

MINERALOGY OF CALCIUM SILICO-PHOSPHATES IN ANGRITES COMPARED WITH RELATED PHASES IN HEATED EUCRITE AND SYNTHETIC ANALOG. T. Mikouchi¹, K. Sugiyama², Y. Kato², A. Yamaguchi³, E. Koizumi⁴, and K. Kaneda⁵, ¹Dept. of Earth and Planet. Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (mikouchi@eps.s.u-tokyo.ac.jp), ²Inst. for Materials Res., Tohoku University, Aoba-ku, Sendai, Miyagi 980-8577, Japan, ³Natl. Inst. of Polar Res., Midori-cho, Tachikawa, Tokyo 190-8518, Japan, ⁴Remote Sensing Tech. Center of Japan, Roppongi, Minato-ku, Tokyo 106-0032, Japan, ⁵Japan Coast Guard, Tsukiji, Chuo-ku, Tokyo 104-0045, Japan.

Introduction: Angrite is a small group of basaltic achondrites showing unusual mineralogy and chemistry mainly composed of Ca-rich olivine, fassaitic clinopyroxene, and anorthite [e.g., 1]. Some angrites display evident quenching textures due to rapid cooling from magmas. In these “quenched” angrites, calcium silico-phosphate (CSP) is a minor, but common late-stage crystallization product [2,3]. CSP is extremely rare in natural occurrence in both terrestrial and extraterrestrial environment, but is a major component in dephosphorization slag [e.g., 4]. The understanding of the formation of CSP is important to better understand crystallization history of quenched angrites. In this abstract, we report our ongoing study characterizing CSP in angrites by comparison with related products in experimentally heated eucrite [5] and synthetic analog from the heating experiment.

Occurrence and Composition: CSP usually occurs as a cluster of tiny euhedral or lathy grains in quenched angrites such as Asuka-881371, Sahara 99555 and D’Orbigny [2,3]. Each grain is mostly up to several tens of μm in size. Some of them show a hexagonal crystal shape on thin sections, probably when they are near perpendicular to c axis. They are present at the Fe-rich rims of fassaitic clinopyroxene associated with other late-stage crystallization phases such as troilite, ulvöspinel, and Fe, Ca-rich olivine. Because of their small sizes, there are some scatters in their chemical compositions analyzed by electron microprobe, but their chemical compositions appear fairly homogeneous in each grain. The representative composition (all in wt%) is 11.7 SiO_2 , 0.2 Al_2O_3 , 1.5 TiO_2 , 4.8 FeO , 0.1 MnO , 49.4 CaO , 29.4 P_2O_5 , 0.3 Cl , 1.0 F and 0.4 SO_3 (Fig. 1). CSP is also found in experimentally heated Hammadah al Hamra 262 (HaH262) eucrite at 1070 °C for 24 hours ($\log P_{\text{O}_2} = \text{IW}-1$) [5]. It is a rare anhedral small grain up to 10 μm in size coexisted with plagioclase. Its chemical composition (all in wt%) is 15.3 SiO_2 , 5.6 Al_2O_3 , 0.8 TiO_2 , 2.7 FeO , 0.1 MnO , 47.8 CaO and 25.8 P_2O_5 (Fig. 1). These compositions are close to silicocarnotite ($\text{Ca}_5(\text{SiO}_4)(\text{PO}_4)_2$) or nagelschmidite ($\text{Ca}_7(\text{SiO}_4)_2(\text{PO}_4)_2$), but slightly different from both of them [2].

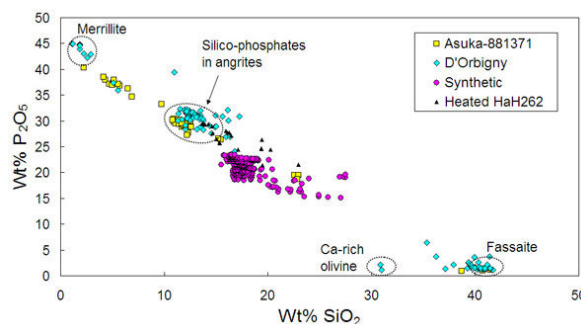


Fig. 1. SiO_2 vs. P_2O_5 contents of CSP in angrites, heated eucrite and synthetic analog.

Micro Raman Analysis: We analyzed CSP in D’Orbigny and heated HaH262 by micro Raman spectroscopy (Fig. 2). The obtained spectrum of CSP in D’Orbigny shows a strong peak at 960 cm^{-1} with three weak broad peaks at 433 , 589 and 667 cm^{-1} [3]. CSP in heated HaH262 shows a similar, but slightly different Raman spectrum from that of angrites. The CSP Raman spectrum has a strong peak near 960 cm^{-1} , but the second strongest peak is at 507 cm^{-1} , and three weak peaks observed in angrite CSP were not present. For comparison, we also analyzed apatite in EET90020 eucrite and whitlockite from Mexico. The apatite spectrum is close to that of angrite CSP, showing a sharp peak at 968 cm^{-1} with two weak peaks at 434 and 595 cm^{-1} . The whitlockite spectrum is similar to apatite, but the strongest peak is at 973 cm^{-1} , and several weak peaks are present unlike apatite.

SEM-EBSD analysis: We analyzed CSP in D’Orbigny and heated HaH262 by FEG-SEM equipped with an EBSD detector to obtain Kikuchi bands for the phase identification. The obtained Kikuchi bands were compared with calculated patterns using structures of several phosphorous-bearing phases. Although we tried silicocarnotite and nagelschmidite structures, either of them did not give matches with the observed Kikuchi bands. As was found in the Raman spectroscopy, the obtained Kikuchi bands well match with those calculated by the apatite structure [3] (Fig. 3). The britholite (REE-bearing Ca silico-phosphate) structure also gave a good match although REEs were not detected in angrite CSP. CSP in heated HaH262

did not give Kikuchi bands probably because the analyzed surface was not well polished. Reanalysis will be done by the meeting.

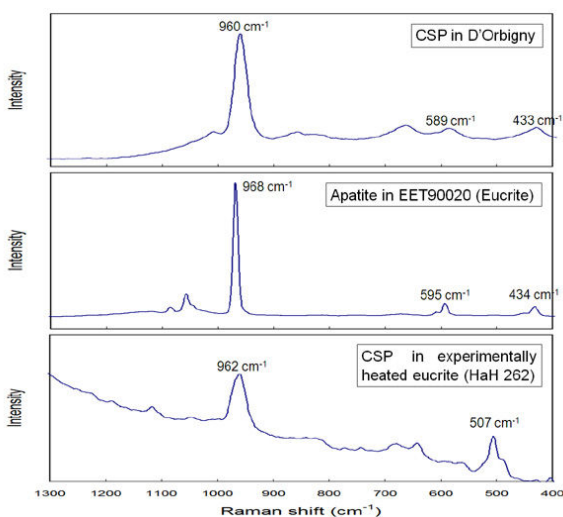


Fig. 2. Raman spectra of CSP in D'Orbigny, apatite in EET90020 eucrite, and CSP in heated HaH262 eucrite.

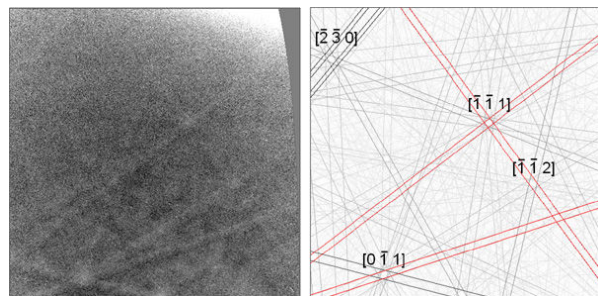


Fig. 3. Observed (left) and calculated (right) Kikuchi bands in a CSP grain in D'Orbigny. The calculated pattern using the apatite crystal structure matches with the observed pattern.

Synthetic Experiment: We prepared a starting material having the composition of 49.2 CaO, 25.7 SiO₂, 12.0 P₂O₅, and 13.1 Fe₂O₃ (all in wt%). It was preheated at 900 °C at first, and then held for 24 hours at 1600 °C. It was cooled down to 1400 °C at 10 °C/hour cooling rate and quenched in the furnace. The run product contains CSP whose composition (all in wt%) is 16.8 SiO₂, 0.6 FeO, 59.3 CaO and 22.6 P₂O₅ (Fig. 1). This composition is different from CSP in both angrites and heated HaH262 in its higher Ca content, but is close to stoichiometric nagelschmidite. Its crystal structure obtained by single crystal XRD gives cell dimensions of $a=10.8241(5)$ Å and $c=21.459(1)$ Å with the space group of $P6_1$ ($P6_5$). It corresponds to the

superstructure of α -Ca₂SiO₄ ($P6_3/mmc$, $a=5.42$ Å $c=7.03$ Å) with $2a$ and $3c$ axial lengths, respectively [6].

Discussion and Conclusion: CSP in angrites occurs at the rim of fassaitic clinopyroxene showing extreme Fe enrichment. Its occurrence suggests that CSP crystallized from the late-stage residual melt enriched in Ca, Si and P. Alternatively, CSP may be a reaction product of fassaitic clinopyroxene and merrillite because they usually coexist. It is interesting that CSP is present in heated HaH262 although its chemical composition is slightly different from that in angrites. The presence of CSP in heated eucrite suggests that they share a similar formation process. In heated HaH262, Ca phosphates, ilmenite and silica (plus minor pyroxene and plagioclase) were clearly melted, resulted in the formation of local melt enriched in Ca, Si and P [5]. The angritic magma at the last crystallization stage may have a similar composition to this partial melt.

Our micro Raman spectroscopic and SEM-EBSD analyses showed that CSP in the D'Orbigny angrite is isostructural with apatite, which is more generally called as a graserite structure. The graserite structure is hexagonal with the space group of $P6_3/m$. In this structure, cations and anions are arranged in two types of columns in a hexagonal arrangement [e.g., 7]. The hexagonal crystal shape on thin sections is consistent with this structure. Because Raman spectrum of CSP in heated HaH262 is slightly different from that of angrite CSP, they probably have different crystal structures. Although we could not synthesize CSP matching that in angrites in our heating experiment, we could obtain a crystal structure of nagelschmidite that was not well characterized so far. This structure is unique in comparison with α -Ca₂SiO₄ because it shows a superstructure of $2a$ and $3c$. The nagelschmidite structure can be explained by the substitution of one of SiO₄ tetrahedra and Ca sites of α -Ca₂SiO₄ by vacancy and PO₄ tetrahedron, respectively.

References: [1] Mittlefehldt D. W. et al. (2002) *Meteoritics & Planet. Sci.*, 37, 345-369. [2] Kaneda K. et al. (2001) *LPS XXXII*, Abstract #2127. [3] Mikouchi T. et al. (2009) *Meteoritics & Planet. Sci.*, 44, A143. [4] Segnit E. R. (1950) *Mineral. Mag.*, 29, 173-190. [5] Yamaguchi A. and Mikouchi T. (2005) *LPS XXXVI*, Abstract #1574. [6] Mumme W. G. et al. (1995) *N. Jb. Miner. Abh.*, 169, 35-68. [7] Mathew M. and Takagi S. 2001. *Journal of Res. of National Inst. of Standards and Technology*, 106, 1035-1044.