

# Laboratory Studies of Epsomite at Temperatures Relevant to Planetary Surfaces



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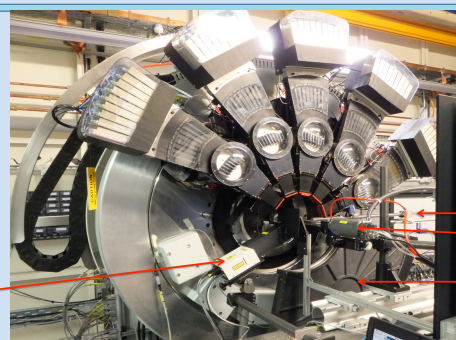
## Introduction

Phase transition studies of Mg-sulphates and characterisation of their in situ hydration are important for planetary exploration in order to allow analysis of current geochemical processes, advance understanding of hydrologic history and the cycles of water and sulphur, and the potential for past and present habitability. Hydrated sulphates are thought to be relatively common in some periglacial environments on Mars and are also thought to be responsible for the high equatorial hydrogen abundance in near surface soils on Mars - it has also been suggested they form part of major rock-forming minerals in the interiors of the icy Galilean moons of Jupiter. Evidence for the presence of sulphate in Martian soils and rocks first emerged from the Viking landings in 1977 [1] and was confirmed by the Pathfinder landers [2], and the Mars Exploration Rovers Opportunity and Spirit [3]. Chemical analyses carried out during these missions showed a strong correlation between sulphur and magnesium, pointing to the presence of magnesium sulphate in significant amounts.

Evidence regarding the composition of Europa's crust includes sputtered atmospheric constituents [4] and near-infrared reflectance spectra of surface regions [5]. The data show evidence of endogenic frozen salt mineral mixtures, including epsomite. Geochemical models suggest salts such as epsomite can be produced by low-temperature aqueous alteration of solar nebula material as seen in carbonaceous chondrites; this is expected to lead to the formation of Mg-sulphate rich material [6].

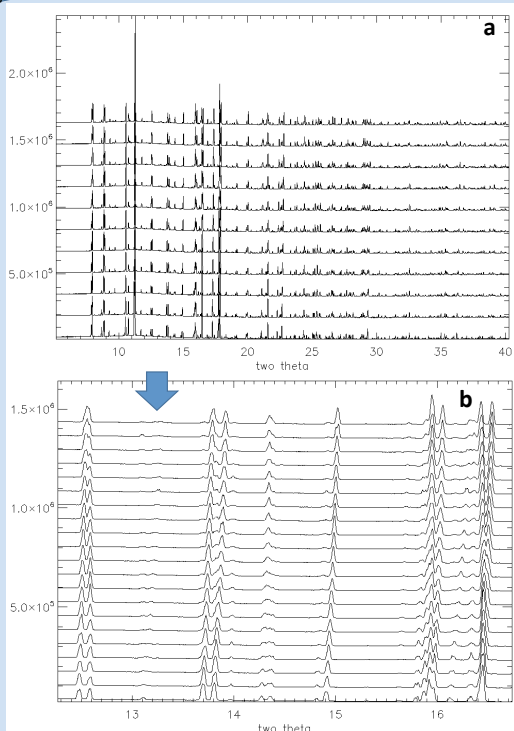
## Experimental Work

Both in situ synchrotron X-ray powder diffraction (SXPd) and in situ Raman laser spectroscopy (532 nm laser, Horiba iHR550 spectrometer) were performed on beamline I11 at the Diamond Light Source UK, with the aim of investigating the thermal expansion (TE) properties of epsomite. A sample of reagent grade  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  was ground and loaded into a 0.7mm borosilicate glass capillary and mounted on the beamline's diffractometer. A  $\text{LN}_2$  cryostream was used, allowing the sample temperature to vary between 90-300K with 10K intervals. A ramp rate of 360K/hr was applied and at each temperature the sample was allowed to equilibrate for 2 min before data collection using the position sensitive detector (PSD) [7][8]. In the case of the SXPd measurements a wavelength of 0.825818 Å was used (calibrated against NIST 640 Si standard).



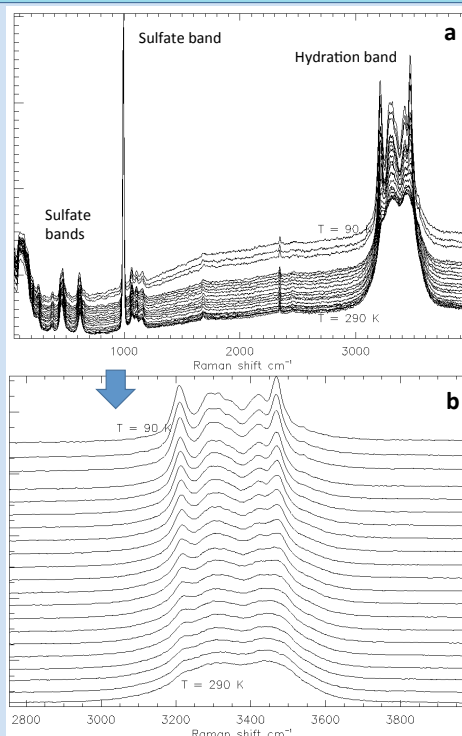
**Fig. 1** Beamline I11 diffractometer with experimental setup

## Results



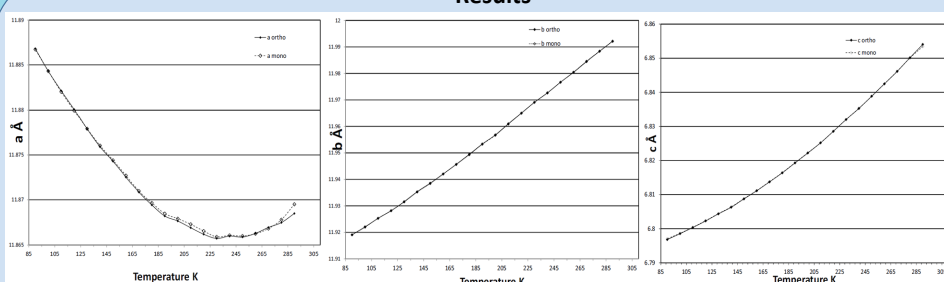
**Fig. 2(a)** SXPd of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Data are shown offset in y-axis for clarity, bottom pattern is for 290K and top pattern is 90K. Intermediate patterns are in 20K intervals.

**Fig. 2(b)** is a zoomed in region of the pattern showing merging and splitting of Bragg peaks with temperature, again offset in y-axis.



**Fig. 3** Raman spectra collected with decreasing temperature; (a) shows the overall spectra while (b) shows a zoomed in image of the hydration band showing progressive sharpening of features due to vibration of water molecules.

## Results



**Fig. 4** Lattice parameters for epsomite as a function of cooling temperature obtained from fits to SXPd data. The b and c axes both exhibit normal positive TE, however the a axis shows a crossing from positive to negative TE at ~235K; this is what is causing the change in appearance of the pattern at low T in fig. 2b.

## Conclusion

We have measured the TE of epsomite between 90-300K. A progressive sharpening of the Raman hydration bands is observed revealing distinct crystallographic sites occupied by the water molecules and attributable to the reduction in vibrational smearing as the temperature decreases. The change in appearance of the diffraction patterns with temperature is due to the change from negative to positive TE of the a lattice parameter rather than the formation of a low-temperature phase as previously proposed [9].

## References

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