LABORATORY SYNTHESIS AND RAMAN STUDIES OF THREE MARTIAN HYDRATED SULFATES

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Introduction:
Hydrated sulfates have been widely observed by martian orbital remote sensing (by OMEGA instrument on Mars Express and CRISM instrument on Mars Reconnaissance orbiter, MRO). Although many types of sulfates (e.g., Ca, Mg, Fe-sulfate) were found to be widespread and in large quantities [1], there are still unknowns about the complex phases especially the Fe-sulfate se-ries. Mixed-valences Iron (II) and iron (III) sulfates were found in evaporate deposits and might exist as romerite (Fe$^{2+}$Fe$^{3+}$)(SO$_4$)$_2$·14H$_2$O) and halotrichite (Fe$^{2+}$Al$^{3+}$(SO$_4$)$_2$·22H$_2$O) [2]. The Mars Exploration Rover (MER) Spirit excavated soils with high albino and relatively white to yellow colors at Paso Robles in Gusev crater and Paso Robles soils may contain coquimbite (Fe$^{3+}$3(SO$_4$)$_2$·9H$_2$O).3]

Raman spectroscopy as a promising planetary spectroscopy technique for studying Martian sulfate will be applied in future Mars missions (e.g., ExoMars and Mars 2020) [4]. Many hydrated sulfates have also been identified at acid mine drainage (AMD) system on Earth [5-7]. But they are often in mixtures without pure phase, Raman spectra of natural sulfates have been conducted by relevant Raman flyby instruments [8]. Meanwhile, conditions of synthesizing process of sulfates can reflect past Martian environment under which formation of sulfates need proper pH, relative humidity (RH), temperature (T), Martian relative pressure (P) and partial water pressure (P$_{H2O}$), etc [9]. Thus we can infer past and present environmental conditions of the Martian surface and subsurface in order to better understand the geological evolution of the Mars.

This paper focuses on the spectroscopic characterizations of three synthesized Fe-sulfates, i.e., halotrichite, romerite, and coquimbite. Our goal is to obtain pure phases of these sulfates and acquire their exact spectroscopic properties for their potential utilizations in future martian remote sensing and in situ investigations.

Sample synthesis
Halotrichite: A single batch of saturated aqueous solution of iron (II) sulfate and aluminum sulfate were prepared using AR grade mate-rials by dissolving FeSO$_4$·7H$_2$O and Al$_2$(SO$_4$)$_3$·18H$_2$O. We took out 15 ml each saturated aqueous solution of iron (II) sulfate and aluminum sulfate. Each of the material used to prepare the saturated solution were placed into the beaker and need fix two soxhlet extraction thimbles on the beaker wall. Then we added adequate solid powder of FeSO$_4$·7H$_2$O and Al$_2$(SO$_4$)$_3$·18H$_2$O to the two soxhlet extraction thimbles in order to make aqueous solution of each soxhlet extraction thimble achieve saturation. Solid powders were repeatedly added in for 7 days and then the residuary solution of baker was heated in an oven (40°C) about 4 days until precipitating white acicular halotrichite crystal[4,10].

Romerite: Mixed saturated solution of iron (II) sulfate and iron (III) sulfate was prepared by dissolving enough FeSO$_4$·7H$_2$O and Fe$_2$(SO$_4$)$_3$·nH$_2$O. First, we measured 1 ml mixed saturated solution by Pasteur pipettes for adding glass jar without cap. Then uncovered glass jar was placed in NaI humidity buffer that maintains ~30% RH at 40°C[9]. After 19 days, a red brown phase romerite had precipitated out.

Coquimbite: Each saturated solution of iron (II) sulfate and iron (III) sulfate were prepared before one week. We need measure 1 ml each saturated solution by Pasteur pipettes for adding glass jar without cap. Meanwhile a drop 73% sulfuric was added. Then uncovered glass jar was placed in relative humidity buffer MgCl$_2$ saturated solution that maintains~31% RH at 50°C. After 7 days, a yellow phase coquimbite had precipitated out [4].

Raman measurements and analysis
Raman spectroscopy probes vibrational and rotated transitions depended on the symmetry of a molecule or a crystal. We collected the Raman spectra of three synthesized sulfates ranging from 100 to 1300 cm$^{-1}$ (Fig. 1a, 1b, 1c). The stretching and bending modes of the SO$_4$ group, O-H and H-O-H are dominant features in their spectra, leading to their easy phase identifications even within mixtures.

An undistorted SO$_4$ group with tetrahedral symmetry has four modes of vibration in the Raman spectra. For example, in our study symmetrical stretching mode ($\nu_1$) of the SO$_4$ group of romerite is at 1012 and 1037 cm$^{-1}$, whereas $\nu_1$ mode of halotrichite and coquimbite are located at 996 and 1026 cm$^{-1}$ respectively. And asymmetrical stretching mode ($\nu_2$) of the SO$_4$ group of halotrichite is 1142 cm$^{-1}$, but $\nu_1$ mode of romerite and coquimbite are 1195 and 1203 cm$^{-1}$. Within the spectrum of sulfates, bending mode ($\nu_2$ and $\nu_3$) of the SO$_4$ group is low frequency. The $\nu_3$ mode of halotrichite, romerite and coquimbite are at 467, 463 and 503 cm$^{-1}$. Compared to the symmetrical bending mode ($\nu_3$), the asymmetric bending mode ($\nu_4$) of halotrichite, romerite...
and coquimbite are at 620, 661, 600 cm$^{-1}$. Thus these three hydrated sulfates could be easily distinguishable by these characteristic Raman spectral features.

**Discussions**

Formation mechanisms of some hydrous sulfates are still unclear on Mars, because there are often very different phase transition pathways under specific environment conditions. Our studies three sulfates with high hydrated degree (more than 9 water per molecule) could form at temperature range of 313-323 K with enough water supplies. They may get hydrated during Mars high obliquity periods and could probably preserve until today in the subsurface like other highly hydrated salts [11]. Coquimbite may be produced by dehydration and oxidation of romerite at relative lower humidity. And Al-halotrichite could be required for the releasing of Al from feldspar, then it went through dehydration and ion exchange with surrounding minerals in a specific environment until forming romerite.

**Conclusions and future work**

We have performed laboratory synthesis and Raman measurements of halotrichite, romerite, and coquimbite. For future work, we conduct the systematic spectroscopic measurements including visible near-infrared and mid-infrared. We will also start our stability field studies of these three sulfates to better understand their phase diagram and phase transition pathways.

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Figure 1a, 1b, 1c are Raman spectra of halot-richite, romerite, coquimbite, respectively. Red spectra is the standard from RRUFF database (http://rruff.info) and black spectra is taken from our laboratory analogues.