

Comment on Mineral Diversity on Europa: Exploration of Phases Formed in the $\text{MgSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ Ternary

A. Dominic Fortes* and Johannes M. Meusburger



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ABSTRACT: The structure of a new polymorph of $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$, a potentially important mineral on the surface of Europa, one of Jupiter's icy moons, was reported by Maynard-Casely et al. [Maynard-Casely, H. E.; Brand, H. E.; Wilson, S. A.; Wallwork, K. S. Mineral Diversity on Europa: Exploration of Phases Formed in the $\text{MgSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ Ternary. *ACS Earth Space Chem.* 2021, 5 (7), 1716–1725. DOI: 10.1021/acsearthspacechem.1c00073]. The reported structure is unambiguously incorrect because the stoichiometry is wrong; the formula unit contains only half of the SO_4^{2-} oxyanions required. We highlight where this error could have been detected at various stages of the analysis, writeup, and submission process and make recommendations to avoid repetition of the mistake.

INTRODUCTION

Maynard-Casely et al.¹ recently reported the results of a study using synchrotron X-rays into the sub-solidus behavior of mixtures containing magnesium sulfate, sulfuric acid, and water, motivated by an interest in the mineralogy of icy planetary bodies in the outer solar system. In the first instance, we thoroughly support this work. Studies of cosmic analogue materials have the potential to shed light on unexpected chemical interactions and identify novel structural motifs while also helping us to interpret remotely sensed or *in situ* data from extraterrestrial phenomena. Our motivation in writing this comment is not to criticize unduly but to recommend methods and tools for authors, reviewers, and editors to avoid the errors that we highlight below.

AREAS OF AGREEMENT

The analysis carried out by Maynard-Casely et al.¹ includes the identification of four unknown crystalline phases, in addition to a number of previously characterized MgSO_4 hydrates and water ice. For one of these, unknown 1 (UK1), they provide a structure solution based on their X-ray powder diffraction data and interpret the resulting structural model as a new polymorph of $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$ or MS6 (the mineral hexahydrite). Their indexing of the unit cell is similar to that of MS6 (i.e., $\Delta a \sim 7.6\%$, $\Delta b \sim -5.3\%$, $\Delta c \sim -0.2\%$, $\Delta \beta \sim 1.6\%$, and $\Delta V \sim 2.1\%$). We have indexed the powder diffraction pattern provided in their Crystallographic Information File (CIF) and obtain the same lattice parameters as Maynard-Casely et al.¹ with a high figure of merit (FoM).

The evidence presented in the paper that this is a distinct phase from MS6 is convincing, and we agree with that specific interpretation. In the first place, both MS6 and UK1 co-exist in one of their samples (Figure 2 of ref 1). Second, the unit-cell volumes for $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4\cdot 11\text{H}_2\text{O}$ agree reasonably well with published data, indicating that instrument calibration is likely not an issue. Some years ago, we determined the lattice

parameters of deuterated MS6 down to 8 K as an accessory phase in samples of $\text{MgSO}_4\cdot 3\text{D}_2\text{O}$. A comparison of this previously unpublished work² with the values of Maynard-Casely et al.¹ (Figure 1) confirms that their results for the known phase of MS6 are accurate, with the absolute difference in

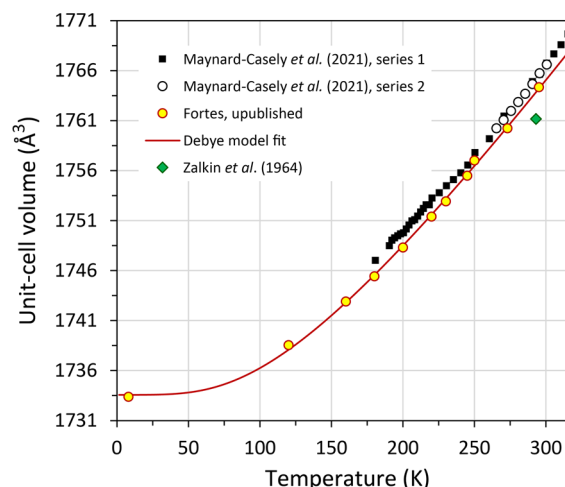


Figure 1. Unit-cell volumes of ordinary protiated MS6 reported by Maynard-Casely et al.¹ (extracted from their Figure 4 by graphical methods) compared to previously unpublished experimental data² for deuterated MS6, acquired by neutron powder diffraction and fitted with a Debye-type model of the thermal expansion. The room-*T* datum from Zalkin et al.³ is also indicated.

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volume potentially being due to deuteration. Third, the Bragg peak intensities of UK1 shown in Figure 6 of ref 1 differ substantially from those of MS6.

It is our view that problems arise in moving beyond basic phase identification and indexing to the structure solution stage. We assert that their final structural model is unambiguously incorrect for the reasons outlined below.

PROBLEMATIC STRUCTURE SOLUTION

The authors used the freely available parallel tempering code FOX^{4,5} for their structure solution, which is an excellent tool for the job but one that requires careful use. In setting up the solution process, the chances of obtaining a correct solution are increased by the choice of space group, with awareness of the site multiplicities, and, for more complex structures, by providing accurate information on how the atoms may be connected. This could be a Z-matrix for molecular species or a geometric description of the likely coordination polyhedra for inorganic crystals.

Maynard-Casely et al.¹ determined from systematic absences that UK1 is a C-centered monoclinic crystal, adopting either space group $C2/c$ (the same as MS6) or Cc . We note that both $C2/n$ and Cn represent alternative settings with the same absence conditions that were apparently not considered. The authors had by this point already made the assumption that this phase was a polymorph of MS6 and used MgO_6 octahedra and SO_4 tetrahedra to describe the structural motifs in the crystal. We consider this at least to be a reasonable starting point but one that should have been revisited after it became clear that the resulting fit to the data was rather poor. The stated Mg–O bond lengths of 2.2 Å are not correct; typical Mg–O bond lengths in the water-rich $MgSO_4$ hydrates are in the range of 2.0–2.1 Å.^{6–9} Longer Mg–O bonds sometimes occur in less hydrated $MgSO_4$ crystals because their polyhedra exhibit an increasing tendency to polymerize, forming corner-sharing dimers or chains.¹⁰ In this case, one may observe MgO_6 polyhedra with greater degrees of distortion as a result of the spread of Mg–O distances between Mg^{2+} and water oxygens (~2.00–2.05 Å) as well as sulfate oxygens (~2.05–2.10 Å).^{11–14} Hence, Mg–O = 2.2 Å should be considered unlikely unless other structural evidence is obtained to support it.

The authors note that they populated the asymmetric unit with two MgO_6 octahedra and one SO_4 tetrahedron. This provides the correct stoichiometry in space group $C2/c$, where the Mg atoms are on special positions with a multiplicity of 4 and the S atoms occupy general positions with a multiplicity of 8. Loss of the 2-fold axis of rotational symmetry and the center of symmetry in Cc with respect to $C2/c$ results in the multiplicity of the general position being reduced from 8 to 4; space group Cc only has sites of 4-fold multiplicity. This poses no problem for the MgO_6 octahedra, which are already on sites with a multiplicity of 4, but to retain the correct overall stoichiometry, the SO_4 tetrahedra formerly on sites of 8-fold multiplicity must be split in two. Hence, the number of SO_4 tetrahedra included in the asymmetric unit must be doubled. The FOX software will not make this change automatically if a different space-group symbol is entered; one must explicitly click on “Scatterers → Duplicate Scatterer” and then select the item to be copied. Having been unable to obtain a solution in $C2/c$, it appears that Maynard-Casely et al.¹ either failed to recognize the need for duplication of the SO_4 unit or recognized the need but unintentionally omitted the action to achieve it and proceeded to a structure determination in space group Cc without ensuring

that the correct number of SO_4 tetrahedra were included in the asymmetric unit. As a result, the structure presented in the paper does not have the correct stoichiometry. This is readily apparent from examination of Figure 8 of ref 1 and from the CIF, which explicitly lists the site multiplicities; their crystal has the formula sum $MgS_{1/2}O_{16}$, when it would properly be $MgSO_{20}$ if it were indeed a polymorph of MS6. The quality of the final structure refinement is low; $wRp = 18.8\%$, including even the use of eighth-order spherical harmonics, is an extremely poor result. Structure-less profile refinement yields $wRp = 4.9\%$ (Pawley method; caption of Figure 6 of ref 1) and $wRp = 3.2\%$ (LeBail method; obtained by us using the data provided in the CIF), and one would thus expect a satisfactory Rietveld structure refinement to be close to this or at least $<5\%$.

POTENTIAL FOR SPOTTING THE ERROR

We next examine where the error could have been detected and evaluate what steps may be taken to avoid such obviously incorrect crystal structures from being published in the future, paying attention to where assumptions could have been challenged or better working practices could be developed.

The first problem that the authors faced was at the stage of making assumptions about the composition. They naturally assumed that the similarity of the lattice parameters implied a structural and compositional relationship to MS6 without giving due weight to the increase in molar volume and the possibilities afforded by the chemistry of the ternary system with which they were working. The presence of sulfuric acid in the mother liquor and the structural similarity between SO_4 and either HSO_4 and/or H_2SO_4 imply the possibility that crystals could form containing any or all of these units. There are a number of compounds in the Inorganic Crystal Structure Database (ICSD) in which a divalent metal cation is coordinated to HSO_4 and/or H_2SO_4 , including $Mg(H_2SO_4) \cdot H_2O$ and $Mg(HSO_4)_2(H_2SO_4)$.^{15–20} Even the notion that such compounds could have formed during their study is not mentioned by the authors, who should certainly have entertained the possibility that the increase in volume and the potential splitting of the sulfate oxyanion into two symmetry inequivalent units was due to the inclusion of HSO_4 , $H(SO_4)_2$, or H_2SO_4 in the structure.

The very basic error in the stoichiometry of the structure could have been captured early in the solution process. It should become habitual, after entering the structural motifs in FOX, to visually inspect the unit-cell contents. Clicking the “Display” button and examining only the asymmetric unit allows for a straightforward “head count” of how many MgO_6 and SO_4 polyhedra (for example) are present, even before running the Global Optimization. In the event that the polyhedra are clustered on top of one another, clicking “Parameters → Randomize Configuration” a one or more times will eliminate this problem.

Clearly, in the absence of the correct number of polyhedra, FOX will attempt to move the “wrong” polyhedra to account for the observed electron density at particular locations in the unit cell. Consequently, one would expect to encounter substantial residual features in a Fourier difference map. After running the Global Optimization, one ought to open the “Display” tab, right click in the display window, and select “Fourier maps” to produce a three-dimensional (3D) plot of the difference densities. This is likely to have revealed features indicating a problem with the solution process.

Nevertheless, this incorrect structure was used as the basis for a rigid-body Rietveld refinement. Obtaining a large wRp value,

even with many texture parameters, should have indicated a serious problem. We note that the authors do not report the overall texture coefficient nor do they report the total number of refined parameters. Having completed the refinement, we expect that the authors examined their structure to characterize it relative to MS6, producing figures, tables of atomic coordinates and bond lengths, and a CIF. Any one of these subsequent actions provided an opportunity to count up the number of polyhedra and observe a disparity. Moreover, the imprecision of the atomic coordinates and the large unphysical difference in B_{iso} for the sulfate oxygens act as warning indicators. We are suspicious of the B_{iso} values for the atoms in the MgO_6 octahedra not being refined and do not accept the explanation provided that this step was omitted as a result of the fact that the O atoms have hydrogens attached.

One extremely important aspect of examining the structure should be to ascertain if the bonding between the structural elements is reasonable. In this case, one would be seeking O...O contacts consistent with the formation of O–H...O hydrogen bonds. Considering the ranges of distances and angles found in other water-rich MgSO_4 hydrates,^{6–14} we expect O...O distances of 2.6–3.0 Å and O...O...O angles in the region of 105°; the exact values will depend upon how strained are the hydrogen bonds, but the approximate values serve as a fair guide for an initial check. With 12 symmetry-inequivalent water molecules, we are seeking 24 potential hydrogen-bonding contacts. Our examination of the structure reported by Maynard-Casely et al.¹ reveals only nine O...O distances and just two pairs of vectors that form an angle that are consistent with ordinary O–H...O hydrogen bonding. There are distances that are too short [$\text{O15}\cdots\text{O2}^a = 2.06(3)$ Å, $\text{O15}\cdots\text{O3}^a = 2.45(3)$ Å, and $\text{O2}^a\cdots\text{O15}\cdots\text{O3}^a = 56.4(9)^\circ$] ($a = \text{symmetry code of } x, 1 - y, \frac{1}{2} + z$), while the majority of distances are too long [e.g., $\text{O13}\cdots\text{O26}^b = 3.33(4)$ Å, $\text{O13}\cdots\text{O11}^c = 3.59(8)$ Å, and $\text{O26}^b\cdots\text{O13}\cdots\text{O11}^c = 70.0(7)^\circ$] ($b = \text{symmetry code of } \frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$, and $c = \text{symmetry code of } \frac{1}{2} + x, \frac{1}{2} + y, z$). Even a cursory examination of the structure and potential bonding geometry thus reveals serious flaws and a likely incorrect solution.

The final checkpoint for identifying problems comes with the crystallographic information file (CIF),^{21,22} which authors will typically deposit as part of their supplementary information. Crystallographic best practice requires the experimentalists to prepare their CIF for publication with care and attention to detail, ensuring that information required for others to understand and reproduce the work is accurately reported. Ideally, a CIF editing tool^{23,24} should be used to ensure that syntax is correct at the very least. Prior to submission, the CIF should be evaluated by the CheckCIF utility of the International Union of Crystallography (IUCr);²⁵ this will highlight issues with the CIF and provide authors with an opportunity to correct the problems or else offer reasons for disregarding the alerts.²⁶ We can be quite sure that Maynard-Casely et al.¹ did not use the CheckCIF utility because when we submitted their CIF we obtained a syntax error message and the checks were not carried out.

Deleting the incorrectly formatted lines allowed the CheckCIF utility to proceed, and we obtained a report (see the Supporting Information) with 17 A-level alerts, defined as “most likely a serious problem—resolve or explain”, 5 C-level alerts, and 11 G-level alerts. Many of these alerts are due to the sparse nature of the CIF, including missing information about the data acquisition and the refinement, which are readily

addressed. However, the CheckCIF report informs us that there is a very short contact distance between S1 and O15 (2.81 Å) and, most telling of all, that the unit cell contains solvent-accessible voids of 86 Å³. This is a quite considerable amount of void space and reflects the fact that the structure is missing half of its complement of SO_4 tetrahedra. The final page of the report draws the asymmetric unit, showing two MgO_6 octahedra and only one SO_4 tetrahedron. If all of the indicators prior to this point had been missed, the CheckCIF report is at least very clear that there are fundamental problems with the crystal structure.

RECOMMENDATIONS

In terms of avoiding these errors in the future, we encourage all authors of crystallographic papers to adopt the best working practice of ensuring that they produce a comprehensive CIF, regardless of whether it is required by a journal for submission or not. This should include use of a CIF editor and the CheckCIF validation utility combined with rigorous error checking to resolve outstanding problems prior to submission. Outside of the core crystallographic journals, the rules concerning adoption of CIF submission and use of CheckCIF as a mandatory step in submission of papers reporting crystal structures are not consistent. Across a range of chemistry journals, we note that the Royal Society of Chemistry of the U.K.,²⁷ the *European Journal of Chemistry*,²⁸ the *Canadian Journal of Chemistry*,²⁹ and the *Australian Journal of Chemistry*³⁰ each require submission of crystallographic data to the Cambridge Crystallographic Data Centre (CCDC), which, in turn, requires the use of CheckCIF, and most of the author guidelines of these journals offer extensive advice on the content that they expect to appear in the CIF. Despite this, we find recent examples of work (e.g., ref 31) in the aforementioned journals where CIF preparation was extremely poor and CheckCIF validation cannot have been done. Among the family of journals of the American Chemical Society (ACS), only *Crystal Growth & Design*, *Inorganic Chemistry*, *Organic Letters*, *The Journal of Organic Chemistry*, *Organometallics*, and the *Journal of the American Chemical Society* presently mandate the same level of due diligence with regard to CIF checking prior to submission.³² Because we have observed an increasing number of papers in *ACS Earth and Space Chemistry* that report crystal structures, we advocate for the adoption of a requirement for submission of a comprehensive CIF that has been thoroughly validated. Furthermore, we recommend that any ACS journal in receipt of a crystal structure determined using either X-ray or neutron diffraction methods also follow this practice.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsearthspacechem.2c00038>.

IUCr CheckCIF/PLATON report on the CIF supplied in ref 1 (PDF)

AUTHOR INFORMATION

Corresponding Author

A. Dominic Fortes — ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom; orcid.org/0000-0001-5907-2285; Email: dominic.fortes@stfc.ac.uk

Author

Johannes M. Meusburger – ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom; Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom; Camborne School of Mines and Environment and Sustainability Institute, Tremough Campus, University of Exeter, Penryn, Cornwall TR10 9EZ, United Kingdom

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsearthspacechem.2c00038>

Notes

The authors declare no competing financial interest.

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