HIGH PRESSURE PROPERTIES OF PLANETARY SULFATE HYDRATES DETERMINED FROM INTERATOMIC POTENTIAL CALCULATIONS.

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Introduction: The presence of salts such as $MgSO_4$ and Na_2SO_4 in chondritic meteorites has led to the suggestion that the water-rich icy moons of the Gas Giant planets are likely to be dominated by multiply hydrated salts such as Fritzsche's salt ($MgSO_4.12H_2O$, MS12), epsomite ($MgSO_4.7H_2O$, MS7) and mirabilite ($Na_2SO_4.10H_2O$, NS10) [1]. In the case of ammonia-bearing icy moons, reactions with sulfate solutions can result in formation of mascagnite ($(NH_4)_2SO_4$, AS), and the recently reported ammonium sulfate tetrahydrate ($(NH_4)_2SO_4.4H_2O$, AS4) [2]. Moreover, hydrated sulfates are clearly important rock-forming minerals and water storage reservoir on Mars [3]. When constructing models of icy moons to explore their structure and evolution, it is therefore extremely important to know the phase behaviour and physical properties of the constituent materials under the appropriate pressure and temperature conditions ($0 < P < 5$ GPa, and $100 < T < 300$ K).

We are, therefore, engaged in a programme of study to determine the phase behaviour and physical characteristics of candidate salt hydrates using both experimental (high-pressure powder neutron diffraction, single-crystal X-ray diffraction, and ultrasonic methods) and computational techniques (*ab initio* methods such as density functional theory, and empirical interatomic potential calculations). The combination of experimental and computational techniques to derive inputs for planetary modeling has proved to be an effective method of investigating the structure and evolution of icy planetary bodies [4, 5]. For highly hydrated salts, typically with large low-symmetry unit cells, *ab initio* calculations are computationally very expensive, even when confined to the athermal limit; calculations at finite temperatures are even more demanding especially in the range of interest. Thus we are currently in the process of fitting interatomic potentials for classical molecular dynamics simulations that will allow us to calculate thermodynamic quantities for these hydrates at the relevant temperatures and pressures with much less computational cost.

Computational method: The calculations reported here were performed with the GULP code (General Utilities Lattice Program) [6]. GULP uses interatomic potentials to calculate thermoelastic properties of solids by calculating the Ewald summation to obtain the energy and energy derivatives for a system. The inputs for GULP are the crystal structure and the coefficients for the interatomic potentials which are to be used. In the current study we have used the Buckingham potential to describe the interaction between the cations and the oxygens, while for the S-O interaction we employ Morse and Three-body potentials. These have the forms:

Buckingham potential:

$$A\exp\left(-r/r\right)-Cr^{-6}$$

Morse potential:

$$D\left\{\left[1-\exp\left(-a\left(r-r_0\right)\right)\right]^2\right\}$$

Three body potential:

$$\frac{1}{2}k_2\left(q_{213}-q\right)^2\exp\left(-r_{12}/r\right)\exp\left(-r_{13}/r\right)$$

where A, C, D, a, $r_{0,}$ k_2 ,ρ θ_{213} and θ are coefficients and r is the interatomic separation [6].

Presently there are no potentials for the hydrated salts of magnesium, sodium or ammonium sulfate so in order to allow the successful simulation of these systems potentials have been fitted to experimental or *ab initio* structural data (either in the literature or acquired by our group). The first step in achieving this was to fit potentials to structural data for the anhydrous species: $MgSO_4$, Na_2SO_4. and $(NH_4)_2SO_4$, each of which exists in at least two polymorphic forms . These potentials were refined by comparison of the output lattice parameters from GULP with published lattice parameters as the potential coefficients were varied [7]. The potentials for the anhydrous materials were then be used as a starting point for the fitting of potentials for the hydrated forms of these salts. Once potentials had been successfully optimised for the hydrated forms, GULP was then be employed to obtain the desired thermodynamic properties as a function of pressure and temperature.

Preliminary Results: We have already fitted potentials for anhydrous magnesium sulfate (α- and β-phases) obtaining lattice parameters to within 0.05 Å of the experimentally determined values at 4 K [8]. Fitting a 3rd order Birch-Murnaghan equation of state to the pressure dependence of the calculated unit cell volume (See Fig. 1) yields a bulk modulus of 63.0 ± 0.5 GPa; this is in excellent agreement with the athermal *ab initio* value, 61 ± 1 GPa, found by one of us (ADF, unpublished). Good agreement between these two studies is demonstrated in Table 1.

The anhydrous magnesium sulfate interatomic potential refinements have shown thus that GULP is very effective as a tool to mimic the behaviour of salts.

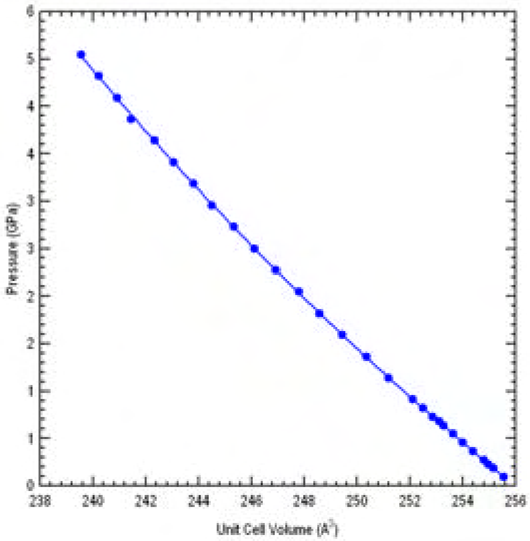

Figure 1. The calculated pressure dependence of the unit cell volume in α-$MgSO_4$.

	This study	*Ab initio* calculations (unpublished)
V_0	256 (2) A^3	276.5 (2) A^3
K	63.0 (5) GPa	61 (1) GPa
K’	5.3 (2)	4.7 (1)

Table1. Comparison of V_0, K, - the bulk modulus and K’ from this study with *ab initio* calculations.

Application of these potentials to the relevant hydrated sulfates will be valuable in supporting existing experimental and *ab initio* data for epsomite [5], and understanding the polymorphism seen at high pressure [9]. In addition, the dodecahydrate, which neutron powder diffraction and single crystal morphology indicate is a complex triclinic crystal [10], will benefit from this computational technique.

Anhydrous sodium sulfate has four known polymorphs as a function of temperature [11]. This richness of structural topologies, and the availability of structural data, means that fitting of interatomic potentials should be very robust. Since the only known hydrate of sodium sulfate (mirabilite) is a complex low-symmetry crystal (space-group $P2_1/c$, Z = 4, *a* = 11.512(3) Å, *b* = 10.370(3) Å, *c* = 12.847(2) Å, β = 107.789(10)°, and V = 1460.3(5) Å^3 [12]), with the added problem of orientational disorder, then there is a strong motivation for being able to carry out cost effective calculations of the thermoelastic properties.

Anhydrous ammonium sulfate (the mineral mascagnite) exists in two forms at ambient pressure, one paraelectric and the other (below 223K) ferroelectric [13]. Work is in progress to fit potentials to these two structures which will be of use in simulating the – presently - little understood tetrahydrate phase.

Conclusion: The evolution and dynamics of the icy satellites are governed by the behaviour of the consitituent materials of the satellites. Modelling of these planetary bodies requires a combination of experimental and computational techniques to obtain the necessary thermoelastic properties and polymorphic phase behaviour. Interatomic potential calculations can make a singificant contribution to this effort, allowing the rapid determination of physical properties for the kinds of complex low-symmetry salt hydrates that may comprise such moons.

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