1 **Noble metal nanonugget insolubility in geological sulfide liquids**

2 Michael Anenburg, John Mavrogenes

3 Research School of Earth Sciences, Australian National University, Canberra ACT

4 2600, Australia

5 **METHODS**

6 The silicate starting material was prepared by mixing NM-nanonugget bearing glass
7 fragments produced in a previous study (Anenburg and Mavrogenes, 2016) with
8 additional oxides to produce a mix of the composition: 54% SiO₂, 12.4% Al₂O₃, 3.6%
9 Fe₂O₃, 14.7% CaO, 3.9% MgO, 3.6% Na₂O, 0.8% K₂O, 1% RbCl, 1% CsCl, and 5%
10 H₂O. The heavy alkali chlorides and high H₂O content were added to produce a non-
11 viscous melt accessible at reasonable experimental temperatures (1100 °C, see
12 below). The NM and Bi budget is inherited from the starting glasses produced for the
13 Anenburg and Mavrogenes (2016) study. The use of Bi is justified for this study by its
14 non-toxicity (compared to other TABS such as As or Te), and by its use as a flux that
15 lowers the melting point of the refractory NM. Once in liquid form, the exact identity
16 of the TABS element bonded with the NM becomes less important as they are all in
17 solution within the liquid.

18 The sulfide starting material was prepared by melting an elemental mix of 25% Fe,
19 12.5% Ni, 14.2% Cu, and 48.3% S in a graphite crucible for ~1 hour. Melting was
20 conducted at 900 °C in N₂ atmosphere. Chromite was prepared by mixing
21 stoichiometric properties of Cr₂O₃ and FeO (prepared by reducing Fe₂O₃ in a 1-atm
22 furnace).

23 Graphite rods, 9 mm long and 4 mm wide, were used as capsule material. A 1.3 mm
24 wide and 7 mm long hole was drilled into each rod, into which the starting materials

were placed as layers. Three experiments are reported in this study: D2905 (consisting of 9.6 mg of sulfide sandwiched between 7.4 and 3.6 mg of silicate on the bottom and top, respectively), D2909 (consisting of 5.2 mg of sulfide sandwiched between 5.3 and 7.6 mg of silicate+chromite on the bottom and top, respectively), and C5774 (consisting of 5.2 mg of sulfide sandwiched between 6.6 and 5.6 mg of silicate on the bottom and top, respectively). A 2 mm thick graphite lid was placed on top of each rod, and the entire graphite assemblies were inserted into a swage-type Ni capsules with a wall thickness of ~1 mm (Hack and Mavrogenes, 2006). The Ni capsules were then inserted into 10 mm wide MgO assembly, surrounded by graphite foils (to be used as heaters), and into a 19 mm talc sleeves. This design ensures that the experimental charge only contacts graphite. The Ni capsule allows containment of any CO₂ gas produced during the reaction between ferrous iron and graphite:

In turn, the CO₂ gas serves as the *f*O₂ buffer in equilibrium with graphite. It is not clear whether pure CO₂ gas existed in our experiments, but in any case the silicate melt was saturated or nearly saturated in CO₂, thus buffering *f*O₂ conditions to CCO or nearly so (Frost and Wood, 1997). The combined use of talc and graphite foil required that the maximum temperature is 1100 °C, because higher temperatures cause rapid degradation of the graphite foil.

The entire assembly was inserted into a 19 mm (3/4") pressure vessel, and run in an end-loaded piston cylinder apparatus with automatic control of temperature and pressure using an in-house system. We used a piston-out method in which pressure was first increased to 5 kbar, and then temperature was increased at a rate of

100°C/min. Temperature was monitored via a type-B thermocouple. Runs D2905 and D2909 ran for 4 hours, and run C5774 ran for 17 hours. Experiments were quenched by turning off power to the heater, causing temperature to drop below 600 °C in ~5 seconds, and reaching room temperature in less than one minute. After each experiment, the capsules were removed from the assembly, mounted in 1" epoxy mounts and the experimental charges were exposed using a coarse diamond lap and sand paper. Final polishing was conducted using successively finer diamond pastes down to a grade of 0.25 µm.

Element maps were conducted using WDS spectrometers on a JEOL 8530F Plus field emission EPMA. Accelerating voltage was 8 kV and beam current was 50 nA. Pixel size varied between maps but was commonly between 100 and 200 nm, and dwell time per pixel was 250 ms. Maps were obtained in two passes, with S (K α -PETJ), Ru (L α -PETL), Ag (L α -PETL), Pt (M α -PETL) and Ni (L α -TAPH) in the first pass, and Bi (M α -PETJ), Pd (L α -PETL), Au (M α -PETL), Ir (M α -PETL) and Cu (L α -TAPH) in the second pass.

Laser ablation was conducted using a Coherent COMPexPro 110 ArF excimer (λ =193 nm), feeding into an Agilent 7700 ICP-MS. Sampling cell was a "HelEx" two-volume vortex cell in an atmosphere of Ar and He, with H₂ added during sample introduction to the ICP-MS. Spot size was 13 µm and laser repetition rate of 3 Hz. The following masses were measured: ²⁷Al, ²⁸Si, ⁴⁴Ca, ⁵²Cr, ⁶⁰Ni, ⁶³Cu, ¹⁰²Ru, ¹⁰³Rh, ¹⁰⁶Pd, ¹⁰⁷Ag, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au, ²⁰⁹Bi.

REFERENCES CITED

Anenburg, M., and Mavrogenes, J.A., 2016, Experimental observations on noble metal nanonuggets and Fe-Ti oxides, and the transport of platinum group elements in silicate melts: *Geochimica et Cosmochimica Acta*, v. 192, p. 258–278, doi:10.1016/j.gca.2016.08.010.

- 75 Frost, D.J., and Wood, B.J., 1997, Experimental measurements of the fugacity of
76 CO₂ and graphite/diamond stability from 35 to 77 kbar at 925 to 1650°C:
77 *Geochimica et Cosmochimica Acta*, v. 61, p. 1565–1574, doi:10.1016/s0016-
78 7037(97)00035-5.
- 79 Hack, A.C., and Mavrogenes, J.A., 2006, A cold-sealing capsule design for synthesis
80 of fluid inclusions and other hydrothermal experiments in a piston-cylinder
81 apparatus: *American Mineralogist*, v. 91, p. 203–210,
82 doi:10.2138/am.2006.1898.

83