Supplementary material

SM1: In-situ measurements of lead isotope compositions using CAMECA IMS1280 at Nordsims

The Pb-isotope composition of sulphides was determined by secondary ion mass spectrometry (SIMS) on polished rock sections using a Cameca IMS1280 instrument located at the Swedish Museum of Natural History, Stockholm (NordSIMS facility), closely following the protocol of Whitehouse et al. (2005). A primary beam of $^{16}O_2$-ions was accelerated onto the sample with an incident energy of ca. 23 kV (-13 kV primary, 10 kV secondary). Illumination of a 200 μm beam aperture resulted in a typical beam current of ca. 10–13 nA and produced a ca. 20 μm elliptical, flat-bottomed crater. The mass spectrometer was operated at high mass resolution (M / ΔM ~ 4860) using an entrance slit width of 75 μm and a common exit slit width of 250 μm on each of four ion counting secondary electron multiplier (EM) detectors. The detectors were positioned in the focal plane to enable simultaneous detection of ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Mass centering was achieved prior to each analysis by scanning the ^{208}Pb signal, which typically ranged from several 100's to >200000 cps in the target grains. EM detector settings were optimized for low background (<0.01 cps) and high efficiency (ca. 95%) by inspection of the pulse height analysis curves. Relative efficiencies were then calibrated by analysis of BCR-2G basaltic glass, using published values (Woodhead and Hergt, 2000); these relative efficiencies were within a few percent of each other. External precisions on ^{207}Pb / ^{206}Pb and ^{208}Pb / ^{206}Pb ratios in BCR-2G were generally ±0.5% RSD or better.

SM2: *In-situ* measurements of sulphur isotope compositions (^{32}S, ^{33}S, and ^{34}S) using CAMECA IMS1280 at Nordsims

Multiple S isotope compositions were measured using a CAMECA IMS1280 instrument at the Nordsim facility using analytical protocols similar to that previously described from this laboratory (Whitehouse, 2013). A ca. 1.0 nA Cs^+ primary beam was operated at 10 kV in focused beam (Gaussian) mode to generate a ca. 10 μm analytical pit on the sample; a 5 μm raster was applied during all analyses to homogenize the Gaussian beam. The secondary ion beam was extracted at -10 kV with the transfer optics operating at a medium field magnification of 90 x with a field aperture of 2500 μm resulting in an imaged area of ca. 30 μm. A normal incidence electron-flooding gun was used throughout measurements to eliminate problems related to charging of non-conducting inclusions in the sulphide standards. Additionally, the electron gun provided charge compensation for the analysis of very small sulphide grains in the insulating silicate matrix of actual samples. For most of the analytical sessions reported, the mass spectrometer was operated at a nominal mass resolution (M/ΔM) of ca. 4000, sufficient to separate ^{33}S from $^{32}S^1H$, using an entrance slit of 85 μm and an exit slit of 500 μm on each of the multi-collector detectors, with the detector for ^{33}S moved slightly relative the peak centre in order to achieve the required higher mass resolution. Triple sulfur isotope data (^{32}S, ^{33}S and ^{34}S) were obtained simultaneously using three Faraday detectors, with amplifiers equipped with a 10^{10} Ω resistor for ^{32}S and 10^{11} Ω for ^{33}S and ^{34}S, housed in a temperature stabilized (heated above ambient), evacuated chamber. In this mode, the detector measuring ^{33}S was located on the axis. Following a 60 s pre-sputter to remove the gold coating over a 20 x 20 μm^2 rastered area, the secondary ion beam was centred onto the ion optical axis of the mass spectrometer by automated scanning

across the field aperture in both x and y directions. This alignment procedure improved reproducibility by compensating for small variations in the secondary ion beam trajectory caused by a combination of residual (after polishing) surface relief on the sample and the angled incidence of the primary beam. The secondary magnet was stabilized to high precision using an NMR sensor operating in regulation mode. Data were collected over 64 s (sixteen cycles of 4 s integrations). Sulfur isotope measurements of reference materials (RM) were conducted in conjunction with analysis of unknowns in thin sections. Two epoxy segments containing reference sulfides were co-inserted into the 25 μm diameter sample holder together with suitably trimmed samples so that their surfaces were at the same level to within a few □m (as checked with a depth gauge). Samples and RMs were coated with ca. 30 nm of Au, and a small amount of conducting Ag paste was painted at the join between the segments and the sample holder to ensure equal electrostatic conditions. Care was taken to ensure that the Ag paste did not encroach more than ca. 1 mm from the sample holder mask onto the central part of the holder where excessive relief might result in instrumental bias; excess paste on the sample mask itself was removed before introduction of the sample into the instrument. The low values of secondary beam adjustment using the dynamic transfer deflector (DTFA) indicated negligible relief difference between the reference segments and the thin sections, and no z-focus adjustment was necessary. Three sulphide RMs described by Crowe and Vaughan (1996) were utilized in this study: Ruttan pyrite was utilized as the primary reference, assuming a $\delta^{34}S$ value of 1.41 ‰ (Cabral et al., 2012), while both Ruttan and Balmat pyrite ($\delta^{34}S$ = 16.52 ‰, Cabral et al., 2012), which have $\Delta^{33}S$ = 0 ‰, were used to define the mass dependent fractionation line used for determining $\Delta^{33}S$. Additionally, the Trout Lake chalcopyrite ($\delta^{34}S$ = 0.3 ‰, Crowe and Vaughan, 1996) was utilised

as an RM. Under the analytical conditions utilized for three-isotope measurements by SIMS, typical count rates of ca. 1.2 x 10^9 cps were obtained on ^{32}S from the RM's, with lower count rates (60-80 % of the RM) from target samples likely reflecting compositional mismatch.

SM3: Sulphur extraction and isotopic measurement of S using bulk-rock samples at the University of Maryland: Dual inlet isotope ratio mass spectrometry (DI-IRMS)

For whole-rock analyses, the sulphur fraction hosted in sulphides was extracted from powdered samples using a heated solution consisting of 20 mL of 8N HCl and 20 mL of an acidified 0.3M Cr(II) solution that extracts total sulphide sulfur, also known as chromium-reducible sulphur (Canfield et al., 1986). The solution was flushed with nitrogen and heated to sub-boiling temperature for three hours. Hydrogen sulphide was carried from the solution by nitrogen gas through a water-cooled condenser and a water trap to remove HCl vapors, and bubbled into a capture solution consisting of a $AgNO_3$ where sulfur was collected as silver sulphide (Ag_2S). The Ag_2S was then stored in the dark for one week for the dissolution of contaminants. Following this step, the Ag_2S was washed with MilliQ water, and dried at 80˚C.

Approximately 4 mg of dried Ag_2S were reacted with fluorine at 250°C to produce sulfur hexafluoride (SF_6). Sulfur hexafluoride was separated from excess fluorine reagent by condensing in a liquid nitrogen cooled trap, and passivating the fluorine using KBr in another part of the apparatus. The trap was warmed to -110°C using an ethanol slush to allow the SF_6 to be transferred to the loop of a gas chromatograph while also retaining HF in the trap. The sulfur hexafluoride was injected into a gas

chromatograph (GC) with a molecular sieve 5A and a HayeSep Q column for further purification. The exiting flow from the GC was diverted to a liquid nitrogen cooled trap to capture the purified SF_6. The SF_6 was stored in a glass manifold and then analyzed for multiple sulfur isotopes using a dual-inlet Finnigan MAT253 at the University of Maryland.

The data were normalized to the Canyon Diablo Troilite (CDT) standard for $\delta^{34}S$. Data are reported using the delta ($\delta^{3x}S$) and the capital delta ($\Delta^{33}S$) notation. Uncertainties on isotopic analyses are estimated to be 0.3 ‰ for $\delta^{34}S$, 0.016 ‰ for $\Delta^{33}S$, and 0.30 ‰ for $\Delta^{36}S$ (2σ). These estimates of uncertainty are determined from a combination of long-term data on fluorination of reference materials and data collected for reference materials subject to the full extraction protocol followed by fluorination (Wu et al., 2018). The estimates of uncertainty for $\Delta^{36}S$ are increased due to the known existence of a mass interference at 131 daltons that may result in low-level scale compression (~ 0.075 ‰/‰). Such compression may impact samples with compositions significantly different from our reference gas ($\delta^{34}S$ ~5 ‰). This contribution to the samples reported here is small since they have small range of $\delta^{34}S$ values, but the larger estimate is included because of uncertainty in the value of CDT.

SM 4: Sulphur isotope measurement of S using bulk-rock samples at the University of Queensland

Multiple sulfur isotope analyses ($\delta^{34}S$, $\delta^{33}S$) were carried out at the University of Queensland Stable Isotope Geochemistry Laboratory using an Elementar Vario Isotope Cube elemental analyser coupled in continuous flow mode to an Isoprime mass spectrometer (EA-CF-IRMS) using the same EA configuration as Baublys et al. (2004). Analytical precision was determined through replicate analyses of samples

and standards. Calibration was via 3 point normalization of international standards IAEA: S1, S2, and S3. Results are reported in per mil relative to V-CDT and have an analytical uncertainty less than ±0.3 ‰ (1σ).

SM 5: ICP-MS whole rock analysis of trace elements

Trace elements were measured at the ICP-MS analytical facility at the Earth Lab at the University of the Witwatersrand, Johannesburg. The samples were analysed for trace elements in solution by digestion of 50 mg of powder in a Mars Microwave digestor in a 2:1 HF:HNO_3 mixture at 160°C for 40 minutes, followed by drying at 80°C. Fluorides were decomposed with a further digestion using pure HNO_3 at 85°C for 24 hours and then dried. The sample was taken up in 300 µl of pure HNO_3 and made up to 50 ml (by weight) together with a mixture of the internal standards Re, Bi, Rh, and In in 5% pure HNO_3. Sample dilution was carried out to bring concentrations within the calibration range. Analysis was carried out using a ThermoScientfic iCAP ICP-MS against external calibration standards made from certified 10 ppm Perkin Elmer and Alfa Aesar solutions to obtain the calibration range of 10, 25, 50, 75, and 100 ppb. International Certified Reference Materials BCR-2 and BHVO-2 were analysed together with the samples, with measured values mostly within 5% of the recommended values.

References to supplementary material

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