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2 **Main Manuscript for**

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4 **The trisulfur radical ion $S_3^{\cdot-}$ controls platinum transport by hydrothermal fluids**

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35 Main Text (incl. abstract, significance statement, ms text, references and figure captions = 4700 words)

36 Figures 1 to 3 (uploaded separately)

37 References 1 to 33

41 **Abstract (177 words):**

42 Platinum group elements (PGE) are considered to be very poorly soluble in aqueous fluids in
43 most natural hydrothermal-magmatic contexts and industrial processes. Here we combined in
44 situ X-ray absorption spectroscopy and solubility experiments with atomistic and
45 thermodynamic simulations to demonstrate that the trisulfur radical ion $S_3^{\bullet-}$ forms very stable
46 and soluble complexes both with Pt^{II} and Pt^{IV} in sulfur-bearing aqueous solution at elevated
47 temperatures ($\sim 300^\circ C$). These novel Pt-bearing species enable (re)mobilization, transfer, and
48 focused precipitation of platinum up to 10,000 times more efficiently than any other common
49 inorganic ligand such as hydroxide, chloride, sulfate or sulfide. Our results imply a far more
50 important, than believed so far, contribution of sulfur-bearing hydrothermal fluids to PGE
51 transfer and accumulation in the Earth's crust. This discovery challenges traditional models of
52 PGE economic concentration from silicate and sulfide melts, and provides new possibilities for
53 resource prospecting in hydrothermal shallow-crust settings. The exceptionally high capacity of
54 the $S_3^{\bullet-}$ ion to bind platinum may also offer new routes for PGE selective extraction from ore
55 and hydrothermal synthesis of noble metal nanomaterials.

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57

58 **Significance Statement (118 words):** Platinum group elements (PGE) are highly valued by
59 many industrial applications, serve as important geochemical tracers of planetary processes, and
60 are among eagerly sought natural resources of critical trace metals. We show here that aqueous
61 sulfur-bearing fluids play a far more important role, than believed, in many natural and
62 technological processes in which PGE are involved. This role is essentially ensured by the
63 radical sulfur ion $S_3^{\bullet-}$ that forms extremely stable and soluble complexes both with Pt^{II} and Pt^{IV} .
64 By enabling enhanced dissolution, transport and precipitation of Pt, these species may be key
65 players in PGE transfer, fractionation, and accumulation in the Earth's crust. They may also offer
66 novel opportunities for optimizing ore processing and nanomaterial synthesis.

67

68

69 **Main Text**

70 **Introduction**

71 The increasing use of platinum in high-technology fields spanning from the automotive and
72 petrochemical industries to pharmaceuticals and nanomaterials, combined with its scarcity in nature
73 (average Pt content in upper continental crust rocks is ~0.5 ng/g), makes Pt a highly valued
74 commodity and eagerly sought natural resource (1-3). Currently assessed georesources of
75 platinum group elements (PGE) are rare and mostly occur in mafic magmatic settings where PGE
76 are concentrated in Fe-Ni-Cu sulfide minerals and melts (2-5). Their formation models are built on
77 purely magmatic differentiation including fractional crystallization and sulfide-silicate partitioning
78 and currently lack a robust assessment of the role of aqueous fluids. Indeed, systematic findings of
79 inclusions of fluids and hydrous minerals in giant PGE magmatic deposits such as Bushveld,
80 Norilsk, Sudbury (6-8) and in PGE-enriched mantle-derived rocks and lavas (9, 10) point to the
81 potential role of post-magmatic aqueous fluids in PGE transfer and redistribution. Furthermore,
82 there is multiple evidence of remobilization and concentration of Pt, as well as other PGE, in
83 various low-to-moderate temperature (200–500°C) hydrothermal environments such as porphyry
84 Cu-Au-Mo and metamorphic and sedimentary-hosted Au deposits, black shales, and serpentinites
85 (4, 11), with Pt concentrations 1000 times its average crustal abundance, making such settings
86 potentially exploitable for PGE. Therefore, knowledge of Pt chemical speciation and solubility in
87 the hydrothermal fluid phase is required to quantify the formation and distribution of Pt resources
88 in nature, to use PGE as geochemical tracers of Earth formation and evolution (e.g., 9, 10), as well
89 as to optimize the rapidly growing Pt use in technological processes involving both aqueous and
90 organic solvents (e.g., 1, 12-14).

91 Paradoxically, existing data on aqueous complexes of divalent Pt^{II} , which is a typical
92 oxidation state of platinum in nature, with most common inorganic ligands such as chloride (Cl^-),
93 sulfate (SO_4^{2-}), and hydroxide (OH^-) (15-17) yield far too small metal aqueous contents (<0.1
94 ng/g) in equilibrium with Pt-bearing mineral phases to account for the observed Pt mobility in most
95 fluids below the magmatic-hydrothermal transition ($<600\text{--}700^\circ\text{C}$). Such fluids, produced by
96 magma degassing or metamorphism or circulating in sedimentary basins, are commonly near-
97 neutral ($4 < \text{pH} < 8$), moderately saline ($<20 \text{ wt\% NaCl}$), and often sulfur-bearing (up to 1–3 wt% S)
98 containing both sulfide and sulfate. Because of the high chemical affinity of Pt for reduced sulfur
99 (18), hydrogen sulfide (HS^-) complexes are more plausible agents to transport Pt by such fluids.
100 However, the reported data on their thermodynamic stability and the resulting solubility of Pt
101 sulfide solids are highly controversial, spanning over almost 4 orders of magnitude, from $<0.1 \text{ ng/g}$
102 Pt in reduced H_2S -dominated fluids (19-21) to $>1000 \text{ ng/g}$ Pt in oxidized sulfide/sulfate-bearing
103 fluids (22). Such discrepancies call upon complexes other than sulfide (and sulfate) and/or metal
104 oxidation states other than Pt^{II} to account for platinum solubility.

105 The current speciation models of PGE in aqueous media ignore, in particular, the trisulfur
106 radical ion, $\text{S}_3^{\cdot-}$, well-known in sulfur non-aqueous chemistry (23) and stable across a very wide
107 temperature (T) and pressure (P) range of magmatic-to-epithermal sulfate/sulfide-bearing fluids
108 (24-28). Moreover, this ligand was recently shown to bind to gold greatly enhancing the efficiency
109 of Au supply to hydrothermal-magmatic porphyry and metamorphic ore deposits associated with
110 subduction zone settings which commonly involve S-rich fluids (29). To quantify the effect of $\text{S}_3^{\cdot-}$
111 on Pt behavior in typical hydrothermal fluids, we used in situ X-ray absorption spectroscopy
112 (XAS, including both near-edge structure or XANES, and extended fine structure or EXAFS) that
113 provides a direct fingerprint of metal redox, coordination and ligand identity. The spectroscopic

114 data were combined with solubility measurements and quantum-chemistry and thermodynamic
115 modeling of Pt speciation in aqueous sulfide/sulfate/S₃^{•-} solutions saturated with platinum sulfide
116 solid PtS(s) at 275–300°C and 500–700 bar (*SI Appendix*).

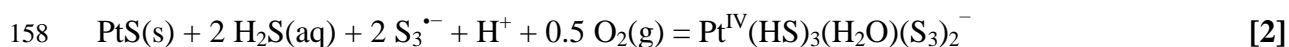
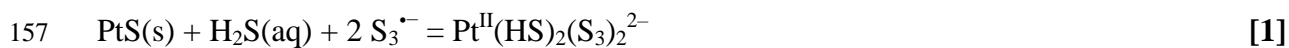
117

118 **Results**

119 Platinum L₃-edge XANES spectra of S₃^{•-} bearing solutions show a systematic evolution as
120 a function of pH and redox (expressed in log₁₀ (bars) scale relative to the conventional hematite-
121 magnetite *f*_{O₂} mineral buffer, HM, *Fig. 1A*). Spectra of the near-neutral (pH 5.9 at 275°C) and
122 relatively reduced (HM–0.2) solution are close to that of Pt^{II}S(s) both in energy position and
123 amplitude, fully consistent with divalent Pt^{II} coordinated by 4 nearest S atoms in a square-planar
124 geometry. By contrast, for more acidic and oxidized compositions, the spectra show a systematic
125 shift to higher energies along with an increase in the white-line amplitude (*Fig. 1A*), indicating a
126 change to higher Pt oxidation state and coordination, which would be closer to those of Pt^{IV}S₂(s) in
127 which Pt is octahedrally coordinated by 6 S atoms. This trend is confirmed by quantum-chemistry
128 simulations of XANES spectra (*SI Appendix*) by considering complexes with HS⁻ and S₃^{•-} ligands
129 of square-planar and octahedral coordination geometry typical for Pt^{II} and Pt^{IV} compounds,
130 respectively (18). The spectrum from the HM–0.2 solution closely resembles the simulation for
131 square-planar Pt^{II}(HS)₂(S₃)₂²⁻, whereas the spectrum from the HM+0.8 solution is best matched by
132 octahedral Pt^{IV}(HS)₃(H₂O)(S₃)₂⁻ (*Fig. 1B*). In contrast, none of the experimental spectra resembles
133 the simulation for Pt^{II}(HS)₄²⁻ (*Fig. 1B*) or other analogous [Pt^{II}(HS)_{*n*}(H₂O)_{4-*n*}]^{2-*n*}]-type species
134 commonly adopted in the literature (19-21), thus strongly supporting the predominance of new
135 [S₃^{•-}]-type species at our conditions.

136 These findings are fully supported by the EXAFS data that show a systematic increase of
 137 the first-shell mean Pt-S distance (from 2.32 to 2.36 ± 0.007 Å, 2 SD), and coordination number
 138 (from 4 to 5 ± 0.5 S atoms, 2 SD), from the most reduced and least acidic (HM-0.2, pH 5.9) to the
 139 most oxidized and most acidic (HM+0.8, pH 4.9) solutions, along with the presence of 2 ± 1 second-
 140 shell S atoms at 3.50 ± 0.02 Å in the second Pt shell of all solutions (*SI Appendix*, Figs. S2-S4;
 141 Table S1). Oxygen neighbors that may stem from OH groups or H₂O molecules in the Pt nearest
 142 atomic shell, were found to be below the detection limit of ≤ 1 O atom (*SI Appendix*). The
 143 amplitude of changes of the 1st shell Pt-S distances (>0.04 Å) and coordination numbers (from 4 to
 144 5) with f_{O_2} and pH (*SI Appendix*, Fig. S4) definitely implies a mixture of different species, and
 145 cannot be explained by the presence of only divalent Pt^{II}-S complexes, which are commonly square
 146 planar and have a very narrow range of Pt-S₄ distances (2.30–2.32 Å; e.g., refs. 18, 30). Therefore,
 147 our findings are more consistent with the presence of both Pt^{II} and Pt^{IV} species in variable
 148 proportions in solution. Furthermore, the detection of 2nd shell S atoms provides compelling
 149 evidence for the presence of the S₃^{•-} ligand in both types of Pt complexes.

150 Using these key constraints from in situ spectroscopy, we applied thermodynamic modeling
 151 to the two sets of PtS(s) solubility data, one obtained simultaneously with the XAS spectra at
 152 275°C/700 bar (Figs. S1A, S5, Table S1) and the other from batch-reactor measurements at
 153 300°C/500 bar conducted within similar ranges of redox, pH and solution composition (Figs. S1B,
 154 2, Table S2). Both datasets were found to be consistent with the formation of two complexes,
 155 Pt^{II}(HS)₂(S₃)₂²⁻ and Pt^{IV}(HS)₃(H₂O)(S₃)₂⁻, that control the solubility at near-neutral pH/more
 156 reducing conditions and acidic pH/more oxidizing conditions, respectively (Fig. 2):



159 Fig. 2 shows that the presence of relatively minor concentrations of $S_3^{\bullet-}$ in solution (~10 mmol,
 160 versus >100 mmol of H_2S/HS^-) leads to 4 to 5 order-of-magnitude enhancement of PtS(s)
 161 solubility compared to predictions for the commonly assumed hydrogen sulfide complexes from
 162 literature data obtained using reduced H_2S -dominated solutions (19, 21). The relative affinities of
 163 Pt^{II} to the $S_3^{\bullet-}$ and HS^- ligands may be evaluated using a symmetrical ligand exchange reaction
 164 between $Pt^{II}(HS)_2(S_3)_2^{2-}$ and the $Pt(HS)_4^{2-}$ complex of the same electric charge and coordination:



166 The value of the reaction [3] equilibrium constant at 300°C and 500 bar is $10^{8.7}$ as derived by
 167 combining the data of this study (Tables S3 and S5) and those for $Pt(HS)_4^{2-}$ from ref. (19). This
 168 value means that the affinity of Pt^{II} for one $S_3^{\bullet-}$ ligand is at least $\sim 10^4$ greater than for one HS^-
 169 ligand. Such remarkable affinity to $S_3^{\bullet-}$ may be related to a favorable combination of the electronic
 170 configurations of both Pt^{II} having two empty 5d shell orbitals ($[Xe]4f^{14}5d^86s^0$) and the radical $S_3^{\bullet-}$
 171 ion having an unpaired electron to fill these orbitals in a chemical bond, coupled with favorable
 172 steric factors yielding a highly stable symmetrical complex geometry with 2 $S_3^{\bullet-}$ ligands in trans-
 173 position (Fig. 1B). Remarkably, the affinities of aurous gold (Au^I) for $S_3^{\bullet-}$ and HS^- are very similar
 174 as attested by an equilibrium constant of ~ 1 for an analogous ligand exchange reaction: $Au(HS)_2^- +$
 175 $S_3^{\bullet-} = Au(HS)(S_3)^- + HS^-$, studied across a temperature range of 200–500°C (29). Compared to Pt^{II}
 176 or Pt^{IV} , Au^I has its 5d shell filled ($5d^{10}$), which may render bonding with the different sulfur
 177 ligands less specific. Furthermore, the 4 and 6-coordinated geometries of Pt offer more flexibility
 178 and less steric strain for binding to 2 $S_3^{\bullet-}$ ligands, compared to Au^I whose stable coordination is
 179 limited to quasi-linear geometries (L-Au-L, e.g., refs. 29, 33). These tendencies are also in good
 180 agreement with the generally more chalcophile (i.e. sulfur loving) character of Pt that forms far
 181 more stable (poly)sulfide solid phases than those formed by Au (e.g., 18, 30). The equilibrium

182 constant values derived for reactions [1] and [2] (Table S5) allow Pt solubility predictions across
183 the wide compositional range of natural and technological S-bearing hydrothermal fluids (Fig. 3).

184

185 **Discussion and Applications**

186 The discovery of stable soluble platinum-trisulfur ion complexes in aqueous fluids offers
187 new applications in geoscience, chemistry and material science.

188 First, the large enhancement of Pt solubility in hydrothermal ore-forming fluids in the
189 presence of $S_3^{\bullet-}$ explains the multiple cases of PGE enrichment in a variety of hydrothermal sulfide
190 deposits of common metals (Cu, Mo, Zn, Au, Ag), which may become a novel economic source of
191 platinum in near future. Our predictions of Pt solubility (Fig. 3) show that $\mu\text{g/g}$ levels of metal
192 concentrations may easily be transported by typical epithermal fluids at temperatures around
193 300°C . Our predictions are in marked contrast with former models based on ‘traditional’ sulfide
194 and chloride ligands that account for less than ng/g levels of Pt in such fluids. Consequently,
195 breakdown of $S_3^{\bullet-}$ within rather narrow S concentration (0.1–1 wt%), pH (3–7) and f_{O_2} (HM \pm 1)
196 windows upon the evolution of a S-rich hydrothermal fluid would yield focused Pt precipitation in
197 high tenors from a fluid volume 10^3 to 10^5 times smaller than would be required to precipitate the
198 same platinum amount if the [Pt- S_3] complexes were ignored. Compared to gold, whose speciation
199 is dominated by hydrogen sulfide complexes in most hydrothermal solutions of near-neutral pH
200 below 350°C ($\text{Au}(\text{HS})_2^-$; Fig. 3D) because of the much greater abundance of the $\text{HS}^-/\text{H}_2\text{S}$ ligands
201 than $S_3^{\bullet-}$, platinum mobility is far more strongly enhanced in the presence of even small amounts
202 of $S_3^{\bullet-}$. Therefore, this ligand may control the fractionation of PGE from Au as well as other more
203 common metals such as Cu, Zn, Pb, or Ni. These metals have a weaker chemical affinity to $S_3^{\bullet-}$

204 and their speciation is dominated by complexes with far more abundant chloride in most
205 hydrothermal fluids (29).

206 Second, on a larger mantle-crust scale, S-bearing aqueous fluids may play a far more
207 important role in PGE behavior than believed. Even though our exploratory data set does not
208 currently allow extrapolations to higher, closer to magmatic, temperatures, the growing stability
209 of $S_3^{\bullet-}$ as well as of its higher-temperature (>500°C) counterpart $S_2^{\bullet-}$ (26, 28), suggests that both
210 radical ions may play a key role in PGE mobility in hydrothermal-magmatic systems. As a
211 result, the radical ions may promote PGE transfers from deep magmas or metamorphic rocks in
212 subduction zones to aqueous fluids and their massive transport up to shallow crust settings,
213 thereby explaining the observed PGE enrichment in gold and base metal porphyry-epithermal
214 deposits, black-shale sedimentary environments, and serpentinites. Our findings of stable PGE
215 complexes with $S_3^{\bullet-}$, if further confirmed across a wider T - P range, may shift the long-standing
216 paradigms on PGE deposit formation by purely magmatic processes, in the light of multiple
217 evidence of aqueous fluid presence (6-8, 11). Quantifying the role of such S-bearing fluids
218 requires more systematic data on PGE interactions with the sulfur radical ions over the
219 magmatic-hydrothermal T - P range. Our results demonstrating a strong Pt enrichment in S-
220 bearing fluids, in which the aqueous sulfate and sulfide forms of sulfur coexist, may offer novel
221 perspectives in the exploration of alternative PGE economic sources in hydrothermal settings
222 that host both sulfate and sulfide mineral assemblages. Furthermore, our study points to an
223 important role of slab-derived fluids under redox conditions of the sulfate-sulfide coexistence
224 common in subduction zones and favoring the abundance of $S_3^{\bullet-}$ and $S_2^{\bullet-}$ (e.g., 28). Such fluids,
225 often enriched in sulfur, may be capable of selectively mobilizing Pt and, by analogy,
226 electronically similar Pd^{II} and Ir^I , from the mantle wedge. On the other hand, other, less

227 chalcophile PGE such as Ru, Rh or Os, generally having weaker affinities for soft ligands like
228 (poly)sulfides (18), would be much less affected. These differences in the affinity to $S_3^{\bullet-}$ may
229 thus induce fluid-mineral fractionations among different PGE thereby impacting their both
230 elemental and isotopic signatures in mantle-derived rocks that are widely used as geochemical
231 tracers of planetary accretion and core-mantle evolution (e.g., 9, 10).

232 Third, the discovery of highly soluble $S_3^{\bullet-}$ complexes with both Pt^{II} and Pt^{IV} may open
233 new routes for hydrothermal synthesis of PGE-based nanomaterials increasingly used in
234 catalysis, medicine, and electronics. Trisulfur ion may offer an interesting alternative to organic
235 thiolate ligands currently used as precursors in the synthesis of Au and Pt nanoparticles and
236 their stabilization in solution (31, 32). Furthermore, the specific solubility pattern of PtS(s) and,
237 by analogy, of Pt metal as a function of solution pH and redox potential, passing through a
238 maximum at slightly acidic pH and an H_2S/SO_4 ratio of ~4, corresponding to the maximum of
239 $S_3^{\bullet-}$ abundance (Fig. 3), may be explored for optimizing Pt nanoparticle preparation and
240 functionalization both through reduction/oxidation and acidification/basification. Such unique
241 solubility dependence thus offers greater flexibility and a larger redox, pH and temperature
242 window for synthesis protocols both in aqueous or organic solvents than those currently based
243 on H_2 reduction of Pt^{II} chloride or thiolate complexes unstable at elevated temperatures (e.g.,
244 12-14). Our findings thus extend the choice of S-ligands and provide more potential for tuning
245 the molecular mechanisms that control the shape, atomicity, structure, and resulting reactivity of
246 the formed nanoparticles of noble metals.

247

248 **Methods Summary** (See *SI Appendix* for detailed description of experimental and model
249 systems, methods, and uncertainties)

250

251 **X-Ray Absorption Spectroscopy and Solubility Measurements.** Platinum solubility and chemical
252 molecular speciation were investigated in aqueous PtS(s)-saturated solutions of thiosulfate and elemental
253 sulfur that yield variable equilibrium amounts of hydrogen sulfide ($\text{H}_2\text{S}/\text{HS}^-$), (hydrogen)sulfate (HSO_4^-
254 $/\text{SO}_4^{2-}$) and S_3^{2-} ion, and provide redox and acidity (pH) buffering of the system (e.g., 29, 33). In situ X-
255 ray absorption spectroscopy (XAS) measurements at Pt L_3 -edge (11.564 keV) were performed at BM30-
256 FAME beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France), using a
257 hydrothermal apparatus developed at the Néel Institute. This setup enables simultaneous acquisition of
258 high-quality fluorescence spectra from dilute solutions (down to 0.1 mmol Pt) to extract ligand identity,
259 molecular structure and metal redox state and to directly determine the total dissolved Pt concentration
260 (33). Measurements were conducted at 275°C and 700 bar. The XAS experiments were complemented
261 by batch-reactor measurements of PtS(s) solubility at similar conditions (300°C, 500 bar) using
262 hydrothermal reactors allowing controlled sampling or quenching of the fluid that was processed and
263 analyzed using recent protocols developed for trace metals in S-rich solutions (20).

264 **Molecular simulations and XANES spectra modeling.** Both static Density Functional Theory (DFT)
265 and First Principles Molecular Dynamics (FPMD) simulations of the geometries and interatomic
266 distances of selected [Pt-HS- S_3]-type complexes were performed following approaches developed for a
267 similar Au- $\text{HS}^-/\text{H}_2\text{S}-\text{S}_3^{2-}$ system (29). The calculated molecular structures were compared with
268 experimental XAS-derived distances and coordination numbers to better constrain the stoichiometry of
269 complexes. In addition, XANES spectra of such complexes were simulated using the FDMNES package
270 (SI Appendix) and compared with the experimental spectra to further constrain the Pt coordination and
271 oxidation state in the fluid phase.

272 **Thermodynamic analysis of platinum speciation and solubility.** Platinum solubility in experimental
273 solutions was modeled in terms of dominant [Pt-HS- S_3] complexes using the constraints imposed by the
274 spectroscopic and molecular data, and based on available robust thermodynamic properties of aqueous
275 sulfur species including S_3^{2-} (SI Appendix, Table S3). The derived stoichiometries and formation
276 constants for the two dominant Pt^{II} and Pt^{IV} complexes (reactions [1] and [2]) are consistent with the
277 whole set of experimental data. The generated reaction constants values allow PtS(s) solubility to be
278 predicted in S-bearing epithermal fluids (~300°C, 500 bar) as a function of pH, oxygen fugacity and total
279 sulfur content with an overall precision of better than ± 1 order of magnitude (SI Appendix).

280

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293

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375

376 **Figure captions**

377

378

379 **Fig. 1.** Platinum L₃-edge XANES spectra of S-bearing aqueous solutions in equilibrium with PtS(s) at
 380 indicated pH and oxygen fugacity (relative to the conventional hematite-magnetite mineral buffer, HM)
 381 recorded at 275°C and 700 bar and compared with reference compounds (A) and quantum-chemistry
 382 simulated XANES spectra of representative [Pt-HS-S₃]-type complexes with structures optimized using
 383 molecular modeling (B). Vertical dashed lines are an eye guide to indicate differences in the experimental
 384 spectra (A) with changes of pH and oxygen fugacity, and (B) among the calculated spectra of the shown Pt^{II}
 385 and Pt^{IV} species (see *SI Appendix, Fig. S1A* and Table S1 for solution composition and speciation).

386

387

388 **Fig. 2.** Direct evidence for platinum-trisulfur ion complexes from PtS(s) solubility measurements in aqueous
 389 thiosulfate solutions as a function of pH and S₃²⁻ ion concentration at 300°C and 500 bar. Thiosulfate
 390 irreversibly breaks down on heating by providing sulfate, sulfide and S₃²⁻ ion (*SI Appendix*). Symbols
 391 represent the measured Pt concentrations (error bars = 2 SD); solid red line shows the predicted total Pt
 392 solubility according to the speciation model of this study that includes the two indicated Pt^{II} and Pt^{IV}
 393 complexes with S₃²⁻ and HS⁻ ligands (dotted blue and purple lines); dashed green curve shows the sum of
 394 concentrations of Pt(HS)_n²⁻ⁿ complexes from the literature, where n = 2, 3 or 4 (19, 21); dashed black curves
 395 indicate the free concentration of the two ligands, HS⁻ and S₃²⁻. The break in the species curve pattern at pH
 396 ~5 reflects the onset of molten sulfur (S_{liq}) formation at more acidic pH (Table S3 for data sources and Fig.
 397 S1B for details on S aqueous speciation).

398

399

400 **Fig. 3.** Platinum dissolved concentration in equilibrium with PtS(s) in hydrothermal fluid at 300°C and
 401 500 bar and its comparison with gold as a function of (A) total dissolved S concentration at pH ~5 and f_{O2}
 402 buffered by sulfide-sulfate equilibrium with (H₂S)_{tot}:(SO₄)_{tot} molal ratio of 4:1 corresponding to the
 403 maximum of S₃²⁻ abundance; (B) oxygen fugacity corresponding to common redox buffers, QFM –
 404 quartz-fayalite-magnetite, NNO – nickel-nickel oxide, PPM – pyrite-pyrrhotite-magnetite, and HM –
 405 hematite-magnetite; (C) fluid acidity, pH = -log₁₀ a(H⁺) at f_{O2} buffered by sulfide-sulfate equilibrium
 406 (H₂S:SO₄ = 4:1); (D) in equilibrium with gold metal as a function of pH at the conditions identical to (C).
 407 In all panels, the curves denote the concentrations of S₃²⁻ (blue, in µg/g of S, same scale as for Pt and Au),
 408 sum of known Pt/Au-Cl, Pt/Au-HS, Pt-SO₄ and Au-OH species (green) and the total Pt or Au solubility
 409 (red) including Pt(HS)₂(S₃)₂²⁻ and Pt(HS)₃(H₂O)(S₃)₂⁻ or Au(HS)S₃⁻. The difference between the two
 410 latter curves (vertical pink arrow), corresponds to the contribution of [Pt-S₃⁻]- or [Au-S₃⁻]-type
 411 complexes. The thermodynamic properties of Au/Pt-Cl-HS-SO₄ species and other fluid constituents are
 412 from Table S3.

413

