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Cu-Fe-S Phases in Lunar Rocks

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Abstract

The sulfide minerals reported to be present in lunar rocks include troilite, mackinawite, the discredited mineral "chalcopyrrhotite", sphalerite, chalcopyrite, and cubanite. Apollo 12 sample 12021,134 contains these last two minerals, and the first chemical analyses of the Cu-Fe-S phases are presented. These minerals occur along cracks and grain boundaries within troilite and are probably exsolution products formed at low temperatures (*i.e,* 100°–300°C) from a cupriferous troilite.

Introduction

The opaque minerals, although constituting only a minor amount of a given sample, have proven useful as indicators of the genesis and cooling histories of the lunar rocks (*e.g.,* Reid, 1971; Taylor and McCallister, 1972; Taylor *et al,* 1973b). The most abundant opaque mineral is ilmenite, and many of the oxide phases in lunar rocks are unique (*e.g.,* armalcolite as per Anderson *et al,* 1970). In addition to native Fe metal, native Cu, and schreibersite, the remaining opaque minerals consist of sulfides.

The most abundant sulfide mineral in lunar rocks is troilite. It commonly occurs with native Fe in a eutectic texture and probably results from crystallization of an immiscible sulfide liquid (Skinner, 1970). Other sulfides which have been reported include mackinawite, $(Fe,Ni)_{1+x}S$ (Simpson and Bowie, 1970; El Goresy *et al,* 1971a; Taylor *et al,* 1971); the discredited mineral "chalcopyrrhotite" (El Goresy *et al,* 1971a, b); chalcopyrite (El Goresy *et al,* 1972b); and sphalerite (El Goresy *et al,* 1973; Taylor *et al,* 1973a). However, because of the small grain size of most of these minerals, troilite and sphalerite are the only sulfide minerals which have been chemically analyzed prior to this study.

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Cu-Fe-S Minerals

"Chalcopyrrhotite", a discredited mineral (Yund and Kullerud, 1966; Cabri, 1967), has been reported from Apollo 12, 14, and 15 rocks (El Goresy *et al,* 1971a, b; 1972a, b). It was described as a yellowish, chalcopyrite-colored phase which appears isotropic and is always found within troilite. It is probable that this phase is either talnakhite, a mineral originally described by Cabri (1967) and having a composition of $Cu_9Fe_8S_{16}$ (Cabri and Harris, 1971) near chalcopyrite or cubanite II, an isotropic form of cubanite (Genkin *et al,* 1966). These are the only two isotropic minerals in this portion of the Cu-Fe-S system. Chalcopyrite was qualitatively identified as occurring on the outside of native Cu rims around FeNi metal grains in Apollo 15 sample 15475 (El Goresy *et al,* 1972b). In light of the phase relations in the Cu-Fe-S system (Barton and Skinner, 1967) at low temperatures, the phase is more probably cubanite. The grain size was too small for positive identification. None of these Cu-bearing phases had been completely verified by quantitative chemical analyses prior to this study. A preliminary discussion of this investigation was presented by Taylor *et al* (1973c).

Within the Sample Library at the Lyndon B. Johnson Space Center (formerly the Manned Spacecraft Center), Houston, Texas, an Apollo 12 sample

(12021,134; a porphyritic basalt) was found to contain yellow Cu-Fe-S phases up to 10 μm across in association with troilite (Fig. 1). The phenocrysts, up to 2 cm in length, consist of pyroxenes with pigeonite cores mantled by augite-to-ferroaugite rims set in a variolitic groundmass of pyroxene and plagioclase. The opaques consist of ilmenite, native iron, troilite, titanian chromite, chromian ulvöspinel, and the Cu-bearing phases. These latter are *chalcopyrite and cubanite* (Figure 1). This is thus the *first reported occurrence of cubanite in lunar rocks* and the *first confirmation of the presence of chalcopyrite.*

TABLE 1. Electron Microprobe Analyses of Chalcopyrite and Cubanite in Apollo 12 Sample 12021,134

	cpy (4)*	$CuFeS_2$	cub (3)*	$CuFe_2S_3$
Cu	33.6	34.6	22.8	23.4
Fe	30.0	30.4	40.4	41.2
Co	0.85	--	0.87	--
S	35.2	35.0	35.7	35.4
Total	99.7		99.8	

*Number of analyses.

The chalcopyrite and cubanite appear to have similar genesis in that both occur along cracks and grain boundaries within troilite. Both show the appropriate anisotropism for the respective phases and, therefore, neither is the supposedly isotropic "chalcopyrrhotite." The microprobe analyses of these minerals, the first Cu-Fe-S mineral analyses reported from lunar rocks, are shown in Table 1. No other elements were detected in quantities $\geq$0.05 wt percent. It is noteworthy that this is the first report of the presence of cobalt in Cu,Fe sulfides. It would appear from the analyses that cobalt substitutes for iron in these structures. X-ray scans of an assemblage

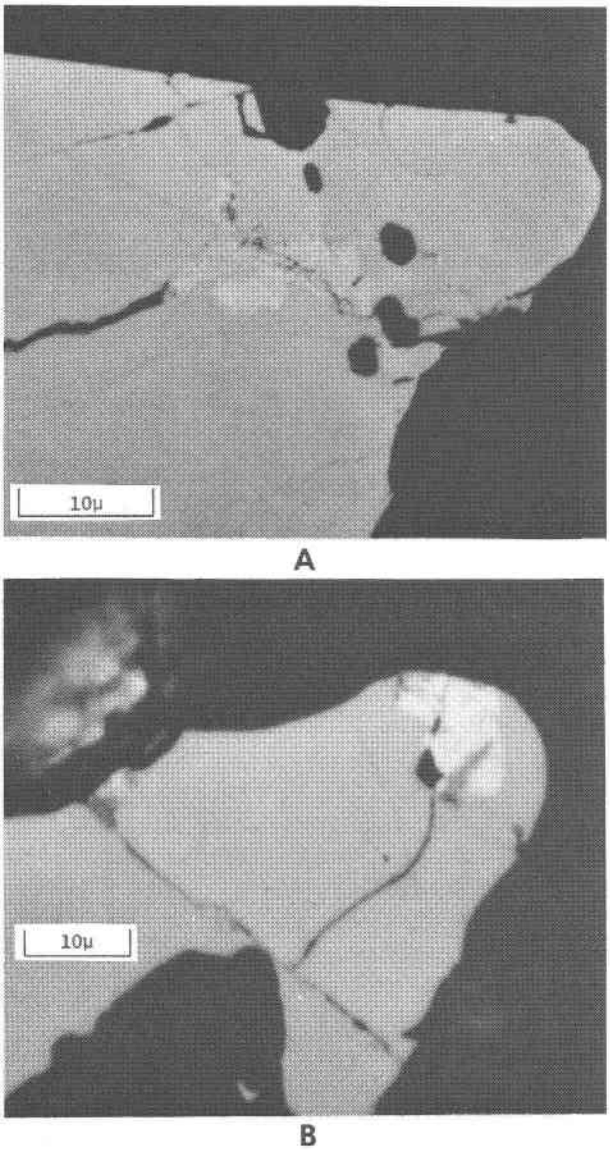

FIG. 1. Photomicrographs of (A) Chalcopyrite and (B) Cubanite in Apollo 12 sample 12021,134. Gray is troilite; light gray to white is Cu,Fe sulfide.

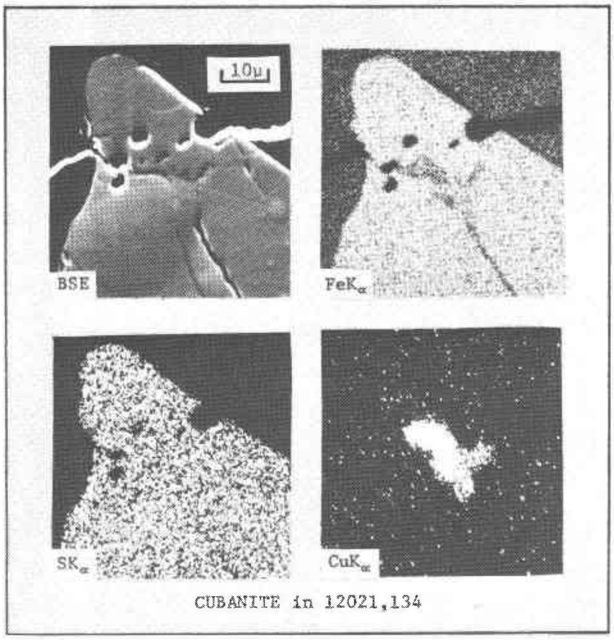

FIG. 2. X-ray scans of chalcopyrite within troilite in Apollo 12 sample 12021,134. The same specimin as shown in Figure 1A.

further verify the nature of the occurrence of these Cu,Fe sulfides (Figure 2).

Chalcopyrite is not stable with troilite, FeS, but is stable with pyrrhotite, $Fe_{1-x}S$, below 334°C (Yund and Kullerud, 1966). It is possible that the Fe-S phase immediately adjacent to the chalcopyrite is pyrrhotite; however, if present it is less than 10 μm in width. The troilite beyond this distance is stoichiometric FeS, and the Fe sulfide within this 10 μm distance could not be accurately determined due to the interference effect of the chalcopyrite and the diffuse contact with the Fe sulfide.

It is possible that the troilite contained small amounts of Cu at higher temperatures and that exsolution of this Cu occurred at lower temperatures as a result of slow subsolidus cooling. Subsolidus re-equilibration of sulfides to temperatures below 300°C is exemplified by the presence of mackinawite in many lunar troilites, a phase only stable below $\approx$150°C (Zôka *et al*, 1973).

Taylor *et al* (1973b) recently investigated the cooling rates of rock 12021 versus 12052. Based on the *Zr partitioning* between coexisting ilmenite, they concluded that rock 12021 has undergone considerable subsolidus re-equilibration as a result of slow subsolidus cooling. These data support the slow cooling (*i.e.,* re-equilibration) hypothesis for the genesis of the Cu-Fe-S minerals.

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