MINERALOGY AND CRYSTALLOGRAPHY OF CALCIUM SILICO-PHOSPHATE IN NORTHWEST AFRICA 4590 ANGRITE. T. Mikouchi[1], K. Sugiyama[2], W. Satake[1] and Y. Amelin[3], [1]Dept. 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), [2]Inst. for Materials Res., Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan, [3]Research 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-881371 [2,3] and later found in additional samples [e.g., 4], but it has not been well characterized because of its small size (up to several tens of μm) and low abundance (less than 1 vol.%). Ca silico-phosphate is extremely rare in nature and no matching mineral with that in angrites has been known. Nevertheless, it is one of the major careers of REEs in angrites and thus its detailed characterization is important. In our previous study using micro-Raman spectroscopy and SEM-EBSD, we found that Ca silico-phosphate in angrites has a glaserite-type crystal structure (e.g., apatite) [5-7], but no X-ray diffraction (XRD) study has been performed yet. Recently, a new angrite NWA 4590 was found that showed a heterogeneous olivine gabbroic texture [8]. This new angrite contains Ca silico-phosphate grains reaching several hundreds of μm. In this abstract we report mineralogy and crystallography of Ca silico-phosphate in NWA 4590 and compare with those in other angrites.

Sample and Analytical Methods: Single crystals of Ca silico-phosphate (~a few hundreds of μm) were extracted from NWA 4590 and embedded in resin (Fig. 1). They were first analyzed by SEM-EDS (Hitachi S-4500) to see the constituent elements, and then analyzed by JEOL JXA-8900L electron microprobe by using well-characterized natural and synthetic standards. In order to estimate an $Fe^{3+}/\Sigma Fe$ ratio of Ca silico-phosphate, micro-XANES measurement using synchrotron radiation was performed at BL-4A, Photon Factory, KEK, Tsukuba, Japan [9]. Micro-FTIR (JASCO IRM-3000) was employed to see whether water was present in Ca silico-phosphate. After these measurements, one of Ca silico-phosphate grains was removed from resin (Fig. 1), and XRD analysis was performed by using Rigaku RAXIS-RAPID operated at 46 kV and 36 mA. The same Ca silico-phosphate grains were also used to determine REE abundance by LA-ICPMS and for chronological study. These results are found in complimentary abstracts in this volume [10, 11].

Results: Ca silico-phosphate grains in NWA 4590 are nearly homogeneous in composition. The representative composition (all in wt%) is 8.76 SiO_2, 0.44 Al_2O_3, 0.69 TiO_2, 2.51 FeO, 0.04 MnO, 50.84 CaO, and 33.96 P_2O_5 with the total sum of *ca*. 97 wt%. The SEM-EDS analysis did not show the presence of either F or Cl (Fig. 2). The micro-XANES measurement showed that the $Fe^{3+}/\Sigma Fe$ ratio is about 0.8 (Fig. 3), suggesting that most Fe is present as Fe^{3+}. Such high Fe^{3+} abundance is consistent with oxidizing condition during angrite formation [e.g., 1]. In fact, the presence of Fe^{3+} 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 $(Ca_{4.36}, Fe_{0.16})(PO_4)_{2.30}(SiO_4)_{0.70}$.

The XRD analysis of Ca silico-phosphate in NWA 4590 showed that it has a hexagonal crystal system with the Space Group of $P6_3/m$. 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., D'Orbigny) [5-7]. It is obvious that $(SiO_4)^{4-}$ tetrahedra partly replaces $(PO_4)^{3-}$ 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 $Ca_5(PO_4)_3 \cdot (F,OH,Cl)$, 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.

References: [1] Mittlefehldt D. W. et al. (2002) *Meteoritics & Planet. Sci., 37*, 345-369. [2] Prinz M. and Weisberg M. K. (1995) *Antarct. Meteorites, XX*, 207-210. [3] Warren P. H. and Davis A. M. (1995) *Antarct. Meteorites, XX*, 257-260. [4] Kaneda K. et al. (2001) *LPS XXXII*, Abstract #2127. [5] Mikouchi T. et al. (2009) *Meteoritics & Planet. Sci., 44*, A143. [6] Mikouchi T. et al. (2010) *LPS XL*, Abstract #2343. [7] Mikouchi T. et al. (2010) *Antarct. Meteorites, XXXIII*, 53-54. [8] Kuehner S. and Irving A. (2007) *LPS XXXVIII*, Abstract #1344. [9] Monkawa A. et al. (2006) *Meteoritics & Planet. Sci., 41*, 1321-1329. [10] Amelin Y. et al. (2011) *LPS XLII*, This volume. [11] Amelin Y. et al. (2011) *LPS XLII*, This volume. [12] Kuehner S. and Irving A. (2007) *Eos, Trans. AGU, 88*, Fall Meet. Suppl., Abstract P41A-0219. [13] Ito J. (1968) *American Mineral., 53*, 890-907. [14] Mathew M. and Takagi S. 2001. *J. Res. National Inst. Standards Tech., 106*, 1035-1044. [15] Arcos D. et al. (2006) *J. Biomed. Mater. Res., 78A*, 762-771.

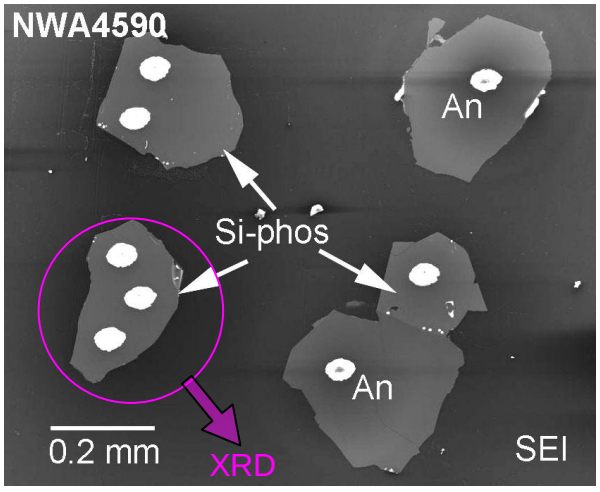

Fig. 1 SEM image of Ca silico-phosphate grains (Si-phos) in NWA 4590. Bright spots on the grains are holes due to LA-ICPMS analysis. An: anorthite.

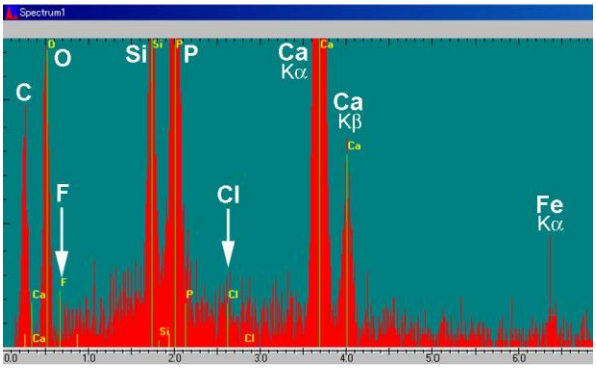

Fig. 2 EDS of Ca silico-phosphate in NWA 4590. Note the absence of Cl or F.

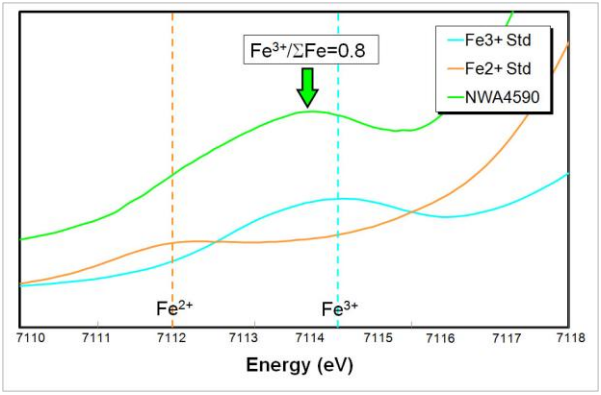

Fig. 3 Pre-edge peaks of Fe K-edge XANES spectra of Ca silico-phosphate in NWA 4590 and standard samples. The estimated $Fe^{3+}/\Sigma Fe$ ratio of Ca silico-phosphate in NWA 4590 is about 0.8.

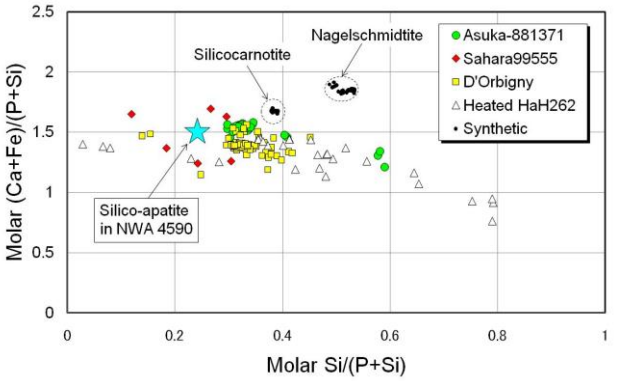

Fig. 4 Molar Si/(P+Si) vs. (Ca+Fe)/(P+Si) in Ca silico-phosphates from angrites, experimentally heated Hammadah al Hamra 262 (eucrite) and synthetic phases (silicocarnotite and nagelschmidtite). Silico-apatite in NWA 4590 has slightly lower Si/(P+Si) ratio compared to Ca silico-phosphates in other angrites,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