

FROM SURREY TO THE
MOONS OF JUPITER (VIA MARS):
THE STORY OF EPSOMITE

A. D. Fortes

Department of Earth Sciences
University College London, Gower Street
London, WC1E 6BT, United Kingdom.
Author email: andrew.fortes@ucl.ac.uk

"Je prens la hardiesse de presenter à V(otre). A(ltesse). ce petit ouvrage, dont j'ai pris le sùjet d'un certain sel qu'on tire par le feu des Eaux d'Eveshamⁱ, c'est une Ville d'Angleterre dans le Comté de Surrey tres renommée pour cela."

Christian Schnetter, May 10th 1715
(from a letter of introduction to his inaugural dissertation)

"I pray boldness to present to Your Highness this small work for which I have taken the subject of a certain salt that is drawn by heat from the waters of Epsom, a town in the English county of Surrey, after which it is renowned."

INTRODUCTION

Magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), the salt produced at, and named after, the Surrey town of Epsom where it was first described, has played a number of roles under the scientific spotlight over the past four centuries. Its first use and scientific description was as a laxative and a headache remedy. During the 18th century, it was central in Joseph Black's experiments upon magnesium compounds, and not long after found its place amongst the pages of mineralogical classifications by Torbern Bergman, René Haüy, and James Dana. Its physical properties were established in the following 150 years, using increasingly advanced techniques, most recently neutron diffraction. During the last 30 years, *in situ* chemical evidence, coupled with geochemical modelling, has shown that epsomite is likely to be an abundant mineral in the soils of Mars, possibly forming considerable subsurface equatorial deposits. And in the last decade, evidence has been found that epsomite may constitute a significant fraction of the Galilean satellites, Europa, Ganymede and Callisto, which orbit Jupiter.

(*Top: The alchemical symbols for magnesium and sulfur.*)

DISCOVERY and EARLY DESCRIPTION

If you consult a modern text, such as *Hey's Mineral Index* (1993), then one might be forgiven for believing that the discoverer of the mineral epsomite was Jean Claude de la Métherie (1806). This is not true. Although de la Métherie was clearly the first man who intended to call the mineral epsomite (it is mis-spelt as “épsonite,” but one could easily blame this on “le rédacteur”), the first correct use of the name “epsomite” in print was by François Beudant (1824). In fact, de la Métherie was neither the first to classify $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as a mineral, nor by any means the first to describe it. Indeed, de la Métherie (1806) cites the earlier chemical analysis of Torbern Bergman, referring to Bergman's *Opuscula* (1779) and *Sciagraphia* (1782), a later edition of which de la Métherie himself edited (Bergman 1792).

Before the name epsomite was adopted, this substance passed under a great variety of guises, which I shall list momentarily. Rather late in the 19th century, Krause (1874, 1876) used the name *reichardtite* to describe massive encrustations of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ occurring at the mines in Stassfurt, Germany. This synonym was used in the literature of the time (e.g., Van't Hoff 1905; van Klooster 1917) but seems to have lost favor much after 1920. The earlier synonyms were usually derived from the principal type localities, these being either Epsom (Surrey, England), or Seidlitz and Seidschutz (Bohemia)ⁱⁱ. Thus one finds, for example, the names *sale sedlicensi* (Hoffman 1722), *aengelskt salt*, *sal anglicanum* (Wallerius 1747), *sal anglicus*, *sal epsomensis*, *sal seidlitzensis*,ⁱⁱⁱ and *sal seyschütensis* (Bergman 1782). From the mineral-water spas of Austria we also have the names *sal alpinum* and *gletschersalz* (= “glacier salts”) (Beudant 1824) and, of more uncertain provenance, Vogel (1762) gives us the name *gesundbrunnen salz*—“healthy spa salt.” The salt was often referred to for its strong taste and/or effect on the bowels, resulting in names like *bittersalz* (Vogel 1762), *sal nativum catharticum*—“native purging salt” (Hermann 1721), and *sal catharticum amarum*—the “bitter purging salt” (Grew 1695). Its occurrence as fibrous efflorescences led to its being called “hair salt,” *haarsalz* in German (Klaproth 1802), and *halotrichum*^{iv} (Scopoli 1761, 1772), or *halotrychum bornii* (Kitaibel 1829) in Latin. Well-formed crystals were dubbed *prismatische bitter-salz* by Friedrich Mohs (1804) and, somewhat unnecessarily, *picralum rhombicum*—“rhombic bitter salt”—by James Dana (1837). In still other works, the salt was known simply by its chemistry; *magnesia vitriolata* (Bergman 1782) or *magnésie sulfatée* (Haüy 1801).

The mineral water spring at Epsom was discovered around 1618 by local farmer Henry Wicker; he “found the hole... filled and running over with most clear water. Yet Cattle (though tempted with thirst) would not drink thereof, as having a Mineral tast therein.” (Fuller 1662). The spring water became well known for its potent palliative properties, including the curing of skin diseases such as the “scorbutick itch,” or scurvy, and the alleviation of headaches, to name but two. The waters were most famed, however, for their purgative effect on the bowels, and the name of the salt precipitated from these waters was thus *sal catharticum*, the “purgative salt.” Thomas Fuller (1662) was not sure that the mineral waters were wholly responsible for their reputation; “...no wonder if Citizens comming thither, from the *worst of smoakes* into the *best of Airs*, find in themselves a perfective alteration.”

The earliest scientific description of the salts formed from the waters at Epsom spa is by Nehemiah Grew (1641-1712), physician and Fellow of the Royal Society. Exactly when he began his work on the mineral waters is not clear, but he mentions the growth of epsom-salt crystals in a lecture given to Royal Society in October 1676, published as part of a larger work on the anatomy of plants (Grew 1682);

Hence it is, that Dew or Water on Windows or Plain and Smooth Tables, by virtue of a Nitro-Aerial Salt, is often frozen into the resemblance of little Shrubs. And the like Figure I have often seen in a well filtered Solution of the Salt of any of our Purging Waters, as of Epsom &c. being set to shoot. Produced, as I conceive, by the Nitre, which with the Rain or other Waters, is washed down from the Surface of the Earth, and so mixed with the Mineral Salts.

■

The "resemblance of little *Shrubs*" refers to the well-known frost pattern which decorates the inside surface of a jar containing an evaporating solution of magnesium sulfate. It was this manifestation, amongst others, of the presence of some part of the salt in the *air* which led John Mayow to propose the existence of the "nitro-aerial spirit" (Mayow 1674) that Grew speaks of. This hypothetical "nitrous principle" was thought to combine with an earthly mineral component to form the volatile salts, and was a lingering reminder of Agricola's alchemical classification of the mineral world (Agricola 1546). The use of the word "nitrous" in the early 18th century caused no small amount of confusion, as we will see shortly.

Grew continued his work on mineral waters, showing the salts from these waters to the Royal Society (April 3rd 1679), reading correspondence from others working on salt springs in different parts of the country (May 29th 1679), and reading his own papers to the Society (June 5th and July 3rd 1679). The records of these meetings were eventually collated and published by Thomas Birch (1757, vol. 3, pages 475, 489 and 492), although John Evelyn, another Fellow of the Royal Society, recorded them in his diary at the time (see de Beer 1955). That the full text of his papers on the epsom salt were omitted from the minutes is apparently because he took them away, intending to bring a larger discourse before the Society in lieu. Instead, he spent the next 15 years concentrating on establishing the medicinal virtues of the epsom salts before publishing his results (Grew 1695). This work, in Latin^v, was translated into English by Francis Moulton without permission (Grew 1697a). Grew was rather upset by this and quickly commissioned his own translation (Grew 1697b), giving over a significant fraction of the text to a scathing attack on Moulton's grasp of Latin.^{vi} He subsequently patented his method of making the epsom salts and supported the publication of a further work (Peter 1701) containing affidavits from notable Royal Society Fellows, including Sir Christopher Wren^{vii}, to the effect that he had been the first to show these salts to the Society in 1679 (see Sakula 1982, 1984, and LeFanu 1990 for more on this dispute).

Undoubtedly, the first description in English of what is *certainly* epsomite is that found in Grew (1697a,b) and reproduced in full below.

This *Bitter Purging Salt*, according as the Water wherein it resides is *more or less boiled*, and the *degree of Cold* whereto it is afterwards expos'd, and other Circumstances, shoots into *Chrystals* differently *siz'd*, but in *Figure*, whether small or great, much alike: For most of them, if they have room to shoot in, are so many small *Rectangular Prisms*, with *four Parallelogram Plains*; and, with two of them a little less and opposite, somewhat flattish. Sometimes they are Sexangular, with two or more *Parallel Plains*; but those so very small as hardly to be discerned. About half an Inch in *length*, exceeding their *thickness* five, six, or seven times. Stand upon a crusty *Base* of the same *Salt*. Their *upper ends* much vary'd, with *sometimes three, usually four inclined or sloped Plains, making Obtuse Angles with the Parallelograms aforesaid*, so as to be either *pointed*, or more often *edged, like a Chisel*: of which upper *Plains* there is a *Pentangular* or *Sexangular* one, commonly greater than all the other three put together: to this an opposite, which is *Quadrangular* or *Pentangular*; the other two *Triangular*, and very small, sometimes hardly discernable without a *Microscope*.

There are descriptions of salts produced at springs *other* than Epsom which predate Grew's *Tractatus* (1695) that could well be of epsomite. Martin Lister, another Royal Society Fellow, describes an apparently ubiquitous salt of English spring waters in his work *De Fontibus Medicatis Angliae* (1682) that he calls *nitrum murale*, the properties of which seem to agree with those of the epsom salt. Lister's depictions of several *nitrum murale* crystals (Fig. 1) share a strong resemblance to certain growth forms of epsomite (see Fig. 8 in particular); these may be the first drawings of epsomite crystals. Lister also describes an experiment to freeze Scarborough sea water (Lister 1685) recorded

during December 1684 which produced, after several nights, "Icicles of the *Sea Water* (that) were ... oblong squares, ... and were brittle and transparent." "The *Salt Icicles* after 3 quarters of an hour, lying before the fire did at length dry into a white powder perfect salt, the moisture totally Evaporating."

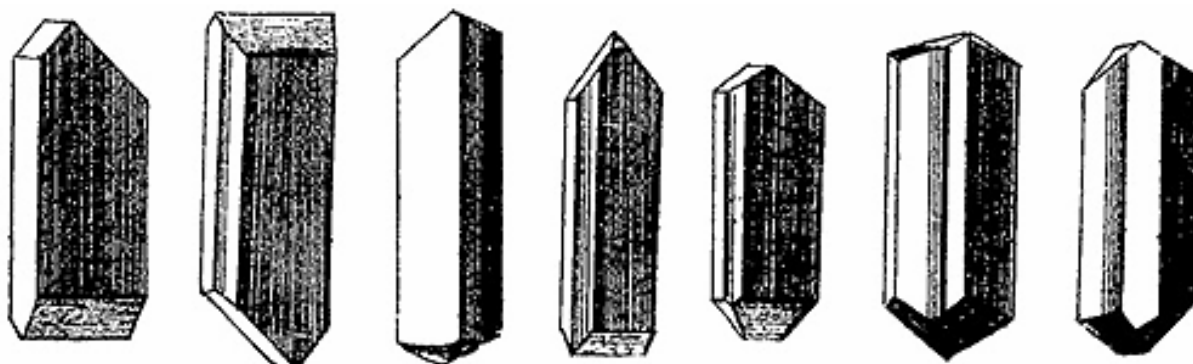


Figure 1. Various crystal habits of Lister's Nitrum Murale (Lister 1682).

The question of ownership, whose was the "true" Epsom salt, may seem trivial, but there was much money to be made from its sale as a pharmaceutical product. In many parts of Britain and continental Europe, salts were being produced in large quantities, either from spring waters or from sea water, hence the proliferation of different names for the salt, listed earlier. Often, after separation of common sea salt, the residual liquor (or *bittern*) would be made to crystallise bitter salts, either by evaporation or boiling, which were then marketed for their medicinal properties. There was some argument during the 18th century as to whose salt was the "genuine article." One must distinguish, however, between two types of "counterfeit" epsom salt. First, there is the natural spring salt which is not from Epsom itself, and secondly there are the artificially manufactured salts.^{viii} Since the latter were mass-produced, they were often cheaper, and consequently viewed rather as a poor-man's substitute. Debunking the first type of counterfeit epsom salt fell to chemists like John Brown who showed, for example, that the salts produced at Epsom, Lymington, Portsmouth, Shooter's Hill, and Newcastle were one and the same (Brown 1723). In continental Europe, Andrei Hermann (1721) identified the purging salts from Epsom, with salts from Seidlitz, Pymont, Eger, Schemnitz^{ix} and Herregrund.^x In spite of complaints from Charles Lucas who, in his *Essay on London Waters* (1756), rails against the critics of "counterfeit" epsom salts, "who vaunt in their imaginary knowledge of the chemic art," one still finds many later papers on the subject. For example, Henry Cavendish (1766) compares salts from various London springs, and William Brownrigg (1774) compares bitter salts from the marine saltpans and the coal mines near his home in Whitehaven with salts from the Scarborough saltpans and the Epsom spring.

On the second type of counterfeit epsom salt, Simon Boulduc (1718) compares methods of preparing artificial epsom salt, concluding that a mixture of alum with the liquor of salt of Tartar yielded an indistinguishable substance. His son, Gilles François Boulduc, in his own work on the production of epsom salt from sea-water (Boulduc 1731), wrote:

My Father recognized his error some time afterwards, and if God had preserved him to this day, as he was in good faith and esteemed the truth, he would have had the honour to declare his mistake. As regards science, it is easy to fall into error, but not so easy to recognize the error and admit it.^{xi}

The saltworks at Prestonpans, just east of Edinburgh, were to be the source of the Epsom salts used by Joseph Black in his experiments upon *magnesia alba* ($MgCO_3$) and *magnesia usta* (MgO), Black having found, probably during experiments conducted in 1752, that the epsom salt was composed of vitriolic (sulfuric) acid and magnesia (see Guerlac 1957). It took some time for this to

become commonly known; Black's dissertation (1754), in Latin, did not enjoy a wide circulation, and it was not until two years later that his experiments were reported in English (Black, 1756). Within a relatively short time thereafter, the composition became commonly known; Samuel Glass (1764, p30) writes, "... the virtues of these and the like waters depend principally, if not wholly, on their bitter salt; and the purgative quality of this salt on its alkaline *basis*, which is *Magnesia*. This earth is in those waters, indeed, united with the Vitriolic Acid"; and Henry Cavendish (1767) states, "That (earth) contained in Epsom salt is well known to be magnesia." One needs to exercise caution in interpreting some of the chemical usage in the early 18th century; chemists found themselves troubled with many rather vague labels for "principles" and "earths." Glass (1764) tells us:

It was usual with the Alchemists of former times to give the name of *Magnesia* to such substances, as they conceived them to have power of attracting any particular principle from the air. Thus an earth, which from being exposed to the air increased in weight and yielded Vitriol, they called *Magnesia Vitriolata*, and salts which attracted moisture from the same element, *Salia Magnetica*.

Equally, the use of the term "nitrous" by Mayow and Lister is more a reflection of a mental bias, and certainly not a concrete measurement of NO_3^{2-} content, as we would have it today. Charles Lucas (1756) seems particularly aggrieved by Lister's usage of the term "nitre"—perhaps he thought Lister should have known better—but the criticism is quite unfair. Certainly, Lister was not alone; Wittie (1660), for example, says of the mineral salts from Scarborough spa, "I ... think this Spaw of ours proceeds from a Nitrous Mineral within the earth," and neither Lister nor Wittie *invented* the usage. There are those, like the Reverend Stephen Hales, who appreciate that these salts are "...called nitrous; tho' they are not a true Nitre" (Hales 1750). Nonetheless, Dale Ingram (1767) writes, "It is evident by experiments formerly, as well as lately made, that there is less fixed earth and more nitrous principles in these waters than in most others, and no vitriolic acid abounding with sulphur." Ingram also states of the Epsom waters that, "In about 1640, Dr. *Grew* analyzed them, and found that their contents were a soluble bitter acid salt; that this salt consisted of eight parts of nitre, and one of earth, but not a grain of alum, as formerly conjectured." Whilst it is probably true that in the early 1680's Nehemiah Grew believed the salts to contain some "nitrous" components (see Grew 1682), by the time he published his treatise on the bitter purging salt, he was able to devote a whole chapter to the properties of the epsom salt which distinguish it from true nitre (saltpetre, KNO_3). What makes it clear that he knew epsomite not to be a nitrate is the following (Grew 1697b, p21):

If then the *Purging Salt* were a sort of *Nitre*, the *Water* distill'd from the said Mixture would dissolve *Gold* as well as the *Aqua Regia*. But we find no such Gold-dissolving Power in this *Water*.

Ingram, on the other hand, appears to be completely out of touch with his contemporaries' thinking—he is clearly unaware of Lucas's admonition of Lister—and his work is littered with mistakes (Grew, born in 1641, cannot have analyzed the Epsom waters in 1640, for example).

The earliest quantitative chemical composition of epsomite appears in Bergman's *Opuscula* (1779), although Dana (1837) incorrectly cites Rudolph Vogel's *Practisches Mineralsystem* (1762). Other early analyses are given by Kirwan (1782), Henry (1810), Gay-Lussac (1820), and Stromeyer (1821).

EXTERNAL FORM and PROPERTIES

During the 19th century, many researchers undertook the characterization of epsomite crystals, measuring the solubility, specific gravity, interfacial angles (goniometry), and the optical and electrical properties along different directions in the crystal.

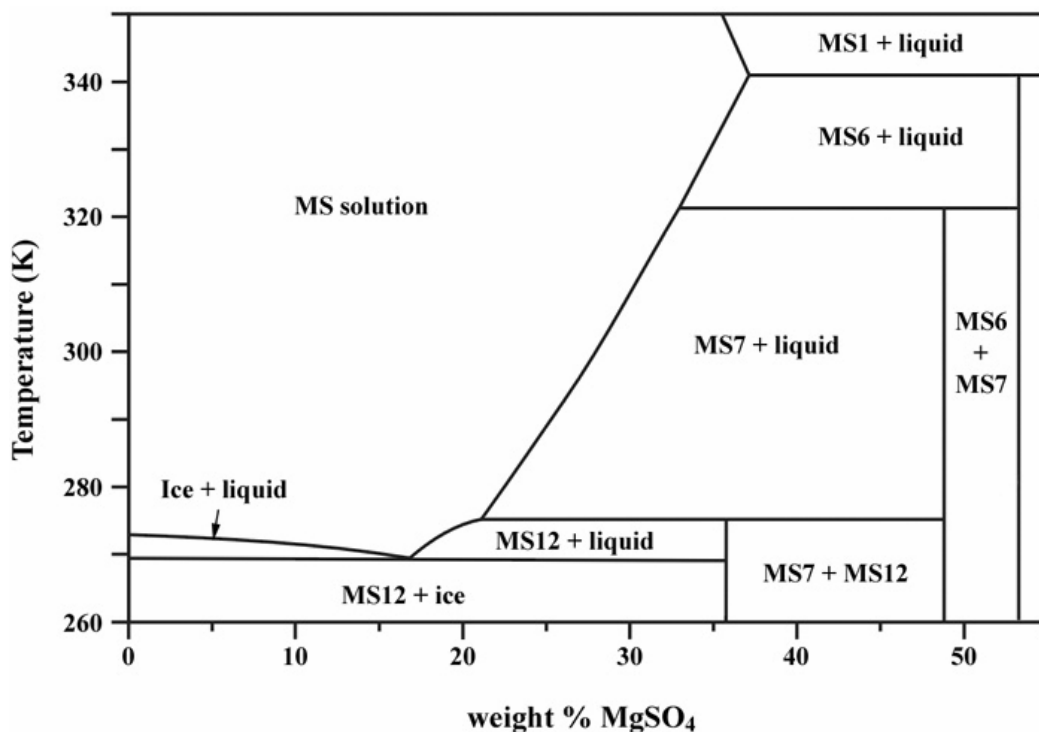


Figure 2. The generally accepted equilibrium binary phase diagram of the system $\text{MgSO}_4 - \text{H}_2\text{O}$. MS7 = epsomite; MS12 = Fritzsche's salt; MS6 = hexahydrate; and MS1 = kieserite.

Solubility

In Nehemiah Grew's time, it was well known that epsomite is very soluble; Grew (1697b) says, "this Salt (is) much more *dissoluble* than most other Salt," and Shaw (1734) remarks, "...this Salt appears to be the most soluble, in Water, of any Salt..."; both Friedrich Hoffmann (1722) and Hermann Boerhaave (1732) give crude values for the solubility of epsom salts in cold water and their results are tabulated in Lucas (1756).

Epsomite in contact with a saturated solution is not stable at all temperatures however (Fig. 2). Below 1.8°C (274.95°K) the stable phase is a dodecahydrate ($\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$); this was discovered by Carl Julius Fritzsche (1837) after observing the crystallization behavior of solutions left out in the winter. The ice-dodecahydrate eutectic at -3.9°C (269.25°K), and the dodecahydrate-heptahydrate peritectic at $+1.8^\circ\text{C}$ were established by Frederick Cottrell, this work being published by Van't Hoff *et al.* (1901). Even today, little is known about this dodecahydrate phase or its dehydration reaction to epsomite. It was suggested by Schirow Takegami (1922) that an octahydrate was stable over a large temperature range before dehydrating to epsomite. However, Benrath and Schröder (1927) failed to find any evidence of the octahydrate, and D'Ans (1933) concluded that Takegami had made a mistake in his data analysis. Viola (1923), in a footnote, states that $\text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ is isomorphous with $\text{FeSO}_4 \cdot 8\text{H}_2\text{O}$, but this appears to be a misinterpretation of work by Herman Kopp on the heptahydrate (see below under A Polymorph): *iron* sulfate forms hepta-, ennea-, and decahydrates, but no octahydrate.

Above 48.3°C , the crystal structure of epsomite loses the one water molecule which is not coordinated to magnesium, forming $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (the mineral hexahydrate). The earliest qualitative observation^{xiii} of this dehydration reaction is the following, from Romé de l'Isle (1772, p55):

The crystals of this salt are transparent, like the most beautiful ice, but when they are

exposed to dry air they quickly lose their transparency by evaporation of the water of crystallization.^{xiii}

The first quantitative study of this phenomenon was made by Eilhart Mitscherlich in the early 1820's (reported at the time by Haidinger 1826). Løwel (1855) observed the hexahydrate forming at much lower temperatures in very strongly supersaturated solutions. The dehydration of epsomite to hexahydrate (and other lower hydrates), both in solution and in air, has been studied extensively over the last 180 years; a few of the many papers on the topic are Millon (1845), Wiedemann (1874), Frowein (1887), Lescœur (1889), Foote and Scholes (1911), Bolte (1912), Gaudefroy (1913), Carpenter and Jette (1923), Schumb (1923), Diesnis (1935), Ide (1938), Kamecki and Palej (1955), Hamad (1975), Phadnis and Deshpande (1981), Emons *et al.* (1990), Chou and Seal (2003).

The solubility of epsomite was initially investigated by Louis Gay-Lussac (1819). Some later works, amongst them studies of the solubility as a function of temperature, include Løwel (1855), Tobler (1855), Schiff (1859a), de Coppet (1872), van der Haide (1893), Étard (1894), Van Klooster (1917), Archibald and Gale (1924), Rakusin and Brodski (1927), Blasdale and Robson (1928), Smits *et al.*, (1928), Ting and McCabe (1934), Bodaleva and Lepeshkov (1956), Novikova (1957), Archer and Rard (1998). See D'Ans (1933) for a useful summary. Løwel (1855) remarked on the ability of this system to form supersaturated solutions which could persist for months before crystallizing (see also Tomlinson 1868, 1871).

Density and Thermal Expansion

Grew (1695, 1697a,b) observed that the specific gravity of epsomite was less than common salt and nitre, but greater than alum. The specific gravity was first quantified by Jean Henri Hassenfratz (1798), many other researchers contributing data during the following century (e.g., Joule and Playfair 1849: Schiff 1859b: Buignet 1861: Pettersson 1879: Thorpe and Watts 1880: Johnsen 1907). Joule and Playfair's memoir also provides the first value of the thermal expansion coefficient from measurements of the density of epsomite between $\sim 0^\circ\text{C}$ and 32°C . Their value, $\alpha_v = 101.9 \times 10^{-6} \text{K}^{-1}$, is therefore an average in that temperature range, but compares extremely well with results derived from modern neutron diffraction; Fortes *et al.* (2004, 2005) found $\alpha_v = 107 \times 10^{-6} \text{K}^{-1}$ at 17°C in deuterated epsomite. The latter work also revealed some peculiarities in the thermal expansion, observing that the crystallographic *a*-axis expands upon cooling (so-called negative linear thermal expansion, NLTE). Indeed all three axes exhibit thermal expansion behavior which results in their experiencing large changes in axial compressibility below $\sim 150^\circ\text{K}$ (see Fortes *et al.*, 2004, 2005).

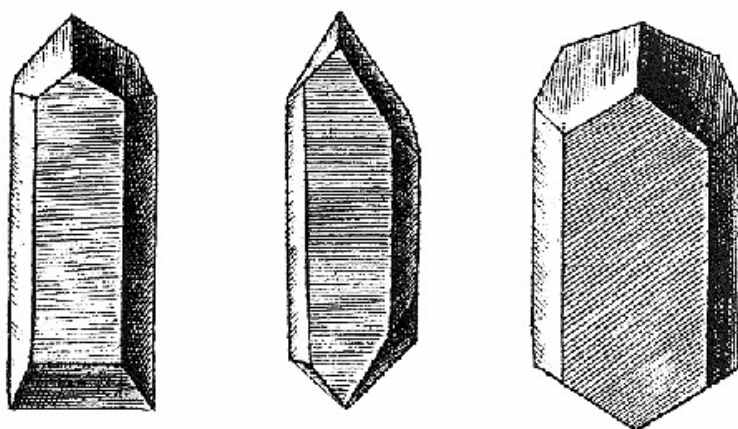


Figure 3. Crystals of *Sel d'Epsom* illustrated by Romé de l'Isle (1772).

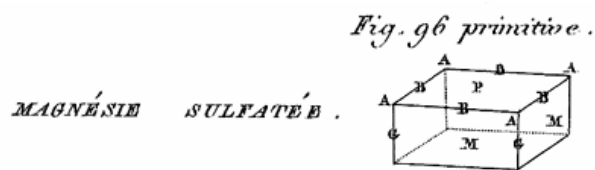


Fig. 97 pyramidée Fig. 98 dioctaédre Fig. 99 soustractive Fig. 100 équivalente .

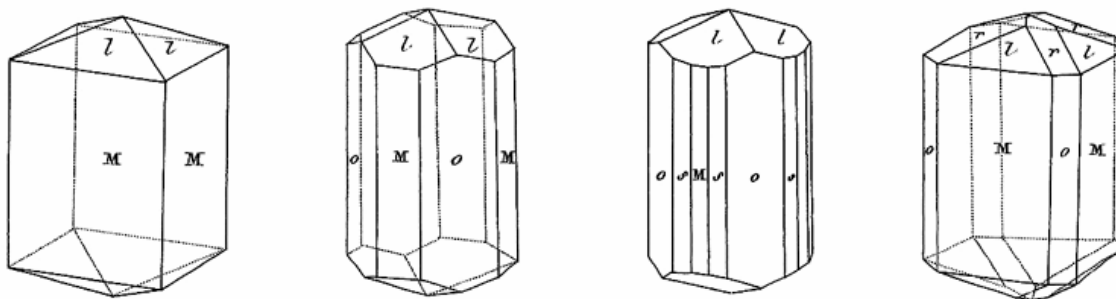


Figure 4. Epsomite crystals illustrated by Haüy (1823). Forms depicted are; $M\{110\}$, $o\{010\}$, $P\{001\}$, $l\{111\}$, $r\{101\}$, and $s\{120\}$.

Crystal Morphology

The first proper crystallographic treatment of epsomite does not appear until the late 18th century. Romé de l'Isle (1772) provides us with descriptions and sketches of several habits of epsomite crystals (Fig. 3), and with the means to distinguish it from other salts. René Haüy (1809) quantitatively describes the basic habit of the crystal for the first time, “Prisme droit à bases carrées”—a right prism with a square base. This is not quite correct; epsomite's dominant form is a right prism with a rhombic base. That is, the interfacial angle $(110):(1\bar{1}0) = 89^\circ 30'$ and not $90^\circ 00'$. However, as Table I shows, Haüy's measurements—done with a contact goniometer—agree very well with calculations of interfacial angles based on the most accurate unit-cell dimensions found by neutron diffraction.

Index (see Fig. 4)	Haüy (1823)	Calculated*
$M : l$	$129^\circ 14'$	$129^\circ 06'$
$M : o$	$135^\circ 00'$	$134^\circ 41'$
$M : s$	$161^\circ 34'$	$161^\circ 30'$
$l : l$	$126^\circ 52'$	$126^\circ 43'$
$l : r$	$153^\circ 26'$	$153^\circ 22'$
$o : r$	$120^\circ 00'$	$119^\circ 45'$
$o : r$	$153^\circ 26'$	$153^\circ 11'$

* from the unit cell at 295°K measured by Fortes *et al.* (2004, 2005) for $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$.

The first very accurate measurements made with an *optical* goniometer appear in the works of Henry James Brooke (1823). Goniometric data and/or illustrations of the crystal habit also appear in Miller (1839), Rammelsberg (1854), Grailich and von Lang (1857), Dufet (1889), Groth (1908), Viola (1923) and Voronkov (1958); see Figures 5-10.

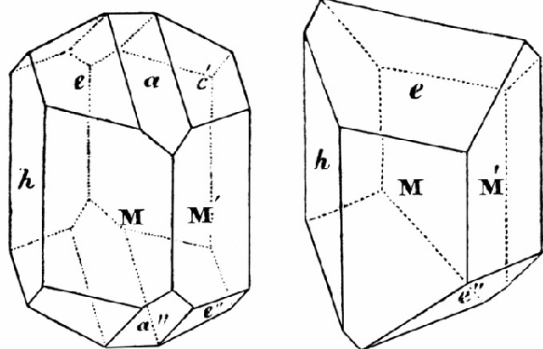


Figure 5. Epsomite crystal from Brooke (1823). Forms depicted are; $M\{110\}$, $h\{010\}$, $e\{111\}$ and $a\{101\}$.

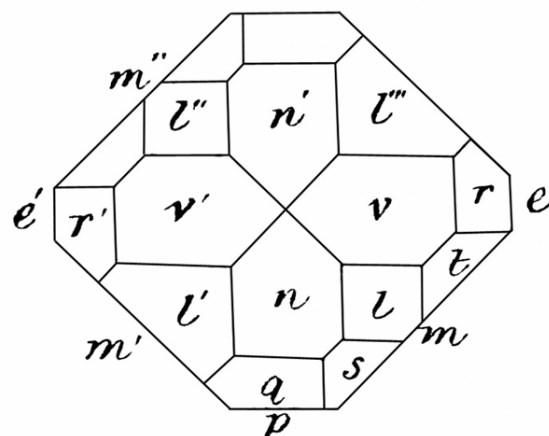


Figure 6. Epsomite crystal from Miller (1839) [also reproduced in Phillips (1852) and in later editions of Dana's System of Mineralogy]. Forms depicted are; $m\{110\}$, $n\{101\}$, $p\{100\}$, $e\{010\}$, $v\{011\}$, $l\{111\}$. $A\{201\}$, $s\{211\}$, $r\{021\}$, and $t\{121\}$.

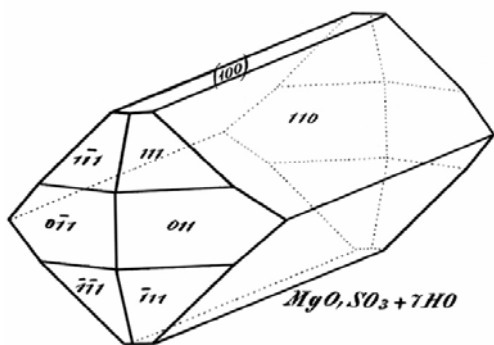


Figure 7. Epsomite crystal from Grailich and von Lang (1857).

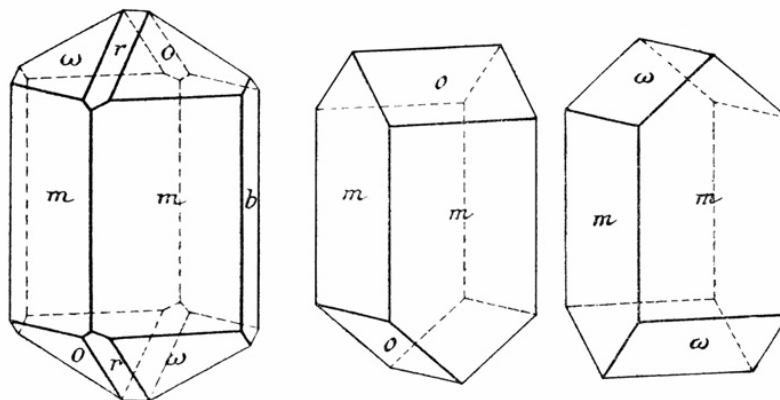


Figure 8. Epsomite crystal forms from Groth (1908) [also reproduced in Cardoso (1930, p25)]. Forms depicted are; $m\{110\}$, $b\{010\}$, $r\{101\}$, $w\{1\bar{1}1\}$, $o\{111\}$.

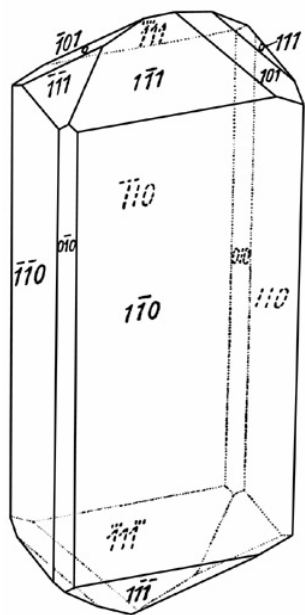


Figure 9. Epsomite crystal from Viola (1923).

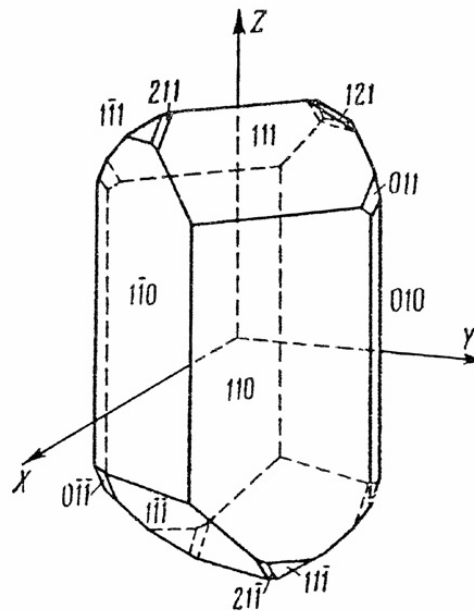


Figure 10. Epsomite crystal from Voronkov (1958), grown with borax.

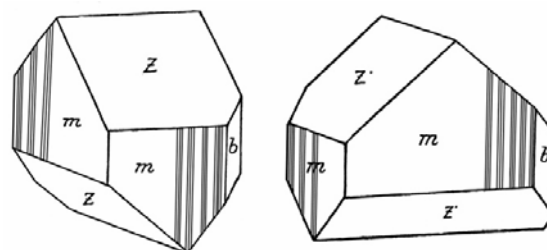
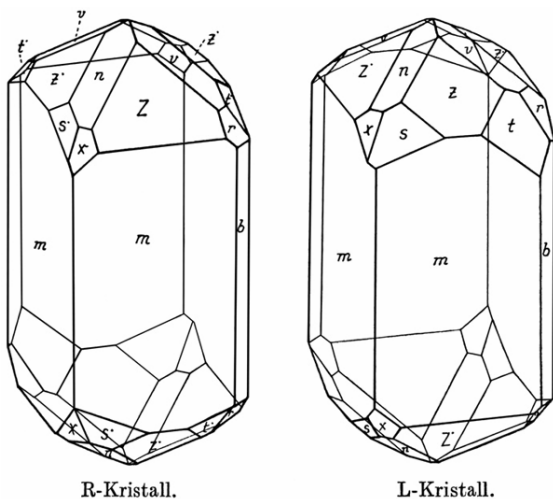


Figure 11 a-d. Left and right-handed epsomite crystals (Mahl 1929). The forms depicted are: $b\{010\}$, $a\{100\}$, $g\{210\}$, $m\{110\}$, $f\{120\}$, $v\{011\}$, $n\{101\}$, $r\{021\}$, $x\{201\}$, $z\{111\}$, $t\{121\}$, and $s\{211\}$.

Optical and Electrical Properties

The subtleties of the molecular architecture are revealed, not only through the external crystal shape, but by the way in which electrical and magnetic fields, and electromagnetic radiation interact with the crystal. If epsomite were indeed tetragonal, as Haüy's first measurements suggested, then the crystal would be optically uniaxial. The earliest optical studies of epsomite showed it to be biaxial, with an angle between the two optic axes ($2V$) of about 50° . A number of researchers published measurements of the optical properties, axial indices of refraction and $2V$ (de Senarmont 1851: Descloizeaux 1853: Grailich and von Lang 1857: Topsøe and Christiansen 1874: Dufet 1878: G. Adolphe Borel 1895); Esper Larsen (1921), in his guide to the optical properties of minerals, gives the values found by Topsøe and Christiansen (1874), and it is these which appear in modern mineralogical texts (see Appendix).

It was originally observed by Henri Dufet (1904) that epsomite crystals rotate the plane of transmitted plane-polarized light. This occurs because the epsomite crystal can exist in one of two different forms which are mirror images of one another; these two chiral forms, or enantiomorphs, are said to be either left-handed or right-handed. The “handedness” of the crystal, its *absolute configuration*, can be observed directly if the {211} forms are manifested. Pocklington (1906) observed entirely left-handed crystals, and Mahl (1929) published a superb study of chirality in epsomite crystals, along with some beautiful illustrations (Fig. 11).

The transmission of electromagnetic radiation as a function of wavelength is not constant. In the infrared, for example, there are regions where the crystal becomes quite opaque; this occurs because the vibrational frequency of the incident radiation resonates with a vibrational frequency of some inter-molecular or intra-molecular bond in the crystal, and is absorbed. Most such absorptions occur in the infrared, and the spectrum can be diagnostic of certain molecular building blocks or bond types. Measurements of the infrared spectra of minerals were first made in the 1880's. Systematic mineralogical studies were made around 1900 by William Coblenz of the Carnegie Institute in Washington. Although Coblenz mentions epsomite in a paper on hydrated salts (Coblenz 1905), and he later reports the infrared spectra of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Coblenz 1906), the first published IR spectrum of epsomite seems to be by Crowley (1991). Spectra were also published by Drake (1995), Ramalingom *et al.* (2001) Dalton (2003) and Dalton *et al.* (2005) for the purposes of identifying evaporite minerals on Earth and elsewhere using multispectral imaging techniques.

Morphological crystallographic studies showed that epsomite crystals possess three orthogonal 2-fold rotation axes, what we would describe as point-group symmetry 222. Since this point group has no center of symmetry, epsomite can exhibit piezoelectric properties—the development of an electrical polarization with the application of mechanical stress. The piezoelectric properties of epsomite are reported by Spitzer (1951), Koptsik (1956) and Voronkov (1958). Pyroelectricity (the development of an electrical polarization with the application of heat) is disallowed by the space-group symmetry of epsomite. David Brewster (1825) reported the detection of a pyroelectric response, although he says that “the action... is comparatively feeble.” Arnaud de Gramont (1884) subsequently demonstrated that epsomite is not pyroelectric.

The axial dielectric constants, now termed the relative permeability (the electric polarization occurring upon application of an external electric field), were first measured by Charles Borel (1893) and subsequently by Voronkov (1958). Voronkov's values for the dielectric constants disagree significantly with Borel's; similarly Voronkov's elastic constants (see below under Thermoelastic Properties and in the Appendix) are in conflict with others. This may be because Voronkov doped his solution with borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), a well-known method of altering the growth habit first observed by Karl von Hauer (1878). This ought not to affect the bulk physical properties of the crystal, but there is no other obvious explanation for the discrepancies.

The diamagnetism of epsomite is noted by Faraday (1846), Knoblauch and Tyndall (1850), Plücker and Beer (1851), and Grailich and von Lang (1858).

EPSOMITE at the ATOMIC SCALE

Crystal Structure

X-ray diffraction experiments upon epsomite first appear in the literature in the mid-1920's, the space-group and unit cell dimensions being determined by Cardoso (1926, 1930^{xiv}) and Westenbrink (1926a-c, 1927). The space-group assignment was confirmed by Barnes and Hunter (1932) as being (in modern notation) $P2_12_12_1$. Although the atomic structure of the isomorphous nickel sulfate heptahydrate had been solved much earlier (Beevers and Schwartz 1935)^{xv}, the structure of epsomite was not established until much later as part of a wider study

of salt hydrates by Werner Baur (1964). Further details of the structure were obtained by X-ray diffraction (Calleri *et al.*, 1984) and neutron diffraction (Ferraris *et al.*, 1973). Neutron diffraction is necessary to locate the hydrogen atoms in the structure; today it is normal to substitute deuterium for hydrogen because it produces a cleaner diffraction pattern, but Ferraris *et al.* (1973) used a synthetic *hydrogenous* crystal. More recent work (Fortes *et al.*, 2004, 2005) was the first to involve neutron diffraction analysis of fully deuterated crystals, carrying out a detailed structure refinement on $\text{MgSO}_4 \cdot 7\text{D}_2\text{O}$ at 2 K.

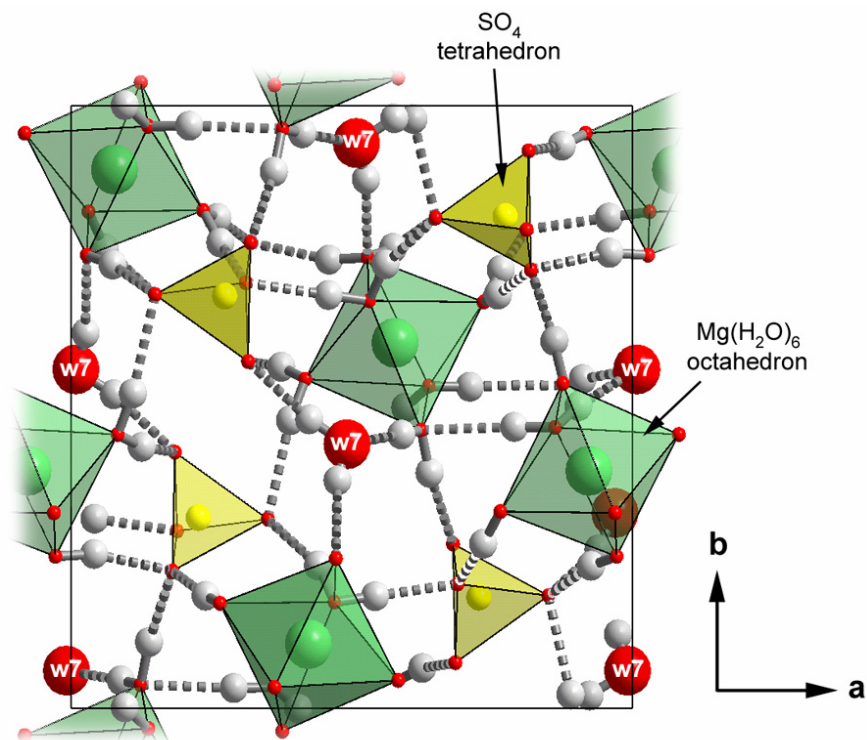


Figure 12. The crystal structure of epsomite viewed down the crystallographic *c*-axis. Magnesium, green; sulfur, yellow; oxygen, red; and hydrogen, grey. Covalent O-H bonds are shown as solid rods, and hydrogen bonds are depicted with broken rods. The water molecule that is not coordinated to magnesium is marked as w7.

The epsomite structure (Fig. 12) consists of $\text{Mg}(\text{H}_2\text{O})_6$ octahedra, SO_4 tetrahedra, and a “spare” seventh water molecule. The Mg-coordinated water molecules donate hydrogen bonds to the sulfate oxygens (which are all h-bond acceptors), and to the seventh water. The latter, by virtue of not being coordinated to the magnesium atom, is readily lost on warming to yield $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.

Thermoelastic Properties and High-pressure Polymorphs

Prior to the work of Fortes *et al.* (2004, 2005) very few measurements had been made upon epsomite at high pressure and/or low temperature. The only measurements at low temperature related to the isobaric heat capacity, C_p , measured from 15 to 300° K (Cox *et al.*, 1955) in order to quantify the correction to their measured heat capacity of hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), wherein it occurred as a minor accessory phase. However, the C_p values for the heptahydrate were not published and appear to be lost. Hence, there only remains the measured value of C_p for the heptahydrate in the range 311° to 321° K (Kopp, 1865) and four values, determined by Differential Scanning Calorimetry, at 223°, 263°, 283°, and 303° K (Fortes *et al.*, 2004, 2005).

273°, and 298° K (Prieto and Kargel, 2001). However, the molar heat capacity of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Barieau and Giauque 1950) is in quantitative agreement with the few known values for epsomite at high temperature, and values for this compound are known from 4° to 300° K.

The earliest high-pressure work was carried out by Percy Bridgman (1948a,b) upon polycrystalline and single crystal epsomite at pressures up to 4 GPa in a piston-cylinder apparatus. Bridgman observed a sluggish phase transition between 1.0 and 1.5 GPa, and suggested two further sluggish transitions at ~2.5 GPa.

The piston compression method was subsequently employed by Livshits *et al.* (1963) in work on crystalline hydrates of magnesium sulfate. These authors claimed to have observed the following series of phase transitions; I ↔ II (~0.45 GPa); II ↔ III (~1.2 GPa); III ↔ IV (~1.6 GPa); and IV ↔ V (~2.5 GPa). Of these, the II ↔ III transition may correspond to Bridgman's first phase change, and the IV ↔ V transition to one of Bridgman's 2.5-GPa phase changes. Livshits *et al.* (1963) also reported weak evidence for breaks in their pressure–volume curves at ~0.2 GPa and at 0.7 to 0.8 GPa.

More recently, a number of groups have studied melting relations in the H_2O - MgSO_4 system (Hogenboom *et al.*, 1995, to 0.4 GPa; Grasset *et al.*, 2001a,b, to ~2 GPa; Nakamura, 2003, to ~5 GPa). Of these studies, Grasset *et al.* (2001) noted, by visual means, a probable polymorphic phase transition in epsomite at 0.6 GPa. It is not known which, if any, of the phase transitions reported earlier (Bridgman, 1948a,b; Livshits *et al.*, 1963) this might correspond to.

Bridgman's work also offers us the first determination of the volumetric and axial incompressibility of epsomite. However, subsequent measurements of the nine independent elastic constants by Sundara Rao (1950), Voronkov (1958), and Alexandrov *et al.* (1963) produced contradictory results. Through a combination of quantum mechanical calculations and high-pressure neutron diffraction, Fortes *et al.* (submitted paper) were able to resolve the argument, showing the thermoelastic parameters of Bridgman (1948a,b) and of Alexandrov *et al.* (1963) to be accurate (see Appendix). The elastic moduli of Sundara Rao (1950) are too large by a factor of ~2, and there are significant discrepancies seen in Voronkov's paper. This gives cause to be suspicious of his piezoelectric and dielectric results as well (as noted above under Optical and Electrical Properties).

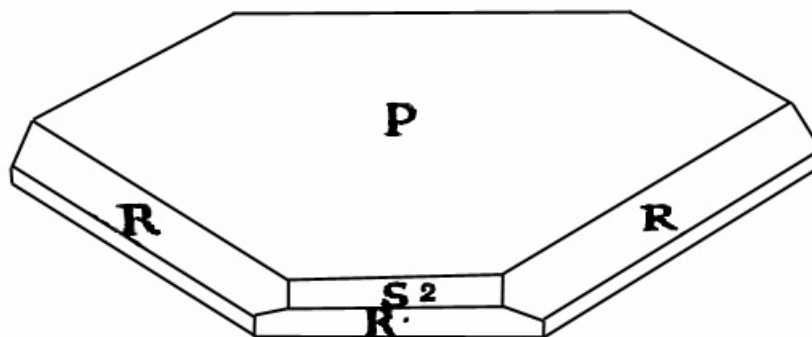


Figure 13. De Marignac's 1857 representation of the 7HOb polymorph.

A Polymorph: Læwel's Sel à 7HOb.

Many chemical handbooks report solubility curves for *two* phases of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, only one of which can be epsomite. In the scientific literature, the solubility curve of this “beta” phase is often presented with little or no comment (*e.g.*, Smits *et al.* 1928; Himawan 2002). Even more cryptically, papers such as Ramalingom *et al.* (2001)^{xvi} refer to two forms of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, terming epsomite β - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The latter is particularly baffling since the cited reference (Rayan *et al.*, 1974) discusses α - and β - forms of *anhydrous* MgSO_4 , both of which are orthorhombic!

■

The origin of the second solubility curve can be traced back to Henri Lœwel (1855). Lœwel was working with strongly supersaturated solutions, and observed that when his jars were stoppered he often produced salts different from those that formed when the jars were left open. The familiar epsom salt ("sel à ordinaire 7HOa") crystallized as prismatic needles; however a *second* salt—analysed and also found to be a heptahydrate, "sel à 7HOb"—formed triangular or hexagonal plates. Shortly afterwards, Jean Charles Gallissard de Marignac (1857, 1902) presented the only other known observations of the crystal, including interfacial angles (Fig. 12). Subsequently, Herman Kopp (1863) determined that the 7HOb salt was isomorphous with monoclinic iron sulfate heptahydrate. The crystallographic index of Paul von Groth (1908) reports these data on pages 431-432. Retgers (1889) offers the only value for the density of the 7HOb polymorph, and is the last original piece of work up to the present day on this material.

One might almost be tempted to dismiss the existence of this second heptahydrate, especially in light of failed attempts^{xvii} to reproduce it (Tomlinson 1868), were it not for the following description, ostensibly of epsom salts, given in Peter Shaw's superb book on Scarborough mineral waters (1734):

The form of its Crystals... appear like small icy Plates, all of them transparent, when singly view'd against the Light; but white when lying in a heap, and view'd by Reflection.

The description of platy crystals may well be the first recorded observation of Lœwel's 7HOb salt. Later (p108), Shaw goes on to describe the "First Salt" which crystallizes from Scarborough mineral waters:

We pick'd out a few of these Crystals which appear'd to be the most perfect, or truest shot; and examining them, by the Eye, found they consisted of two broader, and two narrower sides; each two being equal and parallel; but the former thrice the breadth of the latter. The two broader sides terminate, at one end of the Shoot, in a small inclined Plane, forming a sharp Ridge; and the two narrower sides terminate pyramidal, at the other end of the Shoot, in two small Planes, inclined the contrary way from the former, and rising also to a small Ridge, or Point.

Although it is a near textbook description of epsom salts—and Brownrigg (1774) proved that it was indeed epsomite—Shaw concluded that this salt was *not* the same bitter purging salt found in the waters of Epsom, because the latter, as far as he was concerned, formed platy crystals, not prismatic crystals.

BEYOND THE EARTH

While certainly an abundant terrestrial evaporite, epsomite could have remained nothing more than an arcane curiosity were it not for discoveries made in the last 30 years on distant planetary bodies in our solar system. Not only might epsomite be a major reservoir for water in the Martian regolith, but it might be the bizarre product of brine volcanism on icy moons around the gas giant planets. Indeed crystals of epsomite may yet hold the vital piece of evidence that life existed beyond the Earth.

The Salts of Mars

In 1976, the Viking landers reached the surface of Mars and carried out the first *in situ* analyses of the local soils, using X-ray fluorescence spectroscopy. It was found that the salts are highly cohesive and contain abundant sulfur and chlorine. This led to the conclusion that the soil was partially cemented by sodium chloride and Mg/Fe sulfate salts (Toulmin *et al.* 1977; Clark and van Hart 1981). Subsequent geochemical modelling suggested that highly acidic groundwaters could cause rapid weathering of basaltic rocks to form hydrous Fe and Mg sulfates, such as jarosite

($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and epsomite (Brass 1980; Burns 1988). More recent work has modeled the stability of different salt hydrates in the shallow (down to few hundred meters) Martian regolith (*e.g.*, Zolotov *et al.*, 1997).

In 1997, the α -particle X-ray spectrometer (APXS) on the Sojourner rover measured a strong correlation between MgO and SO_3 in the soils at the Pathfinder landing site (Ares Vallis), indicating the presence of an MgSO_4 mineral (Wänke *et al.* 2001). Spectroscopic data showed evidence for Fe-sulfates consistent with the acidic groundwater models, jarosite and schwertmannite ($\text{Fe}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$). The Mars Odyssey 2001 orbiter carried a neutron spectrometer to measure the distribution of hydrogen in the near-surface ($< 1\text{m}$) soils. Near the polar regions, the observed high hydrogen abundances are probably due to ice (permafrost). In the equatorial regions, near-surface ice is predicted to be unstable, and regions of high equatorial hydrogen abundance have recently been attributed to hydrated Mg-sulfates (Fialips *et al.* 2004; Vaniman *et al.* 2004).

Most recently of all, there have been observations of diagenetically altered sedimentary deposits at the Mars Exploration Rover B ("Opportunity") landing site in Meridiani Planum (Vaniman *et al.*, 2004). This sediment appears to have interacted with acidic groundwater to produce both jarosite and hematite (unambiguously identified by Mössbauer spectroscopy) and hydrated Mg-sulfates, probably kieserite and epsomite (Chipera *et al.*, 2005).

The Martian observations are significant, not least because they point definitively to extensive bodies of surface water on Mars in the past, and such locations are promising places to look for extinct (or extant) life (Rothschild, 1990), but because evaporites like epsomite typically contain fluid inclusions: on Earth, these inclusion can trap bacteria, and biogenic signatures in evaporites may easily be detected robotically using Raman spectroscopy. A Raman spectrometer must, therefore, surely be a prime instrument for flight on future Mars landers (*e.g.*, Ellery and Wynn-Williams 2003).

The Moons of Jupiter

The presence of salts such as MgSO_4 , Na_2SO_4 , and Na_2CO_3 in chondritic meteorites led to the suggestion that the water-rich icy moons of the gas giant planets would have ice mantles dominated by multiply hydrated salts, including epsomite, Fritzsche's salt ($\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) (Kargel 1991) with implications for the geophysics and astrobiology of these objects (Hogenboom *et al.*, 1997; Kargel *et al.*, 2000; Spaun and Head, 2001; McKinnon, 2002). The volume change accompanying hydration of epsomite, for example, has been implicated in the rifting of the ice crusts on Jupiter's moons (Day *et al.* 2002; Hogenboom *et al.* 2002). This suggestion has been supported by observational evidence from the Near Infrared Mapping Spectrometer (NIMS) instrument aboard the Galileo spacecraft, which orbited Jupiter from 1995 to 2003. NIMS acquired multispectral images of the surfaces of Jupiter's icy moons, Europa, Ganymede, and Callisto and these spectra have been interpreted by some as showing deposits of hydrated alkali salts (Dalton 1998, 1999; McCord *et al.*, 1998, 2001a,b; Dalton *et al.*, 2005). Such salts seem likely to be the result of brine volcanism, the eruption of salt water from oceans deep beneath the surfaces of these icy worlds.

At present, we know far too little about the structure and behavior of epsomite, and related substances, at high-pressure and low-temperature to be able to model the interiors of moons whose bulk is dominated by such salts. Technological advances in sample environments for *in situ* neutron diffraction at extreme P-T conditions are opening new avenues of study that may allow us to better understand the geology and geophysics of Jupiter's moons.

SUMMARY

In the four centuries since the discovery of the Epsom spring, the salts produced there have helped us to understand problems in medicine, physical chemistry, crystallography, and now planetary science. Even today, research into the properties of epsomite at conditions far removed from ambient,

i.e., high pressures and low temperatures, is providing new insights into the subtle forces which control the behavior of molecular crystals.

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REFERENCES

I have endeavoured to present the most thorough citations possible; in the case of very long articles, and books, which perhaps cover substances other than epsomite, then the page number(s) of interest are given in brackets after the main citation. For many French- and German-language papers, where the author is named as Monsieur, or Herr X, then I have substituted the correct first name(s).

- AGRICOLA, G. (1546): *De natura fossilium*. Basileæ (Basle).
- ALEXANDROV, K. S., T. V. RHYZHOVA, and A. I. ROSTUNTSEVA (1963): Elastic properties of some sulfate heptahydrate crystals. *Soviet Physics. – Crystallography* **7**, 753-755. [Translated from, Упругие свойства кристаллов группы семиводных сульфатов. *Kristallografiya* **7**, 930-933 (1962)].
- ARCHER, D. G., and J. A. RARD (1998): Isopiestic investigation of the osmotic and activity coefficients of aqueous MgSO₄ and the solubility of MgSO₄·7H₂O (cr) at 298.15K: Thermodynamic properties of the MgSO₄ + H₂O system to 440K. *Journal of Chemical and Engineering Data*, **43**, 791-806.
- ARCHIBALD, E. H., and W. A. GALE (1924): The system magnesium sulfate - sodium sulfate and a method for the separation of the salts. *Journal of the American Chemical Society* **46**, 1760-1771.
- BARIEAU, R. E., and W. F. GIAUQUE (1950): ZnSO₄·7H₂O. ZnSO₄·6H₂O. Heat capacities, entropies and crystal perfection at low temperatures. Heats of solution and transition. *Journal of the American Chemical Society* **72**, 5676-5684.
- BARNES, W. H., and R. G. HUNTER (1932): Confirmation of the space-group of Epsomite. *Nature* (London), **130**, 96.
- BAUR, W. H. (1964): On the crystal chemistry of salt hydrates. IV. The refinement of the crystal structure of MgSO₄·7H₂O (Epsomite). *Acta Crystallographica* **17**, 1361-1369.
- BEEVERS, C. A., and C. M. SCHWARTZ (1935): The crystal structure of nickel sulphate heptahydrate NiSO₄·7H₂O. *Zeitschrift für Kristallographie* **91**, 157-169.
- BENRATH, A. (1941): Über die löslichkeit von salzen und salzgemischen in wasser bei temperaturen oberhalb von 100°. III. *Zeitschrift für Anorganische und Allgemeine Chemie* **247**, 147-160.
- BENRATH, A., and W. SCHRÖDER (1927): Über das Octahydrat des Magnesiumsulfats. *Zeitschrift für Anorganische und Allgemeine Chemie* **161**, 155-158.
- BERGMAN, T. O. (1779): *Opuscula Physica et Chimica*. Uppsala. (vol. 1., p405)
- BERGMAN, T. O. (1782): *Sciagraphia regni mineralis, secundum principia proxima digesti*. Lipsiæ (Leipzig).

- BERGMAN, T. O. (1792): *Manuel du minéralogiste, ou sciagraphie du règne minéral, distribué d'après l'analyse chimique. Nouvelle édition., considérablement augmentée par J. C. Delamétherie.* Paris. (vol. 1., pp119-121)
- BEUDANT, F. S. (1824): *Traité élémentaire de Minéralogie*, Paris. (p445)
- BIRCH, T. (1757): *The history of the Royal Society of London for improving of natural knowledge from its first rise: in which the most considerable of those papers communicated to the Society, which have hitherto not been published, are inserted in their proper order, as a supplement to the Philosophical transactions.* Vol. 3. London.
- BLACK, J (1754): *Dissertio medica inauguralis de humore acido a cibis orto er magnesia alba.* Edinburgi.
- BLACK, J. (1756): Experiments upon Magnesia Alba, Quicklime, and some other Alcaline substances. Essays and Observations, philosophical and literary. Read before a society in Edinburgh and published by them. Vol. II, 157-225.
- BLASDALE, W. C., and H. L. ROBSON (1928): The system water and the sulfates of sodium and magnesium. *Journal of the American Chemical Society* **50**, 35-46.
- BODALEVA, N. V., and I. N. LEPESHKOV (1956): Исследование растворимости в системе K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O при 55° . *Zhurnal Neorganicheskoi Khimii* **1**, 995-1007.
- BOERHAAVE, H. (1732): *Elementa Chemiae.* Vol. 1. Lugduni Batavorum (Leiden).
- BOLTE, H. (1912): Untersuchungen über die Dissociation einiger kristallwasserhaltigen Salze. *Zeitschrift für Physikalische Chemie* **80**, 338-360.
- BONNELL, D. G. R., and L. W. BURRIDGE (1935): The dissociation pressures of some salt hydrates. *Transactions of the Faraday Society* **31**, 473-478.
- BOREL, C. (1893) Recherche des constants diélectriques de quelque cristaux biaxes. *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **116**, 1509-1511.
- BOREL, G. -A. (1895): Sur la réfraction et la dispersion des radiations ultra-violette dans quelques substances cristallisées. Archives des Sciences Physique et naturelles de Genève, 3e période, **34**, 134-157 and 230-249: *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **120**, 1404-1406.
- BOULDUC, S. (1718): Sur le Sel d'Epsom. *Histoire de l'Académie Royale des Sciences, avec les mémoires de mathématique et de physique, Année 1718*, 37-40.
- BOULDUC, G. F. (1731): Recherche du Sel d'Epsom. *Histoire de l'Académie Royale des Sciences, avec les mémoires de mathématique et de physique, Année 1731*, 347-357.
- BRIDGMAN, P. W. (1948a): Rough compression of 177 substances to 40,000 kg/cm². *Proceedings of the American Academy of Arts and Sciences* **76**, 71-87.
- BRIDGMAN, P. W. (1948b): The linear compression of various single crystals to 30,000 kg/cm². *Proceedings of the American Academy of Arts and Sciences* **76**, 89-99.
- BROOKE, H. J. (1823): On the crystalline forms of artificial salts. *Annals of Philosophy* **6**, 38-43.
- BROWN, J. (1722): Observations and experiments on the Sal Catharticum Amarum, commonly called the Epsom Salt. *Philosophical Transactions* **32**, 348-354 and 372-381.
- BROWNRIGG, W. (1774): A Letter from William Brownrigg, M.D.F.R.S. to Sir John Pringle, Bart. P.R.S. relating to some Specimens of native Salts, collected by Dr. Brownrigg, and shewn at a Meeting of the Royal Society, June 23, 1774. *Philosophical Transactions* **64**, 481-491.
- BRASS, G. W. (1980): Stability of brines on Mars. *Icarus* **42**, 20-28.
- BREWSTER, D. (1825): Observations on the pyro-electricity of Minerals. *Edinburgh Journal of Science* **2**, 208-215.
- BUIGNET, H. (1861): Application de la physique à la solution de quelques problèmes de chemie et de pharmacie. 2e partie. Densité de l'eau dans les sels cristallisés. *Journal de Pharmacie et de Chemie* 3e série, **40**, 161-176.
- BURNS, R. G. (1988): Sulfide mineralization: Its role in chemical weathering on Mars. *LPI workshop on Mars Sample Return Science*, N89-18288 10-91, pp48-50.

- CALLERI, M., A. GAVETTI, G. IVALDI, and M. RUBBO (1984): Synthetic Epsomite, $MgSO_4 \cdot 7H_2O$: Absolute configuration and surface features of the complementary {111} forms. *Acta Crystallographica*, Section B: Structural Science, **B40**, 218-222.
- CARDOSO, G. M. (1926): Feinbauliche untersuchungen am Epsomit. *Zeitschrift für Kristallographie* **63**, 19-33.
- CARDOSO, G. M. (1930): Los modernos métodos roentgenográficos aplicados en la determinación de la estructura cristalina de la epsomita. *Trabajos del Museo Nacional de Ciencias naturales.*, Serie Geológica **37**, 5-133. Madrid.
- CARPENTER, C. D., and E. R. JETTE (1923): The vapour pressures of certain hydrated metal sulfates. *Journal of the American Chemical Society* **45**, 578-590.
- CAVENDISH, H. (1767): Experiments on Rathbone-Place Water: By the Hon. Henry Cavendish, F.R.S. *Philosophical Transactions* **57**, 92-108.
- CHIPERA, S. J., D. T. VANIMAN, D. L. BISH, J. W. CAREY, and W. C. FELDMAN (2005): Experimental stability and transformation kinetics of magnesium sulfate hydrates that may be present on Mars. *36th Lunar and Planetary Science Conference*, abstract 1497.
- CHOU, I.-M., and R. R. SEAL II (2003): Determination of epsomite-hexahydrate equilibria by the humidity-buffer technique at 0.1 MPa with implications for phase equilibria in the system $MgSO_4-H_2O$. *Astrobiology* **3**, 619-630.
- CLARK, A. M. (1993): *Hey's Mineral Index: Mineral species, varieties and synonyms*. 3rd edition. Natural History Museum Publications, London.
- CLARK, B. C., and D. C. VAN HART (1981): The salts of Mars. *Icarus* **45**, 370-378.
- COBLENTZ, W. W. (1905): Water of constitution and crystallisation. *Physical Review* (Series I) **20**, 252-258.
- COBLENTZ, W. W. (1906): *Investigations of infrared spectra*. Publication of the Carnegie Institute of Washington, volume 65.
- COX, W. P., E. W. HORNING, and W. F. GIAUQUE (1955): The spontaneous transformation from macrocrystalline to microcrystalline phases at low temperatures. The heat capacity of $MgSO_4 \cdot 6H_2O$. *Journal of the American Chemical Society* **77**, 3935-3938.
- CROWLEY, J. K. (1991): Visible and near-infrared (0.4-2.5 μ m) reflectance spectra of playa evaporite minerals. *Journal of Geophysical Research: Solid Earth*, **96** (B10), 16231-16240.
- DALTON III, J. B. (2003): Spectral behaviour of hydrated sulfate salts: implications for Europa mission spectrometer design. *Astrobiology* **3**, 771-784.
- DALTON III, J. B., O. PRIETO-BALLESTEROS, J. S. KARGEL, C. S. JAMIESON, J. JOLIVET, and R. QUINN (2005): Spectral comparison of heavily hydrated salts with disrupted terrains on Europa. *Icarus* (in press).
- DANA, J. D. (1837): *System of Mineralogy*, 1st edition. London. (p174)
- D'ANS, J. (1933): *Die Lösungsgleichgewichte der System der Salz ozeanischer Salzablagerungen*. Berlin. (pp118-123)
- DAY, S., E. ASPHAUG, and L. BRUESCH (2002): Cumulates, dykes and pressure solution in the ice-salt mantle of Europa. *EOS, Transactions of the American Geophysical Union*, vol. 84, no' 46, Fall Meeting Supplement, Abstract P72B-0507.
- DE BEER, E. S. (1955): *The diary of John Evelyn*. Oxford. (vol. 5., p170)
- DE COPPET, L. C. (1872): Recherches sur la température de congélation des dissolutions salines. *Annales de Chimie et de Physique*, 4e série, **25**, 502-553. (p531).
- DE GRAMONT, A. (1884): Absence de pyroélectricité dans les cristaux de sulfate de magnésie et de sulfate de cobalt. *Bulletin de la Société Minéralogique de France* **7**, 235-236.
- DE LA MÉTHERIE, J. -C. (1806): Tableau des analyses chimiques des minéraux, et d'une nouvelle classification de ces substances, fondée sur ces analyses. *Journal de Physique, de Chimie et d'Histoire Naturelle et des Arts* **62**, 319-365 & 376-405 (p360).
- DE MARNIGNAC, J. -CH. G. (1857): Recherches sur les formes cristallines et la composition chimiques de divers sels. *Annales des Mines*, 5e série, vol. **12**, 1-74. (p50)

- DE MARIGNAC, J. -CH. G. (1902): *Oeuvres complètes publiées Société de Physique et d'Histoire Naturelle*, Genève. (vol. 1., pp479-658)
- DE ROUVILLE, P. (1878): Sur deux échantillons de cristaux naturels de sulfate de Magnésie (epsomite) de dimensions remarquable. *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **87**, p703.
- DESCLOIZEAUX, A. L. (1853): Mémoire sur l'emploi des propriétés optiques biréfringentes, pour la distinction et la classification des minéraux cristallisés. *Annales des Mines*, 5e série, **14**, 339-420. (p375)
- DE SENARMONT, H. (1851): Sur les propriétés optiques biréfringents des corps isomorphes. *Annales de Chimie et de Physique*, 3e série, **33**, 391-436. (pp406-7)
- DIESNIS, M. (1935): Sur la détermination des états hygrométriques critiques. *Bulletin de la Société Chimique de France* **52**, 1901-1907.
- DRAKE, N. A. (1995): Reflectance spectra of evaporite minerals (400-2500nm): applications for remote sensing. *International Journal of Remote Sensing* **16**, 2555-2571.
- DUFET, H. (1878): Sur la variation des indices de réfraction dans des mélanges de sels isomorphes. *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **86**, 881-884; *Bulletin de la Société Minéralogique de France* **1**, 58-62.
- DUFET, H. (1889): Sur la variation de forme cristalline dans des mélanges isomorphes. Sulfates de zinc et de magnésie. *La Société Français de Minéralogie* **12**, 22-31.
- DUFET, H. (1904): Recherches expérimentales sur l'existence de la polarisation rotatoire dans les cristaux biaxes. *La Société Français de Minéralogie* **27**, 156-168.
- ELLERY, A., and D. WYNN-WILLIAMS (2003): Why Raman spectroscopy on Mars? A case of the Right Tool for the Right Job. *Astrobiology* **3**, 565-579.
- EMONS, H. H., G. ZIEGENBALG, R. NAUMANN, and F. PAULIK (1990): Thermal decomposition of the magnesium-sulfate hydrates under quasi-isothermal and quasi-isobaric conditions. *Journal of Thermal Analysis* **36**, 1265-1279.
- ÉTARD, A. L. (1894): Recherches expérimentales sur les solutions saturées. *Annales de Chimie et de Physique*, 7e série, **2**, 503-574. (p551)
- FARADAY, M. (1846): Experimental researches in magnetism. Twentieth series. Philosophical Transactions of the Royal Society of London 136, 21-40: Zwanzigste Reihe von Experimental-Untersuchungen über Elektrizität. *Annalen der Physik und Chemie* (Poggendorff's Annalen) **69**, 289-320. (p299)
- FERRARIS, G., D. W. JONES, and J. YERKES (1973): Refinement of the crystal structure of magnesium sulphate heptahydrate (Epsomite) by neutron diffraction. *Journal of the Chemical Society; Dalton Transactions* **1973**, 816-821.
- FIALIPS, C. I., J. W. CAREY, D. T. VANIMAN, W. C. FELDMAN, D. L. BISH, and M. T. MELLON (2004): Sub-surface deposits of hydrous silicates or hydrous magnesium sulfates as hydrogen reservoirs near the Martian equator: Plausible or not? *35th Lunar and Planetary Science Conference*, abstract 2054.
- FOOTE, H. W., and S. R. SCHOLLES (1911): The vapour pressure of hydrates, determined from their equilibria with aqueous alcohol. *Journal of the American Chemical Society* **33**, 1309-1326.
- FORTES, A. D., I. G. WOOD, M. ALFREDSSON, L. VOČADLO, and K. S. KNIGHT (2005): The thermoelastic properties of MgSO₄·7D₂O (epsomite) from powder neutron diffraction and *ab initio* simulation. Paper submitted to the *European Journal of Mineralogy*.
- FORTES, A. D., I. G. WOOD, M. ALFREDSSON, L. VOČADLO, and K. S. KNIGHT (2004): Neutron diffraction studies of planetary ices. 35th Lunar and Planetary Science Conference, abstract 1252: Epsom Salt on the Moons of Jupiter. *ISIS Science Highlight, ISIS 2004 Annual Report*, RAL-TR-2004-050, CCLRC Rutherford Appleton Laboratory.
- FRITZSCHE, J. (1837): Ueber eine neue Verbindung der schwefelsauren Talkerde mit wasser. *Bulletin scientifique publié par l'Académie Impériale des Sciences de St. Pétersbourg* **2**(13), 193-196; *Annalen der Physik und Chemie* (Poggendorff's Annalen) **42**, 577-580.

-
- FROWEIN, P. C. F. (1887): Die Dissociation kristallwasserhaltiger Salze. *Zeitschrift für Physikalische Chemie* **1**, 5-14.
- FULLER, T. (1662): *The history of the worthies of England*. London. (Part 3, p78)
- GAUDEFROY, C. (1913): Sur les figures de déshydration de types différents obtenus sur les mêmes cristaux. *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **157**, 61-62.
- GAY-LUSSAC, L. J. (1819): Premier mémoire sur la dissolubilité des sels dans l'eau. *Annales de Chimie et de Physique*, 2e série, **11**, 296-315.
- GAY-LUSSAC, L. J. (1820): Analyse de schwefelsauren magnesia. *Annalen der Physik und Chemie* (Gilbert's Annalen) **66**, 34-38.
- GLASS, S. (1764): *An essay on Magnesia Alba, wherein its history is attempted, its virtues pointed out, and the use of it recommended*. Oxford.
- GRAILICH, W. J., and V. VON LANG (1857): Untersuchungen über die physikalischen verhältnisse krystallisirter körper. 1. Orientirung der optischen Elasticitätsaxen in den krystallen des rhombischen systems. *Sitzungsberichte der Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe* **27**, 3-77 (p23).
- GRAILICH, W. J., and V. VON LANG (1858): Untersuchungen über die physikalischen verhältnisse krystallisirter körper. 2. Orientirung der magnetischen verhältnisse in krystallen des rhombischen systems. *Sitzungsberichte der Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe* **32**, 43-67 (p58).
- GRASSET, O., C. SOTIN, O. MOUSIS, and L. MEVEL (2001a): High pressure experiments in the system MgSO₄ - H₂O: Implications for Europa. *31st Lunar and Planetary Science Conference*, abstract 1386.
- GRASSET, O., L. MEVEL, O. MOUSIS, and C. SOTIN (2001b): The pressure dependence of the eutectic composition in the system MgSO₄ - H₂O: Implications for the deep liquid layer of icy satellites. *31st Lunar and Planetary Science Conference*, abstract 1524.
- GREW, N. (1682): The anatomy of leaves prosecuted with the base eye and with the microscope, Read before the Royal Society, Octob. 26. 1676. In, *The Anatomy of Plants with an idea of a philosophical history of plants, and several other lectures read before the Royal Society*. London. (book VI, p158)
- GREW, N. (1695): *Tractatus de Salis Cathartici amari in aquis Ebeshemensibus et huiusmodi aliis contenti Naturâ et usu*. London.
- GREW, N. (1697a): *A treatise of the nature and use of the bitter purging salt contain'd in Epsom and such other waters*. London.
- GREW, N. (1697b): *A treatise of nature and use of the bitter purging salt. Easily known from all counterfeits by its bitter taste*. London.
- GROTH, P. VON (1908): *Chemische Kristallographie, Teil 2: Die anorganischen oxo- und sulfosalze*. Leipzig. (pp428-432)
- GUERLAC, H. (1957): Joseph Black and Fixed Air: Parts I and II. *Isis: an International Review Devoted to the History of Science and Its Cultural Influences* **48**, 124-151 and **48**, 433-456.
- HAIDINGER, W. (1826): Notice respecting Prof. Mitscherlich's observations on the dimorphism of hydrous sulfate of zinc and hydrous sulfate of Magnesia. *Edinburgh Journal of Science* **4**, 301-302: Notiz über Hr. Profess. Mitscherlich's Beobachtungen, den Dimorphismus des wasserhaltigen schwefelsauren zinkoxyds und der wasserhaltigen schwefelsauren Magnesia betressend. *Annalen der Physik und Chemie* (Poggendorff's Annalen) **6**, 191-198.
- HALES, S. (1750): An examination of the strength of several of the principal purging waters, especially of that of Jessop's Well. *Philosophical Transactions* **46**, 446-451.
- HAMAD, S. EL D. (1975): An experimental study of the salt hydrate MgSO₄.7H₂O. *Thermochemica Acta* **13**, 409-418.
- HASSANFRATZ, J. H. (1798): De le pesanteur spécifiques des sels soluble dan l'eau. *Annales de Chimie, ou Recueil de Mémoires concernant la chimie et les arts qui en dépendent*, **28**, 3-18.
-

- HAÜY, R. J. (1809): *Tableau comparatif des résultats de la cristallographie de l'analyse chimique, relativement à la classification des Minéraux*. Paris. (p15)
- HAÜY, R. J. (1801): *Traité de minéralogie*. Paris. (vol. 2, pp333-335)
- HAÜY, R. J. (1823): *Traité de minéralogie*. 2nd edition. Paris. (pp34-35)
- HEIDE, J. K. VAN DER (1893): Die doppelsalze von Kalium- und Magnesiumsulfat: Schönit und Kaliumastrakanit. *Zeitschrift für Physikalische Chemie* **12**, 418-430.
- HENRY, W. (1810): An analysis of several varieties of British and foreign salt, (muriate of soda) with a view to explain their fitness for different economical purposes. *Philosophical Transactions of the Royal Society of London* **100**, 89-122.
- HERMANN, A. (1721): *De nativo sale cathartico in fodinis Hungariæ recens invento, dissertatio epistolica*. Posonii (Bratislava).
- HIMAWAN, C. (2002): Recovery of magnesium sulfate and ice from magnesium sulfate industrial stream by eutectic freezing. In, Chemical Engineering Transactions, volume 1, *Proceedings of the 15th International Symposium on Industrial Crystallisation*, pp951-956.
- HOFFMANN, F. (1722): *Observationum Physico-Chymicarum selectiorum libri III*. Halæ (Halle).
- HOGENBOOM, D. L., J. S. KARGEL, J. P. GANASAN, and L. LEE (1995): Magnesium sulfate-water to 400 MPa using a novel piezometer: densities, phase equilibria and planetological implications. *Icarus* **115**, 258-277.
- HOGENBOOM, D. L., J. S. KARGEL, and M. E. DALY (2001): Stable and metastable high-pressure phases of the sulphuric acid - magnesium sulfate - water system: applications to Europa. *31st Lunar and Planetary Science Conference*, abstract 1739.
- HOGENBOOM, D. L., J. S. KARGEL, M. L. REITER, and Y. N. KHOR (2002): Volume changes attending hydration of quenched magnesium sulfate brine - the tectonics of Ganymede's sulci. *33rd Lunar and Planetary Science Conference*, abstract 1638.
- IDE, K. H. (1938): Zur hydration und dehydration des magnesiumsulfats und seiner hydrate. *Zeitschrift für Anorganische und Allgemeine Chemie* **235**, 305-323.
- INGRAM, D. (1767): *An inquiry into the origin and nature of magnesia alba, and the properties of Epsom waters. Demonstrating that magnesia made with those waters exceeds all others*. London.
- JOHNSEN, A. (1907): Untersuchungen über kristallzwillinge und deren Zusammenhang mit anderen Erscheinungen. *Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilagebande*, **23**, 237-344. (pp315-321)
- JOULE, J. P., and L. PLAYFAIR (1849): Researches on atomic volume and specific gravity. 4. Expansion by heat of salts in the solid state. *Quarterly Journal of the Chemical Society* **1**, 121-139.
- KAMECKI, J., and S. PALEJ (1955): Analiza termiczna i termograwimetryczna siedmiowodnego siarczanu magnezowego. *Roczniki Chemii: Annales Societatis Chimicae Polonorum* **29**, 691-704.
- KARGEL, J. S. (1991): Brine volcanism and the interior structure of asteroids and icy satellites. *Icarus* **94**, 368-390.
- KASATKIN, I. A. (2002): Interferometric study of MgSO₄·7H₂O single crystal growth kinetics from solution. *Crystal Research and Technology* **37**, 193-205.
- KIRWAN, R. (1782): Continuation of the experiments and observations on the specific gravities and attractive powers of various saline substances. *Philosophical Transactions of the Royal Society of London* **72**, 179-xxxv. (p193)
- KITAIBEL, P. (1829): *Hydrographica Hungariæ*. Pestini (Budapest). (Tomus I, p36, 112. Tomus II, p157)
- KLAPROTH, M. H. (1802) LXXXII. Chemische Untersuchung des Haarsalzes von Idria. In, *Beiträge zur chemischen Kenntnis der Mineral-Körper*. Bd. 3. Berlin. (pp104-106)
- KNOBLAUCH, H., and J. TYNDALL (1850). Ueber das verhalten körper zwischen den polen eines magneten. *Annalen der Physik und Chemie (Poggendorff's Annalen)* **81**, 481-498. (p482)
- KOPP, H. (1863): Ueber den pleomorphismus der schwefelsauren magnesia MgO, SO₃ + 7HO. *Annalen der Chemie und Pharmacie* **325**, 369-371.

- KOPP, H. (1865): Investigations of the heat capacity of solid bodies. *Philosophical Transactions of the Royal Society of London* **155**, 71-202. (p156)
- KOPTSIK, V. A. (1956): An investigation of piezoelectric crystals. *Bulletin of the Academy of Sciences, USSR; Physical Series* **20**, 201-207.
- KRAUSE, G. (1874): Reichardtite neues Mineral von Stassfurt. *Archiv der Pharmacie*, 3e sèrie, **5**, 423 and **6**, 41-45: *Zeitschrift für die Gesammten Naturwissenschaften Halle* **44**, p554 (abstract).
- KRAUSE, G. (1876): Reichardtite, a new mineral from Stassfurt. *Journal of the Chemical Society* **29**: Abstracts of Chemical Papers, p. 437.
- KUMAR, C., J. ESTRIN, and G. R. YOUNGQUIST (1930): Crystal growth under nonuniform conditions; experimental observations in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - water system. *Journal of Crystal Growth* **54**, 176-184.
- LARSEN, E. S. (1921): The microscopic identification of non-opaque minerals. *U.S.G.S Bulletin* no. 679, Washington D. C. 294pp. (p241, table)
- LEFANU, W. R. (1990): *Nehemiah Grew: a study and bibliography of his writings*. Winchester, St Paul's Bibliographies; Detroit, Michigan.
- LE MASSON, N. J. M., A. J. J. BOSS, and C. W. E. VAN EIJK (2001) Optically stimulated luminescence in hydrated magnesium sulfates. *Radiation Measurements* **33**, 693-697.
- LESCŒUR, M. H. (1889): Recherches sur la dissociation des hydrates salins et des composés analogues. *Annales de Chimie et de Physique*, 6e sèrie, **16**, 378-403.
- LISTER, M. (1682): *De fontibus medicatis Angliæ*. Eboraci (York).
- LISTER, M. (1685): Some experiments about Freezing, and the difference betwixt common fresh water ice, and that of sea water: also a probable conjecture about the origin of the Nitre of Ægypt. *Philosophical Transactions* **15**, 836-838.
- LIVSHITS, L. D., YU. S. GENSHAFT, and YU. N. RYABIN (1963): Equilibrium diagram of the crystal hydrates of MgSO_4 at high pressures. *Russian Journal of Inorganic Chemistry* **8**, 676-678. [Translated from, Фазовая диаграмма кристаллогидратов MgSO_4 при высоких давлениях. *Zhurnal Neorganicheskoi Khimii* **8**, 1302-1306 (1963)].
- LŒWEL, H. (1855): Observations sur la sursaturation des dissolutions saline. III. Dissolutions sursaturées de sulfate de magnésie. *Annales de Chimie et de Physique*, 3e sèrie, **43**, 405-420.
- LUCAS, C. (1756): Of simple neutral, purging Waters. Of Epsom Water. In, *An essay on waters*. In three parts. Part 2, pp95-103. London.
- MAHL, K. (1929): Zur morphologie des Bittersalzes. *Neues Jahrbuch für Mineralogie, Geologie und Paläontologie*, Beilagebande Abt. A., **59**, 273-296.
- MAYOW, J. (1674): *Tractatus quinque medico-physici quorum primus agit de sal-nitro et spiritu nitro aereo*. Oxonii (Oxford).
- MILLER, W. H. (1839): *A treatise on crystallography*. London. (p85, and plate VI, fig. 86).
- MILLON, E. (1845): Recherches sur la constitution chimique des acides et des bases. *Annales de Chimie et de Physique*, 3e sèrie, **13**, 129-144.
- MOHS, F. (1804): *Sammlung mineralogischer und bergmännischer Abhandlungen*, Wien.
- NAKAMURA, R. S. (2003): High pressure sulfate-water system in the large icy satellites. *EOS, Transactions of the American Geophysical Union*, vol. 84, no' 46, Fall Meeting Supplement, Abstract P51B-0449.
- NEAVE, E. J. W. (1943): The Epsom Spring. *Isis: an International Review Devoted to the History of Science and Its Cultural Influences* **34**, 210-211.
- NOVIKOVA, L. V. (1957): Изучение растворимости системы CaSO_4 - MgSO_4 - H_2O при 35° методом меченых атомов. *Zhurnal Neorganicheskoi Khimii* **2**, 662-668.
- ODOCHIAN, L. (1995) Study of the nature of crystalline water in some magnesium sulfates by thermal methods. *Journal of Thermal Analysis* **45**, 1437-1448.
- PETER, J. (1681): *A treatise of the Lewisham (but vulgerly miscalled Dulwich) wells in Kent*. London.
- PETER, J. (1701): *Truth in opposition to ignorant and malicious falsehood: or a discourse written to vindicate the Honour, and to assert the right of Dr. Nehemiah Grew, &c*. London.

- PETTERSSON, O. (1879): Untersuchungen über die Molekularvolumina einiger Reihen von isomorphen Salzen. II. *Nova Acta Regiae Societatis Scientiarum Upsaliensis*, Seriei Tertiae, **10**, Fasciculus II, 1-26. (p19).
- PHADNIS, A. B., and V. V. DESHPANDE (1981): On the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. *Thermochimica Acta* **43**, 249-250.
- PHILLIPS, W. (1852) *An Elementary Introduction to Mineralogy. A new edition, with extensive alterations and additions by H. J. Brooke and W. H. Miller*. London. (p546-547).
- PLUCKER, J., and A. BEER (1851): Ueber die magnetischen axen der krystalle und ihre beziehung zur krystallform und den optischen axen. *Annalen der Physik und Chemie* (Poggendorff's Annalen) **82**, 42-74. (p73)
- POCKLINGTON, H. C. (1906): Cheirality of form of crystals of Epsom salt. *Nature* (London) **73**, 270.
- POLO, M., N. GÉRARD, and M. LALLEMONT (1971): Étude du système binaire $\text{MgSO}_4 - \text{H}_2\text{O}$. *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, Série C, Sciences chimiques, **272**, 642-645.
- PRIETO, O., and J. S. KARGEL (2001): Specific heat capacity data of some hydrated salts at low temperatures. Applications to Europa satellite. *32nd Lunar and Planetary Science Conference*, abstract 1625.
- RAKUSIN, M. A., and D. A. BRODSKI (1927): Entwässerungsversuche an Metallsalz-hydraten. *Zeitschrift für Angewandte Chemie* **40**, 108-115.
- RAMALINGOM, S., J. PODDER, AND S. NARAYANA KALKURA (2001): Crystallisation and characterisation of orthorhombic $\beta\text{-MgSO}_4 \cdot 7\text{H}_2\text{O}$. *Crystal Research and Technology* **36**, 1357-1364.
- RAMMELSBERG, C. (1854): Ueber das verhältniss, in welchem isomorphe körper zusammen krystallisiren und den einfluss desselben auf die form der krystalle. *Annalen der Physik und Chemie* (Poggendorff's Annalen) **91**, 321-354.
- RAYAN, F. M., W. LEHMANN, D. W. FELDMAN, and J. MURPHY (1974): Fine structure in the optical spectra of divalent Europium in the alkaline earth sulfates. *Journal of the Electrochemical Society*, **1974**, 1475-1481.
- RETGERS, J. W. (1889): Das spezifische gewicht isomorpher mischungen. *Zeitschrift für Physikalische Chemie* **3**, 497-560. (pp534-547)
- ROBSON, H. L. (1927): The system $\text{MgSO}_4\text{-H}_2\text{O}$ from 68 to 240°. *Journal of the American Chemical Society* **49**, 2772-2783.
- ROMÉ de L'ISLE, J. -B. L. (1772): *Essai de cristallographie, ou description des figures géométriques propres à différens corps du regne minéral, connus vulgairement sous le nom de cristaux*. Paris. (pp54-56 and Plate III)
- ROTHSCHILD, L. (1990): Earth analogs for martian life. Microbes in evaporites, a new model system for life on Mars. *Icarus* **88**, 246-260.
- RUBBO, M., D. AQUILANO, M. FRANCHINI-ANGELA, and G. SGUALDINO (1985): Growth morphology of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). *Journal of Crystal Growth* **71**, 470-482.
- SAKULA, A. (1982): The waters of Epsom Spa. *Journal of the Royal College of Physicians of London* **16**, 124-128.
- SAKULA, A. (1984): Dr Nehemiah Grew (1641-1712) and the Epsom Salts. *Clio Medica: Acta Academiae Internationalis Historiae Medicinae* **19**, 1-21.
- SCHIFF, H. (1859a): Ueber die volumveränderung bei lösung von salzen. *Annalen der Chemie und Pharmacie* **109**, 325-332.
- SCHIFF, H. (1859b): Zur theorie der s(pecifisches). g(ewichte). übersättigten lösungen. *Annalen der Chemie und Pharmacie* **111**, 68-82.
- SCHNETTER, C. L. (1715): *Dissertio inauguralis medica de Sale Cathartico Amaro Anglico vulgo Anglis Epsom Salt*. Jenæ (Jena).
- SCHUMB, W. C. (1923): The dissociation pressures of certain salt hydrates by the gas-current saturation method. *Journal of the American Chemical Society* **45**, 342-354.

- SCOPOLI, G. A. (1761): *De hydrargyro Idriensi tentamina physico-chymico-medica. I. De minera hydrargyri. II. De vitriolo Idriensi. III. De morbis fessorum hydrargyri.* Venice.
- SCOPOLI, G. A. (1772): *Principia Mineralogiæ systematicæ et practicæ.* Pragæ (Prague). (p81)
- SHAW, P. (1734): *An enquiry into the contents, virtues, and uses of the Scarborough spaw-waters: with the method of examining any other mineral water.* London.
- SMITS, A., J. RINSE, and L. H. LOUWE-KOOYMANS (1928): Das system wasser-magnesiumsulfat. *Zeitschrift für Physikalische Chemie* **135**, 78-84.
- SPITZER, F. (1951): Neuere synthetische piezoelektrische kristalle in der elektroakustic und hochfrequenztechnik. *Archiv der Elektrischen Übertragung* **5**, 544-552.
- STROMEYER, F. (1821): XXVII. Untersuchung des natürlichen Talkerdehydrats aus New-Jersey in Nordamerika. In, *Untersuchungen über die Mischung der Mineralkörper mit anderer damit verwandten Substanzen.* pp399-409. Göttingen.
- SUNDARA RAO, R. V. G. (1950): Elastic constants of the heptahydrates of magnesium and zinc sulphates. *Proceedings of the Indian Academy of Science* **A31**, 365-370.
- TAKEGAMI, S. (1922): On the octahydrate of Magnesium Sulphate. *Memoirs of the College of Science, Kyoto Imperial University* **5**, 191-199.
- THORPE, T. E., and J. I. WATTS (1880): On the specific volume of water of crystallisation. *Journal of the Chemical Society of London* **37**, 102-117.
- TING, H. H., and W. L. MCCABE (1934): Solubility of magnesium sulfate heptahydrate. *Industrial and Engineering Chemistry* **26**, 1207-1208.
- TOBLER, E. (1855): Ueber die löslichkeit einiger schwefelsauren salze der magnesiareihe in wasser. *Annalen der Chemie und Pharmacie* **95**, 193-199.
- TOMLINSON, C. (1868): On supersaturated saline solutions. *Philosophical Transactions of the Royal Society of London* **158**, 659-673.
- TOMLINSON, C. (1871): On the behaviour of supersaturated saline solutions when exposed to the open air. *Proceedings of the Royal Society of London* **20**, 41-45.
- TOPSÖE, H., and C. CHRISTIANSEN (1874): Recherches optiques sur quelques séries de substances isomorphes. *Annales de Chimie et de Physique*, 5e série, **1**, 5-99; *Annalen der Physik und Chemie*, Ergänzungbandes **VI**, 499-585.
- TOULMIN, P., A. K. BAIRD, B. C. CLARK, K. KEIL, H. J. ROSE JNR, R. P. CHRISTIAN, P. H. EVANS, and W. C. KELLIHER (1977): Geochemical and mineralogical interpretation of the Viking inorganic chemical results. *Journal of Geophysical Research* **84**, 4625-4634.
- VANIMAN, D. T., D. L. BISH, S. J. CHIPERA, AND J. W. CAREY (2004): Salt attack on rocks and expansion of soils on Mars. *American Geophysical Union Fall Meeting*, abstract P21A-0207.
- VAN KLOOSTER, H. S. (1917): Saturated solutions of potassium and magnesium sulphates at 25°C. *Journal of Physical Chemistry* **21**, 513-518.
- VAN'T HOFF, J. H., W. MEYERHOFFER, and N. SMITH (1901): Untersuchungen über die bildungsverhältnisse der oceanischen salzablagerungen, insbesondere des Stassfurter salzlagen. XXIII. Das auftreten von Kieserit bei 25°. *Sitzungsberichte der Preussischen Akademie der Wissenschaften*, **1901**, pp1034-1044.
- VAN'T HOFF, J. H. (1905): *Zur Bildung Ozeanischer Salzablagerungen.* Braunschweig.
- VIOLA, C. (1923): Über bestimmte mischkristalle. *Zeitschrift für Kristallographie* **58**, 583-595.
- VOGEL, R. A. (1762): *Practisches Mineralsystem.* Leipzig. (p282).
- VON HAUER, K. (1878) Krystallogenetische Beobachtungen. *Verhandlungen des Geologischen Reichsanstalt (Wien)* 1878, 315-321.
- VORONKOV, A. A. (1958): The piezoelectric, elastic and dielectric properties of crystals of MgSO₄.7H₂O. *Soviet Physics: -Crystallography* **3**, 722-725. [Translated from Пьезоэлектрические, упругие и диэлектрические свойства кристаллов MgSO₄.7H₂O. *Kristallographiya* **3**, 716-719 (1958)]
- WALLERIUS, J. G. (1747): *Mineralogia, eller Mineral-Riket Indelt och beskrifvit.* Stockholm. (p184-85)

- WÄNKE, H. J. BRÜCKNER, G. DRIEBUS, R. REIDER, and I. RYABCHIKOV (2001): Chemical composition of rocks and soils at the Pathfinder site. *Space Science Reviews* **96**, 317-330.
- WESTENBRINK, H. G. K. (1926a): Thèse de doctorat, Groningue.
- WESTENBRINK, H. G. K. (1926b): Sur l'existence de sels doubles dans la série de mélanges isomorphes $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ et sur des combinaisons à l'état solide en général. Proceedings of the Section of Science. *Koninklijke Akademie Wetenschappen te Amsterdam* **29**, 1374-1384: Over het voorkomen van dubbelzouten in de isomorfe mengingsreeks $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ en over de verbingen in den vasten toestand in het algemeen. *Verslagen Akademie van Wetenschappen te Amsterdam* **35**, 968-978.
- WESTENBRINK, H. G. K. (1926c): Les groupes spatiaux des heptahydrates rhombique et moncliniques des sulfates de métaux bivalents. *Proceedings of the Section of Science. Koninklijke Akademie Wetenschappen te Amsterdam* **29**, 1223-1232: De ruimtgroepen der rhombische en monokliene heptahydraten van de sulfaten der tweewaardige metalen. *Verslagen Akademie van Wetenschappen te Amsterdam* **35**, 913-922.
- WESTENBRINK, H. G. K. (1927): Sur les systèmes spatiaux des heptahydrates rhombiques et monocliniques des sulfates des métaux bivalents et sur la série de cristaux mixtes $\text{Mg}(\text{Zn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. *Recueil des Travaux Chimiques des Pays-Bas* **46**, 105-123.
- WIEDEMANN, G. (1874): Ueber die dissociation der wasserhaltigen salze. *Annalen der Physik und Chemie*, Jubelbandes (1874), 474-490.
- WITTIE, R. (1660): *Scarborough Spaw, or, a description of the nature and vertues of the spaw at Scarborough in Yorkshire*. London.
- ZOLOTOV, M. YU., E. V. ZABALUEVA, and R. O. KUZMIN (1997): Stability of hydrated salts and goethite within the dessicated upper layer of the martian regolith. *Lunar and Planetary Science Conference* **28**, p633.

APPENDIX: PHYSICAL PROPERTIES OF EPSOMITE

As noted in the text, measurements by Voronkov (1958) are open to doubt, possibly due to his use of borax as a growth modifying medium.

Ideal composition: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Molecular weight: $246.47 \text{ g mol}^{-1}$

Magnesium: 9.861 wt %

Sulfur: 13.009 wt %

Oxygen: 71.404 wt %

Hydrogen: 5.725 wt %

Unit cell dimensions (measured by neutron diffraction of deuterated epsomite; Fortes *et al.*, 2004, 2005)

at 295 K,

$a = 11.8659 \pm 0.0002 \text{ \AA}$

$b = 11.9981 \pm 0.0001 \text{ \AA}$

$c = 6.8551 \pm 0.0001 \text{ \AA}$

$V = 975.96 \pm 0.02 \text{ \AA}^3$

giving a calculated density for *hydrogenous* epsomite = 1677 kg m^{-3}

at 2 K,

$$a = 11.8959 \pm 0.0001 \text{ \AA}$$

$$b = 11.9075 \pm 0.0001 \text{ \AA}$$

$$c = 6.7864 \pm 0.0001 \text{ \AA}$$

$$V = 961.30 \pm 0.02 \text{ \AA}^3$$

giving a calculated density for *hydrogenous* epsomite = 1703 kg m⁻³

Coefficient of volume thermal expansion (determined by neutron diffraction of deuterated epsomite; Fortes *et al.*, 2004, 2005)

at 295 K: $109 \times 10^{-6} \text{ K}^{-1}$

at 150 K: $54 \times 10^{-6} \text{ K}^{-1}$

at 50 K: $13 \times 10^{-6} \text{ K}^{-1}$

Molar heat capacity (interpolated from the data of Prieto and Kargel, 2001)

at 295 K: $\sim 380 \text{ J mol}^{-1}$

Optical properties (room temperature). The values quoted here are from Topsøe and Christiansen (1874); these figures, given to 3 decimal places in Larsen (1921), are the values cited in most modern texts.

Refractive indices $n_\alpha = 1.4325$
 $n_\beta = 1.4554$
 $n_\gamma = 1.4608$
 $2V = 51^\circ 25' \text{ (-ve)}$

Birefringence: 0.0283

Dielectric constants (room temperature)

Borel (1893)

$$k_1 = 8.28$$

$$k_2 = 6.05$$

$$k_3 = 5.26$$

Voronkov (1958)

$$\kappa_{11} = 5.40 \pm 0.06$$

$$\kappa_{22} = 5.23 \pm 0.03$$

$$\kappa_{33} = 5.79 \pm 0.05$$

Piezoelectric constants (room temperature). From Voronkov (1958); the values are quoted as being "expressed in CGSE units", and are presumably esu dyne⁻¹.

$$d_{14} = -6.0 \pm 0.3 \times 10^{-8} \text{ esu dyne}^{-1}$$

$$d_{25} = -7.2 \pm 0.3 \times 10^{-8} \text{ esu dyne}^{-1}$$

$$d_{36} = 10.8 \pm 0.03 \times 10^{-8} \text{ esu dyne}^{-1}$$

Elastic constants (room temperature). Alexandrov *et al.* (1963) gives the elastic stiffness moduli, c_{ij} , which I have used to calculate the elastic compliances, s_{ij} . Errors are quoted as 2–3 % on c_{ii} and 10–12 % on c_{ij} .

	Stiffness (GPa)		Compliance (GPa ⁻¹)
c_{11}	32.5	s_{11}	0.0516
c_{22}	28.8	s_{22}	0.0620
c_{33}	31.5	s_{33}	0.0567
c_{12}	17.4	s_{12}	-0.0194
c_{13}	18.2	s_{13}	-0.0186
c_{23}	18.2	s_{23}	-0.0246
c_{44}	7.8	s_{44}	0.1282
c_{55}	15.6	s_{55}	0.0641
c_{66}	9.0	s_{66}	0.1111

Bulk elastic moduli. Column A: moduli calculated from the elastic stiffness coefficients of Alexandrov *et al.* (1963) at room temperature. Column B: parameters from the fitting of a 3rd order Birch Murnaghan equation of state (BMEOS) to the compression data of Bridgman (1948b) at room temperature. Column C: parameters parameters from the fitting of a 3rd order BMEOS to the compression data of Fortes *et al.* (2004) at 290 K; $\partial K/\partial P$ was fixed at the value found in quantum mechanical calculations (see column E). Column D: parameters parameters from the fitting of a 3rd order BMEOS to the compression data of Fortes *et al.* (2004, 2005) at 50 K. Column E: parameters parameters from the fitting of an integrated 3rd order BMEOS to the internal energy of the epsomite crystal calculated using density functional theory (Fortes *et al.*, 2005).

		A	B	C	D	E
Bulk modulus, K	(GPa)	22.2	21.6	21.5	25.0	23.2
$\partial K/\partial P$		-	5.0	5.3	5.3	5.3
Shear modulus, G	(GPa)	8.6	-	-	-	-
Young's modulus, E	(GPa)	22.9	-	-	-	-
Poisson's ratio, η		0.328	-	-	-	-

FOOTNOTES

ⁱ A variant of Ebesham, derived from the ca. 7th century name of the village - Ebbisham.

ⁱⁱ Now Novosedlice, part of the city of Teplice, in The Czech Republic.

ⁱⁱⁱ Not to be mistaken for Seidlitz powder, a mixture of sodium bicarbonate and rochelle salt.

^{iv} *Not* the modern mineral halotrichite, $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$.

^v The reason being given that, "*he hath given us all his other Works in English, yet composed this in Latin, to secure it to the Use of Experienced Physicians, and from the Hands of busy Quacks.*"

^{vi} Some entertaining examples include, "The Translator, ... not knowing the English of *Sextans*, no more than of many other Words before-going," and, "Can any thing be more scurvily render'd?"

^{vii} "I Do remember, that about nineteen years past, Dr. *Grew* shewed to the Royal Society at one of their Meetings in *Gresham* College, several Parcels of Crystallized Salts, by him made of the Purging Waters about *London*. And I do not remember, that any Salts of that Sort, were before that time, presented to the Society by any Person." Sir Christopher Wren, affidavit of June 4th 1698 (Peter 1701, p27).

^{viii} Most often common sea salt plus sulfuric acid, after Johann Glauber's recipe, hence Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), itself a potent laxative.

^{ix} Schemnitz is the modern town of Banská Štiavnica in Slovakia.

^x Herrengrund is now Špania Dolina in Slovakia. The name means Ruler's Valley, and Hermann makes frequent reference to it in latin as *Vallis Dominorum*.

^{xi} "Mon Pere reconnut même san erreur quelque temps après, & si Dieu lui avait conservé des jours, comme il étoit de bonne foi, qu'il aimoit la vérité, il se seroit fait honneur de déclarer hautement sa

méprise. En matiere de Physique, il est facile de tomber dans l'erreur, mais il n'est pas également facile de la reconnoître, & d'en sortir."

^{xii} Wallerius (1747) *does* observe that the salt becomes like flour, and loses its lustre, in the open air ("...blir ock i fria luften mjöligt och förlorar sin glants."), but does not comment on the likely mechanism, as Romé de l'Isle (1772) does.

^{xiii} "Les Cristaux de ce sel sont transparens comme la plus belle glace; mais lorsqu'ils sont exposés à un air sec, ils perdent très-prompement leur transparence par l'évaporation de l'eau de leur cristallisation."

^{xiv} This work contains the earliest known photographs of epsomite crystals.

^{xv} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was actually used in the solution of the Ni-bearing structure by the method of measuring the structure factor differences for specific Bragg reflections.

^{xvi} An otherwise fine piece of work.

^{xvii} Including my own.