

## **Analytical Methods**

### *Optical CL Microscopy*

Optical CL photomicrography was carried out on polished thin sections using an Olympus Vanox microscope coupled with a Relion III CL system, at the School of Earth Resources, China University of Geosciences, Wuhan. The low-vacuum Relion system was set to an electron source operated at 15–20 kV and about 500–800  $\mu\text{A}$ .

### *Electron Probe Microanalysis (EPMA)*

Major- and minor-element composition of tourmaline was determined using the JEOL JXA-8100 electron microprobe at the Institute of Geology, Chinese Academy of Geological Science (CAGS), Beijing. Analysis of apatite was carried out using a JEOL JXA-8230 electron microprobe at the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS, Beijing. Operating conditions in both labs involved an accelerating voltage of 15 kV, a probe current of 10–20 nA, and a beam diameter of 3–5  $\mu\text{m}$ . Natural minerals and synthetic materials were used as standards, all of which were tested for homogeneity before their utilization for quantitative analysis. Matrix corrections were performed using the ZAF correction program supplied by the instrument manufacturer. The analytical precision for major elements measured in both labs is generally better than 1%.

### *LA-ICP-MS Trace Element Analysis*

Trace-element analyses of tourmaline and apatite were done in two different labs: the Wuhan Sample Solution Analytical Technology Co., Ltd. (Wuhan) and the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources (CAGS). The first lab uses a 193-nm GeolasPro ArF excimer laser ablation system coupled with an Agilent 7700e ICP-MS, and the other lab uses a 193-nm RESolution S-155 ArF excimer laser ablation system coupled with a Bruker M90 ICP-MS. In both labs, analyses of tourmaline and apatite were performed directly on polished thin sections using a similar analytical set-up. Helium was applied as the carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP-MS. A “wire” signal smoothing device was included in the laser ablation system (Hu et al. 2015). Each analysis incorporated a background acquisition of ~20 s followed by 45–50 s of data acquisition from the sample. The frequency of the laser was set to 5.5–6 Hz. For the analysis of tourmaline, the spot size was 44  $\mu\text{m}$ , and element contents were calibrated against the reference materials SRM610, BHVO-2G, BCR-2G, and BIR-1G (Liu et al. 2008) using the Si measurement from EPMA as the internal standard. For the analysis of apatite, the spot size was 38  $\mu\text{m}$ , and element contents were calibrated against the reference materials SRM610, SRM612, BCR-2G, BIR-1G, and GSE-1G (<http://georem.mpch-mainz.gwdg.de/>), using the Ca measurement from EPMA as the internal standard. Data obtained from both labs were processed using the Excel-based software ICPMSDataCal (Liu et al. 2008, 2010). The analytical precisions for most

trace elements (in particular those used in the discussion) from both labs are generally better than 10%.

#### *LA–MC–ICP–MS Boron Isotope Analysis of Tourmaline*

Boron isotopic compositions of tourmaline were measured in situ on polished thin sections using a Neptune Plus MC–ICP–MS and a matching New Wave UP213 laser ablation system at the Institute of Mineral Resources, CAGS, Beijing. Detailed analytical procedures and data reduction followed those of Hou et al. (2010). The laser ablation spot diameter was 25  $\mu\text{m}$  with an output frequency of 10 Hz, and an energy density of 8 J/cm<sup>2</sup>. The He carrier gas was set to 0.8 L/min. During analysis, both B isotope signals (L3: <sup>10</sup>B; H4: <sup>11</sup>B) were collected on Faraday cups simultaneously. Before connecting to the laser, the Faraday cups were adjusted with 2  $\mu\text{g/mL}$  H<sub>3</sub>BO<sub>3</sub> (a product of Alfa Company) and their masses were calibrated. The data were collected statically and simultaneously in cycles of 200 with an integration time of 0.131s. The acquisition lasted for about 27s in total. Mass bias of the instrument and the fractionation of isotopes were calibrated using the standard sample-bracketing (SSB) method. Tourmaline IAEA B4 ( $\delta^{11}\text{B} = -8.36 \pm 0.58 \text{ ‰}$ ; Tonarini et al. 2003) was used as the external standard, and tourmaline IRM RB1 ( $\delta^{11}\text{B} = -12.97 \pm 0.97 \text{ ‰}$ ; Hou et al. 2010) was used as an internal standard. The observed internal precision for a single analysis was usually better than 0.5 ‰ (1 SD). Results are reported in

$$\delta^{11}\text{B} (\text{‰}) = [({}^{11}\text{B}/{}^{10}\text{B})_{\text{sample}}/({}^{11}\text{B}/{}^{10}\text{B})_{\text{standard (IAEA B4)}} - 1] \times 1000.$$

### *LA–MC–ICP–MS Strontium-Neodymium Isotope Analysis of Apatite*

The in situ apatite Sr isotope measurements were conducted on a Neptune Plus MC–ICP–MS in combination with a Geolas HD excimer ArF laser ablation system at the Wuhan Sample Solution Analytical Technology Co., Ltd. The Neptune Plus was equipped with nine Faraday cups fitted with  $10^{11} \, \Omega$  resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor Kr, Rb, Er, Yb, and Sr. The combination of the high-sensitivity X-skimmer cone and Jet-sample cone was employed. In the laser ablation system, He was used as the carrier gas for the ablation cell. Following a 40 s period of background analysis, apatite grains were ablated with a 60  $\mu\text{m}$  beam, for 60 s at an 8 Hz pulse frequency, and a constant laser fluence of  $\sim 10 \, \text{J}/\text{cm}^2$ . A signal smoothing device (Hu et al. 2015) was used downstream from the sample cell to eliminate the short-term variation of the signal. All data reduction for the MC–ICP–MS analysis of the Sr isotope ratios was conducted using “Iso-Compass” software (Zhang et al. 2020). The interference correction strategy was the same as the one reported by Tong et al. (2016) and Zhang et al. (2018). During the analysis, two natural apatite samples (Durango and Madagascar) were used as the unknowns for the Sr isotope analysis of the apatite. The in-house apatite standard (MAD) was used to evaluate the reliability of the analytical accuracy and the potential matrix-matched effect during analyses. During

our analyses, the standard MAD yielded average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of  $0.71182 \pm 0.00002$  ( $2\sigma$ ;  $N = 12$ ), which is highly consistent with the accepted values of  $0.71180 \pm 0.00011$  ( $2\sigma$ ) and  $0.71180 \pm 0.00003$  ( $1\sigma$ ;  $N = 8$ ) obtained by in situ LA–MC–ICP–MS and chemically purified solutions (TIMS/MC–ICP–MS) methods, respectively (Yang et al. 2014). The analytical precision for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is generally in the range of 0.0001–0.0003.

The in situ Nd isotope analysis was done using the same LA–MC–ICP–MS instrument at the Wuhan Sample Solution Analytical Technology Co., Ltd. Isotopes  $^{142}\text{Nd}$ ,  $^{143}\text{Nd}$ ,  $^{144}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{146}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{148}\text{Nd}$ , and  $^{149}\text{Sm}$  were collected in Faraday cups in static mode. In the laser ablation system, He was used as the carrier gas within the ablation cell and was merged with Ar (makeup gas) after the ablation cell. Small amounts of nitrogen were added to the Ar makeup gas flow for the improvement of sensitivity of Nd isotopes (Xu et al. 2015). A spot diameter of 44  $\mu\text{m}$  was employed at an 8 Hz pulse frequency and  $\sim 8 \text{ J/cm}^2$  laser fluence. Each spot analysis consisted of a background analysis for 40 s and a data acquisition for 60 s. The signal-smoothing device was used downstream from the sample cell to efficiently eliminate the short-term variation of the signal and remove Hg from the background and sample aerosol particles (Hu et al. 2015). The mass discrimination factor for  $^{143}\text{Nd}/^{144}\text{Nd}$  was determined using  $^{146}\text{Nd}/^{144}\text{Nd}$  (0.7219) along with the exponential law. The  $^{149}\text{Sm}$  signal was used to correct the remaining  $^{144}\text{Sm}$  interference on  $^{144}\text{Nd}$ , using the  $^{144}\text{Sm}/^{149}\text{Sm}$  ratio of 0.2301. The mass fractionation of  $^{144}\text{Sm}/^{149}\text{Sm}$  was corrected by  $^{147}\text{Sm}/^{149}\text{Sm}$  normalization, using the  $^{144}\text{Sm}/^{149}\text{Sm}$  ratio of 1.08680 with the

exponential law. All data reduction for the MC–ICP–MS analysis of Nd isotope ratios was conducted using the “Iso-Compass” software (Zhang et al. 2020). Two natural apatite megacrysts, Durango and MAD, were used as the unknown samples to verify the accuracy of the calibration method for *in situ* Nd isotope analysis. The standard (MAD) was used to evaluate the reliability of the analytical accuracy and the potential matrix-matched effect during analyses. During our analyses, the standard MAD yielded  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.511348 \pm 0.000006$  ( $2\sigma$ ;  $N = 26$ ) and  $^{147}\text{Sm}/^{144}\text{Nd}$  of  $0.081811 \pm 0.000059$  ( $2\sigma$ ;  $N = 26$ ), which are highly consistent with the accepted  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.511322 \pm 0.000053$  ( $2\sigma$ ) and  $^{147}\text{Sm}/^{144}\text{Nd}$  of  $0.0811 \pm 0.0017$  ( $2\sigma$ ) obtained by *in situ* LA–MC–ICP–MS and  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.511348 \pm 0.000016$  ( $2\sigma$ ), and  $^{147}\text{Sm}/^{144}\text{Nd}$  of  $0.0818 \pm 0.0005$  ( $2\sigma$ ) obtained by *in situ* and chemically purified solutions (MC–ICP–MS) methods, respectively (Yang et al. 2014). The analytical precision for  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio is generally better than 0.000025.

### **Tourmaline–Fluid Partition Coefficients**

Keppler (1996) established an indirect method ( $D^{\text{mineral}/\text{fluid}} = D^{\text{fluid}/\text{melt}}/D^{\text{mineral}/\text{melt}}$ ) to estimate the fluid/mineral partition coefficients for trace elements using the partitioning mineral-melt and fluid-melt D values. This method and the calculated  $D^{\text{mineral}/\text{fluid}}$  values have been widely used to determine the fluid composition from the compositions of the minerals that grew from this fluid (van Hinsberg et al. 2017; Codeço et al. 2021). In this study, trace element partition coefficients between tourmaline and borosilicate-saturated melt (1.8, 0.9, 0.7, and 1.0 for Na, Li, Zn, and Sr,

respectively) were derived from a preliminary experiment by van Hinsberg (2011). Fluid-melt D values (7.9, 3.2, 5.5, and 0.6 for Na, Li, Zn, and Sr, respectively) were derived from experimental fluid-melt partitioning values of Zajacz et al. (2008) and Iveson et al. (2019). As a result, the estimated  $D^{\text{tur/fluid}}$  values are 0.2, 0.3, 0.1, and 1.9 for Na, Li, Zn, and Sr, respectively.

### References

- Codeço, M.S., Weis, P., Trumbull, R.B., Hinsberg, V.V., Pinto, F., Lecumberri-Sanchez, and Schleicher, A.M. (2021) The imprint of hydrothermal fluids on trace-element contents in white-mica and tourmaline from the Panasqueira W-Sn-Cu deposit, Portugal. *Mineralium Deposita*, 56, 481–508.
- Hou, K.J., Li, Y.H., Xiao, Y.K., Liu, F., and Tian, Y.R. (2010) In situ boron isotope measurements of natural geological materials by LA–MC–ICP–MS. *Chinese Science Bulletin*, 55, 3305–3311.
- Hu, Z.C., Zhang, W., Liu, Y.S., Gao, S., Li, M., Zong, K.Q., Chen, H.H., and Hu, S.H. (2015) “Wave” signal-smoothing and mercury-removing device for Laser Ablation Quadrupole and Multiple Collector ICPMS analysis: Application to lead isotope analysis. *Analytical Chemistry*, 87, 1152–1157.
- Iveson, A., Webster, J.D., Rowe, M.C., and Neill, O.K. (2019) Fluid-melt trace-element partitioning behaviour between evolved melts and aqueous fluids: Experimental constraints on the magmatic-hydrothermal transport of metals. *Chemical Geology*, 516, 18–41.
- Keppler, H. (1996) Constraints from partitioning experiments on composition of subduction-zone fluids. *Nature*, 380, 237–240.

- Liu, Y.S., Hu, Z.C., Gao, S., Günther, D., Xu, J., Gao, C.G. and Chen, H.H. (2008) In situ analysis of major and trace elements of anhydrous minerals by LA–ICP–MS without applying an internal standard. *Chemical Geology*, 257, 34–43.
- Liu, Y.S., Hu, Z.C., Zong, K.Q., Gao, C.G., Gao, S., Xu, J., and Chen, H.H. (2010) Reappraisal and refinement of zircon U–Pb isotope and trace element analyses by LA–ICP–MS. *Chinese Science Bulletin*, 55, 1535–1546.
- Tonardini, S., Pennisi, M., Adorni-Braccesi, A., Dini, A., Ferrara, G., Gonfiantini, R., Wiedenbeck, M., and Gröning, M. (2003) Intercomparison of boron isotope concentration measurements. Part I: Selection, preparation and homogeneity tests of the intercomparison materials. *Geostandards Newsletter*, 27, 21–39.
- Tong, X.R., Liu, Y.S., Hu, Z.C., Chen, H.H., Zhou, L., Hu, Q.H., Xu, R., Deng, L.X., Chen, C.F., Yang, L., and Gao, S. (2016) Accurate determination of Sr isotopic compositions in clinopyroxene and silicate glasses by LA–MC–ICP–MS. *Geostandards and Geoanalytical Research*, 40, 85–99.
- van Hinsberg, V.J. (2011) Preliminary experimental data on trace-element partitioning between tourmaline and silicate melt. *The Canadian Mineralogist*, 49, 153–163.
- van Hinsberg, V.J., Franz, G., and Wood, B.J. (2017) Determining subduction-zone fluid composition using a tourmaline mineral probe: *Geochemical Perspectives Letters*, 3, 160–169.
- Xu, L., Hu, Z.C., Zhang, W., Yang, L., Liu, Y.S., and Gao, S. (2015) In situ Nd isotope analyses in geological materials with signal enhancement and non-linear mass dependent fractionation reduction using laser ablation MC–ICP–MS. *Journal of Analytical Atomic Spectrometry*, 30, 232–244.
- Yang, Y.H., Wu, F.Y., Yang, J.H., Chew, D.M., Xie, L.W., Chu, Z.Y., Zhang, Y.B., and Huang, C. (2014) Sr and Nd isotopic compositions of apatite reference materials used in U–Th–Pb geochronology. *Chemical Geology*, 385, 35–55.
- Zhang, W., Hu, Z., Liu, Y., Wu, T., Deng, X., Guo, J., and Han Z. (2018) Improved in situ Sr isotopic analysis by a 257 nm femtosecond laser in combination with the



addition of nitrogen for geological minerals. *Chemical Geology*, 479, 10–21.

Zhang, W., Hu, Z.C., and Liu, Y.S. (2020) Iso-Compass: new freeware software for isotopic data reduction of LA–MC–ICP–MS. *Journal of Analytical Atomic Spectrometry*, 35, 1087–1096.