Cryogenic vitrification and 3D serial sectioning using high resolution cryo-FIB SEM technology for brine-filled grain boundaries in halite: first results

G. DESBOIS¹, J. L. URAI¹, C. BURKHARDT², M. R. DRURY³, M. HAYLES⁴ AND B. HUMBEL⁵

¹Structural Geology, Tectonics and Geomechanics, Geological Institute, RWTH Aachen University, Aachen, Germany; ²Natural and Medical Sciences Institute (NMI) at the University of Tübingen, Reutlingen, Germany; ³Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands; ⁴FEI Company, Nanoport, Eindhoven, The Netherlands; ⁵Department of Biology, Utrecht University, Utrecht, The Netherlands

ABSTRACT

The structure of brine films in grain boundaries of halite has been the subject of much controversy over the past 20 years; although a number of innovative methods have been developed to study these structures, much is still unknown and fundamental information is missing. In this study, we investigated different methods of plunge-freezing to vitrify the brine fill of grain boundaries for natural salt polycrystal. This was followed by a preliminary study of the 3D morphology of a vitrified grain boundary in a natural rock salt sample with a focused ion beam (FIB) excavation system. We have shown that brine-filled grain boundaries in rock salt can be efficiently well frozen when dimensions are less than about 1 mm. Coupled with an ion beam tool, cryo-SEM allows 3D observation of the well-frozen grain boundaries in large volumes and high resolution. Initial results of brine-filled natural halite grain boundaries show non-faceted crystal–brine interfaces and unexpectedly low dihedral angles at room temperature and pressure.

Key words: brine, cryo-SEM, FIB, grain boundary, halite, serial sectioning, vitrification

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Corresponding author: Dr Guillaume Desbois, Structural Geology, Tectonics and Geomechanics, Geological Institute, RWTH Aachen University, Lochnerstrasse 4-20, 52056 Aachen, Germany.
Email: g.desbois@ged.rwth-aachen.de. Tel: +49 241 80 95780. Fax: +49 241 80 92358.

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INTRODUCTION

The transport and mechanical properties of rock salt (polycrystalline NaCl) are of importance to the geological evolution of sedimentary basins, and many applications such as subsurface storage of oil, gas and radioactive waste. Water can greatly increase the mobility of grain boundaries in evaporite minerals so that dynamic re-crystallization and solution–precipitation processes can become rapid, even at room temperature (Urai et al. 1986a,b; Drury & Urai 1990; Spiers et al. 1990; Peach et al. 2001; Watanabe & Peach 2002). This is caused by the presence of brine in the grain boundaries. The structure of this brine film has been the subject of much controversy over the past 20 years (Urai et al. 1986a; Den Brok et al. 2002; Urai & Spiers 2007). Although a number of innovative methods have been developed to study these structures, such as infrared spectroscopy (De Meer et al. 2005), interference microscopy (Lohkämper et al. 2003), deformation experiments in transmitted light (Schenk & Urai 2004), electron backscattered (BSE) diffraction (Pennock et al. 2006) and cryogenic scanning electron microscopy (SEM) (Schenk et al. 2006), much is still unknown and fundamental information is missing.

One of the recent developments to study wet grain boundaries is with high-resolution cryogenic SEM after stabilization of the water phase in the grain boundaries at cryo-temperatures. Cryo-SEM is widely used in Life Sciences (Echlin 1978; Sargent1988; Erlandsen et al. 1997; Fauchadour et al. 1999; Walther & Muller 1999; Frederik & Sommerdijk 2005; Marko et al. 2007) but applications in Geosciences are as yet limited to studies of fluid

One of the critical issues of cryo-SEM (Karlsson 2002) is to ensure that plunge-freezing vitrifies the pore fluids to avoid the formation of ice crystals which tend to damage the microstructure. In geoscience studies to date this issue has not yet received much attention. If plunge-freezing is not efficient enough, the brine contained in pores may crystallize or become segregated in two distinct phases (ice crystals and hydrohalite; Schenk et al. 2006).

In this study, we investigated different methods of plunge-freezing (liquid nitrogen, slushy nitrogen and slushy ethane) to find the best cryo-coolant to well freeze the brine fill of grain boundaries for polycrystalline natural salt. This was followed by a preliminary study of the 3D morphology of a well-frozen grain boundary in a natural rock salt sample with a focused ion beam (FIB) excavation system and observation of the frozen fluid at high resolution.

MATERIALS AND METHODS

Samples and experimental procedure

We used three different kinds of samples: (i) 1 mm thick copper rivets with a drop of saturated brine (called ‘standards’ in what follows); (ii) thin films of brine sandwiched between plates of NaCl crystals; and (iii) thin slabs of natural polycrystalline salt. The synthetic ‘salt sandwiches’ were made from two 0.5 mm thick plates of NaCl single crystal clamped together with a drop of saturated brine in between, prepared at least 3 weeks before the cryo-SEM experiments and stored in a container with saturated brine. The rivets with brine and the salt sandwiches were easy to prepare and were used to compare the efficiency of different plunge-freezing procedures for brine vitrification.

The natural sample is a salt mylonite from the Qum Kuh salt glacier in Iran (Schleder 2007). The sample of 5 × 5 × 1 mm was gently cut with a 0.3 mm diamond saw with hexane as lubricant and kept in a container with saturated NaCl solution until the cryo-SEM experiments. For the three kinds of samples, the basic procedure of preparation and imaging is the same (Fig. 1): (i) the sample is plunged in a bath of cryo-coolant with the help of the clamp for the ‘salt sandwiches’ and with tweezers for the salt sandwiches and the natural salt polycrystals, and stirred in the cryo-coolant to improve the cooling rate. (ii) Within the bath of cryo-coolant, the samples are fixed on the pre-cooled sample holder and freeze-fractured with a cold-knife. (iii) The samples are then SEM-imaged at cryo-temperatures, with ion milling if required. The transfer from the bath of cryo-coolant to the cryo-preparation chamber and from the cryo-preparation chamber to the SEM chamber is performed by a cryo-shuttle under vacuum.

Three kinds of cryo-coolants have been investigated: liquid nitrogen, slushy nitrogen and slushy ethane. For nitrogen and ethane, the boiling and melting temperatures are: \( T_{BN2} = -195.8^\circ C \), \( T_{MN2} = -210^\circ C \), and \( T_{BE} = -88.6^\circ C \) and \( T_{ME} = -182.2^\circ C \). This provides a range of cryo-coolants including liquid and slushy phases with different boiling and melting temperatures, and different gaps between \( T_M \) and \( T_B \).

For 3D sectioning of the samples, we used an FIB to cut and remove thin slices in the SEM chamber to image the fresh surface, in ‘slice and view’ imaging mode. Initially the top surface of the sample is sputter-coated with Pt but the freshly cut surfaces are not coated. Before the ‘slice and view’ imaging, we prepared the area of interest by milling ‘channels’ around this area to allow removal of the milling waste (see Fig. 7C).

Analytical techniques and instruments used

The first cryo-SEM experiments were performed at NMI (Reutlingen, Germany), using a Zeiss cryo-SEM (1540XB CrossBeam, Zeiss) with a high-resolution GEMINI field emission column operating at very low acceleration voltage with a thermally assisted Schottky field emission gun that yields a very low energy spread, and a Canion FIB (FIB) from a gallium metal ion source installed at an angle of 54° to the electron beam. The instrument also has an EDX system. Transport and preparation of the samples are done using a Bal-Tec system which allows keeping the samples under cryogenic conditions at each stage of the procedure, in a sample shuttle (VCT 100) which can be attached via a vacuum gate to the freezing bath, a cryo-sputter coater (SCD500) and the microscope.

The study of different methods of plunge-freezing and the ‘slice and view’ imaging of a wet grain boundary were carried out in the Department of Earth Sciences of Utrecht University (the Netherlands). The cryo-SEM available here is a Nova Nanolab 200 Small Dual Beam system from FEI with FIB and EDX facilities. The specifications of these features are comparable with the facilities available in NMI-Reutlingen; but the cryo-transport and the cryo-preparation of the samples were performed in a PP2000T cryo station (Quorum Technologies). This system provides facilities to import pre-frozen samples in the cryo-preparation chamber which provides flexibility to use different plunge-freezing methods and the cryo-preparation chamber includes a sputter coater facility and a cold.
 RESULTS

Vitrification of the grain boundary

One of the critical aims of this study was to validate a method to freeze thin brine films between grains of NaCl. If plunge-freezing is not efficient enough, the brine contained in grain boundaries is crystallized and segregated into two distinct phases (ice crystals and hydrohalite; Schenk et al. 2006). This makes high-resolution study of grain boundary microstructures difficult.

Standards

The results of these experiments are summarized in Fig. 2. For each method of plunge-freezing, a photograph at low magnification shows the fractured surface of the frozen drop of brine in the rivet, and a high-magnification image presents the detail of the frozen brine in BSE mode which enables the identification of the solid phases at constant cryo-temperature (−150°C).

In liquid nitrogen, the frozen brine contains ice crystals surrounded by the eutectic phase, which is evidence of phase segregation during plunge-freezing. In slushy nitrogen, the frozen brine exhibits a phase with absence of visible segregation close to the external rim (40–50 μm) and a dendritic organized structure in the centre. This structure is different from the eutectic phase formed in liquid nitrogen, and is interpreted as incipient phase segregation during plunge-freezing. In slushy ethane, the BSE image does not show organized structures through the whole brine drop. We interpret this as evidence that the brine filling the rivet was well frozen during the plunge-freezing. We prefer here to use the term ‘well frozen’ rather than vitrified because the vitrification (sensu stricto) can only be verified by transmission electron microscopy (TEM). In summary, the order of the grain boundary vitrification efficiency for the three investigated
Fig. 2. SEM photographs (SE and BSE modes) of the standard samples after plunge-freezing either in liquid nitrogen, slushy nitrogen or slushy ethane, showing the different stages of vitrification as a function of the cryo-coolant. The samples are not coated.
plunge-freezing methods is: liquid nitrogen < slushy nitrogen < slushy ethane.

**Synthetic salt sandwiches**

Based on the results shown above we abandoned the liquid nitrogen coolant because of its low efficiency, and investigated 10 synthetic ‘salt sandwich’ samples and with two methods of plunge-freezing (slushy nitrogen and slushy ethane). For both coolants, the samples show similar morphologies. Figure 3 shows typical results for the two methods after freeze-fracturing. At larger scale, the frozen brine film between the crystals indicates a homogeneously solidified material in both cases. At higher magnification, in BSE the segregation patterns are absent, indicating fully well-frozen grain boundaries.

**Natural polycrystalline halite**

We also performed a test with a natural polycrystalline salt plunge-frozen in slushy nitrogen and freeze-fractured (Fig. 4). This sample suggests a well-frozen grain boundary but some of the images could also be interpreted as showing segregation structures. In BSE there are clear contrasts

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**Fig. 3.** SEM photographs (SE and BSE modes) of the synthetic ‘salt sandwich’ samples after plunge-freezing either in slushy nitrogen or slushy ethane. It is clear that the brine film between the crystals is well frozen in both coolants. The samples are not coated. The hackles on the sample surface are formed during cutting with the cold knife.
between domains in the frozen fluid phase; however this geometry does not resemble the segregation patterns observed in the standard experiment (Fig. 2) as formed by well-defined ice crystals surrounding by the eutectic phase. Because to get contrast in BSE there must some chemical or density difference, this geometry could also be due to two fluids.

Freeze-drying

We have also performed a freeze-drying experiment (Fig. 5) where a grain boundary initially well frozen in slushy nitrogen was heated from −150°C to −90°C for 60 min. This sample has undergone dramatic changes showing a frozen brine surface very similar to the one described by Schenk et al. (2006), with a dense pattern of holes and 100 nm size cavities. However, we did not find evidence that these changes caused damage to the surrounding in the form of cracks or fractures.

Application: investigation of wet grain boundaries in natural rock salt

We present some preliminary results of a study of grain boundaries from a rock salt mylonite sample from the Qum Kuh salt glacier (Iran). A detailed description of these samples in outcrop and thin section, using various techniques is presented by Schleder (2007).

SEM investigation of dry natural polycrystalline salt samples

We first studied our samples ‘dry’ in a conventional SEM to compare observations with the cryo-SEM results. Before
SEM imaging, the samples were gently broken, dried in air and coated with Pt sputtering. Observation of grain boundaries in fractured and dried polycrystalline salt samples, can provide information on the grain boundary structure after removal of the fluid and precipitation of an unknown amount of NaCl (Urai 1985, 1987; Urai et al. 1986a,b; Schenk & Urai 2004).

Figure 6 shows SEM images obtained from the salt glacier samples. Figure 6A,B gives the typical indirect evidence of the presence of fluid in the grain boundaries,

Fig. 6. SEM pictures (SE mode) of grain boundaries in a natural polycrystalline salt sample under dry conditions. (A) Efflorescence at grain boundary; (B) a grain boundary with a complicated island-channel (?) structure; (C) pores localized along the grain boundary; (D) wavy efflorescence structures along a grain boundary; (E) triple junction and pores located along the grain boundary; and (F) triple junction showing grain boundary grooving. The sample is Pt-coated.
such as efflorescence structures similar to those reported by Schenk & Urai (2004), formed by evaporation in combination with capillary forces and a mobile and connected fluid, and grain surface which likely formed by solution-crystallization processes in a brine-filled grain boundary.

Interpreting the efflorescence process along the lines of argument of Schenk & Urai (2004) allows study of some aspects of the grain boundaries in detail, and indicates a rich assembly of grain boundary structures in these samples: fluid and gas inclusion arrays, grain boundaries containing thin fluid films, and large grain boundary pores with complex morphologies (Figs 6C–F). However, there are two major problems with this method: first, at the nanometre scale it is not possible to meaningfully interpret the structure of grain boundaries containing thin films or perhaps island-channel structures, because even a very small amount of NaCl precipitation will change this structure in an unpredictable way, and secondly it is very difficult to know what the other (removed) half of a grain boundary looks like (cf. Olgaard & FitzGerald, 1993, for a detailed discussion) and whether it contained a fluid or a gas phase at this location. Therefore, the possibility to quench the fluid-filled boundaries and study them in 3D is a major step forward in this field.

3D investigation of a wet triple junction under cryo-SEM and FIB milling

In a thin slab of the same sample as studied dry, we investigated the 3D structure of a halite grain boundary (Fig. 7) under cryogenic conditions. Our area of interest was a triple junction surrounded by three grains with different crystallographic orientation in the plane of observation. The freeze-fracture morphology shows the \{0 0 1\} cleavage planes, which allow estimation of the crystallographic orientation of the surrounding grains (Fig. 7B). The mis-orientations of all three surrounding grains are large, and all three boundaries are high-angle grain boundaries.

We performed 54 ‘slice and view’ steps of this volume, with the thickness of each slice around 500 nm. In Fig. 8, we show a BSE image corresponding to every third slice, i.e. with a spacing of 1.5 μm. In Fig. 9, the last slice is shown to give an overview of the morphology of the volume surrounding the slices. All the cross-sections are non-coated.

The images (Figs 8 and 9) of the uncoated plunge-frozen grain boundaries show features similar to those

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**Fig. 7.** SEM photographs (BSE mode) of a triple junction located in a natural polycrystalline salt sample. (A) Overview at larger scale; (B) the overview at smaller scale reveals the cleavage planes which indicate the different crystallographic orientation of the three adjacent grains; (C) the dashed line shows the location of the channels milled to drain the milling waste during the excavation. The sample is Pt-coated.

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Fig. 8. SEM images (BSE mode) of progressive slices of brine-filled high-angle grain boundaries in a polycrystalline glacier salt sample. The grain boundary was well frozen by plunge-freezing in slushy nitrogen. The cross-sections are not coated.
the dihedral angle is around 30° than 100 nm, the resolution in these images). The value of the 'healed' grain boundary (it may contain a fluid film thinner than a few micrometres. Another interesting feature (black arrow (Fig. 8K) is the lobate morphology of the grain surface, whereas on the other side of the grain boundary the crystal–brine boundary is flat; these lobe structures were also observed in the sample studied dry.

The third region of interest (black circle Fig. 8R) is a 'healed' grain boundary (it may contain a fluid film thinner than 100 nm, the resolution in these images). The value of the dihedral angle is around 30°, in contradiction to the dihedral angle given by Holness & Lewis (1997) for these conditions (∆σ < 1 MPa; 20°C < T < 40°C). Along this 'healed boundary', there are some small cracks which may have been initiated during plunge-freezing by differences in thermal expansion between the surrounding crystals, by freeze-fracturing, or by volume changes during no visible segregation.

**DISCUSSION**

**The best cryo-coolant for wet salt samples**

Numerical simulations of the cooling of our samples indicate that the centre of a salt sandwich reaches the temperature of slushy ethane in about 0.01 sec, giving a cooling rate of approximately 20 000 K sec⁻¹. This is faster than the values quoted by Moor (1971) as required to vitrify water in biological specimens. Keeping in mind that the brines in our samples have a high concentration of dissolved NaCl and it is not known how this affects vitrification efficiency, it seems reasonable to expect that the brine in our samples is well frozen.

Our experiments performed with the synthetic 'salt sandwiches' plunge-frozen in slushy nitrogen and slushy ethane (Fig. 3) show clearly that the brine filling the grain boundary has been well frozen. On the other hand, the experiments performed with the standards give evidence that crystalline phases segregated during the plunge-freezing in slushy nitrogen. The experiment performed with a natural polycrystalline salt (Figs 8 and 9) plunge-frozen in slushy nitrogen is also well frozen at the grain boundary, but in another sample there is hint that the brine filling the grain boundary is not fully well frozen (Fig. 4). This means that slushy nitrogen may produce variable extents of vitrification of the brine although the thicknesses of the investigated samples are the same in each experiment.

These discrepancies can be explained by the proximity of nitrogen’s boiling and melting temperatures (TBN2 = −195.8°C and TMN2 = −210°C). Because of this proximity, it is easy to exceed the boiling point of the nitrogen just with a slight change of heat energy. There is only limited control of the amount of heat we import into the slushy nitrogen when the sample and eventually the sample holder are plunged in the bath of slushy nitrogen. If the amount of heat energy is enough to exceed the nitrogen boiling temperature, the Leidenfrost effect (Fau-chadour et al. 1999) occurs: the nitrogen boils in the neighbourhood of the sample during the early phase of the plunge-freezing. This covers the sample with a fine vapour layer, which thermally insulates the sample.

The use of slushy nitrogen therefore may produce variable results. Thus, for an optimal control of the freezing of the brine in the grain boundaries in rock salt (around 1 mm thick and less), it is better to use the slushy ethane which offers almost the same range of cryo-temperature as the liquid and slushy nitrogen but for which the Leidenfrost effect is minimal because the difference of its boiling and melting temperatures (TBE = −88.6°C and TME = −182.2°C).
Freeze-drying, cooling and phase segregation

Schenk et al. (2006) showed the potential of the use of cryo-SEM for the study of wet halite salt samples but did not systematically study the structure of the frozen brine in the grain boundaries. They interpreted the structures on the freeze-fractured brine surfaces as ‘segregation pattern’ in reference to the segregation of phases (hydrohalite + ice) in brine which occurs during a freezing (Roedder 1984; Bodnar 1993). We obtained very similar structures in initially well-frozen brine surfaces after a stage of freeze-drying.

These results are consistent, considering that Schenk et al. (2006) used a different procedure of sample preparation after the plunge-freezing. The samples can be sometimes covered by a condensate deposit from water vapour in the cryo-coolant bath. Schenk et al. (2006) have systematically freeze-dried their samples in order to remove the condensate. We interpret the surface pattern observed by Schenk et al. (2006) in frozen grain boundaries to have formed after the segregation of phases, not during too slow plunge-freezing but after freeze-drying of an initially well-frozen grain boundary to clean the sample surface. Based on our observations so far, damage to the samples, during plunge-freezing, freeze-fracturing, or during segregation are minor, although more studies are required to fully understand these effects.

Interpretation of grain boundary microstructures in wet polycrystalline salt samples

Investigations of dried natural polycrystalline salt samples provide indirect observations of fluid morphology in grain boundaries pores (Urai 1985, 1987). Using the cryo-SEM approach, it is possible to study fluid geometry in situ, avoiding artefacts caused by efflorescence and drainage of the fluid. Sectioning the sample with an ion beam after plunge-freezing has been shown to provide superior images at high resolution, in addition to a 3D view.

In 3D, large parts of the grain boundary contain a fluid film of variable thickness, with structures ranging from no visible fluid film at the resolution of the ‘slice and view’ technique to a fluid-filled film several microns thick. This fluid distribution is comparable with some of the structures reported by Schenk & Urai (2005) in wet, artificial fine-grained polycrystalline compacted at high total stress (but presumably at low effective pressure), where significant open porosity can exist (cf. Schoenherr et al. 2007; Schleider et al. in press). This type of fluid distribution is expected to be much less common in domal salt samples, although very little data are available at present.

In the sample studied in Figs 8 and 9 the halite surfaces in contact with the brine are clearly curved, and do not contain crystallographic facets which might be expected for halite which has been in contact with a saturated brine for a long time. There are several possible explanations for this. First, the facets may have been ‘rounded’ during the (metadynamic) recrystallization during natural deformation in the salt glacier or after sampling and storage of the sample. Secondly, the sampled part of the salt glacier may have been dissolving very slowly at the time of sampling, after rainfall some time ago (Talbot & Rogers 1980). It is unlikely that these structures are due to damage to the sample during storage after cutting or the cryo-SEM procedure, because they are also observed in the samples which were fractured and dried (Fig. 6F). Similar lobate structures on grain surfaces have been described in naturally deformed carnallite (Urai 1987) where they were interpreted to be growth structures associated with diffusive mass transfer processes, and in experiments, where the ‘grain boundary groove’ structures observed by Den Brok et al. (2002) were related to stress in the samples. The cusps along the halite–brine interface could also be related to the intersection of subgrain boundaries with the film fluid.

Following Holness & Lewis (1997) and Schoenherr et al. (2007), the dihedral angle \( \theta \) is the main controlling parameter for the distribution of grain boundary fluid in equilibrium. In the case of \( \theta >60^\circ \) the grain boundaries are fluid-free and consist of solid-solid contacts, whereas for \( \theta <60^\circ \) the fluids form an interconnected network of grain boundary triple junction tubes. In Figs 8 and 9 and in the region surrounded by the black circle, the dihedral angle \( (\theta) \) is around 30° which is much lower than the values proposed by Holness & Lewis (1997) for the P–T conditions of our samples. In addition, it is not clear if a true triple point exists in this location, of whether the fluid progressively thins into a nanometre-scale film, perhaps also influenced by the anisotropy of surface energy of halite (Moment & Gordon 1964; Jessell et al. 2007).

Implications for further studies

The main results of this paper are the validation of the technique of freezing with absence of visible segregation and ion-beam cutting of brine-filled grain boundaries in natural polycrystalline salt samples with a diameter of 1 mm, and some interesting observations on the 3D structure of the wet grain boundaries. The technique is promising for a wide range of studies of single- or multiphase grain boundaries which are above their melting point in situ, such as low-permeability reservoir rocks and claystones in which the details of the morphology of the pore space phase distribution are poorly known (Hildenbrand et al. 2006).

In the case of rock salt, water-assisted grain boundary processes have a major effect on the mechanical and transport processes under a wide range of conditions (Urai & Spiers 2007), and this study provides the basis for a wide range of systematic studies of the morphology of grain boundaries.
boundary fluids. First, there are a wide range of natural rock salt tectonites with correspondingly diverse grain boundary structures, and secondly, it should be possible to quench miniature deformation cells containing grain boundary structures under stress, and use the same cryo-SEM technique to study grain boundaries undergoing active deformation. This could give an important contribution to the study of the structure of dynamically stable brine films in grain boundaries in halite (Urai et al. 1986a). Moreover, because most cryo-SEM machines are combined with a micro-chemical analysis tools (EDX), the identification of second-phase impurities, and the measurement of impurity concentrations in the fluid-filled grain boundaries are possible.

CONCLUSIONS

Samples of rock salt containing brine-filled grain boundaries can be efficiently well frozen when dimensions are less than about 1 mm. Coupled with an ion beam tool dedicated for material excavation, cryo-SEM allows 3D ‘slice and view’ observation of the vitrified grain boundaries in large volumes and high resolution. Initial results of brine-filled natural halite grain boundaries show a number of unexpected structures such as non-faceted crystal–brine interfaces and low dihedral angles at room temperature and pressure, calling for further study.

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