

Spectral characteristics of potential complex oxalate on Mars and implication for Mars missions. Wenxi Chen, Xiaohui Fu*, Zhongchen Wu, Jiang Zhang Shandong Provincial Key Laboratory of Optical Astronomy and Solar Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, China (fuxh@sdu.edu.cn).

Introduction: Oxalate is the only known organic matter that can be reserved over geological timescales[1]. As one of the most common biominerals in nature, oxalate is widespread in terrestrial environment. Their formation is commonly related with plants and lower organism like algae and bacteria. Oxalate is therefore considered as a sign of life. Many studies regard that oxalate may also exist on Mars[2,3]. Several previous works have investigated spectral features and thermal decomposition of oxalates[3-5], like calcium oxalates, and copper oxalates, etc. However, the spectra of some double salts, especially phosphate-oxalate, are poorly constrained.

Phoxite, $(\text{NH}_4)_2\text{Mg}_2(\text{C}_2\text{O}_4)(\text{HPO}_4)_2$, is the first mineral contain both phosphate and oxalate groups, which was firstly found in Rowley mine, Maricopa County, Arizona, U.S.A.[6]. Its discover site is an unusual bat-guano-related assemblage of phases that include vanadates, phosphates, oxalates, and chlorides, some containing NH_4^+ . Other secondary minerals found in association with phoxite are antipinite, aphithalite, bassanite, struvite, thenardite, and weddellite[6]. Therefore, it can be considered that phoxite is also a life-related mineral.

In this study, we synthesized phoxite from chemical reagents (MgHPO_4 and $(\text{NH}_4)_2\text{C}_2\text{O}_4$). Multi-spectral methods have been used to identify mineral phases and collect the mid-infrared and Raman spectra of synthesized samples. The spectra obtained here can provide references for both subsequent remote sensing and in-situ exploration Mars missions. This work aimed to find the matching pyrolysis peak to explain the potential existence of phoxite.

Samples and methods: Phoxite were synthesized from oxammite($(\text{NH}_4)_2\text{C}_2\text{O}_4$) and newberyite(MgHPO_4) according to the method of Snow[7]. Both chemical were analytical reagent from Maclin. Due to the fact that magnesium ions and oxalate ions can combine and form glushinskite (magnesium oxalate) precipitation, phoxite cannot be synthesized in solution. grinding method was adopted here Oxammite and newberyite with molar mass ratio of 1:2 were selected and the fine powders were then mixed and ground in a agate mortar. Then the mixed sample was placed in a sealed container with estimated relative humidity 60-80% .

In order to identify the phases in the final products, XRD patterns were collected with a Rigaku Ultima IV diffractometer after 1 and 3 weeks of mixing. Mid-Infrared spectra of the mixed samples were measured

using a VERTEX 70 (Bruker) Fourier Transform Infrared Spectrometer (FTIR). Raman spectra were collected by Renishaw inVia plus, and the excitation light source is 532 nm.

Results: XRD pattern of the mixture is Shown as Fig. 1. The sample is a mixture of oxammite, newberyite and glushinskite. Excluding the characteristic XRD peaks of above phases, the others represent the diffraction pattern of phoxite. Fig.2 compares XRD patterns of the 1 week and 3 weeks products after sample mixing. The 3-weeks products exhibit less oxammite content, according to the intensity of XRD peaks. This indicate that more reactants were consumed with prolonging the reaction time.

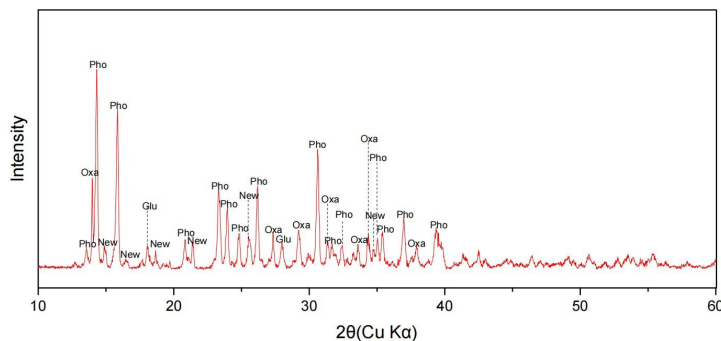


Figure 1: X-ray diffraction pattern of the synthesized sample. Notations are as following: Pho-phoxite; Oxa-oxammite; New-newberyite; Glu-glushinskite;

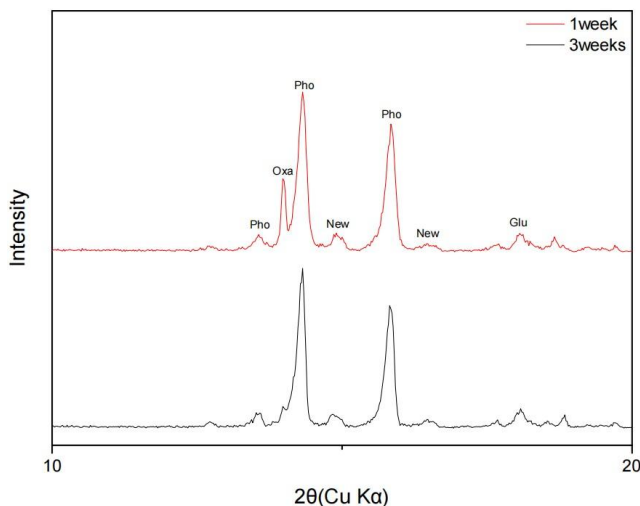


Figure 2: X-ray diffraction pattern of the sample at 1 week & 3 weeks after mixing;

Raman spectrum of the sample was shown in Fig.3. The Raman spectral envelope of phoxite includes the characteristics of both oxalate and phosphate, but the peak position is different with newberyite, oxammite or glushinskite. The strongest peak at 1492 cm^{-1} can be assigned to symmetric stretching vibration of C-O. On its higher-wavenumber shoulder, a weak peak centered at 1648 cm^{-1} can be seen, which is caused by C-O anti-symmetric stretching. Other strong peaks at 964 and 888 cm^{-1} were assigned to P-OH stretching, which is typical phosphate feature. C-C stretching caused peak at 922 cm^{-1} . Other detailed assignments are listed in Table 1.

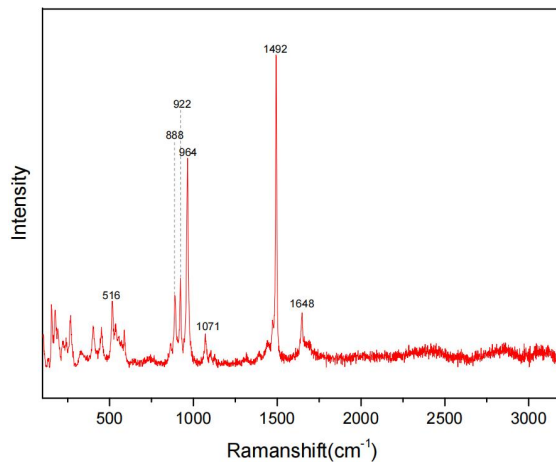


Figure 3: Raman spectrum of the sample;

Table 1. Raman peaks and their assignments

Peak position (cm^{-1})	Assignment
1648	$\nu_a(\text{C-O})$
1492	$\nu_s(\text{C-O})$
1071	$\nu_s(\text{P-O})$
964 888	$\nu(\text{P-OH})$
922	$\nu(\text{C-C})$
587	water libration
537	$\nu(\text{Mg-O})$
516 450	$\delta(\text{PO}_4)$
401	unassigned
267 173 153	lattice modes

Fig.4 shows the mid infrared ATR spectrum of the sample. Infrared spectrum is more complex than Raman spectrum. The peak at 1626 cm^{-1} due to C-O anti-symmetric stretching and the bands range from 1000 to 1300 cm^{-1} corresponding to P-O stretching can be observed, which also show the characteristics of both phosphate and oxalate. The peak at 2814 , 2881 , 3055 cm^{-1} is caused by N-H vibration, which is also the feature of ammonium salt. Detailed assignments are given in Table 2.

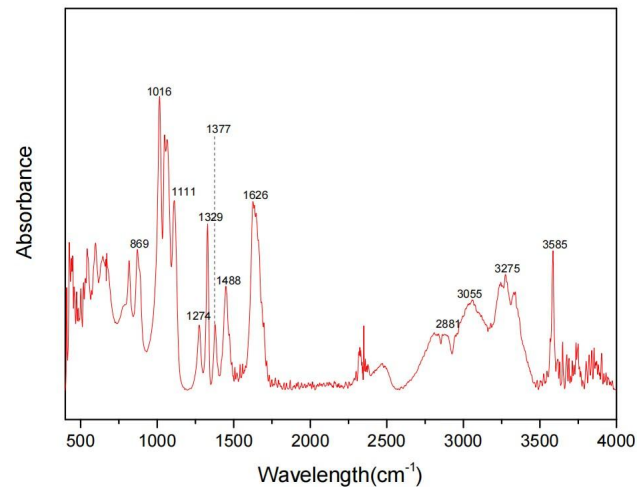


Figure 4: MIR spectrum of the sample;

Table 2. MIR peaks and their assignments

Peak position (cm^{-1})	Assignment
3585 3329 3275 3244	$\nu(\text{O-H})$
3055 2881 2814	$\nu(\text{N-H})$
1626	$\nu_a(\text{C-O})$
1448 1377 1329	$\nu_s(\text{C-O})$
1274	$\nu_a(\text{P-O})$
1111 1064 1049 1016	$\nu_s(\text{P-O})$
869	$\nu(\text{P-OH})$
817	$\delta(\text{OCO})$
597	water libration
543	$\delta(\text{PO}_4)$

Discussions: Here we only synthesized phoxite and obtain multiple spectra of the mineral. In our future work we planned to use STA-FTIR-GC/MS system to perform thermal analysis experiment and compare the evolved gas data obtained by MSL SAM. Then, more important is to discuss its formation mechanism. Because this mineral can be produced by fine powder grinding and mixing in laboration, phoxite possibly form in the martian dust during the dust activities. We will improve the synthesis method and simulate the particle-collision process during the dust activities, and verify whether the sample can be produced on Mars.

References: [1] Hazen R. M. et al. (2013) *Reviews in Mineralogy and Geochemistry*, 75, 7-46. [2] Benner, S.A. et al. (2000) *Proc. Natl. Acad. Sci. USA*, 97, 2425-2430. [3] Applin D. M. et al. (2015) *EPSL*, 420, 127-139. [4] Applin D. M. et al. (2016) *Icarus*, 278, 7-30. [5] Frost R. L. (2003) *Chinese Science Bulletin*, 48, 1844-1852. [6] Kampf A. R. (2019) *American Mineralogist*, 104, 973-979. [7] Snow M. R. & Peter Elliott (2022) *Transactions of the Royal Society of South Australia*, 146:2, 341-347.