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1 *Revised manuscript, version 2*

2 Challenging the traceability of natural gold by combining  
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4

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6

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10

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## 12 **Abstract**

13 Considering the high economic importance and worldwide distribution of gold, the ability to identify its  
14 provenance is critical and challenging to ensuring a responsible supply chain from deposit to consumer,  
15 especially within conflict-affected areas. Here we present an innovative approach to trace the provenance of  
16 natural gold from French Guiana through a combination of geochemical and statistical methods. This approach is  
17 divided in three steps and allows the identification of illicit gold, the certification of the declared gold origin  
18 coming from legal operators and, in some cases, the identification of unknown gold. French Guiana was chosen  
19 as a demonstration case of our approach because it is a well-known conflict-affected area where illegal mining is  
20 widespread. In the first step, we showed that the use of illegal Hg amalgamation can be easily revealed by  
21 looking the gold grain morphology with an optical microscope or by detecting the Hg with laser-induced  
22 breakdown spectroscopy that allow direct detection on the field. In the second and principal step, we  
23 demonstrated that a declared provenance of gold can be certify with a high degree of confidence by measuring  
24 the Ag content of a gold grain population and by checking it against a database with the Kolmogorov-Smirnov  
25 statistic. In the final step that allows the identification of the origin of unknown gold, we used (i) the content of  
26 minor elements (Cu and Hg), (ii) the identification of mineral inclusions and their relative proportions within  
27 samples and (iii) the trace element composition of natural gold grains determined by LA-ICP-MS and coupled  
28 with a permutational multivariate analysis of variance and a similarity percentage analysis. This method allows  
29 the identification of the provenance of 69% of the gold samples; the provenance of other gold populations (31%)  
30 cannot be identified because of their geological similarity with other groups. The traceability of natural gold can  
31 be guaranteeing with our innovative approach, in particular by certifying declared gold population provenance.  
32 Further challenges to be addressed will be the implementation of such approach in others conflict-affected  
33 regions to support the global supply chain of gold.

34

35

## 36 **Keywords**

37 Gold, Geochemistry, Traceability, Statistical test, French Guiana

38

39

## 40 **1. Introduction**

41 As one of the oldest and most important precious metals worldwide, gold holds high economic importance  
42 globally. It has long been traded within both legal and illegal supply chains, which are often closely intertwined  
43 because gold is an easy metal to recover. Even though many major mining companies have turned to large  
44 primary deposits, a significant amount of gold is still produced by artisanal and small-scale operations on  
45 secondary eluvial and alluvial deposits. The latter, when illicit, are responsible for the majority of the extensive  
46 and detrimental deforestation, as well as most of the mercury (Hg) pollution in soils and water (Goix et al.,  
47 2019), human trafficking, and ecosystem destruction (Carisch, 2012). Coupled with the funding of organized  
48 crime and terrorism, illegal gold mining is a global problem (Darlington, 2018).

49 Due to pressure from civil society, major importing countries have imposed certified supply chain  
50 restrictions that follow the principles of due diligence. The American law known as the “Dodd-Frank Act”  
51 includes a condition that requires companies using gold, tin, tungsten and tantalum to make efforts to determine  
52 if those materials came from Democratic Republic of Congo (DRC) or an adjoining country. If so, it requires a  
53 due diligence review of their supply chain to determine whether their mineral purchases are being used to fund  
54 armed groups in DRC (United States Congress, 2010). Following the American example, the European  
55 Parliament and Council adopted EU Regulation 2017/821, which sets forth supply chain due diligence  
56 obligations for Union importers of tin, tantalum, tungsten and gold originating from conflict-affected and high-  
57 risk areas (European Parliament and Council, 2017). This regulation, effective January 1, 2021, implements the  
58 principles of the OECD Due Diligence Guidance at the community level to achieve responsible supply chains for  
59 minerals (OECD, 2016). It obliges the mineral- and metal-importing industry to set up a chain of custody or a  
60 traceability system for their supply chains.

61 Currently, there are two principal ways to ensure traceability of minerals within the due diligence  
62 process: (i) checking the chain-of-custody systems, based on the shipping documentation (“bagging and tagging”  
63 information) that is included in online databases to allow real-time mineral tracking and electronic tagging; and  
64 (ii) analytical fingerprints, based on intrinsic signatures of raw or treated minerals. These two methods are  
65 independent yet complementary. The former is inexpensive and easy to implement on a large scale but does  
66 require additional information to be attached to shipments, which are susceptible to fraud. To date, the second  
67 method appears too onerous for systematic use, but it does reinforce the first by providing some control.

68 The German Federal Institute for Geosciences and Natural Resources (BGR) has developed an analytical  
69 fingerprint of coltan ore using a multi-method approach, which was used to verify and audit the traceability  
70 system based on documentation established in DRC (Melcher et al., 2008). The traceability of heterogenite from  
71 the DRC was investigated through the Trace project (“TRACeability of hEterogenite”; Decrée et al., 2015).  
72 Similarly, several studies have been conducted to investigate compositional profiles of gold. Quantitative  
73 analysis of gold by trace element determination has been performed since the 1960s (Stumpfl and Clark, 1965;  
74 Desborough, 1970). Most of the studies used EPMA results for petrological information about gold formation, as  
75 a tool for gold exploration (Desborough et al., 1971; Guisti and Smith, 1984; Chapman et al., 2000b) or for  
76 provenancing archeological gold artifacts (Chapman et al., 2006). These studies mainly focus on Ag content  
77 because it is the only element systematically present in any gold alloy and it is homogeneous within intra-particle  
78 (i.e. in the grain core). Trace element profiling of gold, which is the most common technique, has been used to  
79 help distinguish legal from illegal gold (Roberts et al., 2016) and to identify the source of the latter (Watling et  
80 al., 1994, 2014; Dixon and Merkle, 2019). The technique consists of quantifying the trace-level components  
81 within gold matrices by laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) and is  
82 mainly based on the assertion that gold will inherit a unique trace element signature related to specific geological  
83 (e.g. hydrothermal or metamorphic event) and extractive processes (Roberts et al., 2016). It is important to note  
84 that composition of gold is generally heterogeneous at sub- $\mu\text{m}$  level (Chapman et al. 2021), which makes the use  
85 of multivariate data more challenging. The previous traceability studies only focus on the identification of  
86 processed and/or refined non-natural gold (i.e. bullion, jewelry, commercial alloys and melted seized gold bars).

87 In their pioneering study funded by the World Wildlife Fund for Nature (WWF), Augé et al. (2015)  
88 used for the first time a combination of minor elements compositions in gold matrices and the nature of micro-  
89 inclusions in gold crystals to determine the origin of four gold samples from French Guiana. Recently, Pochon et  
90 al. (2020) used the Ag distribution in a population of gold grains to identify the origin of natural gold samples  
91 from French Guiana and it assessed the reliability of a field tool (i.e. handheld laser-induced breakdown  
92 spectroscopy, LIBS) as an alternative of the classical laboratory tool (i.e. electron microprobe, EPMA). The two  
93 previous studies in French Guiana have demonstrated their ability to partially trace the provenance of some  
94 limited number of gold occurrences and to distinguish legal from illegal natural gold. Indeed, Hg is used in  
95 small-scale mining to rapidly extract gold from ore as a stable amalgam in the gold recovery process. The  
96 recovered gold contains several wt% Hg (Augé et al., 2015; Legg et al., 2015; Goix et al., 2019). Using Hg

97 content to distinguish illegal versus legal gold has been effective in French Guiana since the use of mercury was  
98 banished in France on January 1, 2006 by prefectoral order. Although nowadays amalgamation is not considered  
99 illegal in all countries, the ratification of the Minamata Convention on Mercury (*i.e.* guidelines to avoid the use  
100 of Hg) by 126 countries as of December 16, 2020, should tend to eliminate the use of Hg for recovering gold.  
101 The ever-increasing number of extraction sites and commercial exchanges requires a more robust and efficient  
102 approach.

103 Thus, we propose an innovative approach to ensure the traceability of natural gold that combine  
104 mineralogical (optical and scanning electron microscopy), geochemical (EPMA, LIBS and LA-ICP-MS) and  
105 statistical (Kolmogorov-Smirnov statistic, permutational multivariate analysis of variance and a similarity  
106 percentage analysis) methods. Although similar in many ways, the remit of our approach is distinct to those used  
107 for gold compositional studies that investigate responsible ore forming processes for improving gold exploration  
108 or the understanding of gold metallogeny, and that requires a strong geological knowledge for tracing the  
109 hydrothermal history. Here, we provide practical and workable tools for verifying the provenance of natural gold  
110 in order to speed up the decision-making. They could play an essential role in the due diligence certification  
111 systems and demonstrate responsible sourcing, especially within conflict-affected areas where illegal gold  
112 mining is common. In order to performed and assess our proposed approach, the French Guiana was chosen as a  
113 perfect demonstration case because it is well-known conflict-affected area due to widespread illegal gold mining  
114 leading to mercury pollution and deforestation of Amazon rainforest.

115

## 116 **2. The nature of French Guiana gold**

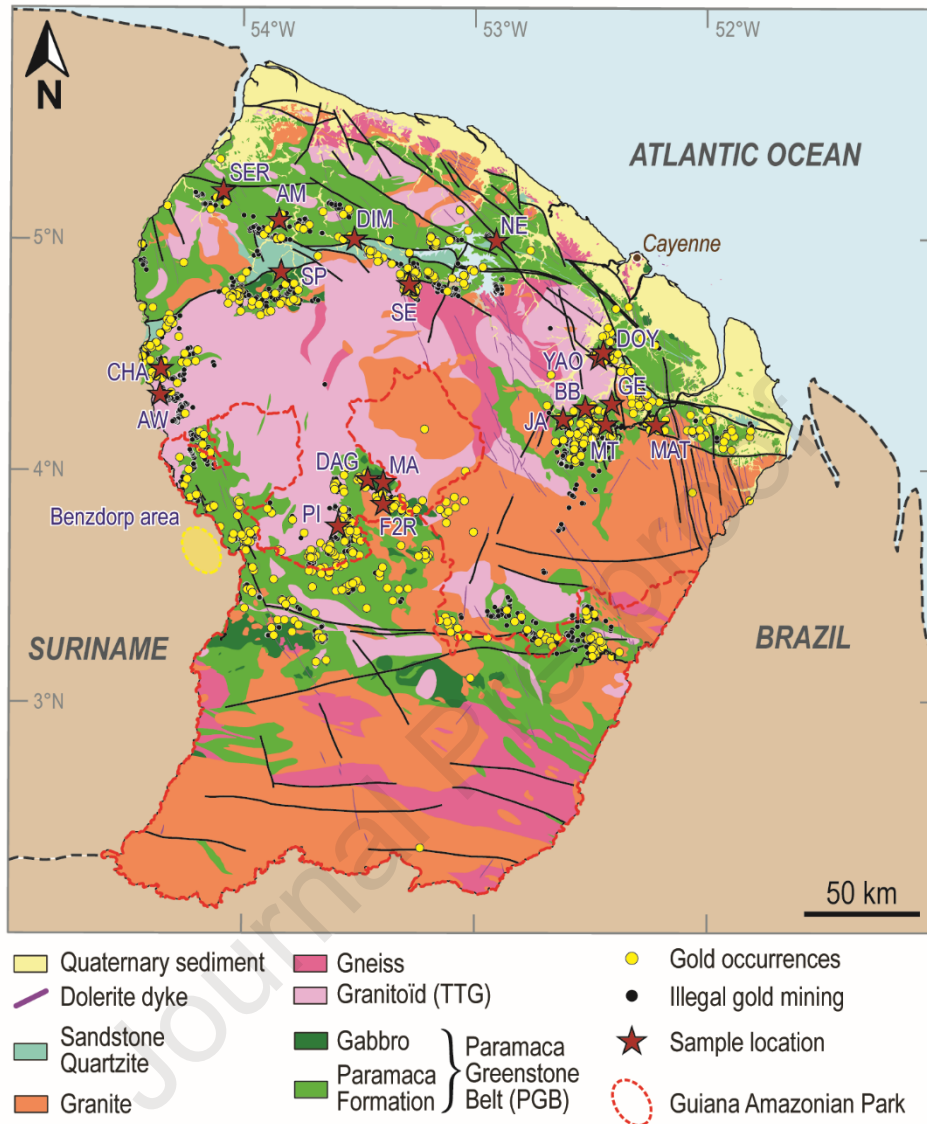
117 The French Guiana is part of the large Guiana Shield of about 900,000 km<sup>2</sup>, covering the northern part of Brazil,  
118 the eastern part of Columbia, the eastern part of Venezuela and the Guyana, the Surinam and the French Guiana.  
119 In spite of the existence of important mineral resources (gold, petroleum, niobium, tantalum, bauxite, kaolinite),  
120 only few easily accessible publications have been produced on the geology and economic potential of the French  
121 Guiana, most of the existing data being part of the Bureau de Recherches Géologiques et Minière (BRGM)  
122 internal reports (*e.g.* Milési et al., 1995; Vanderhaeghe et al., 1998; Delor et al., 2003). Gold deposits are mainly  
123 located in the mid-north part of the French Guiana (Fig. 1). They are mainly hosted by the Paleoproterozoic  
124 Paramaca Greenstone Belt that is interpreted as the remnant of a volcanic arc sequence formed during the  
125 Transamazonian orogeny. It forms two regional-scale synform structures located to the north and south of the

126 Mesorhyacian Central TTG (Tonalite Trondhjemite Granodiorite) complex (Delor et al., 2003; Enjolvy, 2008).  
127 Four types of primary gold deposits have been identified (Marcoux and Milési, 1993; Milesi et al., 1995, 2003;  
128 Franklin et al., 2000; Guiraud et al., 2020): (i) gold-rich volcanogenic massive sulphide (VMS, *e.g.* Montagne  
129 d'Or); (ii) stratiform/stratabound gold deposits hosted by volcano-sedimentary rocks, where gold is associated  
130 with disseminated sulphides (*e.g.* Dorlin); (iii) gold-bearing polygenic conglomerates with disseminated gold  
131 (*e.g.* Montagne Tortue); and (iv) orogenic gold deposits which consist of quartz-carbonate-sulphides veins and  
132 stockworks (*e.g.* Yaou, Esperance, Camp Caïman), essentially hosted by volcano-sedimentary rocks and  
133 granitoids. The primary gold deposits discussed in this study (Dagobert, Repentir, Mataroni, Saint Elie and  
134 Doyle) belong to the orogenic type. It is important to note that the VMS deposits remain rare and that gold-  
135 bearing conglomerates and stratabound gold deposits are mostly overprinted by late orogenic gold event  
136 (Marcoux and Milési, 1993; Milési et al., 2003), making the orogenic gold the most frequent in French Guiana.  
137 Most gold deposits are hosted in Paleoproterozoic greenstone belts (Cassard et al., 2008), and consequently share  
138 several affinities such as fluid composition, the nature of the host rocks and the source of the metals (Goldfarb  
139 and Groves, 2015). Nevertheless, most of the gold production of the French Guiana is coming from placers of  
140 Pliocene to Quaternary age explaining that this type of deposit is the most illegally extracted and consequently  
141 represent the major part of samples in this study. In most cases, placer gold deposits are thus mainly composed  
142 of gold grains coming from primary orogenic gold deposits and may have one or several contributing sources.

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**Fig. 1** Simplified geological map of French Guiana showing the main lithostructural framework and location of gold

149

populations, including those from Suriname (Benzdorp area). Red stars correspond to the sample location used in this study.

150

Gold populations: AM, Amadis; AW, Awa ; BB, Bois Bandé; DIM, Dimanche; GE, Grillon Est; JA, Jalbot; NE, Nelson; PI,

151

Petit Inini; SP, Saint Pierre; SER, Serpent; CHA, Chantal; YAO, Yaoni; MAT, Mataroni; F2R, F2 Repentir; DAG, Dagobert;

152

SE, Saint-Elie; SE(SA), Saint-Elie (Saint-Auguste); DOY, Doyle; MT, Montagne Tortue; MA, Marc.

153

### 154 3. Sampling and methods

#### 155 3.1 Sample descriptions

156 The natural gold used for this study consists of 69 samples from 21 gold populations and comes from the French  
 157 Guiana and in a lesser extent from Suriname (Fig. 1). The view was taken to remain anonymous the samples  
 158 origin to avoid the disclosure of their geochemical signatures (Table 1). Only 6 populations (*i.e.* 13 samples) are  
 159 from primary deposits, the remainder being alluvial in origin (*i.e.* 15 populations and 56 samples). This limited  
 160 number of primary gold samples is not a sampling bias, but rather it reflects the fact that the majority of gold  
 161 extracted in French Guiana is alluvial. Among alluvial gold populations, one population (*i.e.* 5 samples) comes  
 162 from the Benzdorp area in the neighboring country of Suriname, known to be extracted by Hg amalgamation,  
 163 and were used as a reference for illegal gold (Kio-A-Sen et al., 2016). Sixteen samples previously studied by  
 164 Augé et al. (2015) as part of a project funded by the WWF to test the feasibility of the analytical traceability of  
 165 gold from French Guiana were re-analyzed in this study. Each sample consists of about 20-40 individual gold  
 166 grains between 0.05 and 3 mm across, embedded in epoxy resin blocks and polished to expose the core of the  
 167 gold grains. Overall, some 2200 gold grains were used for this study.  
 168

**Table 1. Description of the samples from French Guiana gold populations.** Number of studied gold grains within brackets

Gold population group	Region	Type of gold	Sample name
A	French Guiana	Primary	A1 (41), A2 (58)
B	French Guiana	Primary	B1 (56)
C	French Guiana	Primary	C1 (62), C2 (44), C3 (52)
D	French Guiana	Alluvial	D1 (42), D2 (16), D3 (18)
E	French Guiana	Alluvial	E1 (47), E2 (28)
F	French Guiana	Alluvial	F1 (34)
G	French Guiana	Alluvial	G1 (26), G2 (21), G3 (36)
H	French Guiana	Alluvial	H1 (31), H2 (28)
I	French Guiana	Alluvial	I1 (29), I2 (25), I3 (25), I4 (26)
J	French Guiana	Alluvial	J1 (35), J2 (15)
K	French Guiana	Alluvial	K1 (26) <sup>1</sup> , K2 (27) <sup>1</sup> , K3 (34)
L	French Guiana	Primary	L1 (15), L2 (34)
M	French Guiana	Alluvial	M1 (23), M2 (34), M3 (30), M4 (28), M5 (30), M6 (31)
N	French Guiana	Alluvial	N1 (22), N2 (31), N3 (30), N4 (29), N5 (29), N6 (29), N7 (33), N8 (40)
O	French Guiana	Alluvial	O1 (31), O2 (35)
P	French Guiana	Alluvial	P1 (31), P2 (40), P3 (28), P4 (31), P5 (35)
Q	French Guiana	Alluvial	Q1 (29), Q2 (32), Q3 (31)
R	French Guiana	Alluvial	R1 (39), R2 (30), R3 (35), R4 (31)
T	French Guiana	Primary	T1 (20), T2 (22), T3 (9), T4 (30)

U	French Guiana	Alluvial	U1 (25), U2 (20), U3 (46), U4 (14) <sup>2</sup>
Surinam	Benzdorp (Surinam)	Amalgam	S1 (42), S2 (16), S3 (18), S4 (31), S5 (34)

<sup>1</sup> samples declared as alluvial gold whereas it is amalgam gold and <sup>2</sup> primary gold sample from U group

169

170

### 171 3.2 Mineral chemistry using quantitative electron microprobe analysis

172 Quantitative analyses were carried out on gold grains using a Cameca SX-Five electron probe micro-analyzer  
 173 (EPMA) at the ISTO-BRGM laboratory (Orléans, France) (Appendix A.1). The major and minor elements  
 174 analyzed were Au, Ag, Cu, Pd and Hg. Pure cinnabar standards were used for Hg, whereas pure metals were  
 175 used for the other elements. Each analysis was performed on the core of a gold grain which better reflect the  
 176 primary signature of the grain, the composition of the rims of alluvial gold particles being modified by  
 177 subsurface conditions (Groen et al., 1990). Run conditions were an accelerating voltage of 20 kV, a beam current  
 178 of 40 nA, and counting times of 30 s on-peak and 15 s background.

179

### 180 3.3 Mercury measurements using a handheld LIBS analyzer

181 The needs of fast and real-time measurements on the field led us to use a direct method for the Hg detection.  
 182 Mercury analyses were carried out using a commercial SciAps © Z-200 C+ handheld laser-induced breakdown  
 183 spectroscopy (LIBS) analyzer. Its portability and broad spectral range (*i.e.* 190-625 nm) make it a suitable tool  
 184 for real-time measurements in the field or a field laboratory (Connors et al., 2016; Harmon et al., 2017).  
 185 Spectrometers are calibrated daily by ablating a piece of stainless steel inside the LIBS system in order to correct  
 186 spectral shifts. Each analysis was performed under constant argon flow with a pressure of 10 psi. All the raw  
 187 LIBS data were divided by the signal intensity of the Au emission line at 479.24 nm, which represents the  
 188 matrix-dominant element and consequently the maximum signal intensity. To assess the performance of the  
 189 instrument, about 500 LIBS analyses were performed on gold grains. They come from 5 French Guiana gold  
 190 populations legally extracted by small-scale artisanal miners and 3 Suriname populations extracted by Hg  
 191 amalgamation. Each single-shot consists of 8 cleaning (laser) pulses to ensure tape breakthrough, followed by  
 192 the collection of 32 averaged spectra at the same location to minimize the affected surface area on the gold  
 193 grains (due to their small size) and to avoid striking mineral inclusions.

194

### 195 **3.4 Identification of mineral micro-inclusions**

196 A reflected light optical microscope and a scanning electron microscope (SEM) were used to locate and identify  
197 the nature of mineral inclusions within the gold alloy. The use of an SEM-EDS (energy dispersive X-ray  
198 spectrometer coupled with an SEM) is strongly recommended considering the small size of the micro-inclusions  
199 in the gold grains. More than half (58%) of the micro-inclusions are less than 10  $\mu\text{m}$ . In addition, the intense  
200 optical reflectance of gold affects the classical reflectance of the inclusions. The SEM observations were carried  
201 out on a tabletop Hirox SH-3000 SEM with a 20 kV voltage and coupled to a Bruker-AXS EDS system.

202

### 203 **3.5 Quantitative analysis of trace elements using LA-ICP-MS**

204 Trace element concentrations were determined in situ using the laser ablation inductively coupled plasma mass  
205 spectrometer (LA-ICP-MS) at the BRGM laboratory (Orléans, France). The following isotopes were monitored:  
206  $^{33}\text{S}$ ,  $^{48}\text{Ti}$ ,  $^{52}\text{Cr}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{58}\text{Ni}$ ,  $^{59}\text{Co}$ ,  $^{63}\text{Cu}$ ,  $^{64}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{76}\text{Se}$ ,  $^{78}\text{Se}$ ,  $^{82}\text{Se}$ ,  $^{103}\text{Rh}$ ,  $^{105}\text{Pd}$ ,  $^{106}\text{Pd}$ ,  $^{107}\text{Ag}$ ,  $^{109}\text{Ag}$ ,  $^{112}\text{Cd}$ ,  
207  $^{114}\text{Cd}$ ,  $^{118}\text{Sn}$ ,  $^{120}\text{Sn}$ ,  $^{121}\text{Sb}$ ,  $^{123}\text{Sb}$ ,  $^{130}\text{Te}$ ,  $^{195}\text{Pt}$ ,  $^{197}\text{Au}$ ,  $^{202}\text{Hg}$ ,  $^{208}\text{Pb}$ ,  $^{209}\text{Bi}$ . Sulfur ( $^{33}\text{S}$ ) was monitored to avoid signal  
208 interference of sulphide inclusions, whereas  $^{57}\text{Fe}$  and  $^{48}\text{Ti}$  were used to avoid signal interference from Fe-Ti  
209 oxide inclusions. Gold ( $^{197}\text{Au}$ ) was monitored to verify that the ablated matrices comprised only gold.

210 The BRGM's LA-ICP-MS system consists of a CETAC Excite excimer laser (193 nm) coupled to a  
211 ThermoScientific XSERIES 2 quadrupole inductively coupled plasma mass spectrometer (ICP-MS). The laser is  
212 equipped with a HelEx® 2 volume ablation cell, which optimizes the material transport to the ICP-MS. The  
213 ablated material is carried by He, which is then mixed with N<sub>2</sub> and Ar, before injection into the plasma source.  
214 The instrument was aligned, and mass calibration performed before each analytical session on the NIST SRM  
215 612 reference glass. A beam diameter of 85  $\mu\text{m}$  was used to enhance the signal and reach very low detection  
216 limits for analyzed trace elements. Ablation areas were carefully selected because a wide beam diameter  
217 increases the chances of ablating solid micro-inclusions or ablating part of the modified rim in small gold grains.  
218 A single analysis consists of 20 s of gas blank followed by 40 s of ablation. A repetition rate of 8 Hz and a laser  
219 beam energy of 3.06 J/cm<sup>2</sup> were used during analyses.

220 Quantification of gold was carried out using  $^{107}\text{Ag}$  as the internal standard. The Ag content were determined by  
221 EPMA. For each analytical session, we used the following bracketing procedure: one analysis of the RAuP7 and  
222 RAuP3 gold reference materials from MBH for every 10 gold grain analyses, and one analysis of NA-Au-31 and  
223 NA-Au-30 (Kovacs et al., 2009; Milidragovic et al., 2016) for every 20 analyses. This sequence was repeated up

224 to the end of the session. Ni, As, Cd, Sn and Te were calibrated using reference material NA-Au-31. The  
225 remaining elements were calibrated using RAuP7. Reference materials NA-Au-30 and RAuP3 were used to  
226 monitor the quality of analyses. They were treated as unknowns to control the reproducibility and accuracy of  
227 analyses. Data reduction was carried out using Iolite software (Paton et al., 2011). Analyses of RAuP3 show high  
228 accuracy and very good precision, with a mean relative difference (RD) of ~4% and a relative standard deviation  
229 (RSD) of ~8% for all considered elements (Appendix A.2). Isotopes  $^{121}\text{Sb}$  and  $^{208}\text{Pb}$  were slightly overestimated  
230 by 12-14% and were also slightly heterogeneous, with an RSD of 14-16%. Note that  $^{209}\text{Bi}$  has the largest RSD of  
231 18%. The NA-Au-30 analyses show good accuracy and very good precision, with a mean RD of ~12% and a  
232 mean RSD of ~8%.  $^{114}\text{Cd}$  and  $^{118}\text{Sn}$  are underestimated by 25% (Appendix A.2). Chapman et al. (2021) have  
233 highlighted that trace elements can be heterogeneously distributed within a gold particle at 5-10  $\mu\text{m}$  scale. But  
234 our LA-ICP-MS analytical conditions, that use a larger ablation spot (85  $\mu\text{m}$ ), yielded reproducible analyses  
235 within a same gold particle, meaning that our gold grains can be considered as homogeneous at the scale of our  
236 ablation spot.

237

### 238 3.6 Statistical tests

239 The empirical distribution functions and the Kolmogorov-Smirnov (KSD), the maximum distance between two  
240 empirical cumulative distribution functions (CDFs), was used to characterize and compare the distribution of Ag  
241 content among different samples. It was chosen for its widespread use in raw material traceability studies, such  
242 as coltan, tin, tungsten and gold (Gäbler et al., 2013, 2017, 2020; Martyna et al., 2018; Pochon et al., 2020).  
243 Indeed, the KSD is used as a measure of similarity between two samples by comparing their CDFs. Having the  
244 same distribution does not necessarily prove that two samples have the same origin, but we take sides here that  
245 samples are considered as coming from the same population when they share the same distribution, as many  
246 authors does (*e.g.* Sheskin, 2011). Therefore, a small KSD value indicates a high degree of similarity, whereas a  
247 large KSD value rather reflects a low degree of similarity. To conclude whether if a KSD value between two  
248 individual samples is the result of common origin between two samples, a decision-making criterion is needed.  
249 In this study, two approaches are used for assessing the relevance of KSD statistics, (i) the “classical” KS test  
250 (Kolmogorov, 1933; Smirnov, 1939; Massey, 1951) and (ii) the approach developed by Gäbler et al. (2017), that  
251 we renamed KS17 approach for avoiding confusing with the KS test.

252 The KS test make use the critical distance (D critical; *i.e.* the critical distance that should be exceeded to  
253 consider two CDFs as significantly different) as a decision criterion. If KSD is less than D critical and if the p-  
254 value (*i.e.* value of probability) is higher than the level of significance ( $\alpha$ ), then the “null hypothesis” (*i.e.* two  
255 samples have the same distribution) cannot be rejected, and the two samples are considered to be from the same  
256 origin. For this study,  $\alpha = 0.05$ . This commonly used value gives a confidence degree of  $1 - \alpha$  (95%). D critical is  
257 dependent on sample size and the level of significance (Smirnov 1939), indeed, a low sample size yields a higher  
258 D critical. The KS17 approach uses an empirically-deduced decision criterion based on KSD values for all  
259 possible comparisons of reference samples from a given mine site and calculated as follows:

$$260 \quad DC = X + 3\sigma \quad (1)$$

261 where DC is the decision criterion, X is the mean and  $\sigma$  is the standard deviation calculated from the KSD  
262 values. When this empirically decision criterion is applied, samples are considered to originate from the declared  
263 origin if their KSD value is smaller than the DC when compared to the single reference samples of the declared  
264 origin. This deposit-specific DC is dependent on the number of references samples from the same mine site.  
265 Therefore, this method is not suitable when only two or three reference samples are available from the same  
266 mine site due to the low number of computed KSD values. However, in the case where the studied mine site has  
267 a low number of reference samples, a standard DC can be derived by taking into account all others available  
268 mine sites with at least two reference samples. KSD values are thus calculated for all reference sample pairs  
269 from common mine sites and the DC is calculated as given in Equation (1), but, with X as the mean of all KSD  
270 values of reference sample pairs with common origin but not related to any reference sample coming from the  
271 studied mine site (Gäbler et al., 2017, 2020).

272 LA-ICP-MS datasets contain non-detected values that are below the detection limit. They are thus  
273 censored compositional data that cannot be considered as continuous data and must be transformed before any  
274 statistical analyses (Aitchison, 1982; Helsel, 2011). Before performing multivariate statistical analyses and to  
275 avoid “fabricating” data by replacing values below the detection limit with arbitrary values, we chose to rank  
276 values by a nonparametric method after censoring at the highest detection limit following the recommendations  
277 of Helsel (2011). Ranking was only applied to data of gold populations that are compared between them,  
278 meaning that the obtained rank values for data from three compared gold populations (*e.g.* groups A, B and C)  
279 will be different from the obtained rank values for data from other gold populations (*e.g.* groups D, E and F).  
280 Thus, all considered values are ranked and the attributed rank for data below the detection limit is specific for

281 each considered element and each samples comparison. Permutational multivariate analysis of variance  
 282 (PERMANOVA), a nonparametric multivariate statistical test (Anderson, 2001, 2017), was used to compare  
 283 different gold populations using their trace element compositions. Although originally used in ecological studies,  
 284 this test is now used across many fields such as chemistry, social sciences, environmental sciences, and more  
 285 recently in geochemistry (Monnier et al., 2018, 2021; Launay et al., 2021). PERMANOVA is a geometric  
 286 partitioning of multivariate data using a dissimilarity measure (*e.g.* Bray-Curtis distance). It quantifies the  
 287 dissimilarity between each sample of one group (*i.e.* gold population in our case) considering element  
 288 concentration and test the null hypothesis that the centroids and dispersion were equivalent for each sample  
 289 comparison, using a pseudo F-ratio constructed by inter-point geometric approach (scalar correlations based on  
 290 the distance measure), such as:

$$(SS_A/SS_R) \times (N - g/g - 1)$$

291 where  $SS_A$  (among-group sum-of-squares) is the sum of the squared distances from individual group centroids to  
 292 the overall centroid,  $SS_R$  (within-group sum-of-squares) is the sum of the squared distances to centroids from  
 293 individual sampling units to their own group centroid,  $N$  is the total number of observations, and  $g$  is the number  
 294 of groups. PERMANOVA assumes only the exchangeability of the dataset under a true null hypothesis. In this  
 295 study, PERMANOVA was used to relate gold samples to their provenance, when the Ag content distribution was  
 296 not sufficient to distinguish the distinct origins. The rejection of the null hypothesis (*i.e.* a p-value lower than  
 297 0.05) means that the trace element composition differs between the groups compared. The distance measure was  
 298 calculated with the Bray Curtis dissimilarity index (Bray and Curtis, 1957), which is better at taking into account  
 299 the absence or presence of an element than the classical Euclidian index, and consequently is better suited for  
 300 ordinal data. The smaller the pseudo-F ratio, the more the two compared populations share similarities. A ratio  
 301 equal or lower than 1 is traditionally taken to mean that the populations are indistinguishable, because it  
 302 indicates that among-group distances ( $SS_A$ ) are equal or lower than within-group distances ( $SS_R$ ). The  
 303 significance of the variables was tested and obtained by 9999 permutations (Anderson, 2001). Similarity  
 304 percentage analysis (SIMPER; Clarke, 1993) was performed to determine the contribution of each trace element.  
 305 Indeed, it calculates the contribution of each trace element to the dissimilarity between each two groups, using  
 306 the Bray-Curtiss dissimilarity matrix. This allows the identification of variables that are likely to be the major  
 307 contributors to any difference between groups detected by PERMANOVA. All statistical analyses were  
 308 performed using a combination of software such as XLSTAT, PAST 4.02 (Hammer et al., 2001) and R.

309

#### 310 **4. Results and Discussion**

311

312 The steps in our multi-method analytical approach to gold traceability answer three guiding questions (Fig. 2).

313 The first is “Has mercury been used to extract the gold?”. This step aims to identify gold grains illegally

314 extracted by Hg amalgamation that should not be allowed in the supply chain. The second is, “Does the gold

315 correspond to its presumed provenance?”. This step uses the statistical distribution of silver (Ag) in gold grains

316 and is considered the most discriminative way to certify gold population provenance declared by owners. The

317 third question is, “What is the origin of unknown gold?”. This last step aims to identify the origin of gold from

318 dubious sources (*i.e.* seized gold) by looking at the minor and trace element composition and the mineral

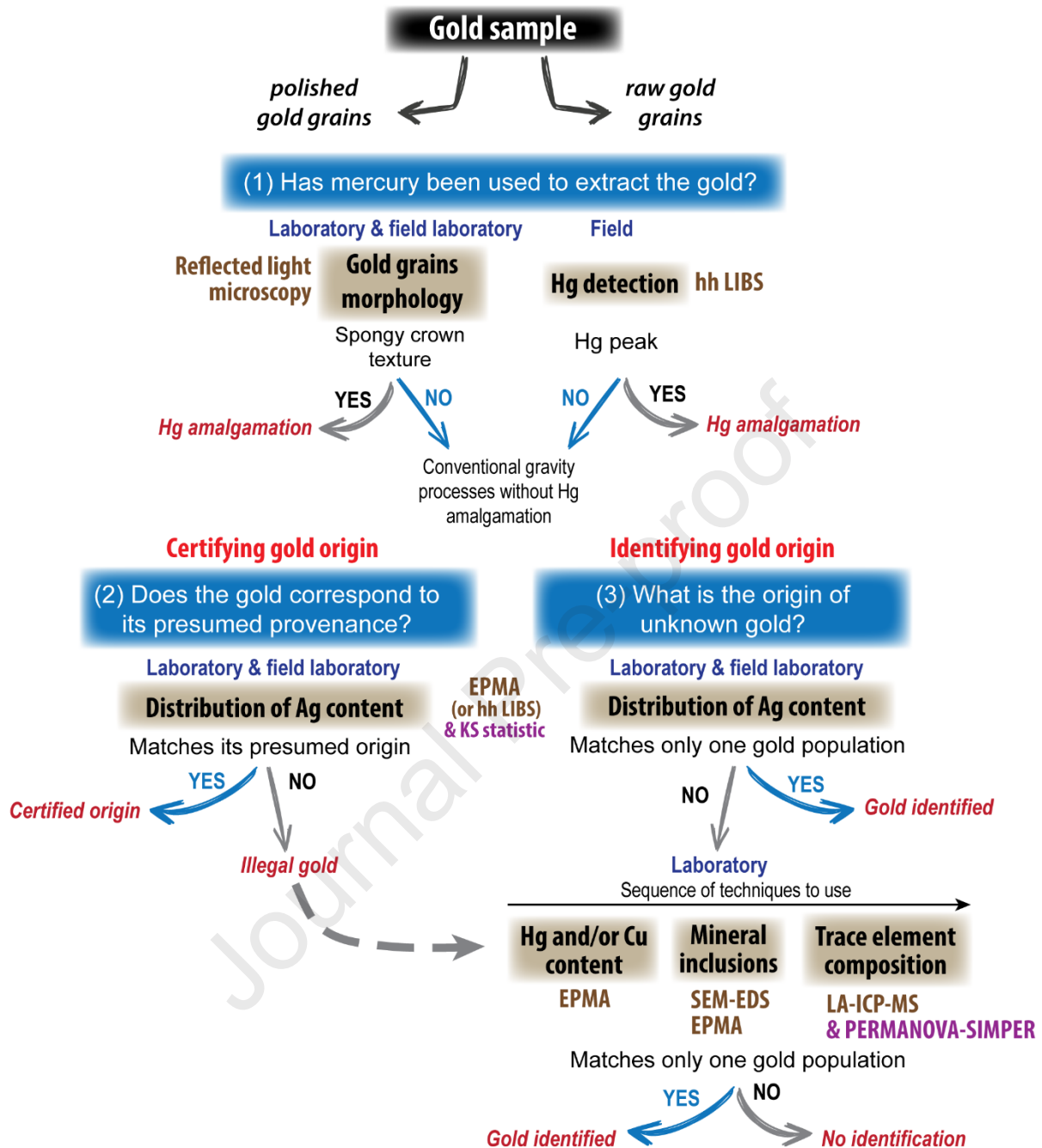
319 inclusion assemblage, in addition to the statistical distribution of Ag. This question is especially relevant in the

320 case of gold without declared origin, gold diverted from the legal supply chain or gold seized by authorities

321 when combating illegal gold mining operations.

322





323

324 **Fig. 2** Overview of the multi-method approach for the traceability of natural gold. This approach is based on the analytical  
 325 fingerprint of gold grains, and the steps answer three guiding questions as part of the due diligence process. “hh” correspond  
 326 to handheld. See text for further explanations.

327

#### 328 4.1 Reliable and efficient ways to identify extracted gold with mercury

329 Mercury is used in small-scale mining (SSM) to rapidly extract gold as a stable amalgam in the gold recovery  
 330 process. The recovered gold contains several wt% Hg (Augé et al., 2015; Legg et al., 2015; Goix et al., 2019).

331 By taking advantage of the known physicochemical properties of gold (Giusti, 1986; Grant et al., 1991; Townley  
332 et al., 2003; Youngson et al., 2002; Márquez-zavalía et al., 2004) and because the use of mercury in gold mining  
333 is prohibited in France, we propose two easy methods to quickly identify gold recovered by the Hg  
334 amalgamation process, namely simple reflected light optical microscopy in the laboratory and a handheld LIBS  
335 analyzer in the field.

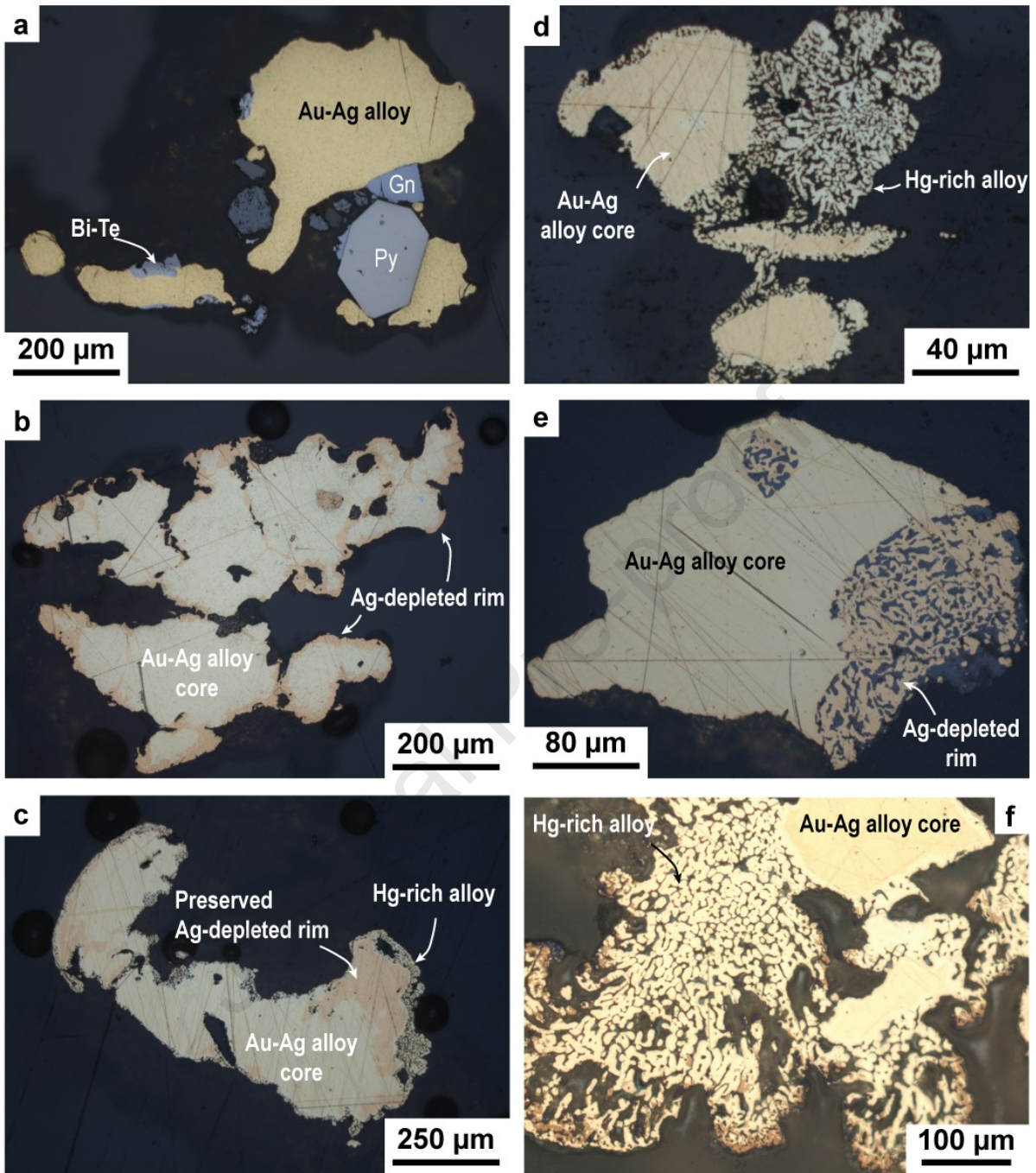
336

#### 337 **4.1.1 Gold grain morphology: a source of easy-to-use information**

338 Although the information on gold grain morphology is not considered a discriminating factor for traceability, it  
339 can be very useful, as a first check, for identifying the type of gold grains. Three main types of gold are easily  
340 recognizable in French Guiana: primary gold mined from bedrock deposits, alluvial gold mined from the  
341 erosional products of former bedrock deposits, and gold from either source recovered using mercury. Primary  
342 gold grains are characterized by an irregular outline composed of angular edges, embayments and primary  
343 crystal imprints (Fig. 3a). In contrast, alluvial gold grains exhibit a rounded habit and more yellowish rims  
344 related to natural Ag-depletion under depositional and transport conditions (Fig. 3b). Primary and alluvial gold  
345 grain populations thus constitute two different types of gold that must be compared separately. Among the  
346 samples of polished gold grains studied by optical microscopy, gold amalgams have the most noticeable  
347 morphological characteristics compared to classic primary and alluvial gold. They invariably exhibit a light  
348 yellowish and highly porous alloy induced by the evaporation of mercury, typical of the so-called spongy crown  
349 texture (Fig. 3c and d). This texture has been observed in almost all the gold grains recovered by Hg  
350 amalgamation from the neighboring Suriname artisanal mines (Augé et al. 2015), highlighting this feature as a  
351 major indicator of illegally extracted gold in French Guiana. Some natural alluvial gold grains may exhibit a  
352 similar texture acquired during natural processes (Fig. 3e), but they can be easily distinguished by studying  
353 samples of polished gold grains under an optical microscope. Gold amalgams have a rim with a light-yellow  
354 color whereas natural grains have a rim of pure gold with a dark yellow color. Furthermore, the spongy crown  
355 texture of gold amalgams is the result of porosity (*i.e.* empty holes that were created by the vaporization of Hg  
356 (Fig. 3f)), whereas such a texture in natural grains results from overgrowth with other minerals that have since  
357 partially eroded away (*e.g.* Fe-oxides; Fig. 3e). Although the presence of spongy crown texture may also be of  
358 natural origin due to cinnabar reduction (Youngson et al., 2002), this natural process remain scarce. When a  
359 sample only consist of gold with such spongy crown textures, it is more likely that the presence of Hg was

360 anthropogenic. In our dataset, two samples (samples K1 and K2) from the group K containing only amalgams  
361 were excluded from the traceability process. Among the other samples, only 12 grains (< 1% of the dataset) with  
362 amalgam morphologies were identified. The very low proportion of gold amalgams in the studied samples  
363 suggests they were mined without use of mercury amalgamation, and the mercury is likely either natural in  
364 origin or the result of inheritance due to nearly 150 years of Hg amalgamation use before its banishment in 2006.

Journal Pre-proof



365

366

367 **Fig. 3** Reflected light optical microscope images of different types of gold grains from French Guiana and Suriname. (a)

368 Primary gold grain with irregular outline composed of angular edges, embayments and classic primary mineral inclusions of

369 galena (Gn), pyrite (Py) and bismuth telluride (BiTe). (b) Alluvial gold grain with typical Ag-depleted rim around Au-Ag

370 core. The rim is secondary, probably the result of self-electrorefining or dissolution-precipitation processes (Groen et al.

371 1990). (c and d) Hg-amalgamated gold grains displaying classical spongy crown texture. The Hg-rich alloy coats the

372 preserved Ag-depleted rim. (e) Alluvial gold grain with Ag-depleted rim composed of pure gold and Fe-hydroxides showing

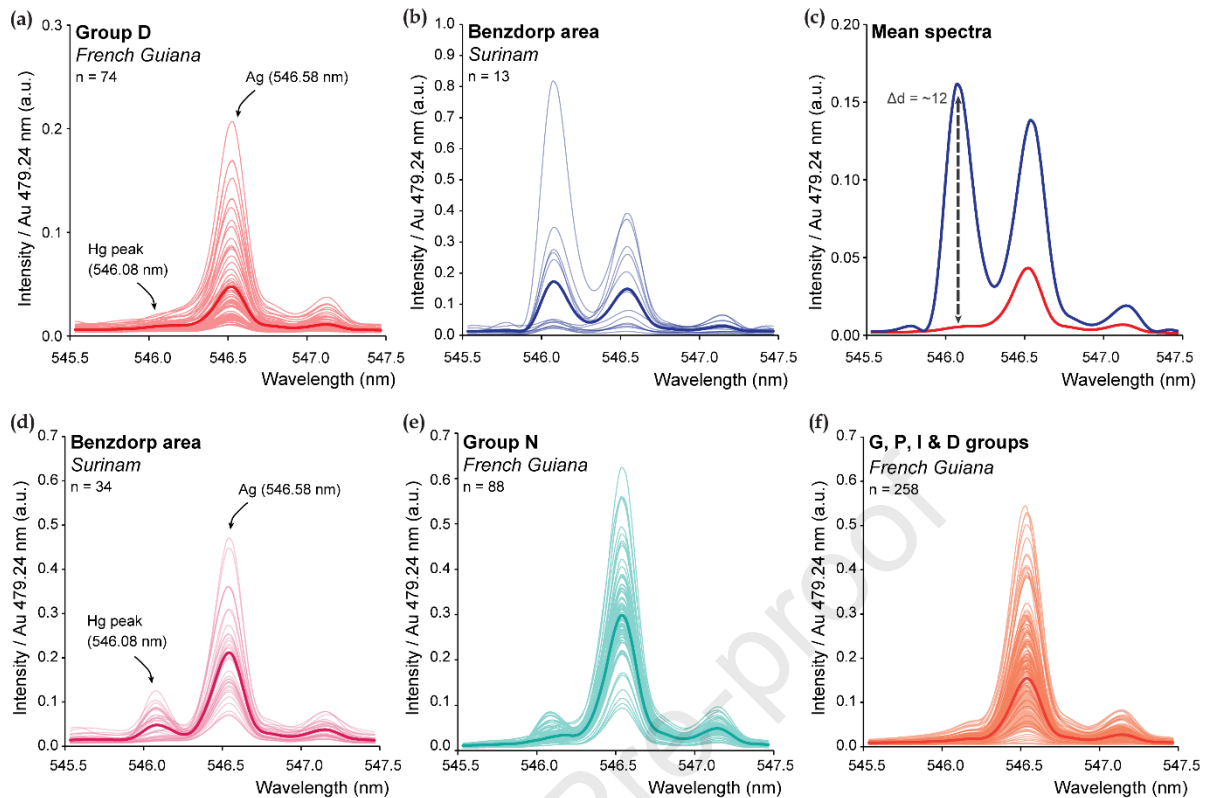
373 a “brain-like” texture, commonly thought to be the product of a natural electrolytic mechanism that purifies the gold. (f) Hg-  
374 amalgamated gold grains displaying classic spongy crown texture (Benzdorp area, Suriname)

375

#### 376 4.1.2 A novel spectroscopic method to detect mercury

377 To track illegally mined gold grains in the field, a fast and easy method is needed to measure the presence of Hg  
378 at the surface of raw gold grains (*i.e.* no sample preparation), compared to optical microscopy characterization  
379 which requires polishing. The use of a novel technique such as the handheld LIBS is promising because the  
380 focused laser beam (50  $\mu\text{m}$ ) is narrow enough to take measurements on small gold grains. For this study, the  
381 emission line at 546.08 nm was selected for Hg (among other possibilities) because it is the most intense. As  
382 expected, LIBS analyses of raw gold grains from the group D did not detect Hg at the surface of the gold grains  
383 (Fig. 4a). This gold population comes from a legal mining operator who extracted the gold by conventional  
384 gravity techniques. On the other hand, LIBS analyses on samples from a Suriname (*i.e.* extracted with Hg  
385 amalgamation) show a strong peak at 546.08 nm (Fig. 4b), indicating the presence of Hg at the surface of the raw  
386 gold grains. When the mean spectra of each population are plotted together (Fig. 4c), the relative difference in  
387 the amplitudes of the peak intensities is large enough to confidently distinguish populations of gold grains  
388 extracted with mercury from those extracted without. Even when the cores of polished gold grains were analyzed  
389 (Fig. 4d), the peak at 546.08 nm was still significantly higher, meaning that Hg used during the amalgamation  
390 process can even be detected in the grain core. It is also important to note that the presence of Hg is not  
391 uncommon within natural gold (Von Gehlen, 1986; MacKenzie and Craw, 2005; Chapman and Mortensen,  
392 2016; Chapman et al., 2000a, 2010a, 2010b, 2017), in the orogenic gold as well as in the alluvial gold. However,  
393 Hg is relatively homogeneously distributed in the core (Von Gehlen, 1986; MacKenzie and Craw, 2005),  
394 compared to amalgam where Hg is mainly localized in the rim and heterogeneously distributed. Indeed, even  
395 though Hg can be detected in some grains from the group N (Fig. 4e), a naturally Hg-rich gold population  
396 (Appendix A.1), the mean intensity of the spectral line of interest (546.08 nm) is half that of the Suriname  
397 samples. Finally, the 258 analyses from the other gold populations of French Guiana, extracted without Hg, do  
398 not display a peak at 546.08 nm (Fig. 4f), making the LIBS technique both dependable and useful for this  
399 application.





400

401

402 **Fig. 4** Laser induced-breakdown spectra of raw (a-c) and polished (d-f) gold grains with a focus on Hg and Ag emission lines  
 403 (i.e. between 545.5 and 547.5 nm). (a and b) LIBS spectra for natural raw gold from the group D (French Guiana) and  
 404 amalgamated gold from Benzdorp (Suriname). (c) The mean spectra of the two gold populations are displayed on the same  
 405 plot to show the relative difference in the amplitude of peak Hg intensity. LIBS spectra of polished gold coming from the  
 406 Benzdorp area (d), the naturally Hg-enriched group N (French Guiana) (e), and G, P, I and D groups (f). Bold lines  
 407 correspond to the mean values of each gold population.

408

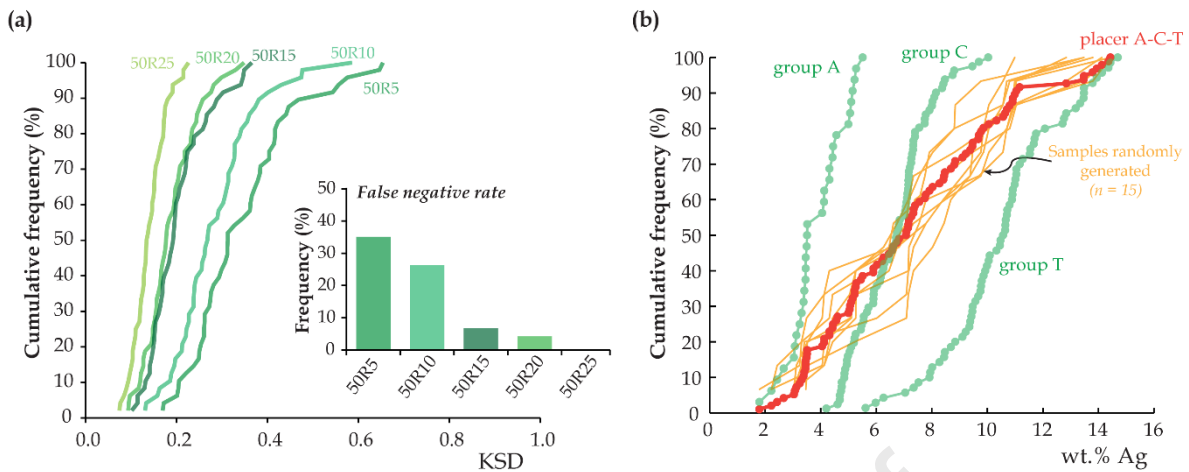
#### 409 4.2 A methodological approach to the certification of responsible gold supply chains

410 In this study, the method used for gold traceability particularly focus on the Ag content because it is the only  
 411 element (with gold) systematically present in any gold alloy and homogeneous within the grain core. Moreover,  
 412 the CDF of the Ag content, when coupled with the KS statistic, greatly helps to discriminate distinct populations  
 413 of gold grains and thus trace gold grain provenance (Pochon et al., 2020). In this study, Ag content was  
 414 measured by EPMA. A similar approach using handheld LIBS on “polished” gold grains was deemed practical  
 415 (Pochon et al., 2020), as was an SEM-EDS (Velazquez, 2014).

416 The reproducibility of such data has already been evidenced (Chapman et al., 2000b, 2010a; Moles and  
417 Chapman, 2019) by resampling several aliquots at a given location but at different time (sometimes several years  
418 later). The obtained CDFs of the Ag content of these gold samples yield similar pattern, highlighting that (1) a  
419 gold sample can be considered as a representative aliquot of a population and (2) that results are reproducible.  
420 Thus, our dataset (i.e. similarly sampled) can be considered as representative aliquots of each studied gold  
421 population. In addition, we have also verified from what sample size our data are reproducible by performing a  
422 statistical procedure of random resampling of our dataset and compare it. Indeed, the comparison of subsamples  
423 obtained by the resampling allow the evaluation of the reproducibility of the sample distribution. The entire  
424 group N has been chosen to evaluate the sample size required (i.e. the number of gold grains needed by sample)  
425 to obtain accurate and reproducible results, because it contains the most gold grains analyzed (i.e. 165 analyses)  
426 and a large range of Ag contents (0.13 and 19.05 wt. %). We thus randomly sampled without replacement fifty  
427 samples with different sample size: 5, 10, 15, 20 and 25 analyses. All possible KSD of two-sample comparisons  
428 were computed (i.e. 1225 combinations for each different sample size) and displayed in Fig. 5a. Because the D  
429 critical is dependent on the sample size, we evaluated the rate of false negative response with the specific-deposit  
430 DC from the KS17 approach. Unsurprisingly, resampling shows that the reproducibility is dependent on the  
431 sample size. Indeed, a low number of analyses tend to increase the KSD between samples coming from the same  
432 provenance and consequently leads to an increase of false negative response (35.1 % and 26.4 % for a sample  
433 size of 5 and 10, respectively). Although the more analyses we have the better the result, it appears that data are  
434 reproducible from a sample size of 15 analyses (see 50R15, Fig. 5a), because the number of false negative  
435 response drastically decrease to only 6.7 % (4.2 % for a sample size of 20). With a mean sample size higher than  
436 15, our dataset can be considered as representative aliquot of a given population. Because the major part of our  
437 dataset consists of alluvial gold coming from placer, the primary source of gold grains can be multiple. We thus  
438 have assessed the ability of the KSD approach to identify samples coming from a placer composed of distinct  
439 contributing primary populations. To do so, we randomly generated a placer from three primary gold populations  
440 (i.e. A, C and T groups) and randomly sampled without replacement ten samples with a sample size of 15 (Fig.  
441 5b). Results show that all randomly selected samples well fit with the placer, meaning that the number of  
442 contributing primary sources has no effect on our method and in the studied Ag content range.

443

444



445

446 **Fig 5 (a)** Cumulative distribution functions of the Kolmogorov–Smirnov statistic (KSD) applied to the Ag content for all447 possible two-sample comparisons. 50R5 means that 50 samples of 5 analyses have been randomly sampled, and so on. **(b)**

448 Cumulative distribution functions of the Ag content of randomly generated placer and randomly selected samples.

449

450 For successful application of our approach in gold traceability, it is essential that two samples from the

451 same location must be identified as brother samples coming from the same gold population. At the opposite, two

452 samples coming from different place must be identified as non-brother samples. The “classical” KS test and the

453 KS17 approach were applied to dataset. Thus, all possible comparisons between brother samples have been

454 evaluated together. The same was done with non-brother samples. For evaluating the “classical” KS test, 92 two-

455 sample comparisons of brother samples and 1148 two-sample comparisons of non-brother samples were

456 possible. Results are plotted in Fig. 6a. KSD is normalized to the D critical and log10-transformed for a

457 straightforward comparison between two samples. If the value is less than 0, the two samples are considered as

458 brother samples. Thus, we can see that curve of brother samples fall into the brother field (see green field in Fig.

459 6a) with only 2.2 % of FN rate (for false negative rate), whereas the larger part of non-brother curve fall into the

460 non-brother field (see orange field in Fig. 6a) with a FP rate of 28.9 % (for false positive rate). Regarding the

461 KS17 approach, a greater number of comparison were possible (134 two-sample comparisons of brother samples

462 and 2193 two-sample comparisons of non-brother samples). The number of pair-wise comparisons is higher in

463 the KS17 approach, because the “classical” KS test does not take into account permutations. Indeed, the pair-

464 wise comparison N2 vs N3 and N3 vs N2 would yield a distinct result in the KS17 approach, because the

465 establishment of the decision criterion (DC) is based on a leave-one-out method that change with permutations,

466 whereas the D critical is only based on the sample size (which remains unchanged when we permuted data).

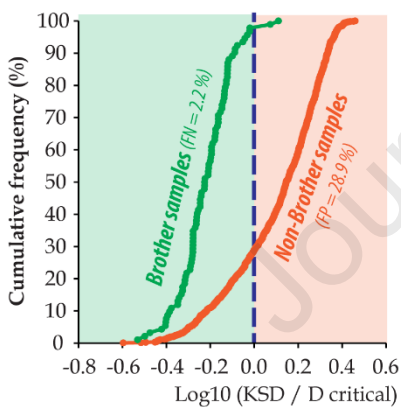


467 Results of KS17 approach are different when using standard or deposit-specific DC as decision criterion (Fig.  
 468 6b). Brother curves mainly fall into the brother field with a FN rate of 10.4 % for the standard DC and a null FN  
 469 rate for the deposit-specific DC. The major part of non-brother curves fall into the non-brother field with a FP  
 470 rates of 32.6-35.0 % for the deposit-specific and standard DC, respectively. Both approaches using KS statistic  
 471 yielded very low FN rates results (*i.e.* 0–10.4 %) which is suitable and expected in traceability purposes. Using a  
 472 deposit-specific DC seems to reduce the FN and FP rates (Gäbler et al., 2020).

473 Thus, the evaluation of our data show that our gold samples can be regarded as representative aliquots  
 474 of a population, and thus the Ag content can be used to verify if a gold sample comes from its declared  
 475 provenance. The use of deposit-specific DC from the KS17 approach is more appropriate for traceability when  
 476 there is sufficient reference samples (*i.e.* at least 5 reference samples for one mine site), but the “classical” KS  
 477 test should be used instead of the standard DC when there is not sufficient data. For this reason, we used the  
 478 “classical” KS test in the remainder of this study.

479

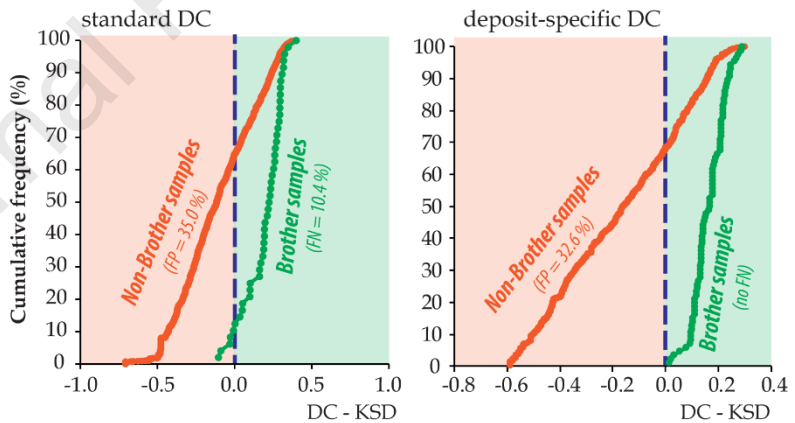
(a) “classical” KS test



480

481

(b) the KS17 approach

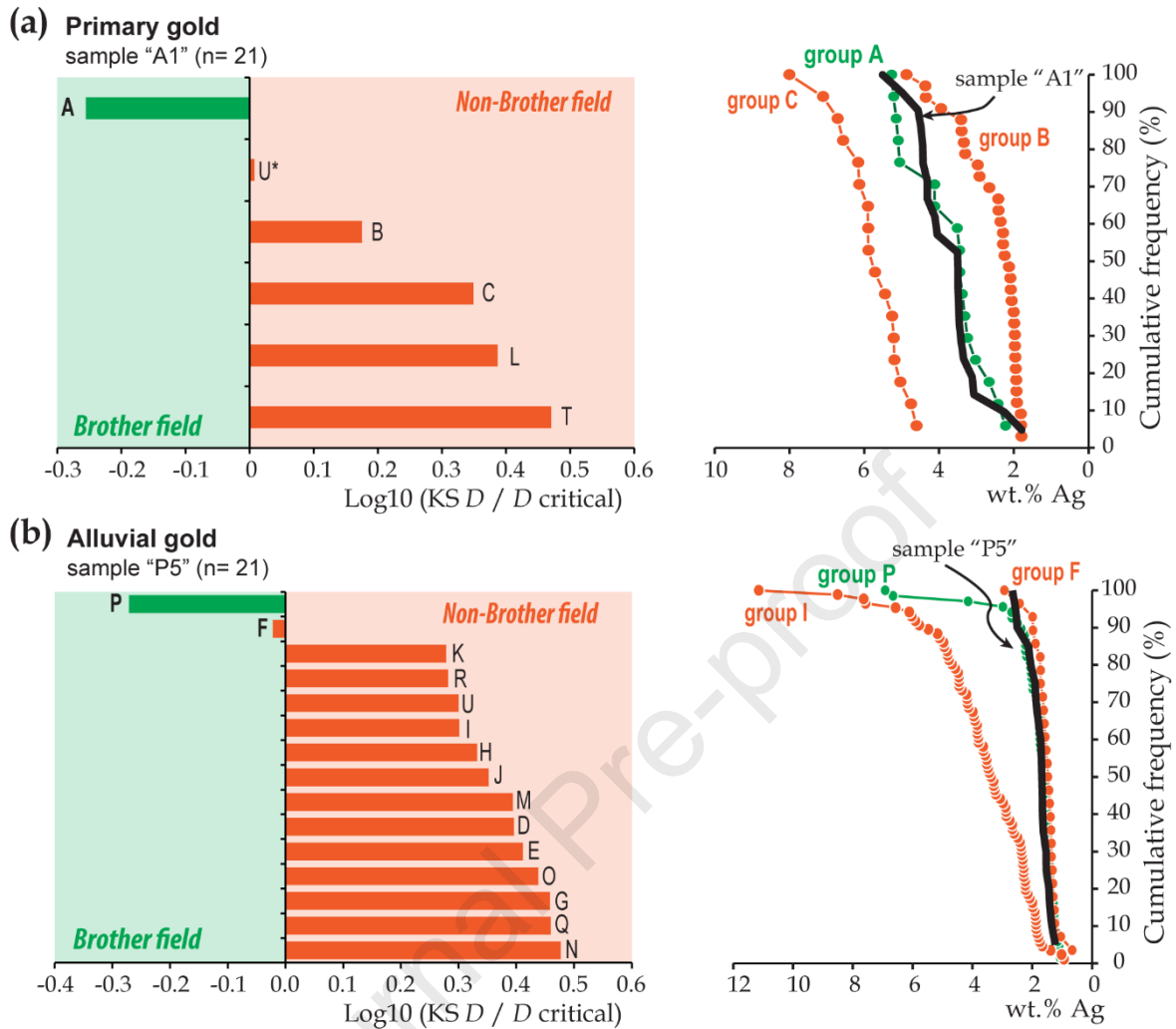


482 **Fig. 6** Cumulative distribution functions of the KSD applied to the Ag content for brother and non-brother samples coupled  
 483 to the decision-making criterion related to (a) the “classical” KS test and (b) the KS17 approach from Gäbler et al. (2017). FN  
 484 and FP stand for the proportion of false negative and positive response, respectively. See text for further explanations.

485

486 To illustrate our approach within traceability process control, we have displayed two characteristic  
 487 examples in the Fig. 7. Primary and alluvial gold grain populations are compared separately because their  
 488 morphological characteristics are distinct and therefore constitute two different types of gold (*i.e.* a gold sample  
 489 declared as being primary cannot be alluvial). The color code from the Fig. 7 follows the same reasoning than

490 that of the Fig. 6. The green represent the brother field whereas the orange represent the non-brother field. It  
491 means that if the result of a brother comparison falls into the orange field, there is a FN response, and inversely.  
492 When the sample in question have a documented origin, results show that the two gold samples (i.e. samples A1  
493 and P5) can be statistically identified to their gold population using their Ag contents. Indeed, the  $\log_{10}$  (KSD/D  
494 critical) value obtained (green bar) from the comparison between the sample A1 and the group A fall into the  
495 brother field (green field), meaning that the declared origin of sample A1 as belonging to group A is correct (Fig.  
496 7a). Moreover, the cumulative distribution curve of sample A1 fits perfectly with that of the group A. Same  
497 reasoning can be applied to the sample P5 (Fig. 7b). The declared origin of sample P5 as belonging to group P is  
498 correct. However, when we do not have documented origin, the sample P5 could be also belong to the group F,  
499 and therefore requiring further study to identify its unique provenance. Not surprisingly, this type of case is  
500 frequent and will become even more so as the number of studied gold occurrences increases, although other  
501 analytical tools can be used to improve the discrimination (see the following section). Nevertheless, Ag content  
502 is still considered the cornerstone of gold traceability studies because the process is efficient, and the parameter  
503 is sufficiently accurate to certify the declared gold population provenance in “routine” traceability studies. Even  
504 if Ag contents and KS statistic alone cannot distinguish all gold grain populations, they do help identify gold  
505 grain origin by reducing the number of possibilities, making this step the most decisive in our approach to the  
506 analytical traceability of natural gold.



507

508

509 **Fig. 7** Bar chart of the KS statistic (coupled with the decision-making criterion, D critical) and cumulative distribution curves  
 510 of the Ag content of primary gold **(a)** and alluvial gold **(b)** samples illustrating our approach for verifying gold grain declared  
 511 origin. Each sample was compared to all the studied gold populations, simulating a known database to which we could refer.  
 512 Group A only refers to sample A2 in this case study, as there are only two subsamples that make up group A. The gold  
 513 population of group P is composed of subsamples P1, P2, P3 and P4. The group U\* is composed of only one sample (U4).  
 514 This sample is primary gold and comes from the same location of alluvial gold samples U1, U2 and U3. For this reason, they  
 515 are treated separately. "n" correspond to number of electron microprobe analyses.

516

517 Adopting such an approach requires guidelines for implementation, knowledge about the presumed  
 518 provenance of the sample, and a reference database. For practical implementation, the number of gold grains  
 519 required (and consequently, the number of chemical analyses) appears critical to the traceability process because  
 520 under-sampling may yield more false positives and some false negatives, leading to misinterpretation. Looking

521 at our dataset and the random resampling (Fig. 5), we showed that a sample give reproducible data from 15  
522 analyzed gold grains, but it is clear that the more we have the better. For a relevant database, it appears important  
523 to have reference samples coming from the same location with common origin (brother samples), and reference  
524 samples of different origins that do not share a common origin (non-brother samples). Ideally, at least five  
525 reference samples from the same location should be compiled for the calculation of the deposit-specific decision-  
526 making criterion, a well-tried approach. A database could not encompass all gold deposits around the world but  
527 rather must be established at a country or regional scale. If a traceability process is implemented, the database  
528 will continue to grow as new extraction sites open, and the number of gold populations with similar  
529 characteristics should also grow. In French Guiana, most of gold mining licence lasts for a maximum of 4 years  
530 and can be renewed only once. Extraction sites are thus not all active at the same time, which will reduce the  
531 number of similar gold populations extracted during the same period. This information should be available in the  
532 database, which must be updated regularly by the competent authorities. In addition, providing time information  
533 and deposit-specific location information can be useful in the case of deposits where composition evolves  
534 horizontally and/or vertically.

535 This analytical approach may help control and certify gold production and trade. Such as several  
536 published papers (Gäbler et al., 2013, 2017, 2020; Martyna et al., 2018), we consider a gold sample that matches  
537 its presumed provenance to be certified gold even if it matches other referenced gold samples from the database,  
538 but we believe it should be evaluated and validated on a case by case basis in accordance with current  
539 legislation. Since it is difficult to predict the Ag distribution in a “raw” gold sample without polishing and  
540 chemical analysis, it would be useless to attempt to imitate a particular signature, because it needs time to do  
541 this; a time that illegal miners do not have. The systematic use of Hg amalgamation by illegal miners can be  
542 easily detected by the use of handheld LIBS directly in the field or in a mobile field laboratory. In addition,  
543 certifying responsible gold supply chains directly in the field could be possible. Pochon et al. (2020) have  
544 demonstrated that a handheld LIBS may be also used as an EPMA substitute for determining Ag content in gold.  
545 In this case, manual rough polishing of raw gold grains would expose the core of the grain, thereby reducing the  
546 cost and sample preparation time, and the process could be done in a field laboratory. Our analytical approach is  
547 thus achievable in the field and in a field laboratory, allowing for easier implementation of the due diligence  
548 process, certification of the origin of the gold and demonstration of responsible sourcing.

549

### 550 **4.3 Identifying the origin of unknown gold samples: a challenging issue**

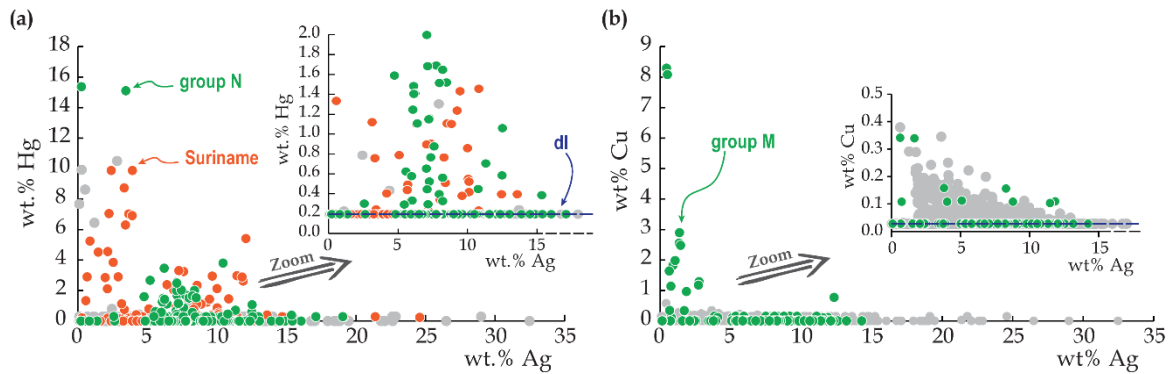
551 In addition to the implementation traceability process for natural gold, it needs complementary tools to help  
552 identify the provenance of gold diverted from a legal supply chain and illegal gold seized by authorities. This  
553 would serve to locate the rightful owner or to locate the area devastated by illegal mining and stop the illicit  
554 extraction. However, when a greater precision is needed, the analytical methods become more expensive and  
555 time-consuming. The use of minor elements (especially Cu and Hg), the identification of mineral inclusions, and  
556 the quantification of trace element fingerprints may help to discriminate gold populations within some specific  
557 case.

558

#### 559 **4.3.1 Input of minor elements**

560 Although the detection limits of a traditional analytical method such as EPMA are often too high to detect Cu  
561 and Hg in every gold grain (Fig. 8a), it is a very useful tool because it allows the number of variables to be  
562 increased. Although the group N is similar to the Q, M, E and G groups in terms of Ag content distribution  
563 (Appendix A.1), the gold from the group N can be easily identified by its Hg content. For example, sample N4  
564 has a mean value of 0.38 wt% Hg with 26% of the gold grains containing a significant amount of Hg, whereas  
565 the Hg concentrations in the gold from the Q, M, E and G groups are generally below the detection limit (*i.e.*  
566 0.28 wt%). The Hg content for sample N4 is specific to the gold from the group N, which also has a mean value  
567 of 0.31 wt% Hg, with mercury detected in 26% of the EPMA analyses. The group N is the only example of  
568 natural Hg-bearing gold known to date in French Guiana with a range composition close to amalgams from  
569 Suriname (Fig. 8a), making its identification relatively easy, but it may be not so easily in areas where Hg is a  
570 common. Indeed, only 3.8 % of our data contains significant Hg content meaning that French Guiana gold is  
571 relatively Hg-poor compared to others goldfields (*e.g.* Von Gehlen, 1983; Chapman, et al., 2000a, 2010a, 2010b,  
572 2017; MacKenzie and Craw, 2005; Chapman and Mortensen, 2016). The same reasoning can be applied to the  
573 gold from the group M based on its significant Cu content (up to 8.3 wt.% Cu, Fig. 8b), detected by EPMA,  
574 compared to the other populations (*i.e.* a mean value of 0.26 wt% Cu with 17% of gold grains containing  
575 significant Cu), thereby allowing for rapid identification of the gold from group M. Such as the Hg content, the  
576 Cu content is not always detected by EPMA (only 21.2 % of our data contains significant Cu content, Fig. 8b),  
577 making difficult the systematic use of these two elements in traceability method.

578



579

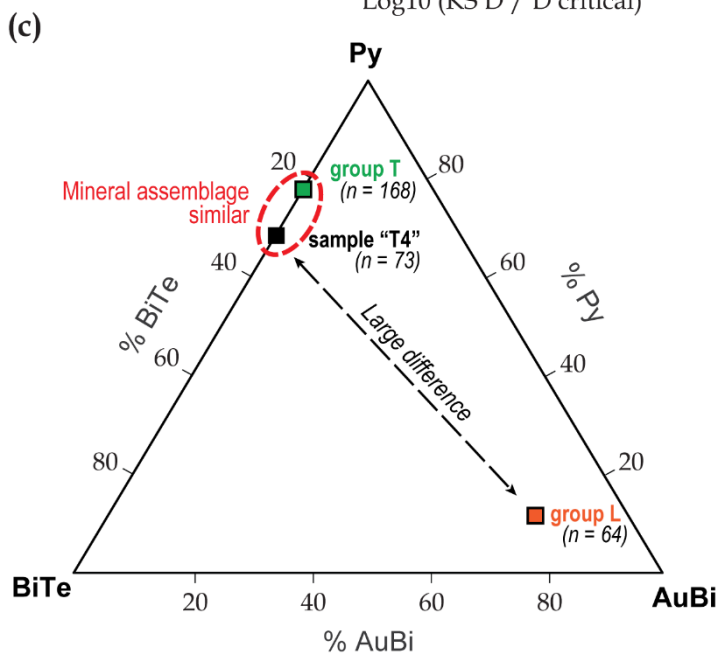
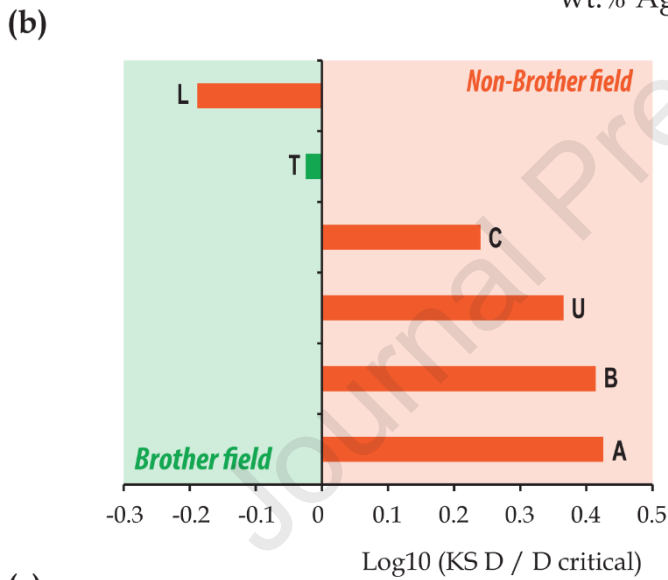
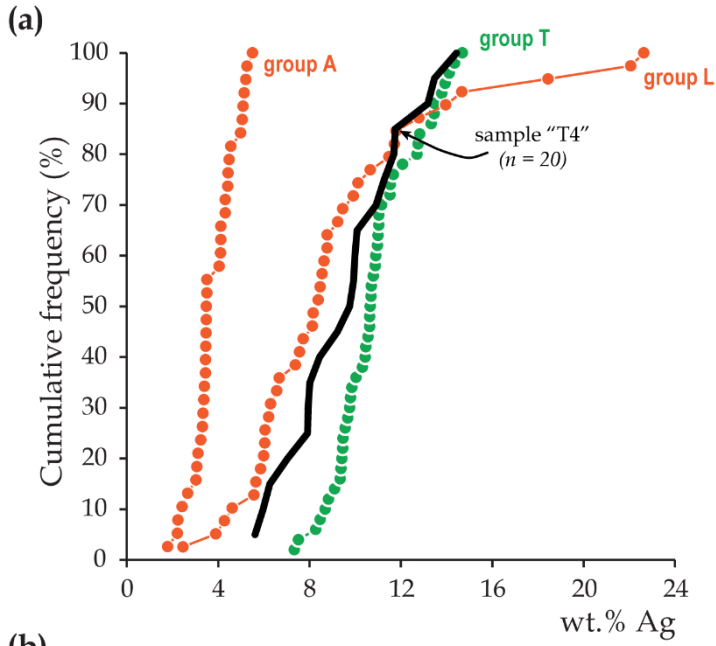
580 **Fig. 8** Binary plots showing the Ag content versus the Hg content **(a)** and the Cu content **(b)** of gold from this study. Grey  
 581 dots consists of others French Guiana gold and “dl” stand for detection limit.

582

### 583 4.3.2 Contributions from mineral inclusions, a source of powerful but fragmentary data

584 Studies on mineral inclusion assemblages to discriminate different gold populations have been performed since  
 585 the 1970s (Desborough et al., 1971), and it is now considered a traditional approach to identifying different  
 586 styles of mineralizing events and a mineral exploration tool for tracking down primary deposits (Chapman et al.,  
 587 2000b). Indeed, the formation of mineral inclusions within native gold is generally interpreted as sub-coeval and  
 588 provides information about the environment of formation (Chapman et al., 2000b). Furthermore, the mineral  
 589 inclusions located in the core of gold grains are preserved by gold’s ability to form an effective natural barrier  
 590 between inclusions and the atmosphere (Chapman et al., 2002). However, to develop a robust interpretation  
 591 based on mineral inclusion data, a large number of gold grains must be collected (*i.e.* about 150 particles for  
 592 Chapman et al. (2021)) and characterized because most are devoid of such inclusions (*e.g.* only 5% of gold  
 593 grains host inclusions in the Klondike Gold District; Chapman et al., 2010a). Thus, all gold grains must be  
 594 carefully examined in order to identify the presence (or absence) and type of inclusions. Unsurprisingly, only a  
 595 few gold grains (less than 17%) host mineral inclusions, providing incomplete information on inclusion  
 596 mineralogy, thereby making robust statistical analyses more challenging. In some cases, when the information on  
 597 Ag content distribution is insufficient, it is possible to use the mineral inclusion information to identify the  
 598 provenance of a gold sample. For example, sample T4 (when considered as an unknown) could belong to either  
 599 the L or T groups based on its Ag content (Fig. 9a and b), but the absence of maldonite inclusions (AuBi) shows  
 600 that it belongs to the T gold population because maldonite was only found in samples from the group L (Fig. 9c).  
 601 But it is important to keep in mind that the absence of such mineral inclusions may also be due to fluvial  
 602 transport that may partly obliterated inclusions information (Melchiorre and Henderson, 2019) yielding

603 incomplete data. In addition, all the samples from the group P (*i.e.* 9, 30, 38, 46 and 47) have similar Ag contents  
604 to the group F, but the mineral inclusion assemblages highlight the differences between them (Appendix A.3).  
605 Mineral inclusions in gold from the group F are mainly galena (~86%) whereas inclusions from the group P are  
606 galena (~55%), Bi telluride (~18%) and Pb telluride (~8%). Thus, sample P5, which could belong to either the P  
607 or F gold populations (Fig. 6b), is easily identified as a brother sample of the group P using mineral inclusion  
608 information. Thereby, mineral inclusions can be very useful to help match samples to gold populations when the  
609 gold grains host sufficient and characteristics mineral inclusions. However, it is not suitable for “routine”  
610 analyses in traceability purposes because it needs quick decision making that is not possible if at least 150 gold  
611 particles are required. This method should be only used to dig deeper into discrimination when required, and  
612 consequently should be used in complement to the KS statistic applied to the Ag content.





614 **Fig. 9** Cumulative distribution plot of the Ag content of primary gold **(a)**. Bar chart of the KS statistic coupled with the D  
615 critical **(b)**. Ternary plot of the statistical counting data on mineral inclusions in sample T4 and gold grains from the T and L  
616 gold populations **(c)**.

617

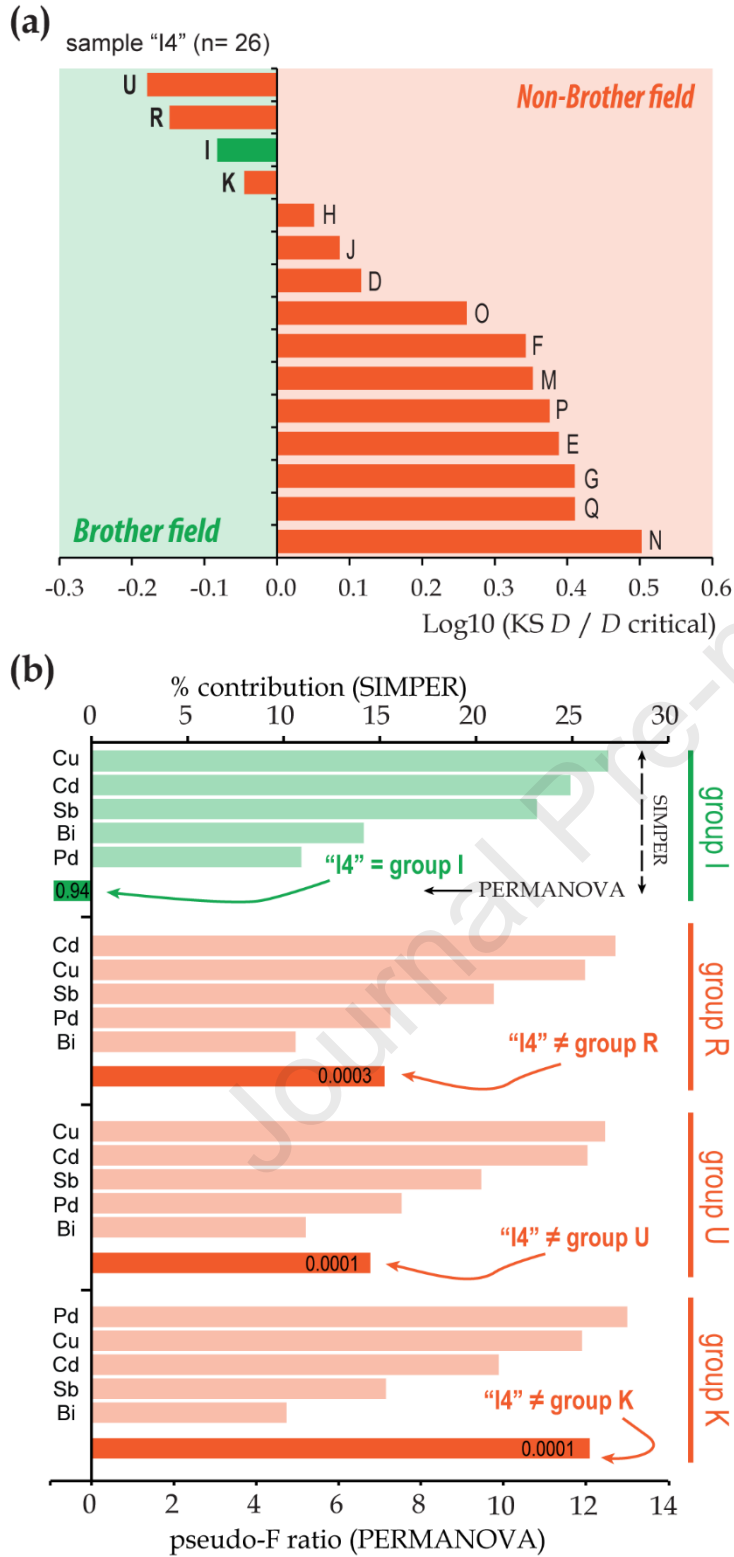
### 618 **4.3.3 Trace element fingerprinting**

619 Deciphering gold fingerprints using trace elements is increasingly used in ore deposit studies (Banks et al., 2018;  
620 Chapman et al., 2021; Liu and Beaudoin, 2021; Liu et al., 2021) and is the most common technique for  
621 identifying the source of illicit gold (Watling et al. 1994, 2014; Dixon and Merkle, 2019). However, in previous  
622 traceability studies this technique is only applied to raw spectral data without any calibration or standardization  
623 with matrix-matched reference materials. In addition, the comparison between different gold populations is  
624 mainly based on trace element patterns and rarely coupled with multivariate statistical analyses. Thus, we  
625 propose here an approach using PERMANOVA and SIMPER analyses on trace element compositions as  
626 determined by LA-ICP-MS to identify gold provenance. The former was used to test the dissimilarity between  
627 gold populations, whereas the latter highlights the trace elements that contribute to the dissimilarity. This  
628 approach was performed on gold samples that could not be matched to a unique provenance using other  
629 analytical methods (Appendices A.4, A.5 and A.6).

630 Sample I4 from the group I is shown as an example of this method in Fig. 10. When treated as an  
631 unknown, the KSD approach on the Ag content (Fig. 10a) identify four possible brothers population for the  
632 sample I4 (I, K, R or U groups). PERMANOVA analyses compared the trace element composition of sample I4  
633 to samples from each of the four possible populations. Only five trace elements (Cu, Pd, Cd, Sb, Bi), analyzed by  
634 LA-ICP-MS, were used (other trace elements were not suitable as they were principally below the limit of  
635 detection). The SIMPER results showed that the average dissimilarity for each trace element varies significantly  
636 from one gold population to another (Fig. 10b). When sample I4 is compared to the I and K populations, the  
637 contributing dissimilarity of Pd varies from 10.9 to 27.9, respectively, making this element the most  
638 discriminative. The PERMANOVA results clearly show a statistically significant similarity in trace element  
639 composition for I4 compared to gold from the group I, yielding a pseudo-F ratio of -0.082 and a p-value of  
640 0.9480. As for the other gold populations (Fig. 10b), the pseudo-F ratio values are significantly higher (from 6.8  
641 to 12.1), and the p-values significantly lower than 0.05 (from 0.0001 to 0.0003). This test undoubtedly indicates  
642 that sample I4 belongs to the group I, successfully tracing its origin.

643           With only five measured trace elements, multivariate statistical analyses were able to confirm the origin  
644 of 12 other samples (Appendix A.5). Consequently, the origin of another 16 samples could not be certified due to  
645 overly similar trace element fingerprints as evidenced by SIMPER results. They clearly show that most trace  
646 elements almost equivalently contribute to the dissimilarity of these samples, explaining the challenge to  
647 undoubtedly discriminate them. In conclusion, the provenance of 69 % of the dataset (*i.e.* 39 of 56 gold samples)  
648 could be correctly identified when the samples were treated as “unknowns”, and the analytical process followed  
649 a specific sequence of techniques (*i.e.* Ag content first, followed by minor element composition, then mineral  
650 inclusion assemblage, and finally trace element composition).

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651

652

653 **Fig. 10** Bar chart of the KS statistic coupled with the D critical performed on the Ag contents of sample I4 compared to other

654 gold populations (a). Results of the similarity percentage analysis (SIMPER) and the permutational multivariate analysis of

655 variance (PERMANOVA) (b). The light colored bars represent the percentage contribution of each element to the  
656 dissimilarities (SIMPER). The dark colored bars represent the pseudo-F ratio (PERMANOVA), and the black values show  
657 the p-value, which reflects the significance of the test.

658

659         When gold samples were treated as unknowns, our approach could not correctly predict the provenance  
660 of 16 samples (~31% of the dataset). This limitation mainly concerns samples from the H, J, O, R and U gold  
661 populations. It becomes difficult to identify these samples and to link them to a unique extraction site when their  
662 origin is assumed to be unknown. Indeed, it is challenging to discriminate alluvial gold populations that share the  
663 same bedrock deposit contributing source (the interconnection of hydrographic networks and the geographical  
664 proximity between the H and J gold populations located only 13 km apart and between the R and U gold  
665 populations only 4 km apart support this assumption) or a bedrock deposit that share similar genetic processes  
666 (*e.g.* fluid composition, the nature of the host rocks and the source of the metals). Indeed, most gold deposits  
667 from French Guiana are hosted within the same Paleoproterozoic greenstone belt and are mostly overprinted by  
668 late orogenic gold event (Marcoux and Milési, 1993; Milési et al., 2003). Consequently, the gold extracted from  
669 placers derived from such primary deposits have similar geochemical signatures. Furthermore, in agreement with  
670 the recent study of Chapman et al. (2021), the trace element content of gold from orogenic environments, such as  
671 French Guiana gold, is relatively low. Only five elements (*i.e.* Cu, Pd, Cd, Sb, Bi) are present in more than 60%  
672 of gold particles, making the multivariate statistic challenging. Using a femtosecond laser coupled with a high-  
673 resolution ICP-MS could enhance the sensitivity of the trace element analysis by pushing down the detection  
674 limit of trace elements, which consequently may increase the number of detected trace elements and enhance the  
675 resulting multivariate statistical tests. But even the most advanced analytical methods will not resolve the  
676 uncertainty for samples with the same geological origin and related genetic processes. Keep in mind that seized  
677 gold is never entirely unknown and that determining its origin follows a forensic investigation that depends on  
678 the context of the seizure, the persons involved and the links to previous cases, and is therefore but one part of  
679 the information that helps trace the origin of the gold (Dixon and Merkle, 2019). Like the use of minor  
680 components or mineral inclusions, the trace elements fingerprint may help to go further into sample  
681 discrimination, but cannot substitute the KS method applied to the Ag content to trace and certify gold  
682 provenance within traceability framework.

683

684 **5. Conclusions**

685 The main motivation of this study was to develop a multi-method approach to support and enhance the due  
686 diligence process of the traceability of gold. We have combined a range of geochemical and statistical methods  
687 in order to help confirm the provenance of legal gold samples and to remove illegal gold samples from the  
688 supply chain. Following three steps, our approach demonstrated that, in French Guiana, it is possible to identify  
689 illicit gold, to certify the provenance of natural gold, and if applicable, identify the origin of unknown gold. First  
690 step showed that the use of Hg amalgamation is easily discernible by the presence of spongy crown texture  
691 around gold grains (*i.e.* 100 % of gold grains extracted by Hg amalgamation have such texture) and also by the  
692 detection of Hg in the field using a compact and lightweight spectroscopic method (LIBS). Indeed, all gold  
693 extracted by conventional gravity methods did not contain significant Hg, except the Hg-rich group N which is  
694 naturally enriched. The second and major step showed that the analysis of the distribution of Ag content coupled  
695 with a statistical KS approach are a powerful tool for certifying the gold provenance. Brother samples were  
696 mostly and correctly identified (*i.e.* only 2.2% of brother samples were misinterpreted with “classical” KS test)  
697 to their presumed provenance. The last and more challenging step (*i.e.* identifying the origin of unknown gold)  
698 requires multi-method approach. The use of the Cu and Hg content can be useful to distinguish gold population  
699 with peculiar signature. The determination of mineral inclusions is powerful to identify a gold population but the  
700 scarcity of such inclusions within gold populations needs large gold grain collection and makes its routine use  
701 complicated. LA-ICP-MS trace element composition, coupled with a permutational multivariate analysis of  
702 variance and a similarity percentage analysis, showed that trace element analyses can greatly help the  
703 identification of unknown gold as long as its source population is referenced in a database. However, it should be  
704 noted that too much similarity between some gold populations (*i.e.* ~31% of the dataset) due to too close  
705 proximity or identical genetic processes cannot be resolved with the most advanced analytical methods.  
706 Application of our innovative multi-method approach in the French Guiana case study has demonstrated that this  
707 approach is relevant and works well. Keeping in mind that gold signatures may be locally more variable, now,  
708 the further challenges consist to enlarge the database and assess this approach in others regions across the world  
709 and to implement this approach to support the global supply chain of gold.

710

711

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713

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721

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## Highlights

- The Ag content is an excellent proxy to certify the origin of natural gold
- Combination of various geochemical methods is needed to identify unknown gold origin
- Laser-induced breakdown spectroscopy is powerful to identify gold extracted by Hg

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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