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Magmatic and hydrothermal controls on diverse Nb mineralization associated with carbonatite/alkaline rocks in the southern Qinlingorogenic belt, Central China: new insights from in-situ chemical and isotopic analyses in a textural context

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Analytical methods

Scanning electron microscope (SEM) analysis

The samples were investigated by backscattered electron (BSE) and cathodoluminescence (CL) imagings, and energy dispersive X-ray spectroscopy (EDS) element mappings. The above investigations were conducted by using a JSM-7800F field emission scanning electron microscope (FE-SEM) equipped with TEAM Apollo XL energy disperse spectroscope and a Gton Mono CL4 detector at the State Key Laboratory of Ore Deposit Geochemistry (SKLODG), Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. The accelerating voltages for BSE and CL imaging were operated at 20 kV and 10 kV, respectively, while the beam currents for both were 10 nA.

Electron probe microanalyzer (EPMA)analysis

Major element compositions of pyrochlore, columbite, rutile, ilmenite, titanite and apatite were determined with a JEOL JXA-8530F field emission electron probe microanalyzer at the State Key Laboratory of Ore Deposit Geochemistry (SKLODG),

Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. A current of 10 nA and a focus beam of 1-10 μm at an accelerating voltage of 25 kV were generally used for these minerals. The standards used for analyses of pyrochlore include monazite for La, Ce, Nd, Th and Y, crome diopside for Ca, U elemental for U, niobium elemental for Nb, PbS for Pb, pyrope for Ti, Fe, Mn, Si, and Al, cubic zirconia for Zr, albite for Na, tantalum elemental for Ta, anhydride for Sr, apatite for F. The standards used for analyses of columbite include almandine garnet for Fe, pyrope for Mn and Ca, tantalum elemental for Ta, benitoite for Ti, niobium elemental for Nb. The standards used for analyses of rutile include pyrope for Fe, vanadium elemental for V, rutile for Ti, niobium elemental for Nb, tungsten for W. The standards used for analyses of ilmenite include pyrope for Mn, Cr, Mg, Al, Si, and Ca, magnetite for Fe, vanadium elemental for V, willemite for Zn, rutile for Ti, niobium elemental for Nb, cubic zirconia for Zr, tantalum elemental for Ta. The standards used for analyses of titanite include pyrope for Fe, Mn, Al, Mg, Cr, and Si, rutile for Ti, Orthoclase for Na, Kaersutite for K, diopside for Ca. The standards used for analyses of apatite include monazite for La, Ce, and Th, pyrope for Fe, Mn, Al, and Si, tugtupite for Cl, benitoite for Ba, niobium elemental for Nb, apatite for S, Ca, F, and P, plagioclase for Na, tantalum for Ta, celestite for Sr. For apatite, due to the characteristic of fluorine diffusion and the specific crystal orientation of the analyzed apatite, the F contents were erratic and should only be considered as semi-quantitative. We use short count times and large beam spots to minimize issues arising from F diffusion (Stormer et al. 1993; Stock et al. 2015). The limits of detection for these measured elements are 50 to

200 ppm.

LA-ICP-MS trace element analysis

Trace element compositions of apatite and titanite were conducted using a Geolas Pro 193-nm ArFexcimer laser ablation system coupled with Element XR HR-ICP-MS and Agilent 7700x ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. Analyses were performed with a beam diameter of 44 μm for titanite，24 μm for apatite with a repetition rate of 5Hz. Helium was applied as a carrier gas. Argon was mixed with carrier gas via a T-connertor before entering the ICP-MS. Each analysis incorporated a background acquisition of ~30 s (gas blank) followed by ~50 s data acquisition from the sample. Elements contents were calibrated against multiple-reference (NIST610 and NIST 612), which were analyzed twice after fifteen analyses of samples. Calcium, which was obtained by EPMA, were used as the internal standard for the analyses of apatite and titanite.

Whole-rock major and trace elemental analyses

One hundred and twenty rock samples of the Miaoya and Shaxiongdong complexes, including syenites, carbonatites, and country rocks, were cleaned with deionized water, and subsequently crushed and powdered with an agate mill. The major- and trace-element composition of rock samples was determined by X-ray fluorescence spectrometry and solution ICPMS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of

Geochemistry, Chinese Academy of Sciences, Guiyang, China. The analytical protocol for trace elements was described in detail by Qi et al. (2000). Replicate analyses, including the samples and reference materials, indicating the analytical precisions for the most trace elements are generally better than 10%.

LA-ICP-MS U-Pb isotope analysis

Titanite U-Pb dating was conducted using a Geolas Pro 193-nm ArFexcimer laser ablation system coupled with Element XR HR-ICP-MS and Agilent 7700x ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China. The beam was set at 44 μm with a repetition rate of 5 Hz. Helium was applied as carrier gas and mixed with argon through T-connector before entering the ICP-MS. Each analysis incorporated 30 s background (gas blank) followed by 50 s of data acquisition. For titanite, OLT-1 titanite standard was utilized to correct U-Pb fractionation and instrumental mass discrimination. Qinghutitanite (QH-1) was measured as unknown sample for quality control. Raw data reduction was conducted off-line by ICPMSDataCal software (Liu et al., 2010). Data were processed using the ISOPLOT program (Ludwig, 2003).

LA-MC-ICP-MS Sr and Nd isotopic analysis

In situ Sr and Nd isotopic analyses of apatite were conducted on 80-100μm-thick polished section, using a Nu Plasma II MC-ICP-MS (Nu Instruments) that was attached to a RESOlution LR ArF193 nm laser ablation system at Nanjing FocuMS Technology

Co. Ltd., China. The analytical protocol for in situ Sr isotope analyses follows the method described in Gao and Zhou (2013). Apatite was ablated in a mixture of helium (370 ml/min) and argon (~0.97 L/min) atmosphere using the following parameters: 20 s baseline time; 40 s ablation time; 40-90 μm spot size; 8 Hz repetition rate; 4.5 J/cm^2 energy density. The analytical accuracy was evaluated with repeated analyses of a modern-day coral and two apatite standards (AP-1 and P1-A) after ten and twenty unknow samples, respectively. The analytical protocol for in situ Nd isotope analyses follows the method described in Yang et al. (2014). The analytical accuracy for in-situ Nd isotopic analyses was evaluated with repeated analyses of one apatite (Namaq2a) and two apatite (AP-1 and AP-2) standards after five and every thirty unknown samples, respectively.

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