

SUPPLEMENTARY MATERIALS

Analytical Methods

Microscope and TIMA analysis

Representative thin section of the studied carbonatite sample was scanned at the Langfang Tuoxuan Rock and Mineral Analysis Service Co., Ltd. A panoramic photograph of the thin section was compiled from approximately 2500 individual micro-petrographic photographs captured using a high-power polarizing microscope. The thin section was also coated with carbon and then scanned by the TESCAN Integrated Mineral Analyzer (TIMA) to create the mineral phase map. The TIMA is a Mira-3 scanning electron microscope (SEM) equipped with four energy dispersive X-ray spectrometers (EDS, EDAX Element 30). Operating parameters were as follows: 25 kV acceleration voltage, 9 nA probe current, and 15 mm working distance. The measurements were conducted using the liberation analysis module and dot mapping mode, with pixel spacing and dot spacing of 3 and 9 μm , respectively.

SEM-EDS analysis

Thin sections were coated with a carbon layer, and then examined using a TESCAN MIRA3 SEM equipped with a Bruker XFlash 5300 detector at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). Backscattered Electron (BSE) images of britholite and humite group minerals were acquired for further in-situ analysis and simultaneous EDS analysis .

EPMA analysis

Major elements of humite group minerals were measured using a JEOL JXA-8530F plus Electron Probe Micro Analyzer (EPMA) at the CAS Key Laboratory of Crust-Mantle Materials and Environments, USTC. Operating parameters were configured with an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 5 μm . Following reference materials were used for instrument calibration: olivine for Si, pyrope garnet for Fe and Al, diopside for Ca and Mg, rhodonite for Mn, rutile for Ti, sanidine for K, jadeite for Na, and topaz for F. Peak counting time was set to be 10 s (Si, Mg, Fe, Ca, Al, Na, REE, and K) and 20 s (Ti, Mn, F) for different elements. Upper and lower background counting times were both set at 5 s for all elements.

Britholites were analyzed by a JEOL JXA-8230 EPMA at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). Operating conditions included an accelerating voltage of 15 kV, a beam current of 50 nA, and a beam diameter of 10 μm . Detailed operating conditions and standards are described in Cao et al. (2019). Modified ZAF (atomic number, absorption, fluorescence) correction procedures were applied during the data reduction.

LA-ICP-MS analysis

LA-ICP-MS analysis of humite group minerals was conducted at CAS Key Laboratory of Crust-Mantle Materials and Environments, USTC. An Agilent 7900 quadrupole ICP-MS, coupled with a GeoLasHD 193 nm ArF excimer laser ablation system (LA), was employed. Operating parameters were set as follow: 32 μm laser beam size, 5 Hz repetition rate and 4 J/cm^2 energy density. Element contents were calibrated against multiple-reference materials (BIR-1G, BCR-2G, and BHVO-2G) without applying internal standardization, and NIST SRM 610 reference glass was used as the monitor standard. Standard materials were repeatedly ablated between 7-8 sample grains. Each analysis cycle comprised a first 20 s for background acquisition and 40 s for data acquisition, followed by 30 s for washout.

Britholite was analyzed using an Agilent 7900x ICP-MS equipped with a RESolution 193 nm LA system, at GIGCAS. Measurements were made using 43 μm laser beam diameter, 6 Hz repetition rate and 4.22 J/cm^2 energy density. NIST SRM 610 and 612 were repeatedly measured between every seven britholite samples, and they served as multiple-reference materials. The acquisition time for the background and sample signal were 20 and 50 s, respectively. Element contents determination was conducted using the ICPMSDataCal software, employing the external calibration without an internal standard method, with analytical uncertainty better than 5% for REE and 10% for other elements (Liu et al., 2008).

Supplementary Table caption

Supplementary Table 1: EPMA analysis result of humite group minerals.

Supplementary Table 2: EPMA analysis result of fluorbritholite-(Ce).

Supplementary Table 3: LA-ICP-MS analysis result of humite group minerals.

Supplementary Table 4: LA-ICP-MS analysis result of fluorbritholite-(Ce).