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Garnet pyroxenite in the Biskupice peridotite, Bohemian Massif: anatomy of a Variscan high-pressure cumulate

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Appendix – analytical methods

A.1 Modal analyses

The modes for each layer were determined by acquiring X-ray maps by electron microprobe, constructing false-color images, and measuring color areas by means of Adobe Photoshop® software.

A.2. Electron probe microanalysis

Minerals were analyzed by wavelength-dispersion spectrometry (WDS) with a Cameca SX50 instrument at the University of Wisconsin. Operating conditions were: 15 kV accelerating voltage, 20 nA beam current (Faraday cup), and beam diameter of 1 μm. Combinations of natural minerals were used as standards for each of the sample mineral species, e.g. orthopyroxene and garnet for Si, Al, Mg, and Fe, rutile for Ti, chromite for Cr, rhodonite for Mn, wollastonite for Ca, jadeite for Na, and microcline for K. Data reduction was performed by Probe for Windows software, utilizing the $\phi(\rho z)$ matrix correction of Armstrong (1988).

A.3. Trace-element ICP-MS analyses

In-situ laser ablation analyses

In-situ trace element analyses were performed on a quadrupole-based ICP-MS Thermo Fisher X-Series II (Charles University in Prague) coupled to a NewWave UP 213 laser microprobe

(NewWave Research; USA) operating at output wavelength of 213 nm. The data were acquired in the time-resolved and peak jumping mode with one point measured per mass peak and processed off-line by Thermo Fisher PlasmaLab software 2.5.11 321. External calibration of the laser-ablation analyses was done using standards NIST 610 and 612 (National Institute of Standards and Technology, USA). For internal standardization ^{29}Si concentrations based on electron microprobe measurements were applied. For details on analytical protocol and correction strategy see Strnad et al. (2005) and Johan et al. (2012).

Solution ICP-MS analyses

The trace-element analyses of mineral separates and whole-rock samples were carried out after modified total digestion in mineral acids (HF + $HClO_4$) and borate fusion (Na_2CO_3 + $Na_2B_4O_7$) in platinum crucibles followed by solution nebulization ICP-MS VG PQ3 (VG Elemental, UK) installed at Charles University in Prague. All the chemicals involved were reagent grade (Merck, Germany) and the acids were double distilled. Deionized water from a Millipore system (Milli-Q Academic, USA) was used for all dilutions.

The analytical precision for all the elements analyzed ranged from 0.5 to 5% relative. The accuracy of this analytical method was checked using the AGV-2 and BCR-2 reference materials (USGS, USA). Trace-element ICP-MS analyses followed the method of Strnad et al. (2005).

Clinopyroxene and garnet separates were prepared using a combination of heavy liquid and magnetic separations, which resulted in > 95 % pure separates. Separates were then leached in hot acids (~60 ºC) to remove possible grain-boundary contamination, using the following leaching steps: garnet – 6N HCl for 1 day, 7N HNO_3 for 1 day and 11N HF for 10 min; clinopyroxene – 6N HCl for 1 hour and 6N HNO_3 for 1 hour.

A.4. Oxygen isotopes

Garnets were hand-picked from crushed samples of each layer and aliquots of 1.5-2.5 mg were analyzed in duplicate by laser fluorination ($\lambda = 10.2$ μm, BrF_5 reagent) and gas-source mass spectrometry at the University of Wisconsin–Madison (Valley et al. 1995). The purity of mineral separates was checked optically and is better than 99%. Analyses were performed in one session and standardized using UWG-2 garnet standard ($\delta^{18}O = 5.80$ ‰ VSMOW, Valley et al. 1995). Six analyses of UWG-2 yielded a raw value of 5.74 ‰ (± 0.10, 2σ).

A.5. Rb–Sr and Sm–Nd isotopes

Analytical methods for Sr and Nd isotope analysis largely followed those of Lapen et al (2005, 2009). Mineral separates Sr and Nd isotope analysis were prepared from different layers by using a diamond saw to cut different layers apart, followed by crushing using a Tungsten Carbide hydraulic press, and mineral separation using a Frantz Isodynamic separator to prepare concentrates of clinopyroxene and garnet and then handpicking pure mineral separates under a binocular microscope. Approximately 50 milligrams of each mineral separate were lightly leached in 5mls of 1M HCl for 10 minutes at room temperature followed by rinsing the mineral 3 times with 18.2MΩ water. Samplers were then spiked using a mixed ^{150}Nd–^{149}Sm spike followed by dissolution in Parr™ bombs using a 10:1 mixture of concentrated HF and HNO_3 for 3 days at 175 °C. Samples were then evaporated and 3 ml of 8 M HCl were added, and the bombs were placed back in a 175 °C oven for 24 h. Following this conversion to chloride, the samples were inspected using a binocular microscope to ensure that all solid particulates material had been dissolved. After sample dissolution, Sr and the REE were separated using a serial extraction procedure involving 2.5 M HCl and cation exchange resin to purify Sr, followed by separation of REE using 2-methylactic acid and cation exchange resin in NH_3^+ form. Total procedural blanks measured for this dissolution and purification procedure were 75 pg for Nd and 5 pg for Sm.

All Sr, Nd and Sm isotope analyses were performed by thermal ionization mass spectrometry on a 7 collector Micromass Sector 54 instrument in the University of Wisconsin-Madison Radiogenic Isotope Laboratory. Strontium was analyzed using a three-jump dynamic multi-collector analysis routine on Ta filaments with H_3PO_4, and an exponential normalization to $^{86}Sr/^{88}Sr = 0.1194$. Reported isotope ratios are the average of 120 ratios with a typical ^{88}Sr ion signal of 3×10^{-11} amps (Tables S3 and S4). Fifteen measurements of NIST SRM-987 yielded an $^{87}Sr/^{86}Sr$ ratio of 0.710276 ± 0.000012 (2σ). Neodymium isotope ratios were analyzed as NdO^+ using a dynamic multi-collection analysis routine on Re filaments with Si-gel and H_3PO_4, and were exponentially corrected for mass fractionation using $^{146}Nd/^{144}Nd = 0.7219$. Reported isotope ratios are the average of 150 ratios with a typical $^{160}NdO^+$ ion signal of 5×10^{-12} amps. Two measurements each of internal laboratory standards AMES I and II yielded $^{143}Nd/^{144}Nd$ ratios of 0.512141 ± 0.000007 (2σ) and 0.511954 ± 0.000043 (2σ), respectively. Samarium was analyzed as Sm^+ on Re filaments loaded with silica gel and phosphoric acid. All Sm data was internally normalized to $^{147}Sm/^{152}Sm \equiv 0.5608$. For determination of isochrons the 2-σ precision for the $^{147}Sm/^{144}Nd$ ratio was 0.2% (a value based on replicate analysis of samples and standards) and the 2-σ precision of the $^{143}Nd/^{144}Nd$ ratio was based on the internal counting statistics of the analysis which closely matches the external precision measured on ultrapure standards. All isochron ages and initials were calculated using IsoPlot version 3.41 using a Model 1 solution (Ludwig 2003); errors for initial $^{143}Nd/^{144}Nd$ and ages are reported at the 95% confidence interval. The ^{147}Sm decay constant used was $6.54 \times 10^{-12}y^{-1}$ (Lugmair and Marti 1978) and ε_{Nd} values were calculated using a present day CHUR $^{143}Nd/^{144}Nd$ of 0.512634 and a $^{147}Sm/^{144}Nd$ of 0.1967 (e.g., Jacobsen and Wasserburg, 1980; and corrected for inter laboratory bias).