

## 6. Crystallography

### 6-1. New Modifications of Pyrrhotite Series Found in Interplanetary Dust Particles

Iron-nickel sulfides are the only phases present in all types of extraterrestrial materials. If sulfides in chondritic meteorites and interplanetary dust particles (IDPs) could be properly characterized in compositions, structures and parageneses, there would be a tremendous gain in our understanding of the early solar system history.

Two examples of our studies on sulfides of IDPs are described in this section. They are entirely new regarding natural or synthetic materials.

All of the diffraction experiments were carried out in a vacuum of  $6 \times 10^{-2}$  Torr by using diffraction equipment developed at BL-4B1 for a micrometer-sized specimen and a micro area of a larger sample.

#### 1) Analysis of chondritic interplanetary dust particle L2005 AE6

The chemical formula of this sample was determined to be  $\text{Fe}_{0.89}\text{Ni}_{0.02}\text{S}$ , analyzed with an electron probe micro analyzer (EPMA). The Laue pattern was obtained by a 30-min. exposure with an average ring current of 297 mA under ring operation at 2.5 GeV.

More than 40 Laue spots were recorded on the imaging plate. An important feature of the Laue pattern is that pairs of satellite reflections accompanied by missing main spots are observed (Fig. 1). This type of pyrrhotite series is classified as the NA type, and its  $c$ -axis is three-times longer than that of the niccolite (NiAs)-type subcell. The pairs of satellites indicate twinning of the NA type. From the positions of satellite reflections, the periodicity of the  $a$ -axis is estimated to be 41.84-times ( $N = 41.84$ ) longer than that of the niccolite type FeS subcell.

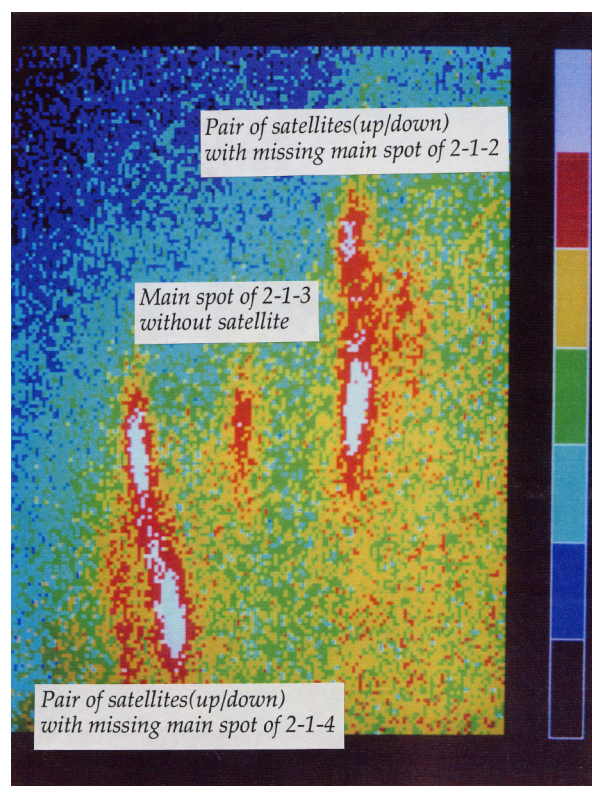


Figure 1.

Pairs of satellite reflections accompanied by missing main spots indexed 2-1-2 and 2-1-4. The main spot with an index of 2-1-3 has no satellite reflections.

#### 2) Analysis of the chondritic interplanetary dust particle L2005 AG17

The chemical formula was determined to be  $\text{Fe}_{0.83}\text{S}$  by the method mentioned above. A Laue pattern of  $1.6 \mu\text{m}\phi$  area of the sample was obtained by a 15-min. exposure with an average ring current of 291 mA. Diffuse streaks are observed along the zone. In order to clarify the diffuse streaks, six oscillation patterns were also taken by monochromatic synchrotron radiation ( $1.0005 \text{ \AA}$ ) with an oscillation range of 30 degrees for each to cover 180 degrees. All of the diffuse diffraction peaks can be well indexed based on the 3C-type pyrrhotite. Four weak, but distinct, powder lines are also observed in all oscillation patterns; these lines correspond to those of magnetite ( $\text{Fe}_3\text{O}_4$ ).

According to the chemical composition of the present sample and the existence of magnetite in the same sample, the crystal structure of the pres-

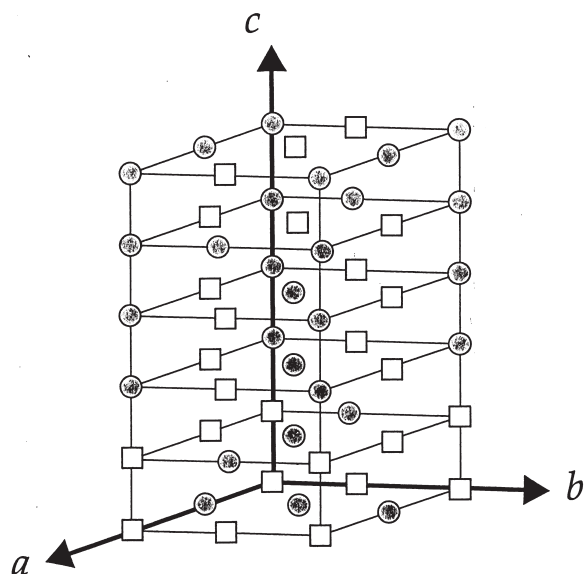
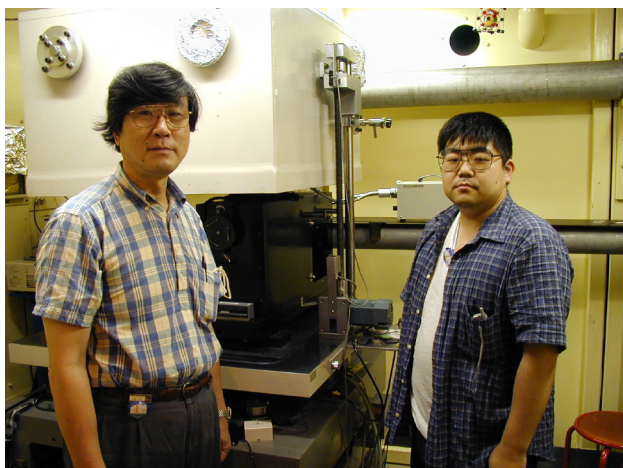


Figure 2. Structure of the newly discovered 3C pyrrhotite. Solely iron sites in octahedra among hexagonally close packing of sulphur atoms are shown with shaded circles and blank squares (vacancies).

ent 3C type must be different from that reported previously having a chemical formula of  $\text{Fe}_{0.875}\text{S}$ . The structure was analyzed based on the extraordinary conditions of missing reflections.

From the obtained structure illustrated in Fig. 2, the chemical formula of the present 3C type is represented as  $\text{Fe}_{0.5}\text{S}$ . The structure exhibits ‘homometry’ as well as ‘diffraction enhancement of symmetry’.

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## 6-2. Identification of Anhydrous and Hydrrous Interplanetary Dust Particles by X-Ray Diffraction Analysis

Interplanetary dust particles (IDPs: Fig. 3) are very small rocky particles coming from space. They are dust particles swept out from small-space objects, such as comets and primitive asteroids, that are composed of chemically very pristine solar-system material. Thus, the chemistry of IDPs is very pristine; the bulk chemical composition of a single IDP with a diameter of  $15\ \mu\text{m}$  is very similar to that of the Sun. IDPs are aggregates of numerous very fine mineral particles (Fig. 3), and each constituent particle is typically less than  $0.1\ \mu\text{m}$  in size. The species and relative abundances of minerals in IDPs reflect the physicochemical condition under which IDPs were formed.

We have utilized synchrotron X-ray radiation to characterize minerals in 15 samples of IDPs. X-ray diffraction analysis of IDPs can be possible only using synchrotron radiation [1], because IDPs are too small and porous to be characterized by X-rays from normal X-ray generators. We used a gandolfi camera, which gives a powder X-ray diffraction pattern of a single IDP. The experiment was carried out at BL-3A; the wavelength of the monochromated

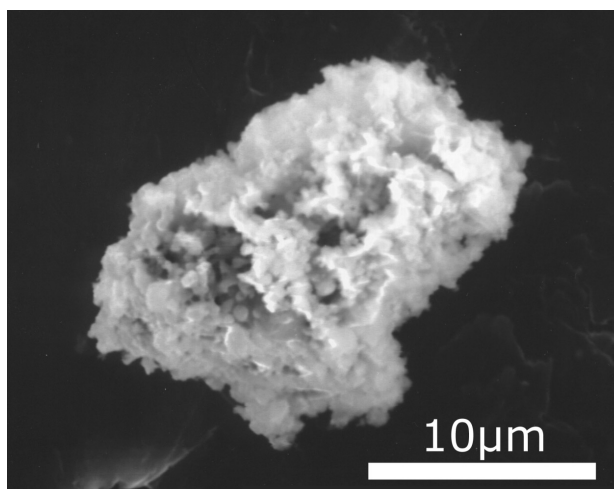


Figure 3. Back-scattered electron image of an interplanetary dust particle.

X-rays was  $2.161 \pm 0.007 \text{ \AA}$ .

The results of an analysis showed that there are two types of IDPs that differ in the bulk mineralogy [1]. The first type consists entirely of anhydrous minerals (Fig. 4a) and the second type contains hydrous minerals, such as saponite and serpentine (Fig. 4b).

The powder X-ray diffraction pattern of the first-type anhydrous IDP (Fig. 4a) shows that Fe-bearing olivine, high-Ca pyroxene, and pyrrhotite are the major mineral phases. Troilite and pyrrhotite coexist in some other IDPs. Pyroxene occurs in variable amounts, but is less abundant relative to olivine. Olivine and pyroxene often show broad X-ray reflections due to compositional heterogeneity and small grain size. The combination and relative abundance of minerals in the anhydrous IDPs are consistent with those thermodynamically predicted for primitive nebular dust. Therefore, the anhydrous IDPs are very pristine solar-system material and preserve the mineralogical characteristics of nebular dust having been present in the early solar system.

On the other hand, the presence of hydrous minerals in the second-type hydrous IDPs (Fig. 4b)

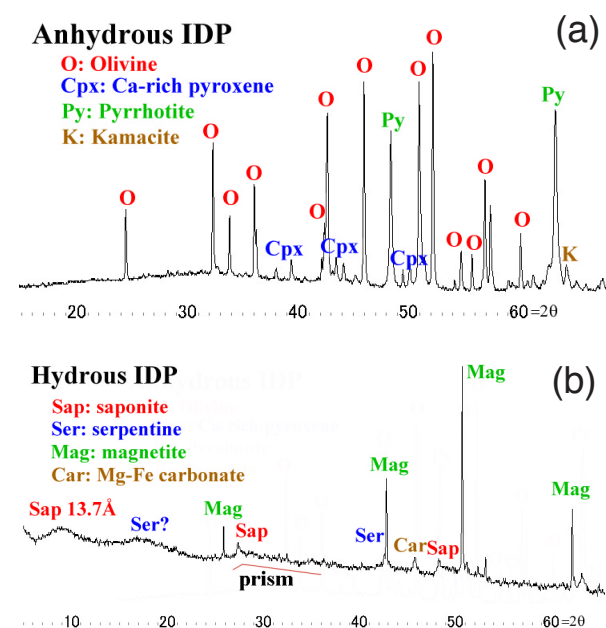


Figure 4. Powder X-ray diffraction patterns of an anhydrous IDP (a) and a hydrous IDP (b).

indicates the presence of water in the parental objects. The mineral species and relative mineral abundances of hydrous IDPs are similar to those of hydrous primitive meteorites. This suggests that the hydrous IDPs have experienced aqueous alteration reactions in the parental objects, like the hydrous meteorites, and lost the characteristics of primitive nebular dust during the alteration.

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## References

[1] T. Nakamura, T. Yada, Y. Nakamuta, N. Takaoka, Y. Terada, I. Nakai and M. Tanaka, *Meteoritics and Planetary Science* 34 (1999) A86.

## 6-3. Mineralogical Characterization of Unique Calcium Silico-Phosphates in Angrite Meteorites

Meteorites are the only available samples which can help us to understand the origin of the solar system and the subsequent evolution of planetary materials. The number of minerals identified in meteorites now reaches 280 and is still constantly growing. Some of them only occur in meteorites, which provide substantial information about their unusual formation conditions. Because of the rarity of meteorites, preparing thin sections and their non-destructive micro analysis (electron microprobe, micro Raman spectroscopy, micro area Laue diffraction) are essential for their characterization. Here we report one example, in which we analyzed a unique Ca silico-phosphate in angrite meteorites, possibly a new mineral.

Angrite is the rarest group of achondrites, and only six specimens are known. Three angrites contain unique Ca silico-phosphates. They are usually present as euhedral or lathy grains at the rim of fassaite clinopyroxene (Fig. 5). The maximum size is  $40 \mu\text{m}$ . Their chemical composition is homogeneous,



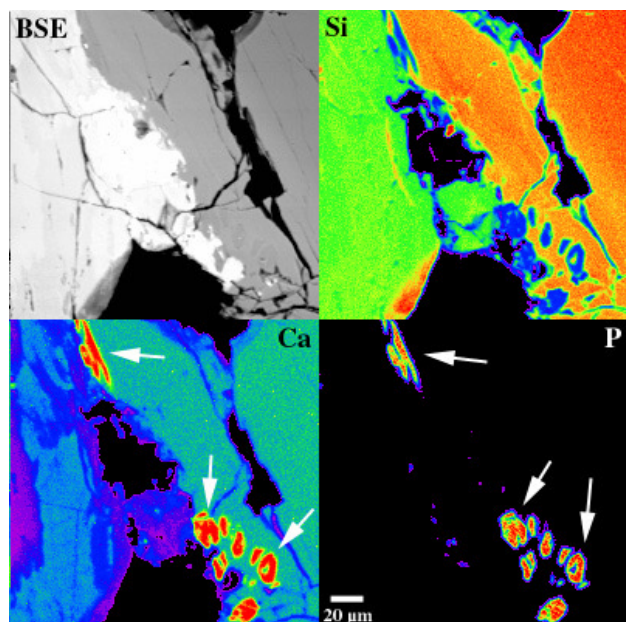


Figure 5. Back-scattered electron (BSE) image and Si, Ca, and P  $K\alpha$  maps of the Ca silico-phosphates (indicated by arrows).

and the cation proportion is possibly  $\text{Ca}_9\text{Fe}(\text{P},\text{Si})_7$  or  $\text{Ca}_{27}\text{Fe}_3\text{P}_{14}\text{Si}_7$ . It is interesting that its composition is close to that of a 1:1 mixture of  $\text{CaSiO}_3$  (wollastonite) and  $\text{Ca}_3(\text{PO}_4)_2$  (whitlockite). A Si-bearing Ca phosphate is also present, showing the same occurrence as Ca silico-phosphates. It has an average composition of  $\text{Ca}_{18.6}(\text{Fe},\text{Al},\text{Ti})_2\text{Na}_{0.4}(\text{PO}_4)_{13.2}(\text{SiO}_4)_{0.8}$ , and a similar stoichiometry to that of merrillite.

We analyzed silico-phosphates by micro Raman spectroscopy. The Ca silico-phosphate shows a sharp peak at around  $958\text{ cm}^{-1}$  and two broad peaks at around  $844$  and  $1048\text{ cm}^{-1}$ , that are different from those of merrillite and apatite, though both have  $958\text{ cm}^{-1}$  peaks, probably due to the P-O bond in phosphates. The Raman spectrum of the Si-bearing Ca phosphate is similar to that of merrillite. These results may suggest that the silico-phosphate has a merrillite structure, replacing some P by Si, although it is possible that the silico-phosphate has a different structure from merrillite because there is no interme-



Figure 6. Micro-area Laue diffraction pattern of Ca silico-phosphate.

diate phase between merrillite and silico-phosphate, and the proportion of P:Si is close to 2:1.

We further analyzed the Ca silico-phosphate by the micro-area Laue diffraction method using synchrotron X-ray radiation (beam diameter:  $1.6\text{ }\mu\text{m}$ ) developed at the BL-4B1 [1]. We obtained sharp diffraction patterns consistent with the unshocked nature of angrites (Fig. 6). The pattern is clearly from a single crystal, ruling out the possibility that it is a mixture of multiple phases. We have tried to give indices for the observed reflections by employing cell parameters of merrillite, but have not succeeded because the large unit cell of merrillite makes the fitting calculation very difficult. Further fitting calculations are in progress by using cell parameters of some other known Ca phosphates (e.g., apatite).

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#### Reference

- [1] K. Ohsumi et al. *Rev. Sci. Instrum.* **66** (1995) 1448.