

## **ANALYTICAL TECHNIQUES**

### **Major and trace elements**

Analyses contained in this compilation were obtained between 1981 and 2008 from a number of geochemical labs, as outlined below. For all samples in this compilation, major elements were determined on fused discs by, except for. Between 1981 and 1983, major elements for the WXTB81- sample series were determined in the labs of the Geological Survey of Canada (GSC), Ottawa by X-ray fluorescence spectrometry (XRF) on duplicate glass button, except for Na<sub>2</sub>O (atomic absorption), FeO (titration against K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and volatiles (infra-red). Between 2002 and 2007, major elements were also determined at the GSC on fused discs except for FeO (titration against K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) with the following calibration range and detection limits:

*GSC Major elements (X-ray fluorescence) (METHOD XRF-100) 2002-07 period*

Analyte	Calibration range (%)	Limit of determination (%)
SiO <sub>2</sub>	0 - 100	0.50
TiO <sub>2</sub>	0 - 3	0.02
Al <sub>2</sub> O <sub>3</sub>	0 - 60	0.40
Cr <sub>2</sub> O <sub>3</sub>	0 - 4	0.02
Fe <sub>2</sub> O <sub>3 total</sub>	0 - 90	0.10
MnO	0 - 1	0.01
MgO	0 - 50	0.10
CaO	0 - 35	0.10
Na <sub>2</sub> O	0 - 10	0.50
K <sub>2</sub> O	0 - 15	0.05
P <sub>2</sub> O <sub>5</sub>	0 - 1	0.02
Ba	0 - 0.30	0.002
Nb	0 - 0.04	0.003
Rb	0 - 0.06	0.002
Sr	0 - 0.20	0.002
Zr	0 - 0.20	0.002

Between 1990 and 1994, major elements were determined as blind duplicates (some triplicate) on fused discs by X-ray fluorescence spectrometry (XRF) at X-ray Assay Laboratories (XRAL), Toronto. FeO was determined in duplicate by dichromate titration and F contents by ion electrode by XRAL.

Between 1981 and 1983, F and Cl for the WXTB81- sample series were determined in duplicate by fusion with lithium tetraborate followed by selective ion

electrode analyses and colorimetric (thiocyanate) analysis, respectively. Other trace elements for these samples were determined on duplicate pressed powder pellets in the Department of Geology by B.W. Chappell by the XRF methods of Norrish and Chappell (1977). Relative percent standard deviation (SD X 100/Mean) on BCR-1 was 5 to 10 percent for Th, U and Ni; 1 to 5 percent for Pb, Sc, Nb, Ce and Cu; less than 1 percent for Ba, Rb, Sr, Zr, Y, V, Zn and Ga.

During 1990 to 1994, pressed powder pellets were used for trace element (Rb, Ba, Sr, Ga, Nb, Zr, Y, Cr, Ni, Cu, Zn, V and Sc) determinations by XRF at Memorial University of Newfoundland (MUN). The rare earth elements (REE) and selected trace elements (U, Pb, Th, Li, Cs, Ta and Hf) were determined by inductively coupled plasma - mass spectrometry (ICP-MS) at MUN using the methods and with the precision and accuracy described by Jenner et al. (1990). ICP-MS and XRF data on the same elements (Rb, Sr, Ba, Y, Zr and Nb) allowed checks on dissolution procedures and inter-technique calibrations. A large proportion of the WXTB81- samples were reanalyzed during this period by ICP-MS at MUN.

During 2002-2007 trace elements analyses were carried out at the GSC. Determinations were based on the total dissolution of the sample using nitric, perchloric and hydrofluoric acids followed by a lithium metaborate fusion of any residual material. For ICPES-110 package analysis was done using ICP emission spectrometry. For the ICPMS-100 and ICPMS-110 packages, analysis was done using ICP mass spectrometry. Elements listed in ICPES-110 may be determined by ICPMS-100 or ICPMS-110 when analyte concentrations were too low for determination by ICP-ES.

Trace elements 1 (ICP emission spectrometry) METHOD ICPMS-110. Sample required: 1.0 g

Element	Limit of determination (ppm)	Element	Limit of determination (ppm)
Ag	5	Pb	10
Ba	10	Sc	0.5
Be	0.5	Sr	5
Co	5	V	5
Cr	10	Y	5
Cu	10	Yb	0.5
La	10	Zn	5
Ni	10	Zr	10
Mo	5		

Trace elements 2 (ICP mass spectrometry): Rare-earth elements + Y METHOD ICPMS-100.

Element	Limit of determination (ppm)	Element	Limit of determination (ppm)
Ce	0.1	Nd	0.1
Dy	0.02	Pr	0.02
Er	0.02	Sm	0.02
Eu	0.02	Tb	0.02
Gd	0.02	Tm	0.02
Ho	0.02	Y	0.02
La	0.1	Yb	0.05
Lu	0.02		

Trace elements 2 (ICP mass spectrometry): Other trace elements METHOD ICPMS-110.  
Sample required: 1.0 g.

Element	Limit of determination (ppm)	Element	Limit of determination (ppm)
Ag	0.1	Pb	2
Bi	0.5	Rb	0.05
Cd	0.2	Sn	0.5
Cs	0.02	Ta	0.2
Ga	0.1	Th	0.02
Hf	0.05	Tl	0.02
In	0.05	U	0.02
Mo	0.2	Zr	0.5
Nb	0.05		

#### *Fluorine, chlorine, and sulphur (METHOD IC-100)*

Fluorine, chlorine and sulphur were determined using a pyrohydrolysis method followed by ion chromatography. For this method, the upper limit of determination was 1%.

Sample required: 0.2 g.

Element	Limit of detection (ppm)
F	50
Cl	100
S	50

Analyses of a granodiorite (WXTB-121) and a basalt (WXTB-135) standard that were carried out in the various labs outlined above revealed no obvious time- or laboratory-related differences in analytical results (see file 'standards\_duplicates.xls' in the Analytical Procedures folder) .

## **Isotopes**

Whole rock oxygen isotopic analyses were performed at the University of Western Ontario using a Fisons-Optima dual-inlet mass spectrometer. Oxygen was extracted from silicate rocks using the  $\text{BrF}_5$  method of Clayton and Mayeda (1963), and quantitatively converted to  $\text{CO}_2$  over red-hot graphite. The oxygen-isotope data are presented in the normal  $\delta^{18}\text{O}$  -notation relative to SMOW (Standard Mean Ocean Water) (Craig, 1961). An oxygen-isotope  $\text{CO}_2$ - $\text{H}_2\text{O}$  fractionation factor of 1.0412 at  $25^\circ\text{C}$  has been employed in these calculations to calibrate the mass spectrometric reference gas. An average  $\delta^{18}\text{O}$  value of +9.66‰ was obtained for more than 50 samples of silicate standard NBS-28 analyzed during the period of this study.

Sr isotopic analyses were carried out in the labs of the Geological Survey of Canada, Ottawa. Rb and Sr concentrations were determined using standard isotope dilution techniques of HF sample dissolution,  $^{84}\text{Sr}$  spiking, ion exchange separation and solid source spectrometry (Finnigan MAT 261 instrument). Sr isotope compositions were determined on a triple  $^{86}\text{Sr}$ - $^{87}\text{Sr}$ - $^{88}\text{Sr}$  collector and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to an  $^{88}\text{Sr}/^{86}\text{Sr}$  ratio of 8.3751. When these determinations were made in 1985-86, the NBS-987 standard strontium salt yielded values of  $0.71025 \pm 8$  (average of 18 runs). Uncertainties in the Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are estimated at 1% and 0.02% (2 sigma) respectively.

Pb isotope measurements were done at the Université du Québec à Montréal on carefully hand-picked populations (5-10 mg) of K-feldspar, a mineral almost devoid of uranium, in order to obtain the best estimate of the initial isotopic composition. The K-feldspar populations were acid leached to remove, in as much as possible, any radiogenic Pb component present in the minerals (e.g., Carignan et al., 1993) and the supernatants and residues were analysed separately. When the supernatant was significantly more radiogenic than the residue, which may indicate the presence of uranium and/or impurities in the K-feldspar populations, the results were discarded and new material analysed. Procedures for Pb separation and isotopic analysis were identical to those described by Carignan and others (1993).

Prior to 2002, Sm/Nd isotopic separations were carried out at MUN, using the techniques described in Swinden et al. (1990). Isotopic measurements ( $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{147}\text{Sm}/^{144}\text{Nd}$ ) were made at MUN, using Finnigan-Mat 261 multicollector mass

spectrometer. Data are reported relative to a value of 0.511850 for  $^{143}\text{Nd}/^{144}\text{Nd}$  in the LaJolla standard. The maximum error on the  $^{143}\text{Nd}/^{144}\text{Nd}$  (m), calculated as twice the standard error of the mean (2SE), is  $\pm 0.000015$ , the maximum error on the  $^{147}\text{Sm}/^{144}\text{Nd}$  (m), calculated as the two-sigma error, is  $\pm 0.2\%$  and the estimated error on an individual epsilon Nd calculation is  $\pm 0.5$  units.

During 2003-04, Sm-Nd isotopic ratios were measured using the Nu Plasma multicollector ICP-MS at the GSC.  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios are reported relative to the value of 0.51186 for the LaJolla Nd standard (Table 6). Nine spiked and unspiked analyses of BCR-1 yielded a weighted average value of  $0.512636 \pm 0.000009$  for  $^{143}\text{Nd}/^{144}\text{Nd}$ . The  $\epsilon^{143}\text{Nd}$  has been calculated for the igneous age, relative to the accepted Chondritic Uniform Reservoir with  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512636$  and  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1966$ .

During 2007, Nd isotopic analyses on samples with a 07SNB-WX- prefix were carried out at the Isotope Geochemistry and Geochronology Research Centre (IGGRC), Department of Earth Sciences, Carleton University. Samples were dissolved in 0.26N HCl and loaded into a 14-ml Bio-Rad borosilicate glass chromatographic column containing a 2 cm-high bed of Teflon powder coated with HDEHP [di(2-ethylhexyl) orthophosphoric acid (Richard et al., 1976)]. Nd was eluted using 0.26N HCl, followed by Sm in 0.5N HCl. Total procedural blanks for Nd were  $< 350$  picograms. Samples were spiked with a mixed  $^{148}\text{Nd}$ - $^{149}\text{Sm}$  spike prior to dissolution. Concentrations are precise to  $\pm 1\%$ , but  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios are reproducible to 0.5%. Samples were loaded with  $\text{H}_3\text{PO}_4$  on one side of a Re double filament, and run at temperatures of 1800-1875°C. Isotope ratios are normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.72190$ . Analyses of the USGS standard BCR-1 yield Nd = 29.02 ppm, Sm = 6.68 ppm, and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.512668 \pm 20$  (n=4). The La Jolla standard produced: Finnegan-MAT 261:  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511876 \pm 18$ , n = 54 (Sept. 1992-Feb. 2004).

In addition to reporting measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in the isotopic table, Nd isotopic data are reported as epsilon values ( $\epsilon_{\text{Nd}}$ ) which measure the deviation in  $^{143}\text{Nd}/^{144}\text{Nd}$  between a given sample and the chondritic uniform reservoir (CHUR) at the time chosen (see DePaolo (1988) for a complete review). Depleted-mantle Nd model

ages ( $T_{DM}$ ) based on both the models of DePaolo (1988) and Goldstein et al. (1984) are also included in the isotopic table.

## References

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