

The trisulfur radical ion S 3 \bullet - controls platinum transport by hydrothermal fluids

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4	The trisulfur radical ion S_3^{-} controls platinum transport by hydrothermal fluids
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25 26 27 28 29	Author contributions: G.S.P. designed research and wrote the paper;, M.A.K., E.D., D.T., C.L., R.V. and G.S.P. performed experiments and modeling; C.L., E.F.B., A.Y.B., J-L.H., G.F. and A.M.S. contributed new reagents/analytical/computational tools; G.S.P., M.A.K., E.D. analyzed data; all authors contributed to data interpretation and manuscript preparation.
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41 Abstract (177 words):

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

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

67

69 Main Text

70 Introduction

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

Paradoxically, existing data on aqueous complexes of divalent Pt^{II}, which is a typical 91 oxidation state of platinum in nature, with most common inorganic ligands such as chloride (Cl⁻), 92 sulfate (SO₄^{2–}), and hydroxide (OH[–]) (15-17) yield far too small metal aqueous contents (<0.1 93 ng/g) in equilibrium with Pt-bearing mineral phases to account for the observed Pt mobility in most 94 fluids below the magmatic-hydrothermal transition (<600–700°C). Such fluids, produced by 95 magma degassing or metamorphism or circulating in sedimentary basins, are commonly near-96 neutral (4<pH<8), moderately saline (<20 wt% NaCl), and often sulfur-bearing (up to 1–3 wt% S) 97 containing both sulfide and sulfate. Because of the high chemical affinity of Pt for reduced sulfur 98 (18), hydrogen sulfide (HS⁻) complexes are more plausible agents to transport Pt by such fluids. 99 However, the reported data on their thermodynamic stability and the resulting solubility of Pt 100 sulfide solids are highly controversial, spanning over almost 4 orders of magnitude, from <0.1 ng/g 101 102 Pt in reduced H₂S-dominated fluids (19-21) to >1000 ng/g Pt in oxidized sulfide/sulfate-bearing fluids (22). Such discrepancies call upon complexes other than sulfide (and sulfate) and/or metal 103 oxidation states other than Pt^{II} to account for platinum solubility. 104

The current speciation models of PGE in aqueous media ignore, in particular, the trisulfur 105 radical ion, S_3^{-} , well-known in sulfur non-aqueous chemistry (23) and stable across a very wide 106 temperature (T) and pressure (P) range of magmatic-to-epithermal sulfate/sulfide-bearing fluids 107 (24-28). Moreover, this ligand was recently shown to bind to gold greatly enhancing the efficiency 108 of Au supply to hydrothermal-magmatic porphyry and metamorphic ore deposits associated with 109 subduction zone settings which commonly involve S-rich fluids (29). To quantify the effect of S_3^{-1} 110 on Pt behavior in typical hydrothermal fluids, we used in situ X-ray absorption spectroscopy 111 (XAS, including both near-edge structure or XANES, and extended fine structure or EXAFS) that 112 113 provides a direct fingerprint of metal redox, coordination and ligand identity. The spectroscopic data were combined with solubility measurements and quantum-chemistry and thermodynamic modeling of Pt speciation in aqueous sulfide/sulfate/ S_3 solutions saturated with platinum sulfide solid PtS(s) at 275–300°C and 500–700 bar (*SI Appendix*).

- 117
- 118 Results

Platinum L₃-edge XANES spectra of S_3^{-} bearing solutions show a systematic evolution as 119 a function of pH and redox (expressed in log_{10} (bars) scale relative to the conventional hematite-120 magnetite f_{02} mineral buffer, HM, Fig. 1A). Spectra of the near-neutral (pH 5.9 at 275°C) and 121 relatively reduced (HM–0.2) solution are close to that of Pt^{II}S(s) both in energy position and 122 amplitude, fully consistent with divalent Pt^{II} coordinated by 4 nearest S atoms in a square-planar 123 geometry. By contrast, for more acidic and oxidized compositions, the spectra show a systematic 124 shift to higher energies along with an increase in the white-line amplitude (Fig. 1A), indicating a 125 change to higher Pt oxidation state and coordination, which would be closer to those of $Pt^{IV}S_2(s)$ in 126 which Pt is octahedrally coordinated by 6 S atoms. This trend is confirmed by quantum-chemistry 127 simulations of XANES spectra (SI Appendix) by considering complexes with HS⁻ and S₃⁻ ligands 128 of square-planar and octahedral coordination geometry typical for Pt^{II} and Pt^{IV} compounds, 129 respectively (18). The spectrum from the HM-0.2 solution closely resembles the simulation for 130 square-planar $Pt^{II}(HS)_2(S_3)_2^{2-}$, whereas the spectrum from the HM+0.8 solution is best matched by 131 octahedral $Pt^{IV}(HS)_3(H_2O)(S_3)_2^-$ (Fig. 1B). In contrast, none of the experimental spectra resembles 132 the simulation for $Pt^{II}(HS)_4^{2-}$ (Fig. 1B) or other analogous $[Pt^{II}(HS)_n(H_2O)_{4-n}^{2-n}]$ -type species 133 commonly adopted in the literature (19-21), thus strongly supporting the predominance of new 134 $[S_3^{\bullet}]$ -type species at our conditions. 135

136 These findings are fully supported by the EXAFS data that show a systematic increase of the first-shell mean Pt-S distance (from 2.32 to 2.36 ± 0.007 Å, 2 SD), and coordination number 137 (from 4 to 5 \pm 0.5 S atoms, 2 SD), from the most reduced and least acidic (HM–0.2, pH 5.9) to the 138 most oxidized and most acidic (HM+0.8, pH 4.9) solutions, along with the presence of 2 ± 1 second-139 shell S atoms at 3.50±0.02 Å in the second Pt shell of all solutions (SI Appendix, Figs. S2-S4; 140 Table S1). Oxygen neighbors that may stem from OH groups or H₂O molecules in the Pt nearest 141 atomic shell, were found to be below the detection limit of <1 O atom (SI Appendix). The 142 amplitude of changes of the 1st shell Pt-S distances (>0.04 Å) and coordination numbers (from 4 to 143 5) with f_{O2} and pH (SI Appendix, Fig. S4) definitely implies a mixture of different species, and 144 cannot be explained by the presence of only divalent Pt^{II}-S complexes, which are commonly square 145 planar and have a very narrow range of Pt-S₄ distances (2.30–2.32 Å; e.g., refs. 18, 30). Therefore, 146 our findings are more consistent with the presence of both Pt^{II} and Pt^{IV} species in variable 147 proportions in solution. Furthermore, the detection of 2nd shell S atoms provides compelling 148 evidence for the presence of the S_3 ligand in both types of Pt complexes. 149

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

157
$$PtS(s) + H_2S(aq) + 2S_3^{-} = Pt^{II}(HS)_2(S_3)_2^{2-}$$
 [1]

158
$$PtS(s) + 2 H_2S(aq) + 2 S_3^{\bullet} + H^+ + 0.5 O_2(g) = Pt^{IV}(HS)_3(H_2O)(S_3)_2^{-}$$
 [2]

Fig. 2 shows that the presence of relatively minor concentrations of S_3^{-1} in solution (~10 mmol, versus >100 mmol of H₂S/HS⁻) leads to 4 to 5 order-of-magnitude enhancement of PtS(s) solubility compared to predictions for the commonly assumed hydrogen sulfide complexes from literature data obtained using reduced H₂S-dominated solutions (19, 21). The relative affinities of Pt^{II} to the S₃⁻⁻ and HS⁻ ligands may be evaluated using a symmetrical ligand exchange reaction between Pt^{II}(HS)₂(S₃)₂²⁻ and the Pt(HS)₄²⁻ complex of the same electric charge and coordination:

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$$Pt(HS)_4^{2-} + 2S_3^{\bullet} = Pt(HS)_2(S_3)_2^{2-} + 2HS^{-}$$
 [3]

The value of the reaction [3] equilibrium constant at 300° C and 500 bar is $10^{8.7}$ as derived by 166 combining the data of this study (Tables S3 and S5) and those for $Pt(HS)_4^{2-}$ from ref. (19). This 167 value means that the affinity of Pt^{II} for one S_3^{-1} ligand is at least ~10⁴ greater than for one HS⁻¹ 168 ligand. Such remarkable affinity to S_3^{-} may be related to a favorable combination of the electronic 169 configurations of both Pt^{II} having two empty 5d shell orbitals ([Xe] $4f^{14}5d^86s^0$) and the radical S₃⁻ 170 ion having an unpaired electron to fill these orbitals in a chemical bond, coupled with favorable 171 steric factors yielding a highly stable symmetrical complex geometry with 2 S_3^{-1} ligands in trans-172 position (Fig. 1B). Remarkably, the affinities of aurous gold (Au^I) for S_3^{-1} and HS⁻ are very similar 173 as attested by an equilibrium constant of ~1 for an analogous ligand exchange reaction: $Au(HS)_2^{-}$ + 174 $S_3^{\bullet} = Au(HS)(S_3)^{\bullet} + HS^{\bullet}$, studied across a temperature range of 200–500°C (29). Compared to Pt^{II} 175 or Pt^{IV}, Au^I has its 5d shell filled (5d¹⁰), which may render bonding with the different sulfur 176 ligands less specific. Furthermore, the 4 and 6-coordinated geometries of Pt offer more flexibility 177 and less steric strain for binding to 2 S_3^{-1} ligands, compared to Au^I whose stable coordination is 178 limited to quasi-linear geometries (L-Au-L, e.g., refs. 29, 33). These tendencies are also in good 179 agreement with the generally more chalcophile (i.e. sulfur loving) character of Pt that forms far 180 181 more stable (poly)sulfide solid phases than those formed by Au (e.g., 18, 30). The equilibrium constant values derived for reactions [1] and [2] (Table S5) allow Pt solubility predictions across
the wide compositional range of natural and technological S-bearing hydrothermal fluids (Fig. 3).

184

185 **Discussion and Applications**

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

First, the large enhancement of Pt solubility in hydrothermal ore-forming fluids in the 188 presence of S_3^{-} explains the multiple cases of PGE enrichment in a variety of hydrothermal sulfide 189 190 deposits of common metals (Cu, Mo, Zn, Au, Ag), which may become a novel economic source of platinoids in near future. Our predictions of Pt solubility (Fig. 3) show that $\mu g/g$ levels of metal 191 192 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 and chloride ligands that account for less than ng/g levels of Pt in such fluids. Consequently, 194 breakdown of S_3^{-} within rather narrow S concentration (0.1–1 wt%), pH (3–7) and f_{O2} (HM±1) 195 windows upon the evolution of a S-rich hydrothermal fluid would yield focused Pt precipitation in 196 high tenors from a fluid volume 10^3 to 10^5 times smaller than would be required to precipitate the 197 same platinum amount if the [Pt-S₃] complexes were ignored. Compared to gold, whose speciation 198 is dominated by hydrogen sulfide complexes in most hydrothermal solutions of near-neutral pH 199 below 350°C (Au(HS)₂; Fig. 3D) because of the much greater abundance of the HS⁻/H₂S ligands 200 than S_3 , platinum mobility is far more strongly enhanced in the presence of even small amounts 201 of S_3 . Therefore, this ligand may control the fractionation of PGE from Au as well as other more 202 common metals such as Cu, Zn, Pb, or Ni. These metals have a weaker chemical affinity to $S_3^{\bullet-}$ 203

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

Second, on a larger mantle-crust scale, S-bearing aqueous fluids may play a far more 206 important role in PGE behavior than believed. Even though our exploratory data set does not 207 currently allow extrapolations to higher, closer to magmatic, temperatures, the growing stability 208 of S_3^{-} as well as of its higher-temperature (>500°C) counterpart S_2^{-} (26, 28), suggests that both 209 radical ions may play a key role in PGE mobility in hydrothermal-magmatic systems. As a 210 result, the radical ions may promote PGE transfers from deep magmas or metamorphic rocks in 211 212 subduction zones to aqueous fluids and their massive transport up to shallow crust settings, thereby explaining the observed PGE enrichment in gold and base metal porphyry-epithermal 213 deposits, black-shale sedimentary environments, and serpentinites. Our findings of stable PGE 214 complexes with S_3 , if further confirmed across a wider *T-P* range, may shift the long-standing 215 paradigms on PGE deposit formation by purely magmatic processes, in the light of multiple 216 evidence of aqueous fluid presence (6-8, 11). Quantifying the role of such S-bearing fluids 217 requires more systematic data on PGE interactions with the sulfur radical ions over the 218 magmatic-hydrothermal T-P range. Our results demonstrating a strong Pt enrichment in S-219 220 bearing fluids, in which the aqueous sulfate and sulfide forms of sulfur coexist, may offer novel perspectives in the exploration of alternative PGE economic sources in hydrothermal settings 221 that host both sulfate and sulfide mineral assemblages. Furthermore, our study points to an 222 223 important role of slab-derived fluids under redox conditions of the sulfate-sulfide coexistence common in subduction zones and favoring the abundance of S_3^{-1} and S_2^{-1} (e.g., 28). Such fluids, 224 often enriched in sulfur, may be capable of selectively mobilizing Pt and, by analogy, 225 electronically similar Pd^{II} and Ir^I, from the mantle wedge. On the other hand, other, less 226

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

Third, the discovery of highly soluble S_3^{-} complexes with both Pt^{II} and Pt^{IV} may open 232 new routes for hydrothermal synthesis of PGE-based nanomaterials increasingly used in 233 catalysis, medicine, and electronics. Trisulfur ion may offer an interesting alternative to organic 234 235 thiolate ligands currently used as precursors in the synthesis of Au and Pt nanoparticles and their stabilization in solution (31, 32). Furthermore, the specific solubility pattern of PtS(s) and, 236 by analogy, of Pt metal as a function of solution pH and redox potential, passing through a 237 maximum at slightly acidic pH and an H_2S/SO_4 ratio of ~4, corresponding to the maximum of 238 S_3^{-} abundance (Fig. 3), may be explored for optimizing Pt nanoparticle preparation and 239 functionalization both through reduction/oxidation and acidification/basification. Such unique 240 solubility dependence thus offers greater flexibility and a larger redox, pH and temperature 241 window for synthesis protocols both in aqueous or organic solvents than those currently based 242 on H₂ reduction of Pt^{II} chloride or thiolate complexes unstable at elevated temperatures (e.g., 243 12-14). Our findings thus extend the choice of S-ligands and provide more potential for tuning 244 the molecular mechanisms that control the shape, atomicity, structure, and resulting reactivity of 245 246 the formed nanoparticles of noble metals.

247

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

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 (H_2S/HS^-), (hydrogen)sulfate (HSO_4^-) $/SO_4^{2-}$) and S_3^{-} ion, and provide redox and acidity (pH) buffering of the system (e.g., 29, 33). In situ X-254 ray absorption spectroscopy (XAS) measurements at Pt L_3 -edge (11.564 keV) were performed at BM30-255 FAME beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France), using a 256 hydrothermal apparatus developed at the Néel Institute. This setup enables simultaneous acquisition of 257 high-quality fluorescence spectra from dilute solutions (down to 0.1 mmol Pt) to extract ligand identity, 258 molecular structure and metal redox state and to directly determine the total dissolved Pt concentration 259 (33). Measurements were conducted at 275°C and 700 bar. The XAS experiments were complemented 260 by batch-reactor measurements of PtS(s) solubility at similar conditions (300°C, 500 bar) using 261 hydrothermal reactors allowing controlled sampling or quenching of the fluid that was processed and 262 analyzed using recent protocols developed for trace metals in S-rich solutions (20). 263

- Molecular simulations and XANES spectra modeling. Both static Density Functional Theory (DFT) 264 and First Principles Molecular Dynamics (FPMD) simulations of the geometries and interatomic 265 distances of selected [Pt-HS-S₃]-type complexes were performed following approaches developed for a 266 similar Au-HS⁻/H₂S-S₃⁻ system (29). The calculated molecular structures were compared with 267 268 experimental XAS-derived distances and coordination numbers to better constrain the stoichiometry of complexes. In addition, XANES spectra of such complexes were simulated using the FDMNES package 269 270 (SI Appendix) and compared with the experimental spectra to further constrain the Pt coordination and oxidation state in the fluid phase. 271
- Thermodynamic analysis of platinum speciation and solubility. Platinum solubility in experimental 272 solutions was modeled in terms of dominant [Pt-HS- S_3] complexes using the constraints imposed by the 273 274 spectroscopic and molecular data, and based on available robust thermodynamic properties of aqueous sulfur species including S_3^{-} (SI Appendix, Table S3). The derived stoichiometries and formation 275 constants for the two dominant Pt^{II} and Pt^{IV} complexes (reactions [1] and [2]) are consistent with the 276 277 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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376 Figure captions

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

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Fig. 2. Direct evidence for platinum-trisulfur ion complexes from PtS(s) solubility measurements in aqueous 388 thiosulfate solutions as a function of pH and S_3 ion concentration at 300°C and 500 bar. Thiosulfate 389 irreversibly breaks down on heating by providing sulfate, sulfide and S_3^{-1} ion (SI Appendix). Symbols 390 represent the measured Pt concentrations (error bars = 2 SD); solid red line shows the predicted total Pt 391 solubility according to the speciation model of this study that includes the two indicated Pt^{II} and Pt^{IV} 392 393 complexes with S_3^{-} and HS^{-} ligands (dotted blue and purple lines); dashed green curve shows the sum of concentrations of $Pt(HS)_n^{2-n}$ complexes from the literature, where n = 2, 3 or 4 (19, 21); dashed black curves 394 indicate the free concentration of the two ligands, HS^- and S_3^- . The break in the species curve pattern at pH 395 ~5 reflects the onset of molten sulfur (S_{lia}) formation at more acidic pH (Table S3 for data sources and Fig. 396 397 S1B for details on S aqueous speciation).

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Fig. 3. Platinum dissolved concentration in equilibrium with PtS(s) in hydrothermal fluid at 300°C and 400 500 bar and its comparison with gold as a function of (A) total dissolved S concentration at pH ~5 and $f_{\Omega 2}$ 401 402 buffered by sulfide-sulfate equilibrium with (H₂S)_{tot}:(SO₄)_{tot} molal ratio of 4:1 corresponding to the maximum of S_3^{-} abundance; (B) oxygen fugacity corresponding to common redox buffers, QFM – 403 quartz-fayalite-magnetite, NNO - nickel-nickel oxide, PPM - pyrite-pyrrhotite-magnetite, and HM -404 hematite-magnetite; (C) fluid acidity, pH = $-\log_{10} a(H^+)$ at f_{02} buffered by sulfide-sulfate equilibrium 405 406 $(H_2S:SO_4 = 4:1);$ (D) in equilibrium with gold metal as a function of pH at the conditions identical to (C). In all panels, the curves denote the concentrations of S_3^- (blue, in $\mu g/g$ of S, same scale as for Pt and Au), 407 sum of known Pt/Au-Cl, Pt/Au-HS, Pt-SO₄ and Au-OH species (green) and the total Pt or Au solubility 408 (red) including $Pt(HS)_2(S_3)_2^{2-}$ and $Pt(HS)_3(H_2O)(S_3)_2^{-}$ or $Au(HS)S_3^{-}$. The difference between the two 409 latter curves (vertical pink arrow), corresponds to the contribution of $[Pt-S_3]$ - or $[Au-S_3]$ -type 410 complexes. The thermodynamic properties of Au/Pt-Cl-HS-SO₄ species and other fluid constituents are 411 412 from Table S3.







