MINERALOGY AND CRYSTALLOGRAPHY OF CALCIUM SILICO-PHOSPHATE IN NORTHWEST AFRICA 4590 ANGRITE. T. Mikouchi1, K. Sugiyama2, W. Satake3 and Y. Amelin4, 1Dept. of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (mikouchi@eps.s.u-tokyo.ac.jp), 2Inst. for Materials Res., Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan, 3Research School of Earth Sciences, Bldg. 61 Mills Road, The Australian National University, Canberra, ACT 0200, Australia.

Introduction: Angrites constitute a small group of basaltic achondrites characterized by unique chemistry enriched in refractory elements and depleted in volatiles with very old crystallization ages, and are important samples to understand differentiation at the very early stage of the solar system history [e.g., 1]. Because of such unique chemistry, angrites are mainly composed of Al-Ti-rich clinopyroxene (“fassaite”), anorthitic plagioclase and Ca-rich olivine with unusual accessory minerals such as Ca silico-phosphate [e.g., 1]. Ca silico-phosphate was first reported in Asuka samples to understand differentia
tion and crystallography of Ca silico-phosphate. Such high Fe abundance is consistent with oxidizing condition during angrite formation [e.g., 1]. In fact, the presence of Fe3+ has been suggested for rhönite and ulvöspinel in NWA 4590 although Fe metal is also present [12]. The micro-FTIR analysis did not show the presence of water, which is consistent with anhydrous nature of angrites. Thus, the chemical formula of Ca silico-phosphate in NWA 4590 is (Ca4.36, Fe0.16)(PO4)2.30(SiO4)0.70.

The XRD analysis of Ca silico-phosphate in NWA 4590 showed that it has a hexagonal crystal structure with the Space Group of P63/m. The obtained cell dimensions are a=9.479(3) Å and c=6.970(2) Å. This structure is identical to that of apatite.

Discussion and Conclusion: The XRD result shows that Ca silico-phosphate in NWA 4590 has an apatite structure, and thus it can be called “silico-apatite”. This result is consistent with micro-Raman and SEM-EBSD study on Ca silico-phosphates in other angrites (e.g., Orbigny [5-7]. It is obvious that (SiO4)6 tetrahedra partly replaces (PO4)3 tetrahedra. If this is the case, trivalent cation such as REEs often replaces Ca (e.g., britholite) in order to compensate charge difference [e.g., 13], which is not found in NWA 4590 silico-apatite (Fig. 2). The near absence of F, Cl, or OH in NWA 4590 silico-apatite should be also noted, which suggests that it may be an oxyapatite. Because the ideal chemical formula of apatite is Ca5(PO4)3(F,OH,Cl), silico-apatite in NWA 4590 lacks Ca relative to (P+Si) even if we consider the presence of Fe (Ca+Fe=4.52, P+Si=3). The presence of vacancy and oxy-component may compensate charge valance to achieve this formula. Oxyapatite is known for silica-substituted apatite that is one of major phases of interest in the field of synthetic bone biomaterial research [e.g., 14, 15]. More detailed analysis and structural refinement (now in progress) are required to conclude it,
and will reveal the site where Fe$^{3+}$ is present. Furthermore, it is also important to obtain its accurate chemical composition by electron microprobe analysis because the analysis of Ca phosphate often gives insufficient total sum even if we consider the presence of F, Cl, or OH.

The Si content of silico-apatite in NWA 4590 is slightly lower than those in other angrites [5-7], but plotted on the same trend found for silico-phosphates in other angrites (Fig. 4). Probably, silico-phosphates in all angrites are silico-apatite although XRD analysis is required to conclude it. The variation of Si/P ratio found in silico-phosphates in different angrites may reflect the Si-P differentiation in the magma from which they crystallized.


Fig. 1 SEM image of Ca silico-phosphate grains (Si-phos) in NWA 4590. Bright spots on the grains are holes due to LA-ICPMS analysis. An: anorthite.

Fig. 2 EDS of Ca silico-phosphate in NWA 4590. Note the absence of Cl or F.

Fig. 3 Pre-edge peaks of Fe K-edge XANES spectra of Ca silico-phosphate in NWA 4590 and standard samples. The estimated Fe$^{3+}$/ΣFe ratio of Ca silico-phosphate in NWA 4590 is about 0.8.

Fig. 4 Molar Si/(P+Si) vs. (Ca+Fe)/(P+Si) in Ca silico-phosphates from angrites, experimentally heated Hamadah al Hamra 262 (eucrite) and synthetic phases (silicocarnotite and nagelschmidtite). Silico-apatite in NWA 4590 has slightly lower Si/(P+Si) ratio compared to Ca silico-phosphates in other angrites, but its (Ca+Fe)/(P+Si) ratio is similar to others.