

SULFURIC ACID OCTAHYDRATE FORMATION FROM A WATER RICH ENVIRONMENT: A POWDER DIFFRACTION STUDY. H. E. Maynard-Casely¹, H. E. A. Brand¹ and K. S. Wallwork¹, ¹Australian Synchrotron, 800 Blackburn Road, 3168, VIC, Australia, helen.maynard-casely@synchrotron.org.au

Introduction: This contribution presents an initial study of a water rich hydrate of sulfuric acid, which is believed to be sulfuric acid octahydrate. The research also demonstrates the experimental opportunities that the powder diffraction beamline at Australian Synchrotron affords to the planetary science community. This study of sulfuric acid hydrate is part of a program of research, being conducted on the beamline, into the thermodynamic and crystalline phase behavior of planetary ices under the conditions of the icy satellites of Jupiter and Saturn. The powder diffraction beamline, operational since 2007 [1], is a multi-faceted user facility able to accommodate the needs of this work, and the wide variety of research employing it.

Sulfuric acid octahydrate: The study of sulfuric acid hydrates has applications in some surprising areas of Earth and planetary sciences. On Earth, the system has impact upon the global climate, being responsible for aerosol formation in our atmosphere [2, 3]. Further out in the solar system sulphuric acid hydrates are prevalent upon the Galilean Satellites [4] with the source of these 'icy minerals' under debate. To realistically model and understand the surface and subsurface features upon these moons the physical properties of constituent icy mineral phases must be well understood. For example, to determine if a significant proportion of the Galilean moons' sulfuric acid hydrate budget is derived internally at initial accretion, or formed from sulphur sputtered from their sister moon Io, thermal expansion of the sulphuric acid hydrates must be known to determine this materials stability and potential for movement within the crust and subsurface ocean [5].

It has already been seen that the $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ system exhibits a rich phase behaviour, with solid phases demonstrated to form with $n = 1, 2, 4, 6, 5$ [6]. Additionally, there is thought to exist a more water rich hydrate, thought to be an octahydrate, $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$, which would be very likely to form in the European subsurface. However, the existence of sulfuric acid octahydrate (SAO) has been debated in the literature in recent years with some workers suggesting that the water rich form would be $\text{H}_2\text{SO}_4 \cdot 9.5\text{H}_2\text{O}$, a hemiennekaidecahydrate [7]. Despite this controversy, there exists a proposed crystal structure for SAO [8] which was later amended with the aid of DTF calculations [9], but no region of thermal stability has been reported for this structure (illustrated in Figure 1).

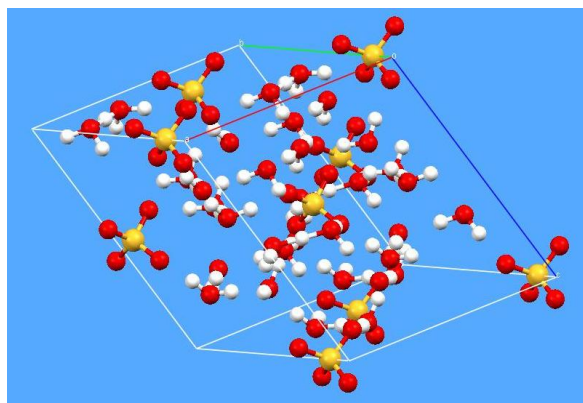


Figure 1 - The crystal structure of sulfuric acid octahydrate, from [7].

Experiment: *In-situ Data Collection,* The powder diffraction station at the Australian Synchrotron, shown in Figure 2, is located on a bending magnet beamline and may be used over the energy range 6–30 keV (0.41–2.07 Å). The instrument has been designed to provide *in situ* high-resolution powder diffraction data from samples under a wide range of environments. For this study, and others of the icy satellites, the Oxford Cryosystems cryostream plus has been used, as it achieves sample temperatures between 80–500 K. High-pressure apparatus, that can probe sample environments up to 50 GPa is also available at the beamline and will be relevant to an extended study of these icy materials. In 2012 it is expected that a cryostat, for use with the high-pressure apparatus, will also come on-line providing sample temperatures down to 4 K.

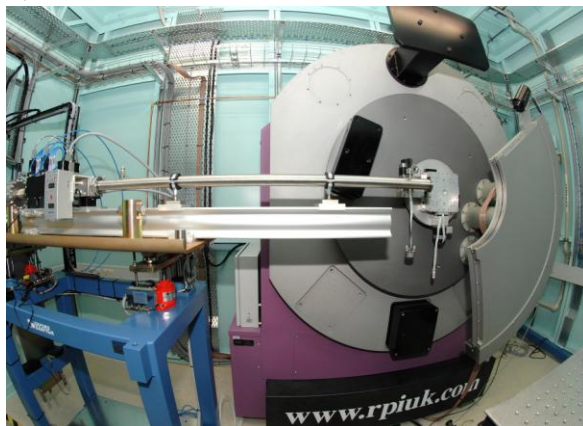


Figure 2 - Inside the experimental hutch, with a fish-eye lens, at the powder diffraction beamline. This shows the strip detector and the highly versatile sample mounting area.

Method. The composition of SAO equates to a 40.49 wt% aqueous sulfuric acid solution. As the intention of this experiment was to investigate if SAO would form from a water-rich solution, a 20 wt% aqueous sulfuric acid solution was prepared and loaded into a 0.3 mm borosilicate capillary. This was then mounted onto the powder diffraction instrument and cooled directly to 100 K. This produced an amorphous sample which, upon heating, crystallised to a good quality powder pattern. This crystalline sample was then cooled and powder diffraction data were collected in 5 K steps to 80K and then in 5 K steps on warming to 220 K.

Result and Discussion:

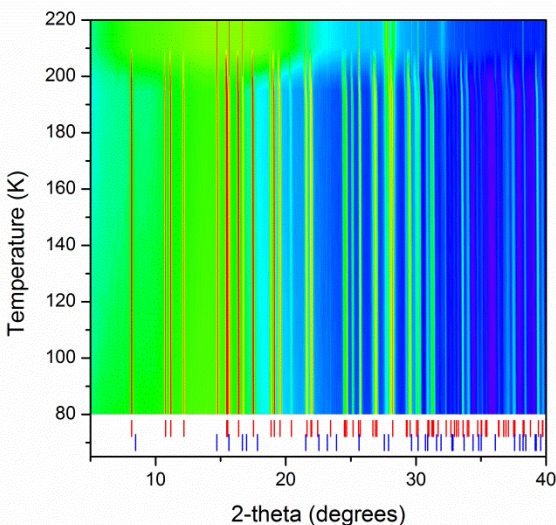


Figure 3 – Thermodiffractogram showing partial diffraction patterns collected between 80 and 220 K; intensity is represented by colour. The top red tick marks indicate expected positions for peaks generated by the SAO structure [8] and the bottom blue tick marks indicate the expected positions for the Ice Ih structure [10]. This figure illustrates the melting of the SAO pattern after 210 K, with crystalline Ice Ih persisting.

The powder patterns, shown in Figure 3, were analysed and found to comprise a mixture of a sulfuric acid hydrate and Ice Ih which persisted between 80 K and 210 K where the sulfuric acid hydrate melted. Between these temperatures no additional peaks or large scale changes in the peak intensities were observed, indicating that SAO is the stable form under these conditions. In contrast to a suggestion that the water rich phase would be a hemienneakaidecahydrate [7], the data obtained here shows a marked similarity to modeled patterns of sulfuric acid octahydrate [8, 9]. The SAO cell reported by Hirsch and Ojamäe [9] was refined to the data at each temperature using the Pawley method, as implemented in the TOPAS v4.2 [11]. From this the volume expansion with temperature can be illustrated.

Figure 4, shows a dramatic increase in expansion in unit cell volume as the sample approaches its melting point prior to 210 K. It must be noted however, that the SAO unit cell does not explain all features observed in the data suggesting that further investigation of the unit cell and symmetry are warranted prior to a more comprehensive study of the structure.

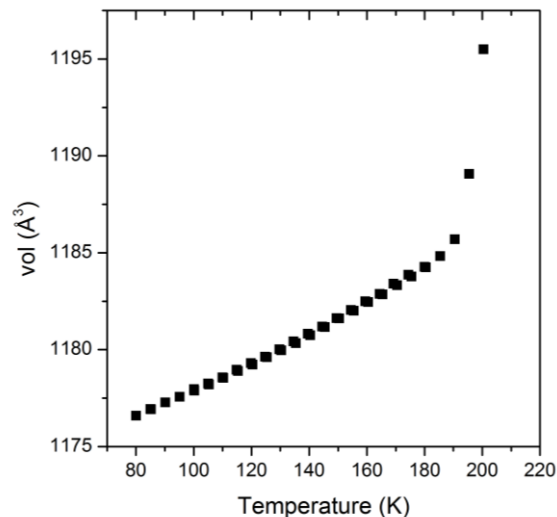


Figure 4 - The variation in volume of sulfuric acid octahydrate unit cell from 80 K to 200 K (N.B the sample melted by 210 K).

Conclusions and Further Work: This preliminary study has shown that a water-rich sulfuric acid hydrate will form from a ‘drowned’ solution and that this phase will persist over a large range of temperatures, making it likely to be an important stable phase applicable to the subsurface region of Europa. Evidence is presented that this hydrate is an octahydrate, although the ill fit of the existing structural models [8,9] suggests that further structural investigation is needed before confirmation. Additionally, it is hoped that the future work of this program of research will begin to probe the high-pressure behavior of this system.

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