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The $^{34}S/^{32}S$ homogeneity of Chemical Vapor Transport (CVT) Reaction-synthesized pyrites

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Abstract

The Chemical Vapor Transport (CVT) Reaction is an important and efficient method of synthesizing pyrite crystals. CVT-grown pyrites have been comprehensively investigated for physical properties and elemental chemical compositions. However, the isotopic compositions have not been investigated. In this study, four series of pyrite crystals (PY3, PY4, PY5, and PY6) were synthesized using the CVT method, with PY5 undoped and the others doped with nickel. The synthesized crystals were characterized qualitatively with confocal laser Raman microspectroscopy and quantitatively by EMPA, LA-ICP-MS, SIMS, and IRMS. The synthetic products are irregular polycrystalline aggregates or cubic and octahedral monocrystals, with characteristic Raman bands at ~344 cm^{-1}, ~380 cm^{-1}/377 cm^{-1}, ~427 cm^{-1}/430 cm^{-1}, and S/Fe weight and atomic ratios of 1.15–1.17 and 2.01–2.04, respectively, indicative of pyrite. The pyrites contain traces of inevitable impurities such as Si and Br. The nickel contents of Ni-doped pyrites are heterogeneous, 39–27 300 ppm for PY3, 24–21 700 ppm for PY4, and 57–2610 ppm for PY6. By comparison, the $\delta^{34}S$ values obtained by SIMS are relatively homogeneous (PY3 = 17.3 ± 0.9‰, PY4 = 17.7 ± 0.8‰, PY5 = 17.9 ± 0.8‰, PY6 = 17.7 ± 0.6‰, ±2SD), and are consistent with IRMS $\delta^{34}S$ values (17.8 ± 0.2‰ for PY3, 18.3 ± 0.9‰ for PY4, 18.2 ± 0.3‰ for PY5, 18.1 ± 0.1‰ for PY6, ±2SD). The homogeneity of $^{34}S/^{32}S$ suggests that CVT has the potential to synthesize reference materials for the determination of sulfur isotopic composition of pyrite using in situ techniques. Additionally, we also investigated the matrix effects of nickel in pyrite on the measurement of $^{34}S/^{32}S$ by SIMS, and a preliminary equation of $\Delta^{34}S$ (‰) = $-0.59 \times Ni\ (wt\%)^{0.27}$ ($R^2 = 0.3$), where $\Delta^{34}S$ is the discrepancy between in situ and bulk $\delta^{34}S$ values, was derived for calibration.

Keywords: CVT reaction, pyrite, $^{34}S/^{32}S$, nickel, matrix effects, SIMS