Celestial and earthly origins of platinum

edited by: A. Cremona

The importance of platinum group metals (ruthenium, rhodium, palladium, osmium, iridium and platinum) in modern industrial chemistry is well known: they constitute, individually and in alloys, the major catalytic systems for oxidation, hydrogenation, petrochemical, environmental reactions, and the global market for noble metal catalysts was valued nearly US$ 19 billion in 2023 [1]. It might be surprising that in the sixteenth century, at the beginning of the exploitation of the Colombian gold deposits by the Spanish conquistadores in South America, platinum was thrown overboard to prevent its fraudulent use. Today as in antiquity, jewelry has always been of great relevance for this element, characterized by a whitish grey metallic color and rather malleable in the pure state, although hardened by addition of other metals of the group, such as rhodium and iridium: its name is a diminutive since it was initially mistaken for a "minor" silver (plata = silver, platina = little silver) [2].

Platinum Group Elements (PGE) can be present both as inclusions and in solid solution in ancient gold objects. Since their association with gold is rare in primary deposits (the former are found almost exclusively in ultrabasic rocks, while the latter is found in acidic rocks), the presence of PGE is an indication that gold came from alluvial deposits in which gold and platinum-bearing grains accumulated due to river transport [3]. Therefore, although the world's largest PGE deposits in Russia and South Africa are linked to ores of copper-nickel sulphides and chromitites in which the noble metal cannot be separated by physical methods, native platinum may be present in alluvial beds mixed with auriferous grains [4].

Pliny the Elder in his Naturalis Historia, probably referring to a river in Northwestern Spain, describes a white lead "recognized only by weight; there are also small pieces, especially in dry streams. Miners wash these sands and cook in the furnaces what is deposited. It is also found in gold mines, those called "alutiae" with water washing the black pebbles spotted a little of white, for which there is the same weight of gold, and thereafter in the basins, with which the gold is collected, remain with this; afterwards they separate into the chimneys and are melted into white lead" [5]. Pliny's words correspond with the description of a modern placer deposit in which "eluvial platinum occurs as blackish, small grains showing mamillary surfaces and lined with limonitic cavities, and with no apparent crystal form. They look like metal droplets" [6] (Fig.1). Therefore, in ancient times it was known that similar densities of noble metals prevent their removal from gold during normal washing and separation procedures.

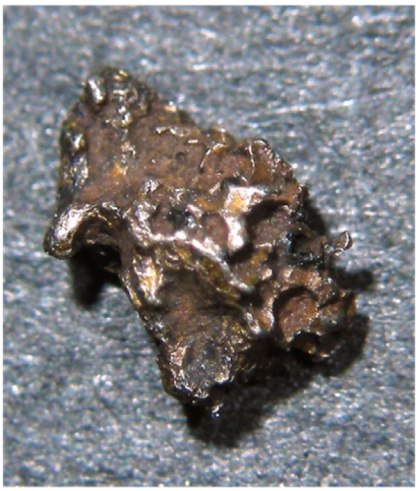

Fig. 1 – Platinum nugget from Yubdo mine (© Thomas Van King)

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Metallurgical processes of the auriferous mineral were practiced in Egypt since the fourth millennium BCE [7]: jewelers produced an alloy of great value with variable content of gold-silver, known to Homer under the name of ἤλεκτρον [8] later latinized to electrum, terms that in both languages also designate amber. Pliny states that "in every gold there is silver in various quantities" [9] and defines the electrum as an alloy containing about 20% by weight of silver occurring both at the native state and synthetically: starting from these concentrations, electrum is visually very similar to silver. Unlike many binary metal systems, gold and silver are mutually soluble in all proportions and the alloy color varies significantly from pale yellow to brilliant white, with the characteristic of "shining more clearly than silver in the light of the lamps". Modern gold essays show that electrum of natural origin is still found in Egypt [10, 11] and there is no evidence that gold and silver (known by the term "white gold") were refined or fused deliberately at the time of the pharaohs [12, 13]. In material selection, color had higher priority than other characteristics and this explains the addition of copper to gold and silver for the synthesis of ternary alloys, since its presence improves both hardness and polychromy.

Unlike silver, whose metallurgy was known, platinum could not be separated from gold during the refining phase by available technologies and therefore remained incorporated as impurity during the process. Traces of metallic platinum were frequently found in gold jewels since the Old Kingdom (c. 2700–2200 BCE) and are visible both to the naked eye and by microscopic examination [14]. On the other hand, native platinum as the main element of a jewel is rare and a unique example is a lead casket of the seventh century BCE discovered in Thebes (current Luxor): conserved at the Louvre Museum, it is considered the first artifact ever made by this metal (Figs. 2 and 3).

Fig. 2 – Shepenwepet's casket, front. Paris, Louvre Museum, E 10814
(© 2003 Musée du Louvre Département des Antiquités Égyptiennes / Christian Décamps)
https://collections.louvre.fr/ark:/53355/cl010007395

Fig. 3 – Shepenwepet's casket, back. Paris, Louvre Museum, E 10814
(© 2003 Musée du Louvre Département des Antiquités Égyptiennes / Christian Décamps)
https://collections.louvre.fr/ark:/53355/cl010007395

Inside the box an ivory tablet is no longer removable for its adhesion to the metal walls. The outer body shows metal hieroglyphs with gold characters on the front and silver on the back side: one of these last characters was made of platinum with impurities of gold and iridium. On the back wall of the lid, the scene of a priestess worshipping the Theban divine triad is represented: Amun, Mut his bride, and their son Khonsu appear in a row from right. The outer body contains a prayer to Khonsu, while silver stars representing the sky are located on the top of the lid. The choice of gold and silver is due to theological reasons: gold corresponds to the sun and silver to the moon, according to astrological and alchemical notations [15].

The ritual case, 142 mm high and 76 mm wide, can be precisely dated because it bears the name of a princess of the Twenty-fifth dynasty, Shepenwepet II (around 679-639 BCE), the powerful daughter of Piankhy, first Egyptian king of Nubian origin, and great priestess of Amun in Thebes. Advanced studies reveal that during that period ancient Egypt reached the peak of its intellectual development and Thebes was the center of this process. Prominent religious and political power was exercised by the Divine Adorers of Amun, assisted by officials leaving testimony with portraits and monuments of their elegant world.

Frenchman Marcelin Berthelot (1827-1907) studied the artifact and reported his experimentation in several works in 1901 [16-18]. The great chemist described that he had been able to examine the object on behalf of the curator of Egyptian Antiquities and had discovered the presence of platinum in one of the hieroglyphic characters submitted to analysis. It was initially mistaken for silver because of its color, but its chemical properties were very different, especially concerning acid resistance. In fact, aqua regia dissolved, in small quantities, yellow platinum chloride that, after mixing with a solution of potassium chloride, showed red crystalline grains under the microscope, but the body of the lamina had resisted, such as is typical of certain platinum minerals rich in iridium and other

elements of the group. Therefore, the resistance to chemical attacks exceeded not only that of gold, but also that of pure platinum, proving the existence of a complex alloy containing different elements of the platinum group.

He concluded that it was prepared with an alluvial mineral, probably occurring with native gold, and that it could have been mistaken for silver even by the ancient Egyptians, as it had been hammered into regular sheets, such as the ones accompanying gold nuggets. There is no doubt that the jewelers would have put aside and subjected to a special treatment a metal with exceptional characteristics: if they had found it frequently, they would have distinguished its infusibility and inalterability with respect to silver. In order to find out if drawings and inscriptions contained other precious metals, it would have been necessary to dissolve another part, but a detached metallic star was made of pure silver and, in view of the uniqueness of the casket, it was considered inappropriate to continue testing. Finally, the chemist concluded that he did not believe that platinum had ever been observed among metals from Egypt: it was not reported in Africa or Arabia in its time, although there were probably examples in the alluvial deposits of Nubia or in the upper regions of the Nile valleys and its tributaries. It was an enigma that could only be solved by the discovery of other Egyptian samples of the kind and the presence of platinum and silver was demonstrated in 1904 in gold nuggets of the Blue Nile, originating from the Ethiopian Plateau [19].

Due to the close relationship between royal families and priests, chemical practice in Egypt (the ancient Kemet) was carried out in workshops associated with temples. The main sectors over which the Divine Adorer of Amun exercised her dominion in Thebes included economic activities, such as crafts, goldsmithing and treasury management, which was typically connected to divine temples in classical antiquity [20]. Religious mysticism extended to precious metals and the specific use to which the different types of gold were destined (from alluvial to mining) was determined by royal decree [21]. Mining and working processes of this metal were delegated by the king to officials with specific titles for the multiple activities related, such as for example the "scribe gold assayer" [22]. From a theological point of view, at the time of the Nubian kings gold was identified with the sun god Amun, with dedications on ritual objects affirming the relationship between the earthly material and the divine sphere. Mining activities received a successful institutional support also in metallurgical development: around 95 ancient gold deposits scattered throughout the Egyptian East desert are known.

The family origins of princess Shepenwepet, combined with the simultaneous southward shift of Egyptian power, strengthen a link with the deposits of Nubia (today's Sudan), already exploited for the presence of gold in previous periods [23]. The ancient region of Kush (called Nubia by the ancient Egyptian name of gold), accessible by Nile navigation, was under full Egyptian control. Given the wealth of its deposits, since the Fourth dynasty (2500 BCE) the pharaoh entrusted the management of quarries and mines to senior officials. Therefore, the precise location of mining sites was a foremost necessity: the only map of topographical interest of Ancient Egypt and one of the oldest in the world, held in the Museo Egizio in Turin, represents on a papyrus a plan of gold mines datable around 1150 BCE (Fig.4). Legends in hieratic, the cursive of time, explain that "the mountains where gold is worked are colored in red" and the term "gold mountains" is repeated several times, as well as the phrase "mountains of silver and gold". A shrine of Amun is also reported at the entrance to the mining area. According to the most accredited interpretation, supported by the presence of a special metagraywacke stone quarry, the analysis of the texts and the orography indicate that the area is located near Thebes in the Wadi Hammamat along the natural path from Coptos (Kuft) on the Nile to the port of Duau (Quseir) on the Red Sea, used since ancient times for commercial expeditions [24]. According to another interpretation, successive to the discovery of the town of Berenice Panchrysos in Nubia, a remarkable correspondence is shown between the topography of the papyrus and that of the satellite image of the archaeological site, in particular with the course of Wadi Allaqi, the extant red auriferous hills, miners houses, roads, paths, and a well [25].

Fig. 4 – Close-up of fragment of the Turin Papyrus map
(© Cat. 1879 + Cat.1969 + Cat.1899 + Cat.2083/182 + Cat.2082/174)
photograph: Federico Taverni / Museo Egizio of Turin

It would be interesting to hypothesize the origin of the metallic platinum of alluvial nature present in Shepenwepet's box. As mentioned, the presence of platinum group metals indicates deposits of alluvial rather than venous nature since PGE hardly associate with gold in the veins but, due to their high density and their non-combination with other substances during erosion, they join gold in river sands and gravels. According to archaeometallurgy principles, the specific chemical composition could also help to identify the area of origin and the mine [26], especially when the noble metal is the primary element of chemical composition. Several works are available on mines exploited in the Pharaonic age: particularly, a study about the ancient gold mines of the Egyptian and Sudanese desert describes around 250 gold production sites in their geological environment and does not indicate the presence of platinoids in the examined samples [27]. Only few and scarce deposits of copper-nickel sulphides and chromites containing noble metals are known in Egypt (mainly osmium, ruthenium and iridium, which were not exploitable due to modernity of the extractive techniques required) and the situation is not different in Sudan and across the crust of the Arab-Nubian shield [28-33].

An attempt could be made to connect the inclusion of the platinum nugget of alluvial origin to a mine or a batch of silver, an element that, due to its scarcity in the Old and Middle Kingdom of Egypt, was considered even more valuable than gold and lacks direct references to local

sources in the old documents [34-36]. Although it might be possible that silver-gold alloy deposits were exploited until vein exhaustion, native silver finds are mineralogically rare. Vague, different and well dispersed are sources of silver import to Egypt in the relatively late era of interest of the seventh century BCE: for our purposes, the proximity of silver and platinum deposits would be important, but in the Mediterranean basin alluvial deposits of the latter are unknown. The Near East is generally mentioned as an area rich in galena (lead sulphide, PbS) and cerussite (lead carbonate, PbCO3) [37], minerals from which silver was extracted by the cupellation process. However, in the Eastern Mediterranean area only gold and electrum of alluvial origin from the valley of the river Pactolus in Anatolia are noted, providing king Croesus' mint with legendary wealth and containing impurities of other noble metals such as osmium and iridium [38]. Further chromitite deposits exist in Western Turkey as well as alluvial deposits in the Ortakale River in Eastern Anatolia, but in every case they contain PGE with prevalence of iridium, osmium, and ruthenium [39]. A study [40] reveals that already in the Tenth dynasty (2175-2135 BCE) Egyptian objects were manufactured with silver from the Attic mines of Laurion but, although deposits of Euboea, Siphnos, Thasos, Thrace and Macedonia [41, 42] further testify to the richness of Greek resources, only rare finds of PGE are encountered today by contemporary prospecting techniques [43, 44]. Other sources indicate that Spain was the largest supplier of silver to Egypt [45], but the Andalusian mines of Rio Tinto, a primary source under Phoenician control in the contemporary era, are devoid of noble metals in their composition, and the relatively recent PGE deposits in the Sierra of Ronda are attributable to chromitite seams [46].

Therefore, new hypotheses should be taken into consideration. The Palermo Stone is one of the most well-known historical documents of Ancient Egypt and reports on a block of black basalt the annals of the first pharaohs and the main events during their kingdoms [47, 48]. It indicates that already since the Fifth dynasty (around 2450 BCE) commercial expeditions were carried out in the land of Punt (identifiable between Northern Ethiopia and the Somali-Eritrean coastal strip), which was rich in luxury goods such as incense, ivory, myrrh and electrum (designated by the specific term ḏʿm) [49, 50]. In 1495 BCE, an expedition of Queen Hatshepsut was well documented in the inscriptions and bas-reliefs of her temple to the god Amun in Thebes and gold and electrum were among the imported goods. The expeditions were organized with flotillas for goods transport, initially proceeding up the high Nile and its tributaries and later following the coastal way of Red Sea. In the vast territory of the Nilotic basin, the presence of different platinum minerals is only ascertained in the alluvial deposits of Yubdo in Northern Ethiopia, where in 1924 platinum was officially "discovered" by Italian geologists who organized extraction on an industrial scale. Both the deposit and nearby areas, including the valley of the Birbir River, were worked for gold by the local population since time immemorial, but platinum was discarded with processing residues since its collection was severely punished by law in order to counter fraud [51, 52]. Presence on the spot of excavations due to gold mining activities, even of considerable proportions, was locally attributed to the "Egyptians". The area of Yubdo is located on the right bank of the Birbir River, with strong seasonal flow changes and tributary of the only Ethiopian river navigable even in modern times, the Baro, an affluent of the White Nile. In Ethiopia, platinum reports outside the territory of Yubdo lack credibility [53] and also recent mineralogical surveys locate in the area possible findings of platinum of alluvial origin [54], reaching in 1940 the peak extraction of 8,230 troy ounces (around 255 kg), among the world's largest productions [55] (Fig.5).

Fig. 5 – Partial map of the Nile River Basin
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Chemical analysis on samples of crude platinum nuggets [56-58], separated with the lens from free gold generally present in the pan concentrates, ascertained that alluvial platinum is predominantly isoferroplatinum Pt3Fe with certain grains of tetraferroplatinum PtFe. The typical composition is the following: platinum around 79-90% by weight, iron between 8-11%, and various PGE inclusions such as an alloy of osmium and iridium (1.41%), iridium (0.82%), rhodium (0.75%), palladium (0.49%), and gold (0.49%). The mineral composition seems sufficiently composite to allow an identification of the metal origin, although alluvial samples variability could create difficulties. However, recent investigations by the Centre de Recherche des Musées de France with non-destructive spectroscopic techniques, e.g. XRF, SEM-EDS, or even more advanced technologies such as Particle Induced X-ray Emission -PIXE- [59, 60] for the analysis of any extant platinum-bearing material, confirmed the absence

of other particles of the same metal on the casket of the princess.
Lots of Nile water passed since the journey of the chiseled grain: meanwhile new "conquistadores" are taking over the unrestful Punt region, and the mystery of its origin is destined to remain unsolved.

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