**STABILITY FIELD OF FIVE CALCIUM SULFATE DOUBLE SALTS AND THEIR POSSIBLE FORMATION ON MARS.**
Enming Ju[1], Erbin Shi[1], Yanqing Xin[1,2], Changqing Liu[1], and Zongcheng Ling[1*] [1]Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. [2]Key Laboratory of Lunar and Deep Space Exploration, CAS. (zcling@sdu.edu.cn).

**Introduction:** Evaporite mineral assemblages have been found in many areas on Mars. Sulfate salts as evaporite minerals can provide geochemical fingerprints of the past chemistry lake basins [1]. That assemblages of saline minerals hold the potential for constraining the characteristics of ancient aqueous fluids once present at the Martian surface and subsurface makes the characterization of evaporative environments important [2]. Calcium sulfate veins are often observed on both Earth and Mars, and veins observed by the Curiosity rover at the Pahrump Hills indicate a protracted history of postdepositional fluid stability in Gale crater [3]. The ratio of Ca, Na, Mg, and K cations in amorphous materials is not enough to completely balance the abundance of $SO_4^{2-}$ [4]. Not all detected calcium sulfates can be explained by different polymorphs of calcium sulfate. Therefore, the presence of mixed-cation sulfates and mixtures of calcium sulfates with other single sulfates must be considered.

This study aims to obtain sufficient spectral information of mixed-cation sulfates for the interpretation of Mars data in the next few years. Five calcium sulfates with double cations were synthesized including syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), calciolangbeinite ($K_2Ca_2(SO_4)_3$), görgeyite ($K_2Ca_5(SO_4)_6 \cdot H_2O$), glauberite ($Na_2Ca(SO_4)_2$), and dobrovolskyite ($Na_4Ca(SO_4)_3$). Stability field experiments were conducted to see which hydration states of them were stable or formed.

**Synthesis of five calcium double salts:** Potassium sulfate and calcium sulfate dihydrate powder were mixed in a ratio of 1:1, ground thoroughly for 10 minutes, and dissolved in 100 mL of deionized water. The solution was put in an oven at 45°C to synthesize syngenite. According to the stoichiometric ratio of $K_2Ca_2(SO_4)_3$, potassium sulfate and calcium sulfate dihydrate powder were mixed and ground in a mortar at a ratio of 1:2 and then put into a crucible. The mixed powder was heated at 900°C for 16 hours in a muffle furnace and cooled to room temperature. For görgeyite, we took 100 mL of deionized water and divide it into three equal parts to dissolve potassium sulfate, potassium chloride, and calcium chloride. After the three reactant solutions were prepared, we mixed them thoroughly in the conical flask. The mixture was heated to boiling point using the universal electric furnace for 20 minutes. To avoid completely evaporation, the mixed solution, we connected the conical flask and reflux condenser. Moreover, glauberite was synthesized by mixing calcium sulfate and sodium sulfate (0.01mol each) in a saturated sodium sulfate solution at 75°C and stirring for ten days. The synthesis method of $Na_4Ca(SO_4)_3$ is similar to $K_2Ca_2(SO_4)_3$, except that $Na_4Ca(SO_4)_3$ requires rapid cooling to room temperature.

**Method:** Raman spectra and humidity buffer techniques were used to study the stability field of the synthesized calcium sulfate double salts. The Raman spectra were obtained at more than ten points to check the homogeneity of these samples. The saturates solutions of LiCl, NaI, KI, and KCl were used to control the Relative Humidity (RH) at different temperatures. The solid was slightly over the aqueous to precisely control the RH%. One saturated salt solution will provide one certain RH% at any desired temperature [5]. Raman spectroscopy was used to monitor the changes of five calcium sulfate double salts under different temperature and RH% conditions.

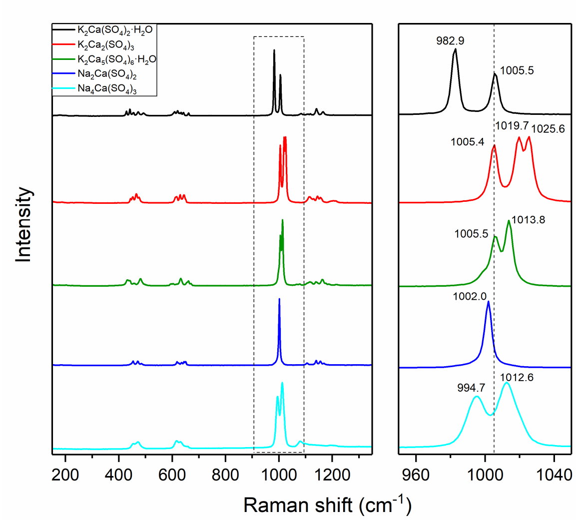


Figure 1. Raman spectra of five calcium sulfate double salts.

**Results and discussion:** As shown in Fig. 1, five calcium sulfate double salts exhibit sharp Raman peaks indicating their good crystallinity. The symmetric vibrational mode ($\nu_1$) of $SO_4$ was highlighted by dotted lines in Fig. 1. From Raman spectra, five calcium sulfate double salts can be readily identified, and the syngenite, calciolangbeinite, and görgeyite all have a peak around 1005.5 $cm^{-1}$.

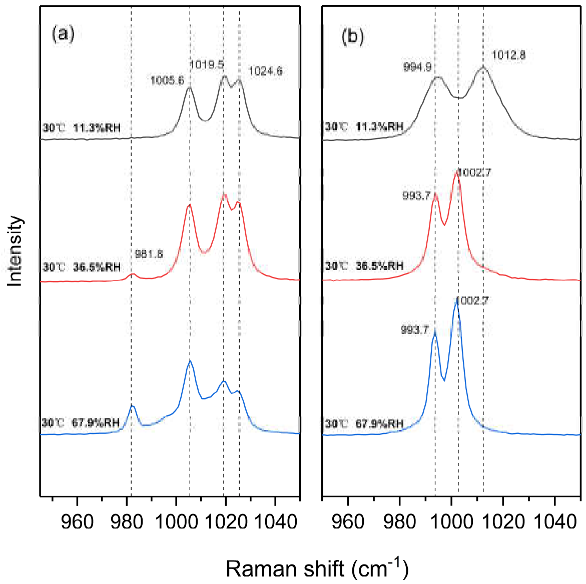


Figure 2. Raman spectra of stability filed results of (a) calciolangbeinite and (b) dobrovolskyite at 30 °C and variational RH% for ten days.

Typical results of stability field experiments are shown in Fig. 2. There are no changes in the Raman spectra of calciolangbeinite and dobrovolskyite under low RH% (~11.3%) conditions at 30 °C for ten days. For calciolangbeinite, the peak at 981.8 $cm^{-1}$ produced under 36.5%RH is weaker than that under 67.9%RH. And with the increase of the intensity of the 981.8 $cm^{-1}$ peak, the two peaks characteristic of 1019.5 and 1024.6 $cm^{-1}$ belonging to calciolangbeinite are weakening. However, the characteristic of 1005.6 $cm^{-1}$ of calcio-langbeinite does not tend to weaken. As shown in Fig 1, the $\nu_1$ mode of syngenite splits into two peaks at 982.9 and 1005.5 $cm^{-1}$. The 981.8 $cm^{-1}$ peak was attributed to syngenite generated in the stability field experiments. Since syngenite has one characteristic peak at 1005.5 $cm^{-1}$, this can explain why the 1005.6 $cm^{-1}$ peak is always obvious during the decomposition of calciolangbeinite. The decomposition reaction can be formulated as:

$$2K_2Ca_2(SO_4)_3 + 3H_2O \rightarrow 2K_2Ca(SO_4)_2 \cdot H_2O + 2CaSO_4 \cdot 0.5H_2O \quad (1)$$

This decomposition process needs further confirmation. XRD (X-ray powder diffraction) will be performed to determine the decomposition of calciolangbeinite. According to the synthesis conditions of syngenite and its growth conditions in nature, syngenite may convert to görgeyite.

For dobrovolskyite, the stability field experiments results are the same under 36.5%RH and 67.9%RH conditions. The 993.7 and 1002.7 $cm^{-1}$ peaks are respectively ascribed to $Na_2SO_4$ and $Na_2Ca(SO_4)_2$. The decomposition process of dobrovolskyite can be determined according to the Raman spectra, and the decomposition process is as follows:

$$Na_4Ca(SO_4)_3 \rightarrow Na_2Ca(SO_4)_2 + Na_2SO_4 \quad (2)$$

For the above two reactions, water promotes the decomposition of calciolangbeinite and dobrovolskyite. The preliminary stability fields experiments of calcio-langbeinite and dobrovolskyite indicate their instability. However, there is no obvious variation in the Raman spectra of görgeyite and glauberite during their stability field experiments.

**Implication for Mars and future work:** Five calcium sulfate double salts were synthesized in high temperature and aqueous solution conditions, and they are also found in some volcanic environments and evaporite deposits on Earth. These natural environments may also occur on Mars, so it is possible to find these minerals on Mars. More studies will be conducted on mixed-cation sulfates, especially those that reflect geologic processes on Martian surface and subsurface. Other stability field experiments of calcium sulfate double salts are ongoing. The data will be collected to support the orbital and in situ detection of them on Mars in the future.

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