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GEOCHEMISTRY

Association of Carbon-Rich Substance and Native Molybdenum in a Lunar Regolith from Mare Crisium

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New finds were made during continuing investigations of minerals in the regolith with a JSM 5610LV low-vacuum electron microscope equipped with EDS JED-2300 (JEOL, Japan). Unlike previous works aimed at studying the finest samples of regolith delivered by A/S Luna-16 (Mare Fecunditatis), Luna-20 (continental ground), and Luna-24 (Mare Crisium), this work was focused on the largest fragments (up to 1 mm in size) from Mare Crisium. The specimen contained regolith fragments extracted from the deepest part of the core corresponding to a depth of 1.84–1.89 m (24184.4–4.9). Numerous attempts were made previously to find interesting mineral phases in such coarse fractions, but nothing interesting was found so far. However, some specimens prepared recently appeared extremely interesting. The specimens were prepared using simple technology: individual particles were taken with a porcupine needle and mounted on two-sided carbon tape preliminarily stacked to the aluminum table of a scanning microscope. The free surface of the table was covered by graphite glue to avoid fluorescence extinction of aluminum.

Our attention was attracted to a large glass splinter (Fig. 1a). It is seen that the lower part of the particle is covered by fractured crust in some places. In the back-scattered image, the crust is significantly darker than particles of native metals at the particle surface, indicating that its average atomic number should be significantly less than that of metals. The X-ray energy-dispersive analysis of this crust in different points showed that it contains, besides carbon and oxygen, only molybdenum peaks. If we ascribe carbon and oxygen to fluorescence in the underlying film, then the crust consists only of Mo. This is obviously inconsistent with its contrast pattern in back-scattered images. We could solve this problem by detailed study of the splintered edge of the glass particle (Fig. 1b). The rupture of the crust along the chip allowed us to see its two-layer structure. The BSE image of the lower layer adjacent to the glass has brightness typical of pure metals, whereas the upper layer is significantly darker even for the matrix glass. The total thickness of both layers at the rupture is too small (no more than 0.5 μm) to determine quantitatively the chemical composition of constituent layers in the scanning electron microscope, but the thickness is sufficient for qualitative analysis.

The preliminary examination of X-ray spectra at the end surface of the ruptured crust confirmed the presence of carbon, oxygen, and molybdenum. Then, the accelerating voltage was decreased to 8 kV in order to reduce maximally the analysis zone and improve conditions for the generation of peaks of light elements, in particular, carbon and oxygen, retaining thereby the possibility to excite peaks of the Mo*L*-series. The crustal fragment broken off in the rupture zone was taken for analysis (Figs. 1c, 1d). The spectrum taken from the central bright (heavy) part of the particle is shown by light color (Fig. 1e), whereas the spectrum recorded from its dark (light) peripheral part is imposed on the image by a dark color. It is seen that the peripheral part of the particle has a significantly higher content of carbon and oxygen than its bright core. Figure 1d shows the secondary electron image of the same particle. In this case, the contrast depends mainly on their morphologies rather than the average atomic number, as in the case of BSE images. The comparison of the BSE image (Fig. 1c), secondary electron image (Fig. 1d), and microprobe data on elements indicates that the central (bright) part of the particle consists of native molybdenum with a light coating dominated by carbon and oxygen. Semiquantitative calculations showed that this film likely contains an insignificant amount of sulfur. However, this assumption remains to be proved.

Thus, we consider that the crust consists of two layers: an internal native molybdenum layer and an external oxygen-bearing carbon-rich substance with possible sulfur admixture. The metallic molybdenum is subordinate or entirely absent in the external layer.

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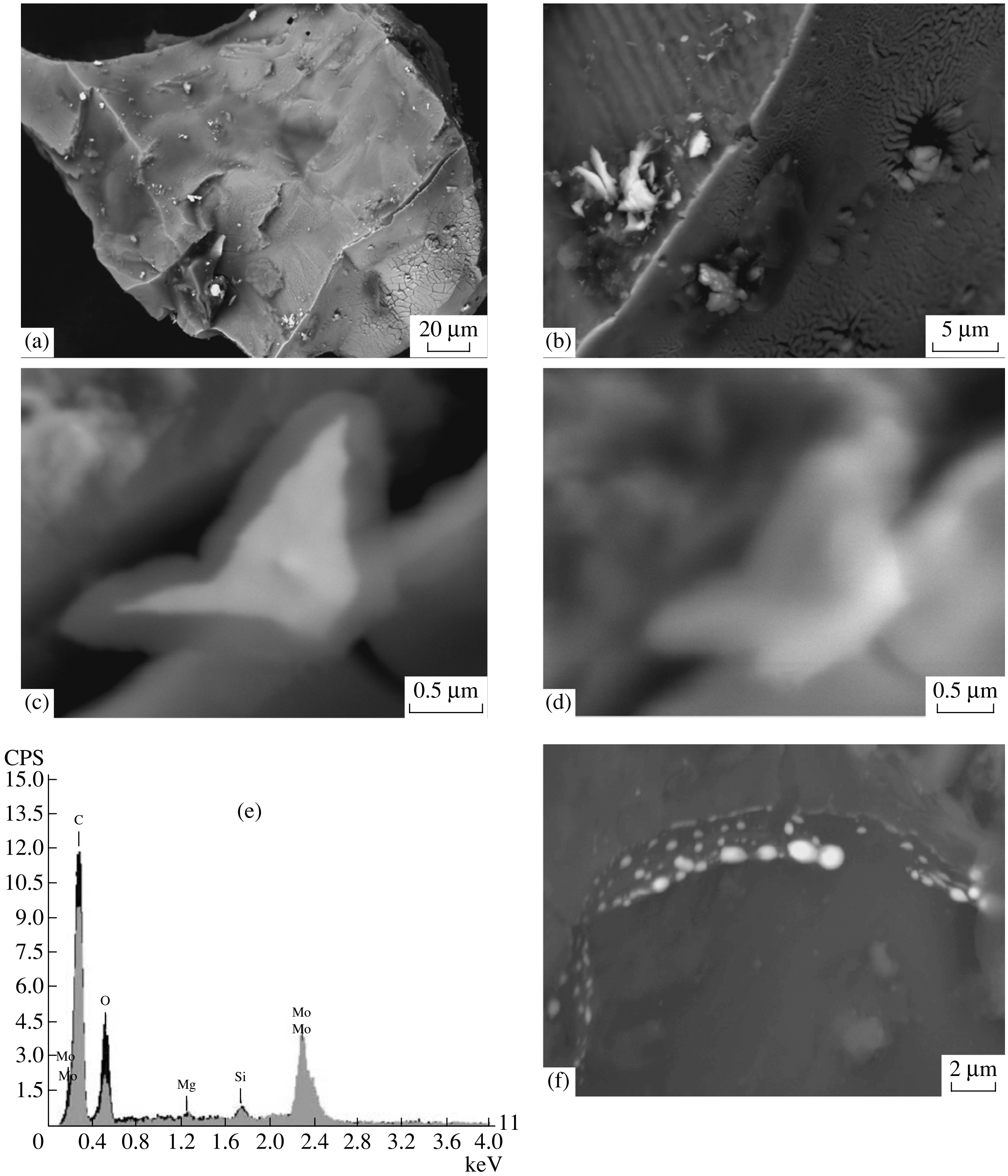

Fig. 1. Crust of native molybdenum on the glass fragment (based on study of samples delivered by A/S *Luna24*). The crust is covered by a carbon–oxygen film. (a–c, f) BSE images; (d) secondary electron image; (e) comparison of ED spectra from internal (light spectrum) and external (black) parts of the particle shown in (c).

Noteworthy is the fact that native molybdenum is observed in other splintered facets of the glass particle as chains of spherical aggregates up to 1 μm in size. They are developed along the walls of exposed cavities and fractures (Fig. 1f). However, they lack an organic film in this case. Hence, the carbon-rich film postdated the molybdenum coating, when the fissures, along which Mo clusters penetrated the glassy matrix, were already sealed.

It was initially suggested that the carbon-rich film could form at the surface of particles due to the impact of exhausts of rocket engines of the automatic station lander. However, this assumption is ruled out by the following fact: the rock fragments were sampled from a depth of more than 1.84 m, and samples taken from the overlying intervals show no signs of contamination.

Native molybdenum has not yet been found at the Earth's surface. Therefore, we do not have any terrestrial analogue for interpretation of the described association of native molybdenum and the carbon-rich phase. The nature of the carbonaceous phase cannot be deciphered by the applied methods. Therefore, we suggest two equally possible interpretations: the detected phase represents either a high-molecular organic hydrocarbon (bituminous substance) or a significantly carbon-rich graphitelike (carbonaceous) substance.

Thus, we can propose two hypotheses to explain the formation of this association: impact (meteorite–comet) nature or exhalative–fumarole nature.

In the case of external impact, we should take into consideration the short-term nature of the process: the high temperature and, possibly, high-pressure phase gave way to a low-temperature phase in fractions of a second (maximum, in a few seconds). Nevertheless, a molybdenum film 0. 25 μm thick could be formed even during this short time if the molybdenum content in the impact area was sufficient. Hence, a significant content of molybdenum should be contained either in the impactor or target object.

The low-temperature stage presumably existed over a longer period than the high-temperature one. This stage could promote the continuation of processes of precipitation of the carbonaceous phase and growth of the micrometer-sized molybdenum spherules in the limited space of cavities by the cluster assemblage mechanism considered in [1]. We do not have any data to judge the real composition of the carbonaceous phase, except for the presence of carbon and oxygen mentioned above. If the impact hypothesis is true, carbon should be located in the impactor, whereas oxygen could be evaporated during the impact from both the impactor and the target, i.e., the lunar surface. Hence, we can assume that the impactor could be represented by both a meteorite and a carbon-bearing comet fragment. The presence of a large amount of molybdenum remains an open issue, because neither meteorites nor lunar substances contain such significant amounts of Mo.

For obvious reasons, high-molecular hydrocarbons and carbonaceous substances have not been reported in the high-temperature volcanic products in the Earth. However, finds of bitumens and cyclic hydrocarbons are known in the areas of low-temperature (solfatara stage) fumarole activity. The participation of hydrocarbons in the magmatism of any composition ranging from the felsic to ultramafic became evident a long time ago.

It is highly probable that hydrocarbons involved in the exhalative (basaltic marine) volcanism of the Moon could be accumulated in air-free conditions in the subsurface mouth parts of the fumaroles and near their vent on the Moon's surface. Thus, the aggregates of native molybdenum could be formed by nanocluster amalgamation during exhalative volcanism on the surface of fractures of gas-conducting channels [1]. With decreasing temperature at the later stage, the aggregates could be covered by solid hydrocarbons. The formation of native molybdenum in this case is constrained only by the sulfur potential in the volcanic gases, because the high potential of sulfur leads to the formation of molybdenite instead of molybdenum. It is conceivable that lunar volcanism was accompanied by large-scale exhalative deposition of different hydrocarbons ranging from methane to bitumens. The total weight of accumulated authigenic hydrocarbons can be higher than that of deuterium-bearing methane and ethane introduced to the moon with the solar wind [2, 3]. In our case, the association with native molybdenum allowed us to find hydrocarbon accumulations, because they could usually be missed due to specific features of the applied technique.

Thus, the chemical composition of the carbon-rich substance detected in our work can support both hypotheses mentioned above. Confirmation of the graphitelike nature of the substance would be an argument in favor of the hypothesis of the xenogenic impact origin of this association. On the other hand, the detection of high-molecular hydrocarbons in the carbonaceous films would unambiguously support their authigenic exhalative origin. The latter hypothesis is also indirectly supported by the significant content of oxygen and, possibly, sulfur. This composition is most probable for bitumens rather than for a carbonaceous substance. Anyway, it is difficult to estimate the impact of solar wind on the formation of a carbonaceous film without knowledge of its composition.

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REFERENCES

1. A. V. Mokhov, P. M. Kartashov, and O. A. Bogatikov, *The Moon under Microscope: New Data on Lunar Mineralogy* (Nauka, Moscow, 2006) [in Russian].
2. C. T. Pillinger, G. Eglinton, A. P. Gowar, and A. J. T. Jull, Phil. Trans. Soc. London **A 284**, 145 (1977).
3. R. C. Murphy, Origins Life Evol. Biosph. **3**, 450 (1972).