

First occurrence of kitagohaite, Pt₇Cu₂, from the Quadrilátero Ferrífero, Brazil

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Abstract

A kitagohaite grain, measuring approximately 1.0 mm, was retrieved from an alluvial gold gravity concentrate from the southeastern Quadrilátero Ferrífero (QFe), Mariana, Brazil. The grain exhibits a cubic structure, whitish-steel-gray, and has a metallic luster. It is composed of Wt. 94.42% Pt and 5.56% Cu (n=9), yielding the empirical formula Pt_{6.78}Cu_{1.22}. This groundbreaking discovery marks the first documented occurrence of kitagohaite in South America. This hydrothermal deposition of kitagohaite indicates that its mineralization is constrained to temperatures <500° C, as inferred by the stability of synthetic Pt₇Cu.

Keywords: kitagohaite, Pt₇Cu, platinum grain, *jacutinga*, Quadrilátero Ferrífero.

1. Introduction and geologic setting

A singular and uncommon platinum isometric grain of kitagohaite (Pt₇Cu) was recovered from an alluvial bulk sample through the process of gold panning (gravity concentration) from the Engenho Podre gold placer. The placer is located in the Gualaxo do Norte River in Mariana, MG, Brazil. The location is geologically set at the southeastern borders of the QFe, an area of approximately 7,000 km², tectonically located in the southern São Francisco Craton (Almeida 1977). Dorr (1969) and Endo *et al.* (2019) characterized the region of this placer in terms of its lithostratigraphic occurrence as a metamorphic complex (granite/gneiss). Specifically, the Paleoproterozoic Santa Barbara Complex is constituted by tonalitic-trondhjemite-

granodioritic (TTG) Orthogneiss, metagranite, and migmatite.

According to Endo *et al.* (2019) and Lobato and Costa (2018), the alluvial placers in the QFe are of Cenozoic origin and it is assumed that the concentration of gold was a consequence of the degradation of several deposit types with different geneses and sizes. Thus, the investigated deposit is situated within the watercourse drainage metasediments belonging to the Estrada Real, Minas, and Rio das Velhas supergroups, as evidenced in a lithostratigraphic study conducted by Endo *et al.* (2019). In this given context, the upstream portion of the examined placer deposit pertains to a specific geological area delineated by the Cabral *et al.* (2009) as an Au-Pd-Pt

belt (Figure 1A-B), which is described as hydrothermal gold-bearing mineralization, anchored in late-orogenic quartz-hematite-(talc-kaolinite) lodes. Alongside Cabral *et al.* (2009), several authors (e.g., Varajão, 1995, Kwitko *et al.*, 2002, Lüders *et al.*, 2005, Sampaio *et al.*, 2009 and Oliveira *et al.*, 2017) have conducted investigations of this palladiferous gold mineralization (Au-Pd-Pt) known as *jacutinga*, which originated during the ca. 0.6-Ga Brasileiro tectonic event (e.g., Alkmim & Marshak, 1998). Oliveira *et al.* (2017) provided insights into the two distinct fluids and chemical processes responsible for the precipitation of Fe-oxides containing Au-PGE (platinum group elements). Their research identified two types of fluids involved

in this process: an aqueous-carbonic fluid and an aqueous-saline metamorphic fluid, which operate within a temperature range of 77 to 305 °C. Additionally, Lüders *et al.* (2005) reported a substantial presence of CO₂ along with an average temperature of 319 ± 45 °C in a related context.

Kwitko *et al.* (2002) documented the occurrence of hongshiite (PtCu) within the sulfide-free hematite-rich

jacutinga mineralization in the Itabira District. Subsequently, kitagoite (Pt₇Cu) was formally characterized by Cabral *et al.* (2014) after further investigation of alluvial grains sourced from Lubero, North Kivu, in the Democratic Republic of Congo. Although Schneider & Esch (1944) and Hansen & Anderko (1958) had previously studied the conditions to generate Pt₇Cu metallurgical and

electrochemical alloys (Cabri *et al.*, 1996). It was only with the observations of Törnroos *et al.* (1998) and Kojonen *et al.* (2008) that this mineral was identified as an alluvial grain in Finnish Lapland. This new report on the uncommon occurrence of Pt₇Cu in the QFe is an important contribution to understanding the hydrothermal fluid mineralization of PGE-Au bearings delineated by Cabral *et al.* (2009).

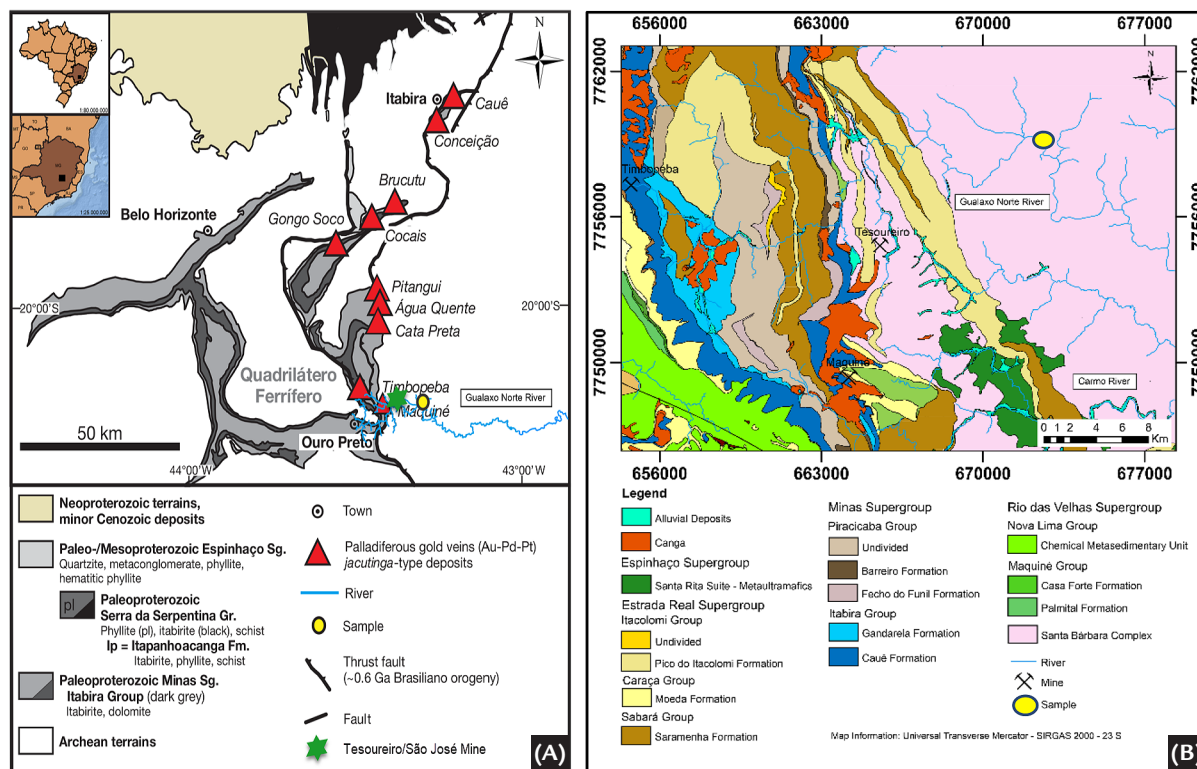


Figure 1 - A) Map of the Au-Pd-Pt belt modified from Cabral *et al.* (2009) and B) Geological setting upstream of the Engenho Podre placer simplified from Endo *et al.* (2019).

2. Sampling, materials, and method

A concentrated sample, weighing approximately 2 g, containing gold grains and nuggets ranging from 0.35-2 mm in size, was extracted from the Gualaxo do Norte River, using a semi-mechanical dredge to pump a gravel slurry into a concentrator trough, followed by manual panning (primarily relying on gravity concentration). After collection, the bulk sample was dried at ambient temperature (~25 °C) to preserve any potential As/Hg sulfides. It underwent a cleaning process using a neodymium magnet, and meticulously examined under a ste-

reoscopic microscope (Quimis, Greenough's Motic SMZ168), revealing the presence of an exceptionally uncommon specimen, whereupon a thin carbon adhesive layer was applied to prepare it for further analysis. Finally, it was analyzed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) (JSM-6510, JEOL Instruments) to investigate its chemical composition. The following specifications were used: accelerating voltage of 20.00 kV, working distance of 15mm and spot size 65. The

results were validated using electron probe microanalysis wavelength dispersive spectrometry (EPMA-WDS) through the JXA-8230 model manufactured by JEOL Instruments. The analysis was conducted with an acceleration voltage of 20.00 kV, a probe current of 40 nA, and a spot size of 1 µm. All specific parameters are outlined in Table 1. The electron microscopy analyses were performed at the Microscopy and Microanalysis Laboratory – LMic, at Geology Department, Universidade Federal de Ouro Preto.

Table 1 - EPMA(WDS) instrument conditions and measurement parameters.

Element	Accel. Voltage	Probe Current	X-ray line	Peak Position	Reference Material	Wt.%
Pt	20 kV	40 nA	Mα	193.252mm	Pt-metal	99.999%
Cu	20 kV	40 nA	Kα	107.403mm	Cu-metal	99.998%

3. Results

The distinctive isometric grain of native platinum (Figure 2) underwent an extensive analysis process involving etching, chemical mapping, and spotted

precise chemical composition assessments using SEM-EDS and EPMA (WDS). With dimensions of approximately 1 mm, the grain exhibited well-preserved facets and

rounded and weathered edges, as depicted in Figure 2 (at 20x magnification). Its appearance featured a whitish steel-gray hue and a robust metallic luster.

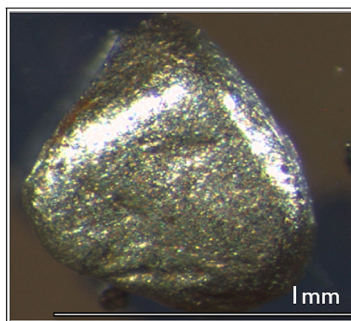


Figure 2 - Stereophotography of the cubic native platinum grain.

As depicted in Figure 3 (A-C), the stoichiometric ratio of Pt-Cu remained uniformly consistent across the entire grain surface prior to polishing. This

maintenance of stoichiometry was observed without any depletion or the presence of heterogeneous zones. This observation is supported by the chemi-

cal maps of Pt and Cu, which provide clearly visual representation of the element distribution.

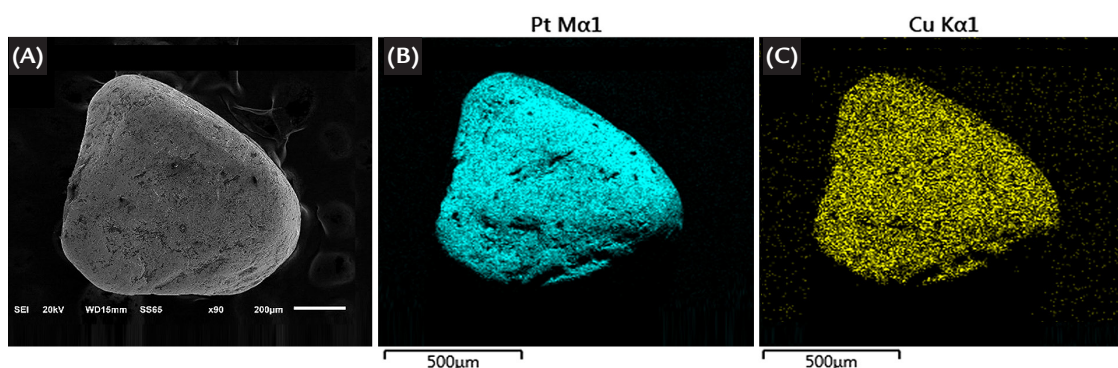
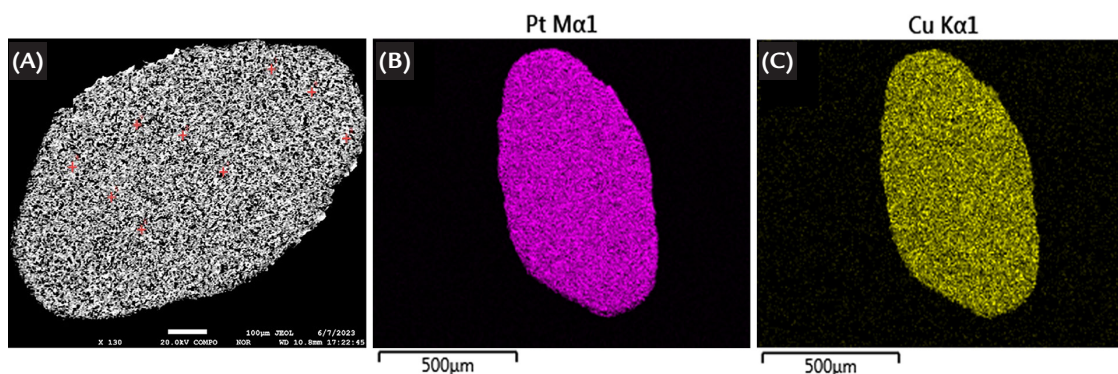


Figure 3 - A) SEM photomicrography; B-C) Pt and Cu distribution on the surface of the studied grain obtained by EDS.

After impregnation with epoxy resin and polishing of the grain, the uniform distribution of Pt and Cu showed that the ratio of these two elements was

preserved across the entire grain, which can be seen in Figure 4B-C (SEM-EDS Chemical map), with 9 spots measured (4A) by EPMA (WDS). The average Wt. %

results are shown in Figure 4D. The uniform distribution reveals the massive grain without depletion or dissolution/reprecipitation effects at the borders.



(D) Element	Wt. %	Range	n	Standard Deviation	Reference Material
Pt	94.42	93.77-94.72	9	0.32	Pt metal
Cu	5.56	5.27-6.19	9	0.31	Cu metal

Figure 4 - A) EPMA photomicrography of the polished grain, and WDS analyzed spots; B-C) Pt and Cu distribution map by SEM-EDS and D) Chemical results of the polished kitagohaite grain, by EPMA (WDS).

All standardized weight percentage results from EPMA (n=9) and SEM-EDS (n=10) have been consolidated in Table 2, with traces of Pd measuring below 0.04 Wt.% being excluded.

Table 2 - EDS and WDS chemical results of the kitagohaite grain.

SEM (EDS)	n1	n2	n3	n4	n5	n6	n7	n8	n9	n10
Wt.%PT	94.9	94.3	94.1	93.9	94.1	94.7	94.5	95.2	93.3	94.0
Wt.%CU	5.7	5.7	5.7	5.6	5.8	5.9	5.8	5.7	5.5	5.6
Total %	100.6	100.0	99.8	99.5	99.9	100.6	100.3	100.9	98.8	99.6
EPMA (WDS)	n1	n2	n3	n4	n5	n6	n7	n8	n9	-
Wt.%PT	94.57	94.64	94.33	93.77	94.53	94.56	94.66	94.72	94.05	-
Wt.%CU	5.42	5.33	5.66	6.19	5.46	5.43	5.32	5.27	5.94	-
Wt. %Pd	<0.04	<0.04	<0.04	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
Wt. % Total	99.99	99.97	99.99	100.0	99.99	99.99	99.98	99.99	99.99	-

4. Discussion

The chemical composition of the examined grain (Wt. % Pt_{94.42} and Cu_{5.56}) closely aligns with the composition outlined by Cabral *et al.* (2014) for the mineral kitagohaite (Pt₇Cu), which is reported to have Wt. %: Pt_{95.06-95.91} and Cu_{4.70-4.89}. Furthermore, the Pt&Cu alloy synthetic models proposed by Schneider & Esch (1944) and corroborated by Carelse & Lang (2006), evaluated the ordered structures

A₇B and ABC₆ whose models involve A-sites occupied by Pt atoms, B-sites occupied by Cu atoms, and if Pt occupies almost C-sites, the structures were (Pt)(Cu)(Pt_{0.98}Cu_{0.02})₆. This explains the slight deviations in the mineral's chemical formula in this study. Moreover, these two investigations suggest the optimal order/disorder temperature (Tc) of synthetic Pt₇Cu is below 500 °C.

In addition to mass percentages of

demonstrated results, considering atoms per formula unit (apfu) is pivotal in accurately characterizing chemical compositions. Apfu provides insights into the proper atomic arrangement within compounds, accounting for varying atomic weights and ratios, resulting in a precise formula determination. In this way, the apfu conversion from weight percent result for this grain is:

Molecular Formula: Pt_{6.78}Cu_{1.22}
 Molar Mass: Pt_{6.78}Cu_{1.22} ≈ (6.78 × 195.08) + (1.22 × 63.55) ≈ 1429.08 g/mol
 Moles of Pt = (94.42 / 195.08) ≈ 0.484 moles - Moles of Cu = (5.56 / 63.55) ≈ 0.087 moles
 apfu of Pt = Moles of Pt / Moles of Cu ≈ 0.484 / 0.087 ≈ 5.54
 apfu of Cu = Moles of Cu / Moles of Cu = 1

Therefore, considering the molecular formula Pt_{6.78}Cu_{1.22}, the apfu for Pt is approximately 5.54, and the apfu for Cu is 1.

Comparing the mineral composition results of this study with all known

Pt&Cu alloy minerals presented in Table 3 (kitagohaite, orthocuproplatinum, hongshiite, and tomamaeite), the remarkable proximity of Wt.% Pt 94.42% and Cu 5.56% underscores intriguing composi-

tional chemical affinities to Pt₇Cu. This analysis highlights the distinctive relationships among these minerals' unique concentration patterns and their potential geological implications.

Table 3 - This work results compared to known minerals of Pt&Cu alloy.

Mineral	Theoretical chemical formula	Theoretical Wt% Pt	Theoretical Wt% Cu
kitagohaite	Pt ₇ Cu	95.55	4.45
this work	Pt _{6.78} Cu _{1.22} *	94.42*	5.56*
orthocuproplatinum	Pt ₃ Cu	90.21	9.79
hongshiite	PtCu	75.43	24.57
tomamaeite	PtCu ₃	50.58	49.42

*Empirical based on Wt.% results from EPMA(WDS).

The natural occurrence of Pt₇Cu - (Pt)(Cu)(Pt_{0.98}Cu_{0.02})₆ - as described in this study, corroborates the observations of Kwitko *et al.* (2002), who described hongshiite (PtCu) in the QFe. It is also enriched with a particular mineral from the platiniferous-gold-

PGE belt, as proposed by Cabral *et al.* (2009). Furthermore, the massive cubic grain with faces and edges preserved indicates near-primary mineralization. Other kitagohaite features corroborate the estimation of transport, such as low hardness (3.5 Mohs scale) and malleable tenac-

ity, which hinder crystal preservation. In addition, the high density of kitagohaite (19,958 g/cm³), which is higher than that of gold, hinders long-distance transportation. Thus, these findings strongly indicate hydrothermal growth of crystals as *jacutinga* mineralization (BIF itabirite-

hosted platiniferous gold lode mineralization). Therefore, one plausible possibility is that a carbonated hydrothermal fluid

below 350 °C, with a low level of HS, provides conditions for kitagohaite growth. Intense weathering under tropical condi-

tions disaggregated lode mineralization to release the grains and nuggets of Au-Ag-Pt alloys and kitagohaite.

5. Conclusion

The presence of the uncommon mineral kitagohaite (Pt₇Cu) in the QFe has been confirmed through EPMA(WDS) & SEM-EDS analysis of alluvial sediments from the Gualaxo do Norte River. The existence of this grain strengthens our understanding of low-temperature and hydrothermal fluid activity, and the preserved isometric faces and edges of the grain are evidence for the proximity of the primary

mineralization. Cabral *et al.* (2009) demonstrated that the connection between jacutinga and platiniferous alluvial deposits suggest a potential span of approximately 240 km of Pd-Pt-containing gold mineralization from Ouro Preto to Diamantina (south–north orientation). Building upon this assertion, the current study introduces an evaluation of lateral variations (east-west) extracted from alluvial metasediments

across the potential trend found in all river courses along this mineralization belt. This extension subsequently enables the integration of the Tesoureiro/São José mine into the Au-Pt-Pd lode (Figure 1A). Owing to its proximity as the nearest identified source of gold mineralization, located approximately 9km upstream from the placer where the grain was retrieved, as depicted in Figure 1B.

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