IMPACT-INDUCED FORMATION OF SUB-MICROSCOPIC MAGNETITE WITHIN CHANG'E-5 SULFIDE GRAINS. Z. Guo[1,2], C. Li[1], Y, Li[1], Y. Wen[1], Y. Wu[1], B. Jia[2], K. Tai[1], X. Zeng[1], X. Li[1], J. Liu[1] and Z. Ouyang[1], [1]Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, guozhuang@pku.edu.cn, [2]School of Earth and Space Sciences, Peking University, Beijing, China.

Introduction: Magnetite is essential in planetary science when addressing questions concerning ancient magnetic fields and indicators of life. Traditionally, the Moon is considered to be extremely reduced. Thus, the oxidation state of the lunar surface points to the formation of metallic iron rather than iron oxides [1].

In the Apollo era, some studies deduced the presence of ubiquitous sub-microscopic magnetite-like phases in Apollo soils, but there was no further in-situ mineralogical evidence for the presence of widespread magnetite crystals in lunar soils [2-3]. Although some micron-sized magnetite grains have been identified in lunar samples, they are closely associated with exogenous carbonaceous chondrite impactors [4].

China's Chang'E-5 mission successfully returned 1.731 kg of new lunar soils from the young lunar mare basalt unit [5]. Considering that the Chang'E-5 ejecta formed at a young age and was subjected to very limited late modification processes, information about the initial response to impact processes on the lunar surface can be obtained. Here we first report the sub-microscopic magnetite formed by eutectic reaction during the impact process in Chang'E-5 lunar soil, and the potential contribution of this magnetite formation to magnetic anomalies on the Moon.

Sample and methods: The Cheng'E-5 samples examined in this study consisted of the fine fractions of lunar regolith soils (CE5C0400YJFM00505 and CE5C0200YJFM00302). The iron-sulfide grains selection, focused-ion-beam sections' preparation and observation was performed by field-emission scanning and transmission electron microscopy (TEM) analysis. Electron energy-loss spectroscopy (EELS) were employed to measure the oxidation state of iron.

Results: *Overview of the iron-sulfide grains in Chang'E-5 lunar soil.* Angular and spherical iron-sulfide grains were observed in Chang'e-5 lunar soil, and the magnetite were confirmed in the interior of spherical iron-sulfide grains. TEM observations showed that the cross sections of the spherical iron-sulfide grains were elliptical with long and short axes of 2.5 and 1.5 μm, respectively, which is similar to the morphology of molten droplets (Fig. 1).

Quantitative TEM-energy dispersive X-ray (EDX) compositional maps indicated that tentacles of pure metallic iron (Fe^0) protruded from the entire surface of the spherical iron-sulfide grains at nearly equal intervals. In addition, the interiors of the grains contained abundant minute inclusions of Fe^0 and magnetite particles with sizes of ~100 nm, and the close spatial association of these two embedded phases suggested co-precipitation formation (Fig. 1). The matrix within the spherical iron-sulfide grains was identified to be intergrowth of troilite and pyrrhotite. EELS spectra and quantitative TEM-EDX results indicated that the iron-sulfide matrix also contained a certain amount of oxygen. Another feature of the spherical iron-sulfide grains was that many pores and scattered vesicles were observed at the edge and interior of the grains.

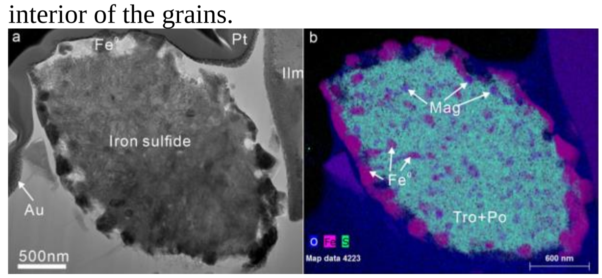

Fig. 1 Spherical iron-sulfide particles containing magnetite in Chang'e-5 lunar soil. Mag: magnetite; Tro + Po: troilite and pyrrhotite.

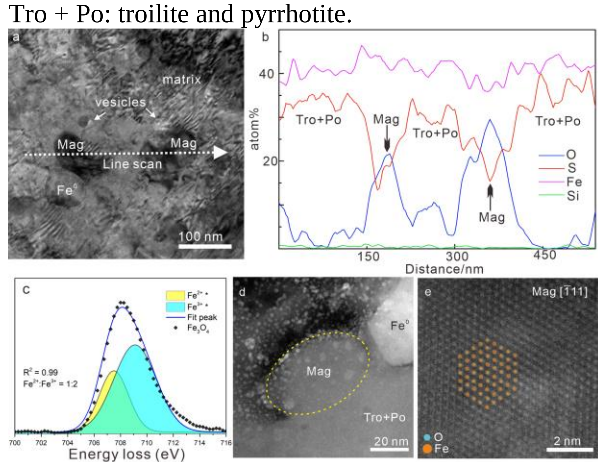

Fig. 2 Identification of magnetite (Mag) in the spherical iron-sulfide grains. Mag: magnetite.

Identification of magnetite in the iron-sulfide grains. TEM-EDX compositional maps and line profiles indicated that the iron-oxide minerals within the spherical iron-sulfide grains were O- and Fe-rich phases. The EELS spectrum of the iron-oxide particles within the spherical iron-sulfide grains showed a pre-peak near 530 eV, a weaker maximum at ~545–550 eV, and a dominant peak at 540 eV. These detailed EELS spectral structures near 530 eV indicate the presence of

Fe_2O_3 in the iron-oxide particles, and they have similar characteristics to those of Fe_3O_4. In addition, the Fe $L_{2,3}$ spectrum of the studied iron-oxide particles was intermediate between the standard single-valence spectra, and the Fe^{3+} to Fe^{2+} ratio in the iron-oxide particles was estimated to be approximately 2:1 by the EELS spectral peak fitting method, which is consistent with the chemical composition of magnetite. Both atomic-resolution annular dark-field scanning TEM images and high-resolution TEM images of the iron-oxide particles can be well indexed by magnetite (Fig. 2). The iron-oxide particles embedded in the spherical iron-sulfide grains were conclusively determined to be magnetite crystals.

Discussion: *Formation mechanism of magnetite.* Sub-microscopic Fe^0 particles coexisted with magnetite in the Chang'E-5 spherical sulfide grains indicates a formation mechanism of magnetite that is generally accepted in the field of hot-rolled steel sheets, namely, co-precipitation of magnetite and metallic iron from iron oxides by eutectoid reaction ($4FeO = Fe_3O_4 + Fe$) [6]. Numerous observations and simulations of extraterrestrial sample have demonstrated that a considerable amount of nonaffine O components from the surrounding O-containing matrix can be incorporated into the metal-sulfide phase and form Fe–S–O systems under high-temperature conditions during impact processes [7-8]. The ellipsoidal shape, large number of pores at the grain edges, and dissolved oxygen within sulfide grain all indicate that the studied iron-sulfide grains experienced high-temperature events and underwent melting. The absence of other molten phases attached to the spherical iron-sulfide grains and the equilibrium crystallization of magnetite and metallic iron within the spherical sulfide grain suggest that the molten iron-sulfide droplets most likely interacted with the silicate gas, which indicate that such unique iron-sulfide droplets were formed in the oxygen-bearing gas columns produced by a large-impact event on the Moon.

The FeO–FeS phase diagram was used to constrain the formation conditions of magnetite and pure metallic iron particles within the iron-sulfide grain, yielding a eutectic temperature of α-Fe, magnetite, and pyrrhotite of below 600 °C [9]. The magnetite and metallic iron particles were commonly euhedral and entirely embedded in the studied iron-sulfide grains, showing that they formed as solid-state precipitates at conditions below the melting point.

Based on the above discussion, a plausible scenario for the complex phenomenon within the iron-sulfide grain is that the molten iron-sulfide droplets reacted with the surrounding silicate vapor during a large-impact event. During the melt stage of iron-sulfide, the surrounding FeO-gas component reacted with the edges of the iron-sulfide droplets in a reduction reaction, forming a substantial amount of iron tentacles around the grains, and some of the FeO gas dissolved in the interior of the iron-sulfide droplet. During the subsequent rapid-solidification process, the FeO dissolved inside the iron-sulfide droplet decomposed to form sub-microscopic magnetite and Fe^0 particles.

Implications for the Lunar magnetic anomalies. Orbiting magnetometer data from Lunar Prospector suggests that magnetic anomalies may be associated with impact basins on the Moon, especially because lunar surface impact ejecta deposits are often strongly magnetized [10]. Wieczorek et al. (2012) performed numerical simulations of large-scale impacts. They found that chondritic projectile materials (Fe metal) from giant impacts can provide the highly ferromagnetic minerals to account for the intensity of the observed magnetic anomalies, and the impact-related materials may be the most plausible carriers of magnetic anomalies [11]. However, in addition to ferromagnetic materials directly injected by the impactor (e.g., FeNi), newly formed ferromagnetic minerals during the large-impact have not been considered. The results of this study of Chang'E-5 lunar soil indicate that iron-sulfide minerals undergo complex eutectic reactions during lunar impact to form highly ferromagnetic minerals (sub-microscopic magnetite and Fe^0), which could also be an important source of ferromagnetic material on the lunar surface.

There are two plausible implications of our study that can help to understand lunar crust magnetic anomalies: (1) ferromagnetic minerals on the Moon are questioned and we provide another candidate (magnetite) and (2) previous studies have only established the relationship between large-impact ejecta and magnetic anomalies, they did not focus on the transformation of the material during impact, and our study has established the soundly correlation between the magnetite formation and impacts.

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