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Reference materials for *in situ* S-Zn isotopes analysis of sphalerite

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This study examined the micro-homogeneity of zinc isotope composition of the NIST SRM 683 and NBS 123 reference materials using femtosecond laser ablation multi-collector inductively coupled plasma-mass spectrometry (fsLA-MC-ICP-MS). NIST SRM 683 and NBS 123 are homogeneous in Zn isotope composition based on numerous measurements performed on twenty chips and four mounts of sphalerite using solution nebulisation (SN)-MC-ICP-MS and fsLA-MC-ICP- MS. The mean $\delta^{66}Zn_{JMC\text{-}Lyon}$ values of NIST SRM 683 and NBS 123 determined by SN-MC-ICP-MS were 0.11 ± 0.02‰ (2 standard deviation (2s), n = 100) and 0.16 ± 0.02‰ (2s, n = 62), respectively. The in situ measurement precision for NIST SRM 683 and NBS 123 was better than 0.06‰ (2s), suggesting NIST SRM 683 and NBS 123 are suitable to serve as microanalytical reference materials for Zn isotope measurement. Zinc isotopic compositions of Zn-rich materials were also determined using fsLA-MC-ICP-MS under wet/dry plasma conditions. Their $\delta^{66}Zn_{JMC\text{-}Lyon}$ values were in agreement with those obtained by SN-MC-ICP-MS analysis, suggesting that fsLA-MC-ICP-MS is suitable to measure Zn isotopic ratios in Zn-rich materials. Thus, this method could potentially analyse spatially resolved Zn isotope compositions at the mineral or even sub-mineral scale, such as to address the process of ore formation or Zn redistribution in near-surface environments. Sulfur isotopes are important tracers in various geochemical processes. In this study, natural sphalerite powders (GBW07270) were ground into ultra-fine powders and then sintered by using a plasma-activated sintering (PAS) method at 1000°C and 50 MPa for 10 minutes. The synthesized sphalerite has smooth surface and dense structure, making it suitable for laser ablation analysis. A large number of *in situ* S isotope measurements were performed on the PAS-synthesized sphalerite by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS), and the LA-MC-ICP-MS results are highly consistent and yield a mean $\delta^{34}S_{V\text{-}CDT}$ value of -5.44 ± 0.20‰ (2SD, n = 1008), which agrees well with that measured by gas source isotope ratio mass spectrometry (GS-IRMS). Therefore, the PAS-synthesized sphalerite is suitable to be a matrix-matched reference material available for *in situ* S isotope measurements of sphalerite.