

# **New potential sphalerite, chalcopyrite, galena and pyrite reference materials for sulfur isotope LA-MC-ICP-MS determination**

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The sulfur isotope system is important in tracing a variety of geochemical processes. Conventionally, sulfur isotopes are mainly analyzed in bulk by gas source (GS-) isotope ratio mass spectrometry (IRMS) and solution nebulization multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). For samples that are fine-grained, complexly intergrown with other minerals or heterogeneous in isotopic compositions, high precision *in situ* sulfur isotope analytical techniques are needed. However, the availability of matrix-matched references for *in situ* sulfur isotope analysis is limited. This study analyzed four sulfide specimens to investigate their potential as reference materials for *in situ* sulfur isotope determination, including three natural sulfide minerals of sphalerite (SPH-1), chalcopyrite (GC-1), galena (NWU-GN), and one resin preserved pyrite powder (RPPY). These four sulfides were analyzed independently in four laboratories using both bulk and microbeam analysis techniques, all of which gave equivalent results within uncertainty with comparable accuracy and precision. The sulfur isotopes of these four sulfides are homogeneous based on a large amount of isotope determination by solution nebulizer multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and laser ablation (LA) MC-ICP-MS, and the isotope homogeneity has been checked using the F-test and the H-index. The mean  $\delta^{34}\text{S}$  values for SPH-1, RPPY, GC-1, and NWU-GN determined by gas source isotope ratio mass spectrometry (GS-IRMS) and the solution nebulizer MC-ICP-MS are  $-7.13 \pm 0.41 \text{ ‰}$  (2s),  $3.66 \pm 0.24 \text{ ‰}$  (2s),  $-0.65 \pm 0.28 \text{ ‰}$  (2s),  $28.21 \pm 0.17 \text{ ‰}$  (2s) relative to Vienna Canon Diablo troilite (V-CDT), respectively, which are proposed as the potential preferred values. Over 400 spot analyses performed on randomly selected fragments for each sulfide by LA-MC-ICP-MS yield highly consistent  $\delta^{34}\text{S}$  values with the preferred values. Thus, SPH-1, GC-1, NWU-GN, and RPPY are considered a set of candidate matrix-matched sulfide reference materials for *in situ* sulfur isotope determination.