digested overnight at room temperature using ~2 mL of high-purity 16N HNO<sub>3</sub> acid in pre-cleaned 15 mL Savillex® Teflon beakers. High-purity acids are produced in-house via Savillex DST-1000, sub-boiling, acid-purification systems. The digested samples were centrifuged, and supernatants were subsequently diluted to ~50 mL with 18MΩ cm<sup>-2</sup> ultrapure boron-free water. Boron-free water is obtained using ion-exchange chromatography involving ~2 mL of B-specific resin Amberlite IRA-743 in a 13.4 cm column pre-cleaned with 2% HNO<sub>3</sub>.

Trace element and boron abundances were determined using a Nu Plasma AttoM High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) in medium-resolution mode ( $M/\Delta M \approx 3000$ ) housed within MITERAC. The instrument's wet-plasma introduction system consists of a cyclonic spray chamber placed within a Peltier cooling device (at 7°C), Meinhard nebulizer, and quartz torch. The instrument was tuned and calibrated with a multi-element 1 ppb standard solution before each analytical session. The concentrations of the trace elements were calculated using a standard/spike addition method (Jenner et al. 1990), which includes corrections for matrix effects and instrumental drift. Boron abundances were calculated based on an external calibration technique involving a boron elemental standard solution (NIST SRM 3107; certified concentration of 999.2 ppm) and using indium as an internal standard for instrument and matrix (if present) corrections. Lab hood and procedural blanks (~80 pg and 0.15 ng B, respectively) were monitored for background B contribution and subtracted when

calculating the final concentrations. The relative uncertainties associated with the trace element abundances range between 3% and 5% ( $2\sigma$  level).

### **Carbon and oxygen isotopes**

Each sample powder (200-300  $\mu\text{g}$ ) was digested using the conventional orthophosphoric acid method involving  $\sim 0.2$  mL concentrated  $\text{H}_3\text{PO}_4$  in sealed tubes at room temperature ( $25^\circ\text{C}$ ) for 24 hours (McCrea 1950). Isotopic determination is obtained by flushing the resulting sample gas with He into a Delta V with Thermo Gasbench Isotope Ratio Mass Spectrometer. Three external limestone standards (NBS 19, YWCC, RoyCC) were used to ensure the validity of the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  results. Carbon and oxygen isotope ratios are reported in per mil notation (‰) relative to Vienna Peedee Belemnite (V-PDB; Craig 1957; Coplen 1995) for  $\delta^{13}\text{C}$  and Vienna standard mean oceanic water (V-SMOW; Coplen et al. 1983, Coplen 1995) for  $\delta^{18}\text{O}$ .

### **Boron isotopic compositions**

Procedures for boron isotope analyses were adapted from Hulett et al. (2016). Sample powders (0.005 - 0.09 g) were digested in 1 mL high-purity, B-free, 2%  $\text{HNO}_3$  acid and centrifuged to remove any non-carbonate phases. Subsequent to digestion, 1 mL of sodium acetate (20 wt.%) was added to the supernatants to adjust the pH to  $>5.5$ . The samples were then purified by ion-exchange column chemistry using a 1 mL pipette tip filled with  $\sim 250$   $\mu\text{L}$  of the B-specific Amberlite IRA-743 resin pre-cleaned with high-purity, B-free, 2%  $\text{HNO}_3$  and conditioned with B-free water. The matrix is rinsed off the columns using 1 mL B-free water and B elutes with 1 mL of high purity, B-free, 2%  $\text{HNO}_3$ , and is then ready for instrumental analysis. Isotope ratio measurements of the purified B sample aliquots ( $\sim 100$  ng total B) were determined

via solution-mode on a Nu PlasmaII multi-collector-ICP-MS (MC-ICP-MS) housed within MITERAC. Each analysis consisted of a 30-second on-peak zero cycle followed by a two-minute analysis cycle involving simultaneous measurement of  $^{10}\text{B}$  and  $^{11}\text{B}$  ion signals on Faraday collectors. A boron-free, wet-plasma introduction system was used to reduce background B signal, which consisted of a PFA nebulizer, PFA spray chamber (housed within a Peltier cooling device at  $7^\circ\text{C}$ ), and demountable quartz torch equipped with a sapphire injector.

To validate the B isotope results, a modern coral standard powder ( $\delta^{11}\text{B} = +23 \pm 0.5\text{‰}$ ) obtained from Dr. E. Troy Rasbury at Stony Brook University was repeatedly digested (aliquots  $\sim 0.003$  g), and underwent the same ion-exchange procedure as each batch of samples. The calculated average  $\delta^{11}\text{B}$  value of this coral standard is  $+23.4 \pm 0.5\text{‰}$  (21 replicates), which agrees with the recommended value. In addition, sample-standard bracketing employing a  $\sim 100$  ppb solution, typically tuned to a 0.7 V signal on  $^{11}\text{B}$  of the NIST SRM 951a boron isotope standard, was used to correct for instrument drift and ensure acceptable reproducibility of  $<0.5\text{‰}$  ( $2\sigma$  level) per analytical session. Boron isotope results are reported using the conventional  $\delta^{11}\text{B}$  (‰) notation relative to the B isotope ratios measured for the NIST SRM 951a standard (e.g., Hulett et al. 2016).

### **Strontium isotopic ratios**

For strontium isotope ratio determinations, Sr was first separated from the sample matrix using 13.4 cm ion-exchange columns containing 4.3 mL of 200-400 mesh AG50W-X8 resin pre-cleaned with 6N high-purity HCl and  $18\text{M}\Omega\text{ cm}^{-2}$  ultrapure water and conditioned with 2.5N high-purity HCl. Purified Sr was eluted with 2.5N high-purity HCl, dried down, and re-dissolved into  $\sim 2$  mL of 2%  $\text{HNO}_3$  for isotopic analysis. Strontium isotope measurements were conducted

on the same MC-ICP-MS described above, but in dry-plasma mode using a DSN-100 desolvating nebulizing system following the protocol outlined in Balboni et al. (2016). Strontium isotope data were acquired in static, multi-collection mode using five Faraday collectors for a total analysis time of 400 s. Any isobaric interference of  $^{87}\text{Rb}$  with  $^{87}\text{Sr}$  was corrected for by monitoring  $^{85}\text{Rb}$ . The accuracy and reproducibility of the results were verified with repeated measurement of the NIST SRM 987 strontium isotope standard, which yielded an average value of  $0.71025 \pm 0.00004$  ( $2\sigma$ ;  $n=4$ ).

## References

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