Fast in-situ X-ray scattering reveals stress sensitivity of gypsum dehydration kinetics

Christoph Eckart Schrank1✉, Oliver Gaede1, Tomasz Blach2, Katherine Carmen Michelle Gioseffi1, Stephen Mudie3, Nigel Kirby3, Klaus Regenauer-Lieb2 & Andrzej P. Radliński3,4

The dehydration of gypsum to hemihydrate has been studied for decades because it is an important model reaction for understanding fluid-triggered earthquakes, and due to the global use of plaster of Paris in the construction industry. The dehydration kinetics of gypsum strongly depend on temperature and water vapour pressure. Here, we perform fast, time-resolved synchrotron X-ray scattering on natural alabaster samples, finding that a small elastic load accelerates the dehydration reaction significantly. The mechanical acceleration of the reaction consumes about 10,000 times less energy than that due to heating. We propose that this thermodynamically surprising finding is caused by geometry-energy interactions in the microstructure, which facilitate nucleation and growth of the new crystalline phase. Our results open research avenues on the fundamental thermo-mechanics of crystal hydrates and the interaction of stress and chemical reactions in crystalline solids with a wide range of implications, from understanding dehydration-triggered earthquakes to the energy-efficient design of calcination processes.

1 Queensland University of Technology, School of Earth and Atmospheric Sciences, Brisbane, QLD, Australia. 2 The University of New South Wales, School of Minerals and Energy Resources Engineering, Anzac Parade, Kensington, NSW, Australia. 3 Australian Synchrotron, Clayton, VIC, Australia. 4 University of Warsaw, Faculty of Physics, Warsaw, Poland. ✉email: christoph.schrank@qut.edu.au
The calcium sulphate dihydrate gypsum (CaSO₄·2H₂O) is the most common sulphate evaporite mineral on our planet. Sulphate evaporites play an important role in Earth’s sulphur cycle and are primary recorders of geochemical fluxes through time. Upon heating, gypsum gradually loses its water, transforming into the hemihydrate, also known as bassanite, (CaSO₄·0.5H₂O) and anhydrite (CaSO₄). While gypsum and anhydrite deposits are common on Earth, bassanite is unstable at its surface. However, bassanite, as well as gypsum, deposits have been detected on Mars, and their origin remains a matter of ongoing debate.

The rate of the gypsum-hemihydrate transformation is dominantly controlled by temperature, T, and the water vapour pressure in the reaction environment, p_H₂O. A temperature increase causes an exponential increase in reaction rate according to the Arrhenius relation: $\dot{\alpha} = A e^{-E/(RT)}$ where $A$ is a reaction-specific constant, $R$ is the universal gas constant, and $E$ is the activation energy. Increasing $p_H₂O$ in the sample environment slows down the evacuation of H₂O from the crystalline phase and results in a negative correlation of $p_{H₂O}$ with $\dot{\alpha}$. In contrast, the effect of mechanical stress on gypsum dehydration kinetics is not well understood. A single study on high-pressure dehydration of single crystals, conducted in the pressure range 343–1085 MPa using a diamond anvil cell under water-saturated conditions, found that a pressure increase decreases the reaction rate. This result contrasts with the conclusions of a comprehensive study on the effects of confining pressure, $p_c$, and pore-fluid pressure, $p_f$, on dehydration kinetics of natural gypsum rock (Volterra alabaster), performed on cylindrical specimens (20 × 50 mm) in a triaxial stress apparatus. It turned out that the reaction rate is negatively correlated with $p_c$, consistent with the rate-inhibiting impact of $p_{H₂O}$, whereas $p_f$ has a negligible effect.

Triaxial dehydration experiments are usually conducted under constant-stress load (often to >100 MPa), which causes complex interactions between the transient hydraulic, chemical, and mechanical processes in gypsum samples. The effects of confining stresses the shrinking of the denser dehydrated phase produces ~30% porosity, the dehydration-induced pore network collapses under high constant-stress load. Therefore, the evolving drainage network loses connectivity, and micro-regions of high pore-fluid pressure can form, which in turn decelerate the reaction dramatically and possibly lead to hydraulic fracturing. Under constant-stress boundary conditions it is thus difficult to separate the effect of mechanical stress on kinetics from the coupled chemo-hydraulic-mechanical processes. This is further compounded by the need to infer the progress of dehydration from proxies, usually the measured volume of expelled excess fluid. This method is not sensitive enough to capture the onset of dehydration and generally leads to an underestimation of the dehydration rate.

To overcome these challenges, we conducted in-situ experiments using time-resolved synchrotron X-ray scattering techniques specifically designed to investigate and quantify the impact of stress on the dehydration kinetics of the gypsum-hemihydrate transformation. Dehydration of axially pre-stressed, heated discs of natural gypsum rock (Volterra alabaster) were monitored in a purpose-built loading cell while collecting 2D small- and wide-angle X-ray scattering patterns (SAXS/WAXS, Fig. 1). Experiments were performed at controlled temperature in the elastic differential pre-stress regime ($\Delta\sigma$), such that the resulting pore network could evolve freely, and the sample did not fracture macroscopically. Details of the pre-stress regime are discussed in Supplementary Note 1. Our experiments provide unambiguous evidence that dehydration kinetics and differential stress are coupled. For the examined dehydration temperatures of 129 °C and 142 °C, the pre-stressed samples dehydrate about two times faster than their low-stress equivalents (Fig. 2, Supplementary Table 1). 3D grain-scale numerical models demonstrate that the elastic differential pre-stress combined with internal stresses due to the elastic anisotropy of the gypsum grains produce substantial, geometrically controlled stress perturbations at the grain scale (Fig. 3). It is hypothesised that these stress perturbations explain the observed acceleration of the dehydration reaction, as predicted theoretically more than thirty years ago.

### Results

**2D SAXS/WAXS patterns.** We report the results of four dehydration experiments (Fig. 2, Supplementary Table 1). Two pre-stresses, low (hand-tight) and high (estimated $\Delta\sigma$<5 MPa in the sample centre, well below the unconfined compressive strength of 25 MPa of Volterra alabaster), were used at different dehydration temperatures, 129 °C and 142 °C (Fig. 2). For each temperature and pre-stress condition, a time series of 2D SAXS/WAXS patterns was acquired, recording X-rays scattered inside a
small interrogation volume in the sample centre. The SALS/WAXS patterns reflect the evolution of nano-structural features in the scale range from 0.15 to 23 nm, which covers characteristic Bragg reflections of gypsum and hemihydrate (Fig. 2a–h) as well as the development of nano-porosity and nano-crystallites of hemihydrate11. Analysis of Bragg reflections enabled in situ tracking of the lattice transformation during dehydration (Fig. 2i, j; see Methods for details).

For three experiments, gypsum fully converted to hemihydrate (Fig. 2c–h). Only the low-stress experiment at $T = 129^\circ C$ retained ~1% of gypsum in the sample centre11 (Fig. 2a, b). The Bragg reflections of the unreacted samples form patchy rings (Fig. 2a, c, e, g), indicating random orientation of grains of a number insufficient to form a powder-like truly isotropic pattern24. The (020)-reflection of the gypsum sample used at $T = 129^\circ C$ and low pre-stress exhibits a noticeable gap in the upper-left quadrant of the (020)-ring, indicating the local alignment of grains in this specific interrogation point (Fig. 2a). As a result of this alignment, local micro-strains, expressed by changes of the width and height of the azimuthally integrated growing hemihydrate (110)-peak24, lead to fluctuations of the 1D conversion curve (black circles in Fig. 2i). Azimuthal intensity variations along the hemihydrate (110)-ring are noticeable in Fig. 2b but perhaps not obvious because of the logarithmic colour scale. The conversion curve for a second, adjacent interrogation point of the same sample with a more uniform microfabric exhibits less fluctuations and shows similar kinetics (Supplementary Fig. 2) because the micro-strains are averaged out. The homogenisation of the Bragg rings in the product (Fig. 2b, d, f, h) indicates growth of smaller, randomly oriented hemihydrate grains, confirmed by ex-situ imaging of the samples (Supplementary Figs. 3 and 4). The high-intensity SALS region around the beam stop contains scattering due to nano-pores, and in the reacting samples, to a smaller degree, also due to nano-crystallites of hemihydrate embedded in gypsum grains11. In the unreacted samples, the SALS iso-intensity profiles are nearly circular (with aspect ratio ≤1.03), suggesting random orientation of nano-pores. The corresponding SALS patterns of reacted samples display a significant increase in intensity caused by growth of nano-pores and nano-crystallites11. In the low-stress experiments, the iso-intensity profiles remain almost circular, with aspect ratios ≤1.05 (Fig. 2b, f). In contrast, their high-stress counterparts have an aspect ratio of ~1.16, which indicates preferential growth of anisotropic nano-pores and/or nano-crystallites along the radial...
expected, grain-boundary cracking commences at grain vertices and triple lines. From these locations, cracks preferentially propagate across grain that formed incipient grain-boundary cracks. The colour scale is the same as in white grain boundaries are located at the outer surfaces of the model cube and thus have no contact stress. positive. The plus-sign in a white circle marks a grain boundary at high angle to the shortening direction, which accordingly is in compression. Completely blue colours. The white circle with the minus-sign marks a grain boundary at low angle to shortening under tensile loading. Compressive stresses are expected\textsuperscript{77}, grain-boundary cracking commences at grain vertices and triple lines. From these locations, cracks preferentially propagate across grain interfaces sub-parallel to the loading direction.

Dehydration kinetics. The striking impact of Δσ on kinetics is revealed by the conversion curves (Fig. 2i, j, see Methods for definition). At both temperatures, increased Δσ accelerates the dehydration reaction by a factor of about 2, as measured by the induction and characteristic times (Fig. 2i, j, Supplementary Table 1). Therefore, higher Δσ promotes both the formation and subsequent growth of nuclei. The conversion curve for T = 129 °C at high pre-stress is very similar to the one at T = 142 °C and low pre-stress. Thus, one can compare the energy needed to accelerate the dehydration reaction by a factor of 2, at T = 129 °C and low stress, through heating or elastic straining. Most significantly, accelerating the dehydration by heating turns out to be more than 10,000 times more expensive energetically than doing so via pre-stress (Supplementary Note 1). The dramatic impact of pre-stress on kinetics does neither depend on nor alter the microphysical dehydration mechanisms, as revealed by post-mortem analyses of scanning-electron microscope images (Supplementary Note 2, Supplementary Figs. 3 and 4).

Discussion
Why does a small differential stress Δσ accelerate dehydration? The answer probably lies in the microstructure of the material. Volterra alabaster contains randomly oriented gypsum grains\textsuperscript{25} with significant elastic anisotropy\textsuperscript{26}. Nucleation of hemihydrate is common within the vacancy-rich water layer of the (010)-plane in the gypsum parent, especially where this plane intersects crystal edges\textsuperscript{16}. Since the critical resolved shear stress on the (010)-plane is ca. 0.5 MPa at low confining pressure\textsuperscript{27}, it is likely that suitably oriented (010)-planes slip slightly under pre-stress (Fig. 3a), which in turn may promote nucleation by producing new vacancies and vacancy clusters\textsuperscript{16}. Moreover, any pre-stress loading results in heterogeneous grain-scale stresses caused by geometric mismatch of the anisotropically deforming, randomly oriented grains (Supplementary Note 3). The resulting local contact stresses may be normal to grain boundaries, especially on interfaces at a high angle to the compression direction, whereas most grain boundaries sub-parallel to the pre-stress direction are under local tension (Fig. 3a) and may start to crack at higher Δσ (Fig. 3b). The observed anisotropy of the final SAXS iso-intensity patterns at high Δσ attests to stress-controlled formation of anisotropic nano-scale structures, such as radially growing inclined cracks or hollow hemihydrate nano-crystallites, in our samples. Increased normal stresses on grain boundaries enhance the chemical potential gradient and fluid pressure gradient locally, which can accelerate the transformation\textsuperscript{20,23,28,29}. Therefore, we hypothesise that the high elastic pre-stress promotes local dissolution of gypsum at grain-interface regions with high contact stresses and facilitates subsequent transport to and precipitation near those with low or tensile contact stresses. This prediction can be tested by examining gypsum rocks with a strong crystallographic preferred orientation such as satin spar. In such materials, transformation kinetics should be less sensitive to pre-stress.

Our results imply that elastic stresses can accelerate dehydration reactions dramatically in crystalline solids with randomly oriented grains. This notion supports the call for the development of a thermodynamically consistent model for the coupling of stress and reaction kinetics in such materials\textsuperscript{28}; it should also inspire a new class of kinetic experiments that explores the effect of small elastic stresses on mineral transformations systematically. Our results hint at a potentially ubiquitous geometric thermodynamic effect of a polycrystalline microstructure. Finally, this work should open new research avenues for the energy-efficient design of calcination processes for gypsum and other solids.

Methods
Starting material. We dehydrated discs of natural alabaster from Volterra, Italy, with a diameter of 10 mm and a thickness of 1 mm. Volterra alabaster is a standard material in experimental rock mechanics because of its small grain size, low porosity, and purity\textsuperscript{9,20,22,25}. This alabaster consists of randomly oriented, subhedral,
tabular gypsum grains with a mean grain size that varies on the scale of centimetres and is generally in the range of 45–123 μm\(^2\). A representative image of the unreacted alabaster is shown in Supplementary Fig. 4a.

**Beamline set-up and data processing.** We used the pinhole-geometry SAXS/WAXS beamline at the ANSTO Australian Synchrotron described in Kirby, et al.\(^30\). A 3 m-long, 22 mm-period in-vacuum undulator source (\(K_{\text{max}}\) of 1.6 at 6.6 mm minimum insertion device gap) and a flat Si(111) double-crystal monochromator provided a photon flux of up to \(10^{13}\) photons per second in the energy range from 5 to 20 keV. X-ray energy of 16 keV, corresponding to the photon wavelength of 0.775 Å, was used in all experiments. Focusing is achieved with a KB mirror pair with Si, Rh, and Pt stripes for harmonic rejection. Four monochromatic slits allow flexible adjustment of the collimation system to minimize parasitic scattering at different camera lengths. The vacuum SAXS camera can be adjusted to camera lengths between 60 and 720 cm. Its rear module contains the beamstop and the SAXS detector. The WAXS detector is located above the frontal nose cone of the SAXS camera. The 169 × 179 mm Pilatus 1 M and the 33 × 169 mm Pilatus 200 K (pixel size of 172 × 172 μm\(^2\)), were used to collect 2D SAXS and WAXS scattering (diffraction) images in transmission mode. The sample-to-detector distances of 1.03 and 0.45 m, respectively (Fig. 1), were calibrated using silver benenate. This set-up covered the real-space size range of ca. [0.15; 1.0] nm on the SAXS detector, and ca. [0.3; 23] nm on the SAXS detector. The corresponding full range of the magnitude of the scattering vector \(q\) covered 2.2 × 10\(^{-2}\) Å\(^{-1}\) to 4.1 Å\(^{-1}\). In this configuration, the SAXS detector monitored the prominent (110)-reflection of hemihydrate while the WAXS detector captured the time evolution of the (020)- and (220)-reflections. The time evolution of these reflections served for tracking of the dehydration reaction, as explained below. 2D diffraction patterns were recorded as uncompressed 32-bit TIFF images. Since the obtained Bragg reflections were circular, 2D SAXS/WAXS images were transformed into 1D curves by azimuthal averaging using the scatterBrain IDL program (http://archive.synchrotron.org.au/aussyncbeamlines/saxswaxs/software-saxswaxs), developed at the SAXS/WAXS beamline at the ANSTO Australian Synchrotron. SAXS intensity curves were converted to absolute units. This procedure entailed correction for background signal through measurements of the empty cell, dark current, intensity normalization, and (220)-reflections served for tracking of the dehydration reaction in our methodological review paper\(^11\). All experiments proceeded to reaction completion except for the one at \(T = 129^\circ\mathrm{C}\) and low pre-stress. Post-mortem powder XRD confirmed that 1% gypsum remained in the sample centre, as can also be seen qualitatively in the SAXS/WAXS images (Fig. 2b) and the post-mortem microstructural images (Supplementary Figs. 3 and 4). The data tables for the conversion curves plotted in Fig. 2 i, are provided in Supplementary Data 1 accompanying this article.

**Scanning-electron microscopy (SEM).** SEM images (Supplementary Figs. 3 and 4) of the surfaces of uncoated reacted and unreacted samples were obtained with the Ultra Plus Field Emission SEM under low vacuum (40 Pa). We used an accelerating voltage of 10 kV, beam intensity index of 12, and a working distance between 9 and 14 mm. A mixed mode of backscattered-electron signal (70%) and secondary-electron signal (30%) helped to eliminate edge effects compared to imaging in pure secondary-electron mode.

**Data availability**

The azimuthally integrated, calibrated, time-series 1D SAXS curves underpinning the conversion curves shown in Fig. 2 and the processed data for the conversion curves as well are provided as electronic supplement (Supplementary Data 1). The authors will arrange for sharing of the uncalibrated, uncompressed 32-bit TIFF images from the SAXS/WAXS detectors upon reasonable request.

Received: 22 September 2020; Accepted: 28 April 2021; Published online: 24 May 2021

References

1. Chang, L. L. Y., Howie, R. A. & Zussman, J. Non-silicates: Sulphates, Carbonates, Phosphates, Halides 2nd edn, Vol. 5B (Geological Society of London, 1998).
2. Blättler, C. L. et al. Two-billion-year-old evaporites capture Earth’s great oxidation. Science https://doi.org/10.1126/science.aae9267 (2018).
3. Spencer, R. J. Sulfate minerals in evaporite deposits. Rev. Miner. Geochim. 40, 173–192 (2000).
4. Rapin, W. et al. Hydration state of calcium sulfates in Gale crater, Mars: identification of bassanite veins. Earth Planet. Sci. Lett. 452, 197–205 (2016).
5. Wray, J. I. et al. Identification of the Ca-sulfate bassanite in Marswth Valls, Mars. Proc. Natl. Acad. Sci. 109, 416–421 (2010).
6. Langevin, Y., Poulet, F., Bibring, J.-P. & Gondet, B. Sulfates in the north polar region of Mars detected by OMEGA/Mars express. Science 307, 1584 (2005).
7. Stawski, T. M. et al. Formation of calcium sulfate through the aggregation of sub-3 nanometre primary species. Nat. Commun. 7, 11177 (2016).
8. Heard, C. J. & Rincon-Remacha, M. Ectopic implications of gypsum dehydration. GSA Bull. 77, 741–760 (1966).
9. Brantut, N. et al. Dehydration-induced damage and deformation in gypsum and implications for subduction zone processes. J. Geophys. Res. https://doi.org/10.1029/2011JB008730 (2012).
10. Bedford, J., Fussess, F., Leclère, H., Wheeler, J. & Faulkner, D. A 4D view on the evolution of metamorphic dehydration reactions. Sci. Rep. 7, 6881 (2017).
11. Schrank, C. E. et al. Tracking metamorphic dehydration reactions in real time with transmission small- and wide-angle synchrotron X-ray scattering: the case of gypsum dehydration. J. Petroil. https://doi.org/10.1093/petrology/ega041 (2020).
12. Zurcher, H. & Prabu, D. Plaster of Paris: past, present and future. J. Clean. Prod. 79, 787–797 (2017).
13. Van Driessche, A. E. S., Stawski, T. M., Benning, L. G. & Kellermeyer, M. in New Perspectives on Mineral Nucleation and Growth: From Solution Precursors to Solid Materials (eds Alexander, E. S., Van Driessche, Matthias Kellermeyer, Liane G. Benning, & Denis Gebauer) (Springer International Publishing, 2017).
14. U. S. Geol. Survey, (ed U.S. Department of the Interior) 200,https://doi.org/10.3133/mcs2020 (Washington, 2020).
15. Först, J. & Cerný, R. Carbon footprint analysis of calcined gypsum production in the Czech Republic. J. Clean. Prod. 177, 795–802 (2018).
16. Wolfers, A., Howell, H. G. & Schiller, K. C. The dihydrate-hemihydrate transformation in gypsum. J. Appl. Cryst. 18, 366–372 (1985).
17. McDaid, H. G. The effect of water vapour upon the dehydration of CaSO\(_4\)\(_2\)H\(_2\)O. Can. J. Chem. 42, 792–801 (1964).
18. Pretulian, J. D., Vieille, L., Quilisotti, S. & Favereon, L. Kinetics and mechanism of the dehydration of calcium sulfate dihydrate: a comprehensive approach for studying the dehydration of ionic hydrates under controlled
temperature and water vapor pressure. J. Phys. Chem. C 124, 26352–26367 (2020).

19. Liu, C., Zheng, H. & Wang, D. The dehydration kinetics of gypsum at high pressure and high temperature. High Press. Res. 35, 273–281 (2015).

20. Llana-Fúnez, S., Wheeler, J. & Faulkner, D. R. Metamorphic reaction rate controlled by fluid pressure not confining pressure: implications of dehydration experiments with gypsum. Contrib. Mineral. Petrol. 164, 69–79 (2012).

21. Ko, S.-C., Olgaard, D. L. & Wong, T.-F. Generation and maintenance of pore pressure excess in a dehydrating system 1. Experimental and microstructural observations. J. Geophys. Res. 102, 825–839 (1997).

22. Olgaard, D. L., Ko, S.-C. & Wong, T.-F. Deformation and pore pressure in dehydrating gypsum under transiently stressed conditions. Tectonophysics 346, 237–248 (2001).

23. Wheeler, J. The significance of grain-scale stresses in the kinetics of metamorphism. Contrib. Mineral. Petrol. 97, 397–404 (1987).

24. Lavina, B., Dera, P. & Downs, R. T. Modern X-ray diffraction methods in mineralogy and geosciences. Rev. Mineral. Geochem. 78, 1–31 (2014).

25. Fusseis, F. et al. Pore formation during dehydration of polycrystalline gypsum observed and quantified in a time-series synchrotron radiation based X-ray micro-tomography experiment. Solid Earth 3, 857–900 (2012).

26. Bass, J. D. in Mineral Physics and Crystallography: a Handbook of Physical Constants Vol. 2, AGU Reference shelf (ed Ahrens, T. J.) (American Geophysical Union, 1995).

27. Williams, S. C. The shear strength of gypsum single crystals on three cleavage planes. Tectonophysics 148, 163–173 (1988).

28. Wheeler, J. The effects of stress on reactions in the Earth: sometimes rather mean, usually normal, always important. J. Metamorph. Geol. 36, 439–461 (2018).

29. Gratier, J.-P., Dysthe, D. K. & Renard, F. in Advances in Geophysics Vol. 54 (ed Renata Dmowska) (Elsevier, 2013).

30. Kirby, N. M. et al. A low-background-intensity focusing small-angle X-ray scattering undulator beamline. J. Appl. Crystallogr. 46, 1670–1680 (2013).

31. Ballirano, P., Maras, A., Meloni, S. & Caminiti, R. The monoclinic I2 structure of bassanite, calcium sulphate hemihydrate (CaSO4 · 0.5H2O). Eur. J. Mineral. 13, 985–993 (2001).

32. Comodi, P., Zanazzi, P. F., Nazzareni, S. & Speziale, S. High-pressure behavior of gypsum: a single-crystal X-ray study. Am. Mineral. 93, 1530–1537 (2008).

33. Lasaga, A. C. Kinetic Theory in the Earth Sciences (Princeton University Press, 1998).

34. Ossorio, M., Van Driessche, A. E. S., Pérez, P. & García-Ruiz, J. M. The gypsum–anhydrite paradox revisited. Chem. Geol. 386, 16–21 (2014).

35. Milsh, H., Priegnitz, M. & Blöcher, G. Permeability of gypsum samples dehydrated in air. Geophys. Res. Lett. https://doi.org/10.1029/2011GL048797 (2011).

36. Ballirano, P. & Melis, E. Thermal behaviour and kinetics of dehydration of gypsum in air from in situ real-time laboratory parallel-beam X-ray powder diffraction. Phys. Chem. Miner. 36, 391–402 (2009).

37. Raghami, E., Schrank, C. & Kruhl, J. H. 3D modelling of the effect of thermal-elastic stress on grain-boundary opening in quartz grain aggregates. Tectonophysics https://doi.org/10.1016/j.tecto.2019.228242 (2019).