

# Rhenium Oxide, Potassium Perrhenate, Iron and Aluminum Hydroxochlorides, Barite, and Celestine in Lunar Regolith

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The continuing study of lunar regolith with a JSM-5610LV low-vacuum electron microscope equipped with EDS JED-2300 JEOL (Japan) made it possible to detect several oxygen-bearing phases and associated native metal in one case. These findings are of special genetic interest. The case in point is an intergrowth of native rhenium with rhenium oxide, oxides of rhenium and potassium, hydroxides of iron and aluminum, and sulfates of barium and strontium.

*Rhenium oxide and potassium perrhenate intergrown with native rhenium.* Native rhenium was first found in a regolith sample delivered by A/S Luna 24 from Mare Crisium [1]. Some rhenium particles up to 10  $\mu\text{m}$  in size were also found in close intergrowths with micrometer-sized crystals in material delivered by A/S Luna 16 from Mare Fecunditatis [2]. Contrast BSE images of these crystals suggest that they belong to significantly lighter elements. Spherical individuals of the particles, in turn, consist of aggregates of rhenium nanocrystals. The particles include traces of Cu and Fe (total content <2%). As far as we know, metallic rhenium was not used in the construction of lunar automatic stations and it could not be introduced into the sample at any stage of its preparation for the analysis.

Native rhenium was first found on Earth as micrometer-sized intergrowths in wolframite from the Transbaikal region [3]. The mineral from this region was marked by a high purity (99.9% Re). A year later, native rhenium was identified as dustlike particles in Ni-bearing iron and silicates of the Allende meteorite [4]. The mineral from the meteorite consisted of 97% Re and 3% Ru.

The new finding of native rhenium in a tiny sample taken at a distance of ~300 km from the first sampling site once more confirms the abundance of heavy metals on the Moon. The previous finding of native rhenium

was ascribed to the relict component of cosmogenic meteorite assemblages [1]. However, new findings of native rhenium in the regolith from Mare Fecunditatis, and especially its nanoglobular morphology, which is very similar to that of previously described native molybdenum [5], suggest the lunar exhalative origin of this metal.

In addition, the regolith sample from Mare Fecunditatis contained irregular and well-shaped micrometer-sized particles in close intergrowths and near spherical aggregates of the native rhenium. The particles appeared significantly darker than native rhenium in a back-scattered electron image. Although we could decipher rather quickly the composition of native rhenium, attempts to determine the composition of these particles were unsuccessful. The contrast BSE image only suggested that they have a significantly lower than average atomic number.

We managed to determine the composition of these aggregates only on a JSM 5610LV (JEOL) scanning electron microscope equipped with a JED-2300 (JEOL) energy-dispersive spectrometer under lowered accelerating voltage.

The irregular particles (Fig. 1a) in close intergrowths with native rhenium turned out to be rhenium oxide. However, quantitative analysis of its X-ray spectrum (Fig. 1b) was impossible because of the fluorescent extinction of oxygen in the organic adhesive tape. The characteristic distribution patterns of oxygen and rhenium unambiguously indicate that these particles are rhenium oxides intergrown with metallic rhenium, but it is impossible to determine their exact composition.

In addition to irregular particles, native rhenium is also found with a rim of microcrystals and their intergrowths (Fig. 1a). Point analysis of spherical bright particles showed that they represent native rhenium. The spectrum from the surrounding particles contained peaks of Re, O, and K (Fig. 1c). Separate crystals analyzed under accelerating voltage of 8 kV only yielded the K/Re ratio of 1 : 1. The fluorescence of substrate prevented the determination of oxygen content.

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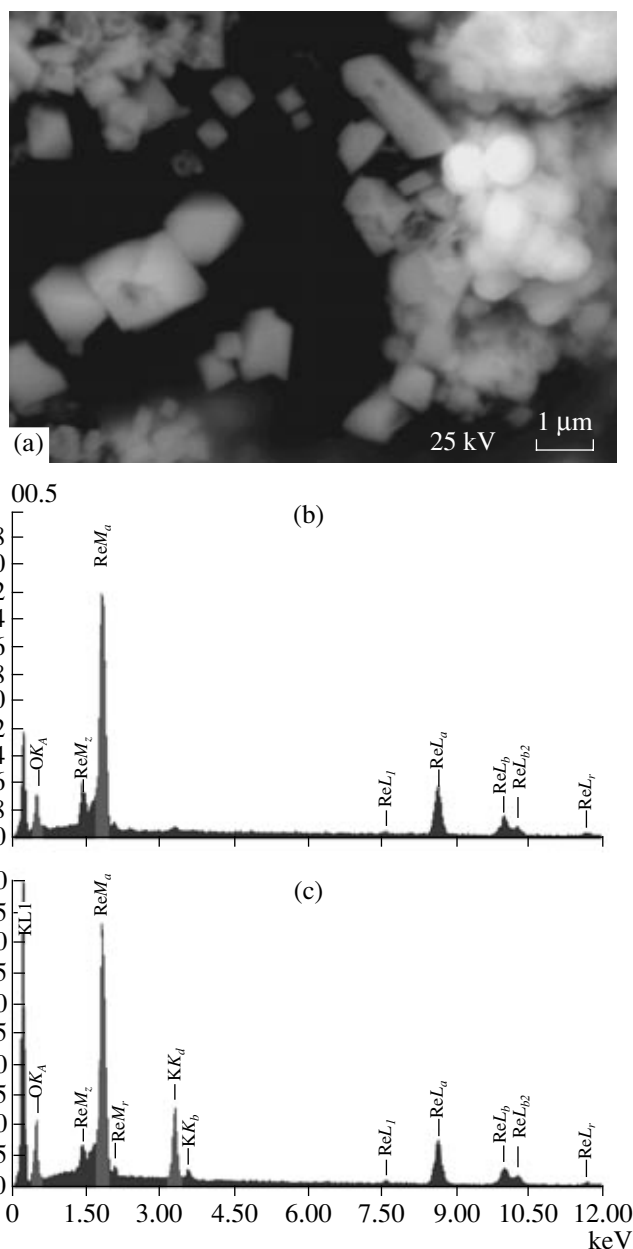
The distribution patterns of O, Re, and K showed that they are contained in well-shaped particles. Since the most stable compound of these three elements is potassium perrhenate,  $KReO_4$ , with Re : K = 1 : 1, the discovered particles can be identified as potassium perrhenate.

The potassium perrhenate was already found in the exhalative products of Kudryavyi Volcano. However, no native rhenium and its oxides have yet been found here.

Formation of rhenium oxides and potassium perrhenates with Re in the highest oxidation state on the Moon seems to be hardly probable. Therefore, we are compelled to assume that both minerals formed on the Earth during oxidation of the fine-dispersed aggregate of native rhenium, according to the reaction  $4Re_0 + 7O_2 = 2Re_2O_7$ . Since the newly formed rhenium oxide is hygroscopic, it interacts with atmospheric water vapor to form rhenium acid ( $Re_2O_7 + H_2O = 2HReO_4$ ), which, in turn, could react with regolith to produce potassium perrhenate.

The close association of all three rhenium phases and the presence of primary metallic rhenium indicate that the aforesaid reactions are in progress. However, the appearance of the aggregates of these three phases has not changed two years after their discovery and identification. However, the native rhenium, which should have been corroded, has retained the ideal spherical undisturbed shape. This is inconsistent with the aforesaid conclusion. In addition, K-bearing phases are absent in the closest surrounding of these aggregates, and selective transportation of K over hundreds of micrometers looks highly hypothetical.

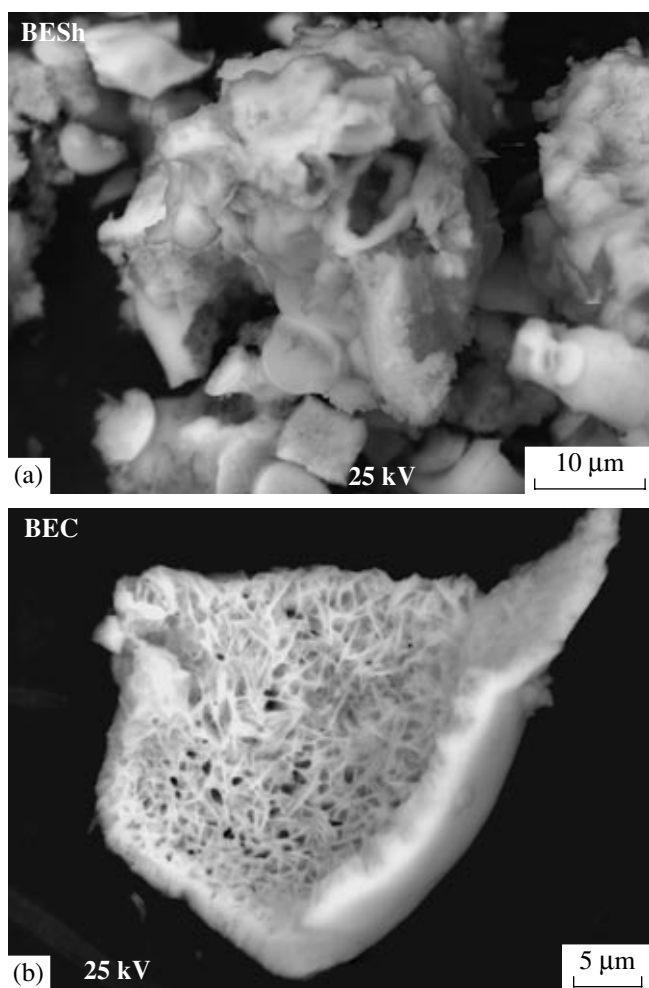
Therefore, we consider an alternative hypothesis of lunar exhalative origin of potassium perrhenate with simultaneous low-temperature formation of spherical aggregates of native rhenium from nanoclusters. At the first stage, an abrupt drop in pressure and temperature can foster the formation of single-element nanoclusters of metals in high-temperature (heavy-element-rich) magmatogenic or impact-related gas jets. At the second stage, these clusters can combine with other clusters at significantly lower temperatures owing to significant surface energy. As was mentioned in the literature [6, 7], with decreasing temperature, the Wulff diagram, reflecting distribution of surface energy, acquires a cloudlike shape, which depends on structural characteristics of a nanoparticle. This indicates that, at lower temperatures, the nanocrystals will aggregate with other particles having a similar surface energy distribution. They will be combined following the principle of 3D puzzle in certain mutual crystallographic positions. Correspondingly, submicrometer particles of native metals and alloys could grow at low temperatures from the gas phase in interstices and fissures of the rocks under conditions close to cosmic vacuum on the lunar surface. Such a mechanism was theoretically substantiated by Askhabov et al. [8].



**Fig. 1.** Luna 16. (a) BSE image of intergrowths of rhenium oxide and potassium perrhenate with native Re (bright); (b, c) X-ray spectra of rhenium oxides and potassium perrhenate, respectively.

In addition to magmatic and impact processes typical of the Moon, such a low-temperature rapid accretion provides the multiple repetition of the process under different parameters and compositions of initial gas. Thus, the accretion can produce a great number of various metals and their composites in the form of micro- and nanoparticles.

Potassium perrhenate can form simultaneously with spherical aggregates of native rhenium from nanoclusters at low temperatures. Rhenium oxides (not obligatorily  $Re_2O_7$ ) could grow in the course of both the for-



**Fig. 2.** Luna 20. BSE images of hydroxychlorides of (a) iron and (b) aluminum.

mation of other rhenium phases and the further decrease in temperature. Such a process requires the presence of some oxygen in the gas jet at the low-temperature stage and its complete absence at high temperatures. This type of environment was not heretofore assumed for lunar conditions.

**Iron and aluminum hydroxychlorides.** A few particles of iron hydroxychloride were found in the lunar highland regolith sample delivered by A/S Luna 20 (Fig. 2a). In addition, particles of aluminum hydroxychloride were found at the surface of native aluminum in the same sample (Fig. 2b). The finding of iron and aluminum hydroxychlorides in the regolith sample is inconsistent with existing concepts on the predominance of extremely low humidity at the lunar surface.

Two hydrous aluminum hydroxychlorides—lesu-kite  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  and cadwaladerite  $\text{Al}(\text{OH})_2\text{Cl} \cdot 4\text{H}_2\text{O}$ —are known on the Earth. They are produced by interaction of aluminum hydroxides  $\text{Al}(\text{OH})_3$  with Cl-bearing solutions in volcanic fumaroles (Tolbachik, Kamchatka) and saline waters under arid conditions

(Cerro Pintados nitrate deposit in Atacama, Chile). Naturally, these processes cannot occur at the lunar surface.

The finding of akaganeite,  $\text{FeO}(\text{OH},\text{Cl})$ , in glassy particles from the regolith delivered by A/S Luna 24 was previously reported in [9]. At that time, we suggested that akaganeite was an authigenic lunar mineral, because it could not be formed and preserved in the regolith sample while on Earth.

Now, based on new findings, we believe that akaganeite could form on the Earth, after the delivery of a lunar regolith sample, by hydration and oxidation of a primary iron chloride (lawrencite  $\text{FeCl}_2$  or molysite  $\text{FeCl}_3$ ) according to the following reactions:  $4\text{Fe}^{2+}\text{Cl}_2 + \text{O}_2 + 6\text{H}_2\text{O} = 4\text{Fe}^{3+}\text{O}(\text{OH},\text{Cl}) + 8\text{HCl}$  or  $2\text{Fe}^{3+}\text{Cl}_3 + 4\text{H}_2\text{O} = 2\text{Fe}^{3+}\text{O}(\text{OH},\text{Cl}) + 6\text{HCl}$ . Molysite  $\text{FeCl}_3$  is the characteristic exhalative product of basaltic magma (Tolbachik, Vesuvius, and others). Lawrencite  $\text{FeCl}_2$  was first found in the Tazewall meteorite. This mineral cannot form in fumarole vents because of the vent's highly oxidizing environment. Only its hydrous analogue, rokunnite  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ , is found on Earth. However, this mineral is even more likely to form during volcanic exhalations at the lunar surface than molysite. It should be taken into account that both iron chlorides are highly hygroscopic. Under atmospheric conditions, they rapidly adsorb a large amount of water and can be dissolved in it. The solution thus formed readily interacts with atmospheric oxygen to hydrolyze and oxidize according to the reactions mentioned above. The reaction can further proceed up to the point of complete removal of Cl and the formation of hydrous iron hydroxides. In our case, this process is facilitated and accelerated by a fine-dispersed state of the initial chlorides. Only a few minutes are required for complete hydration and oxidation of micrometer-sized inclusions of primary chlorides. This time is significantly less than the time required for sampling and preparation of the studied regolith particles.

We carried out a check experiment to study the instability of akaganeite in a dry state. Segregations of new phases formed after metallic constructions of the passenger liner *Titanic* were dredged in 1990. In addition to iron oxides and hydroxides, significant amounts of akaganeite were detected in the newly formed phases [10]. We repeatedly studied the akaganeite-bearing aggregates preserved at room temperature for 12 years. Electron microscopic investigations showed no significant changes in the mineral composition and proportions of various iron hydroxides in the samples. Hence, akaganeite was preserved without alterations in air-dry samples for more than 10 years.

We believe that formation of aluminum hydroxychloride in the studied lunar regolith was governed by the same mechanism as the akaganeite formation i.e., by hydration of primary aluminum chloride under terrestrial conditions during sample preservation and

specimen preparation. On the Earth's surface,  $\text{AlCl}_3$  even is less stable than anhydrous iron chlorides.

The close association with native aluminum is crucial for explaining the origin of hydroxychlorides in the regolith from A/S Luna 20. We believe that both native aluminum and hydroxylchloride formed from volcanic-exhalative  $\text{AlCl}_3$ . It is highly possible that the origin of native aluminum relates to the reduction of  $\text{AlCl}_2$  under lunar conditions. However, not all of the  $\text{AlCl}_3$  was reduced. A part of  $\text{AlCl}_3$  was left in aggregates of native aluminum, while another part formed encrustation on glass contained in the pores. After depressurization of the initial regolith sample, aluminum chloride was hydrolyzed by atmospheric water vapors to form hydroxylchloride, according to the reaction  $\text{Al} + \text{AlCl}_3 + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH},\text{Cl})_3$ .

Microinclusions of supposedly aluminum chloride or one of its hydrated analogues  $\text{AlCl}_3 \cdot n\text{H}_2\text{O}$  were found in native aluminum of clay-salt concretions from mud-volcanic products of the Bulla Volcano, Caspian Sea (M.I. Novgorodova, private communication). The exact composition of this mineral could not be determined due to its high ability to absorb water. Only qualitative determination of its chemical composition was performed. One of the characteristic minerals of the nodules was akdalaite,  $4\text{Al}_2\text{O}_3 \cdot \text{H}_2$ , the possible dehydration product of aluminum hydroxides. This assemblage is analogous to the lunar one.

**Barite  $\text{BaSO}_4$ .** A dense group of particles, which have a higher brightness than surrounding phases and matrix Al in BSE images, was found on the surface of one of the large native aluminum particles (regolith sample, A/S Luna 20) in the surroundings of aluminum hydroxylchloride particles and small silicate particles. Their X-ray spectrum contains high peaks of Ba, S, and O; moderate peaks of Al; and insignificant peaks of Mg, Si, Cl, and Ca. Low-intensity peaks were generated by fluorescence of closely spaced particles of silicates and aluminum hydroxylchloride. The peak of Al was also recorded in the spectrum of Al particles that contained all studied objects. Correspondingly, the bright particles consist of Ba, S, and O. This fact was confirmed by distribution maps of all aforesaid elements over the area.

Barite is characterized by high purity. Based on recalculation of composition after the extraction of matrix, its formula corresponds to  $(\text{Ba}_{0.98}\text{Sr}_{0.02})_{1.00}[\text{SO}_4]$ .

One more barite particle with distinct crystallographic shapes (Fig. 3a) was found in the regolith sample from Mare Fecunditatis. An X-ray spectrum of this particle shows no peak of alien and trace elements, while qualitative calculation of its composition (within the limits of accuracy) yielded an almost ideal formula.

On the Earth, barite is widespread in hydrothermal rocks of variable genesis, temperature, and depth. Its formation is facilitated by high oxygen fugacity, when sulfur occurs in an oxidized state. Otherwise, barium

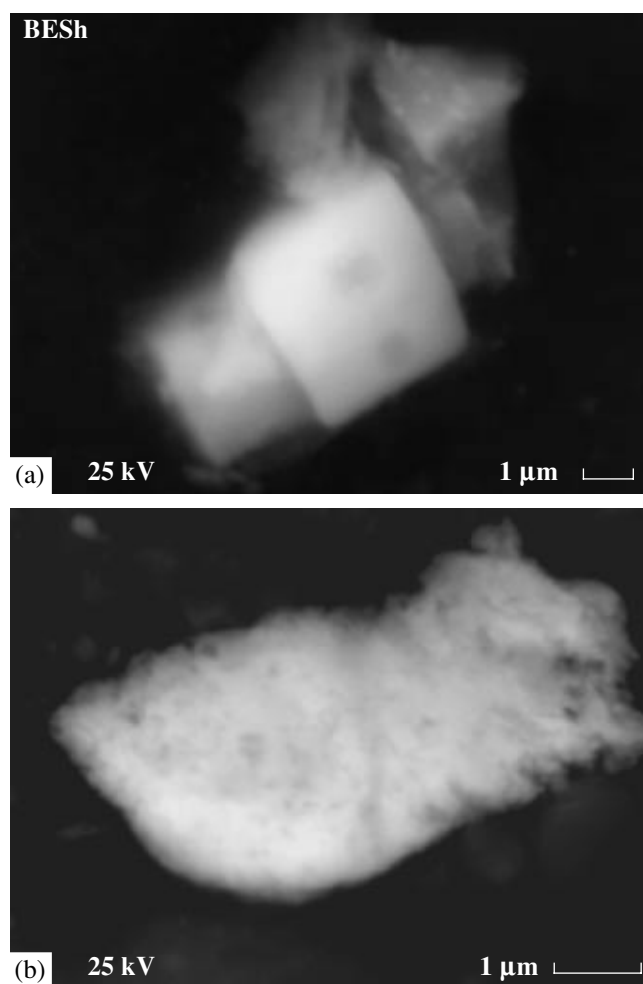


Fig. 3. Luna 16. BSE images of (a) barite and (b) celestine.

carbonates or silicates are precipitated. Barite often forms in zones of mixing of deep-seated reduced-chloride waters with near-surface oxygen-saturated waters. Barite is less common in magmatic rocks. However, it is a typical mineral in some alkaline rocks (primarily, late low-temperature carbonatites). Barite also occurs among late magmatic products of agpaitic rare-metal granites of the Khaldzan-Buregteg Massif in western Mongolia [11]. Magmatic barite also forms in fumaroles during volcanic exhalations. Barite is chemically stable and has low solubility. Therefore, this mineral can accumulate in the weathering crust.

The formation of barite on the Moon seems hardly probable. One can suggest that barite formed in the lunar regolith samples owing to hydrolysis of a hypothetical mineral—barium sulfide ( $\text{BaS}$ )—the analogue of oldhamite and niningerite  $\text{MgS}$ . This mineral is hydrolyzed under terrestrial conditions during contact with water-vapor-saturated air according to the multistage reactions  $2\text{BaS} + 2\text{H}_2\text{O} + 2\text{O}_2 = \text{BaSO}_4 + \text{Ba}(\text{OH})_2 + \text{H}_2\text{S}$  (I),  $2\text{Ba}(\text{OH})_2 + 2\text{H}_2\text{S} + 4\text{O}_2 = 2\text{BaSO}_4 + 4\text{H}_2\text{O}$  (II).

The sum of reactions (I) and (II) yields reaction (III)  $\text{BaS} + 2\text{O}_2 = \text{BaSO}_4$ , which does not proceed under dry conditions. The protomineral BaS can be of lunar volcanic-exhalative or, less probable, cosmogenic origin. As is known, oldhamite and niningerite are characteristic components of some chondrites.

Alternatively, barite can represent a late magmatic mineral formed during the crystallization of subalkaline lunar basalts or an exhalative product (by analogy with terrestrial fumaroles).

*Celestine*  $\text{Sr}[\text{SO}_4]$ . A separate particle  $\sim 10 \mu\text{m}$  in size was found in one specimen from Mare Fecunditatis (Fig. 3b). It represented a homogenous, randomly oriented aggregate of nanocrystals. According to microprobe data, the aggregate consists of Sr, S, and O. Calculations showed that the mineral is pure stoichiometric  $\text{Sr}[\text{SO}_4]$ .

On Earth, celestine mainly occurs in carbonate and sulfate sedimentary rocks. Like barite, it often forms in the zone of mixing of deep-seated reduced-chloride waters with near-surface oxygen-saturated waters. Celestine is also common in hydrothermal rocks related to the high-alkaline intermediate and mafic rocks, as well as in late low-temperature hydrothermal–metasomatic carbonates. Like barite, celestine forms under oxygen-rich conditions with the predominance of sulfate sulfur over a sulfide variety.

As is evident, the formation of celestine on the Moon is hardly probable. Like barite, the mineral found in the lunar regolith was presumably formed by hydrolysis and oxidation of the lunar protomineral SrS under terrestrial conditions following the reaction  $\text{SrS} + 2\text{O}_2 = \text{SrSO}_4$  (with the participation of water vapor according to the reaction for barite). This assumption is also supported by the fine aggregate structure of celestine.

The discovery of common terrestrial minerals, celestine and barite, in the lunar regolith suggests the possible existence of two new minerals, alkali earth sulfides SrS and BaS, on the Moon.

Thus, we can make the following conclusions:

(1) Some of the discovered minerals (native rhenium, molybdenum, and, possibly, some others) presumably formed in two stages: formation of nanosized metal clusters, their aggregation into micrometer-sized particles at low temperatures, and simultaneous forma-

tion of their oxides. An alternative model suggests their formation by decomposition and oxidation of native rhenium under terrestrial conditions.

(2) Findings of common terrestrial minerals, such as celestine, barite, and Fe–Al hydroxychlorides in the lunar regolith suggest the existence of an exotic (anhydrous) volcanic-exhalative mineralization on the Moon. The mineralization is represented by rare or new mineral phases (SrS, BaS,  $\text{AlCl}_3$ , lawrencite  $\text{FeCl}_2$ , or molybdate  $\text{FeCl}_3$ ). Alternatively, we should assume a limited contribution of oxygen during the synthesis of minerals from gas jet.

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