

SUPPORTING INFORMATION (SI)

Isotopic exchange of oxygen, sulfur, hydrogen, and copper
between aqueous phase and the copper minerals brochantite,
libethenite, and olivenite

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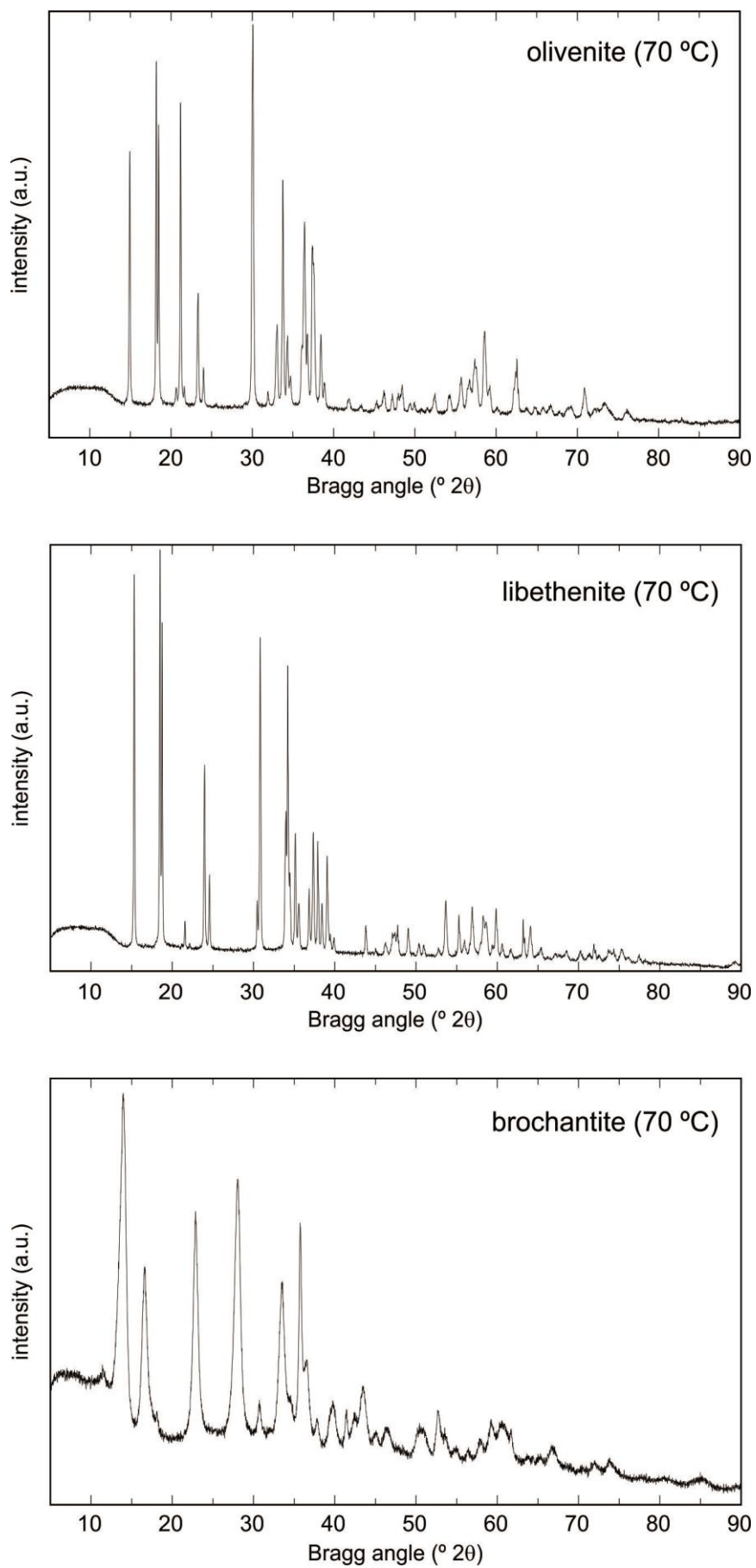


Fig. S1. Powder X-ray diffraction patterns of selected samples.

Methods – vibrational spectroscopy

Infrared spectra of synthetic brochantite, libethenite and olivenite powder samples were acquired on Nicolet™ iS50 Fourier Transform Infrared (FTIR) Spectrometer (Thermo Scientific) equipped with Michelson interferometer and KBr-beam splitter, in Attenuated Total Reflection (ATR) mode. Signal was collected in 150 cycles by an MCT detector in spectral range 400-4000 cm^{-1} , spectra were acquired, and background subtracted and processed in software OMNIC™ Spectra (Thermo Scientific).

Unpolarized Raman spectra were measured using a Horiba Jobin-Yvon LabRam HR800 microspectrometer, mounted on an Olympus BX41 microscope, with a confocally coupled Czerny-Turner type monochromator (focal length 800 mm). A frequency-doubled Nd-YAG laser at 532 nm (Laser Quantum, UK) was used for excitation with power on sample less than 24 mW (a series of tests at various power settings was performed due to possible thermal effect). The Raman-scattered light was collected in 180° geometry through a 50 \times objective lens and dispersed by diffraction grating with 600 g/mm onto a cooled (-70°C) charge-coupled device (CCD) detector. The grating turret accuracy was calibrated between the zero-order line and the laser line at 0 cm^{-1} . Spectral accuracy was verified on the 734 cm^{-1} band of Teflon, the system resolution was 6 cm^{-1} and band definition was improved using 2-fold sub-pixel shift. For each Raman spectrum, the baseline was subtracted (Labspec® v.5 software).

Libethenite

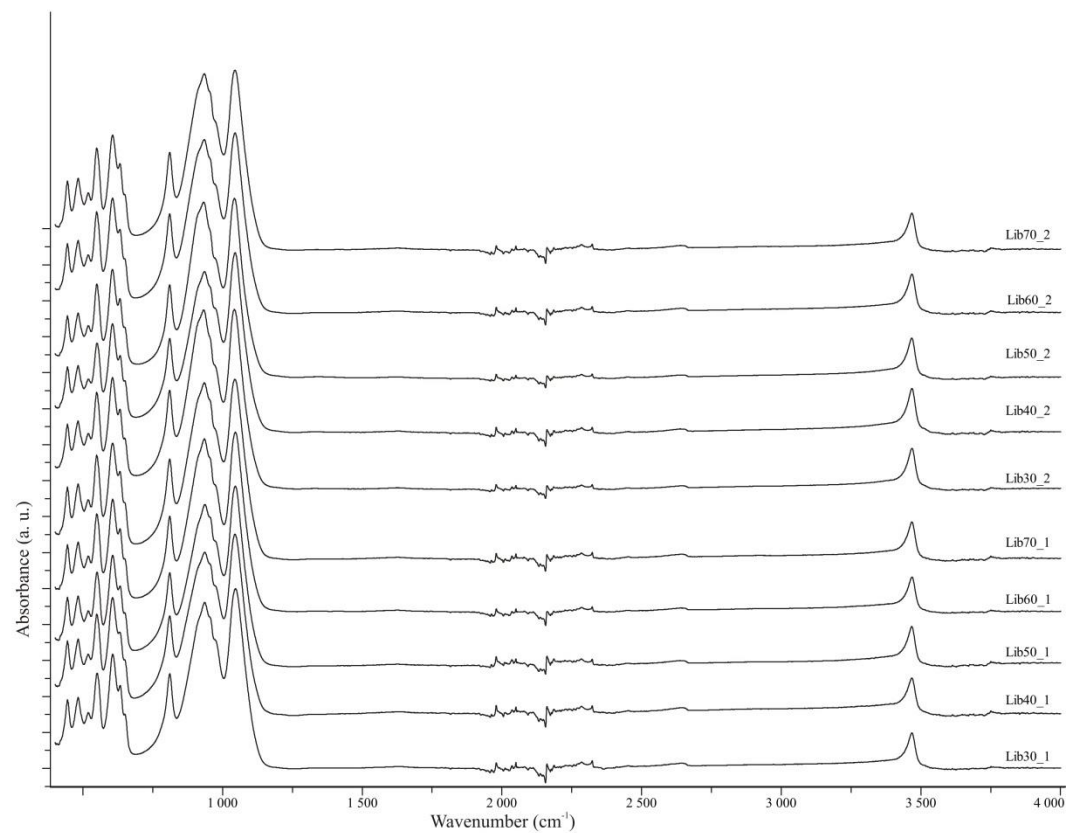
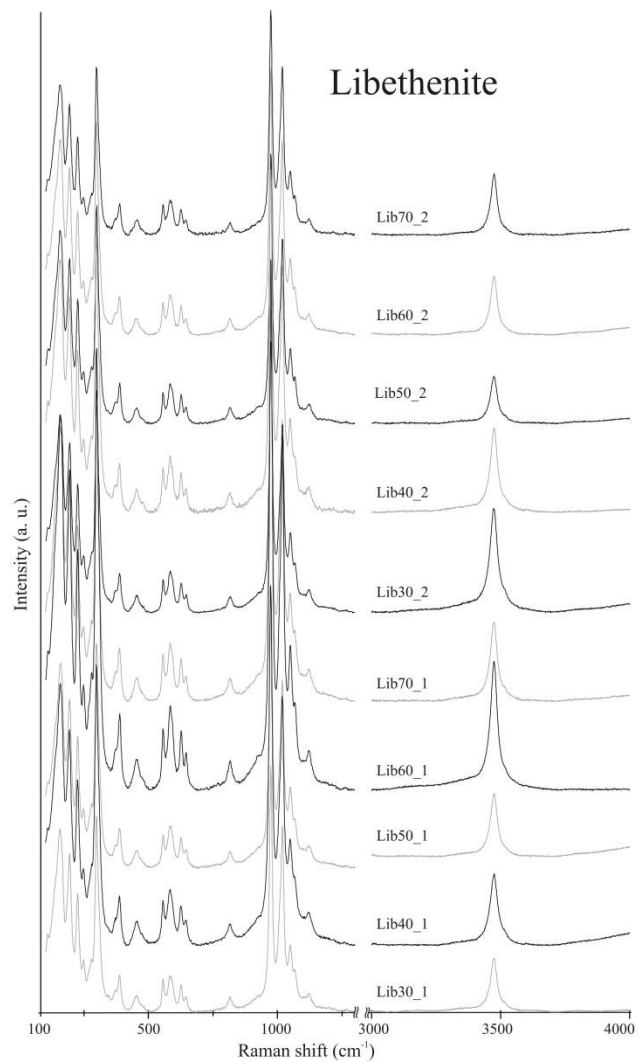


Fig. S2. Raman (left) and infrared (right) spectra of the libethenite samples used for the determination of the isotopic fractionation factors.

Olivenite

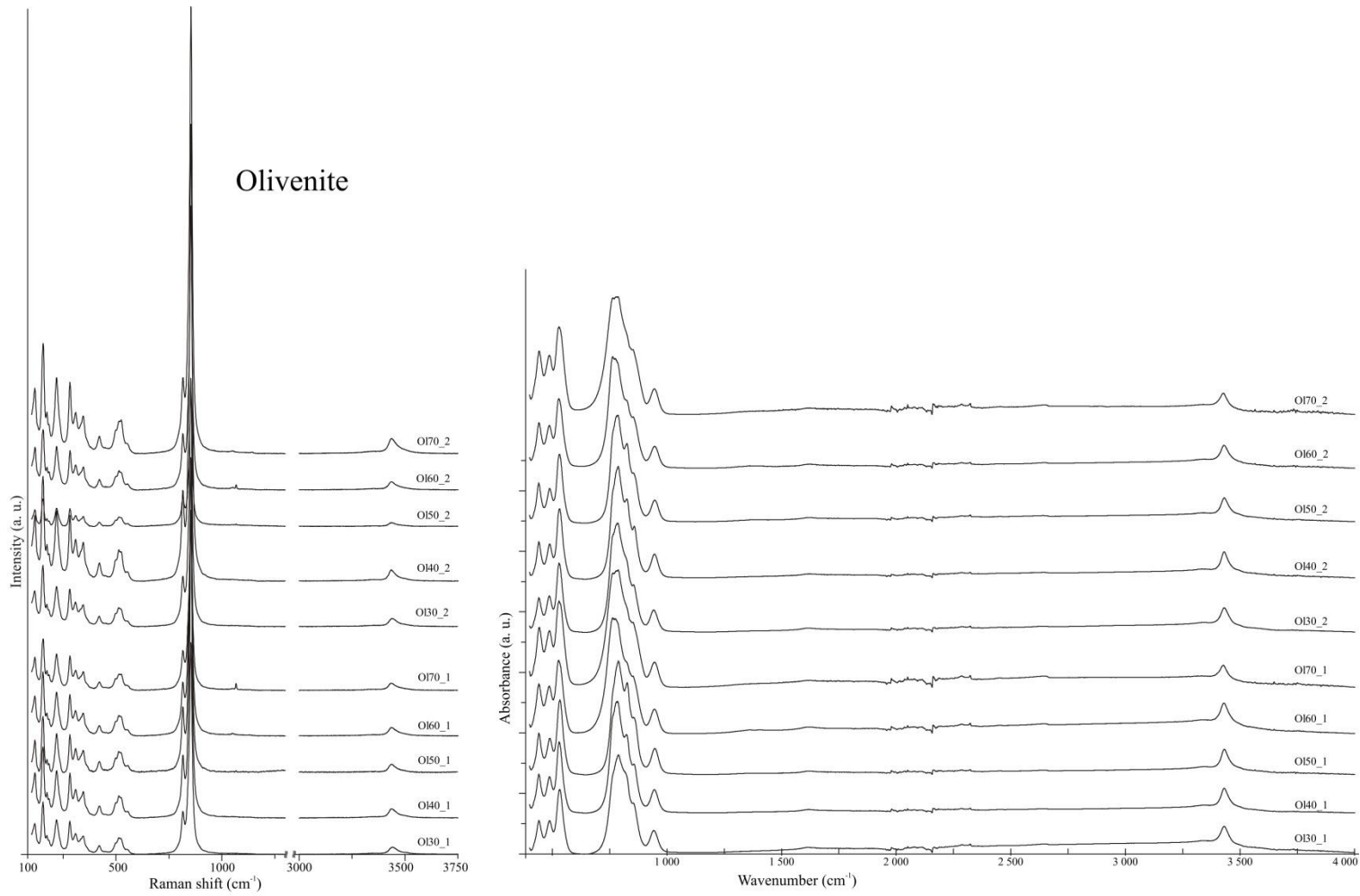


Fig. S3. Raman (left) and infrared (right) spectra of the olivenite samples used for the determination of the isotopic fractionation factors.

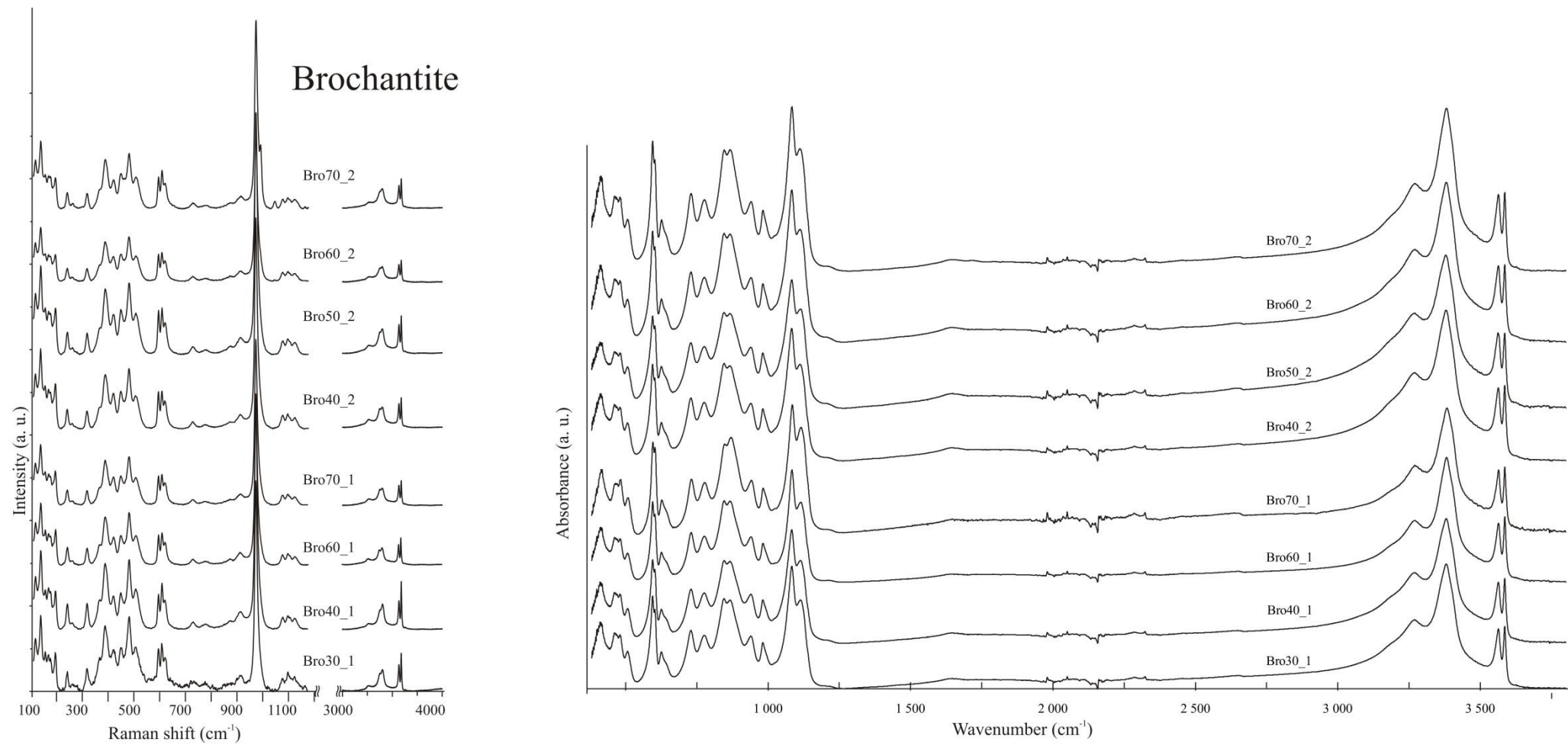


Fig. S4. Raman (left) and infrared (right) spectra of the brochantite samples used for the determination of the isotopic fractionation factors.