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## SEGREGATION OF ANHYDRITE IN SINTERED NATURALLY OCCURRING ROCK SALT

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### Abstract

This study examines the sintering of naturally occurring rock salt in dependence of pressure and temperature as is desired for storage and other applications in saline environments where rock salt is thermodynamically stable and shows a mechanical behavior compatible to the surrounding host material. Rock salt consists mainly of sodium chloride with small impurities of less soluble compounds such as anhydrite,  $\text{CaSO}_4$ . A special interest in the sintering process of naturally occurring rock salt is the segregation of anhydrite to the grain boundaries between individual sodium chloride crystals. Our study has shown that sintering naturally occurring rock salt at different pressures and time periods will influence the segregation of anhydrite. Experiments support a greater segregation of anhydrite resulting from an increased pressure and shorter time period treatment. As the solubility of anhydrite is less than sodium chloride, the sintered samples of naturally occurring rock salt show greater stability towards dissolution than pure sodium chloride.

**Key words:** Segregation, Sinter, Anhydrite

### Introduction

Naturally occurring rock salt has been of great interest for several different applications such as in the food industry as spice and conservation ingredient, in form of caverns for gas storage and for nuclear waste as storage medium. Naturally occurring rock salt shows unique features of halite such as thermal expansion coefficient, viscosity and solubility. The viscous property of rock salt makes it suitable for sealing desired objects from the surrounding with flexibility accounting for factors such as the movement of the surrounding medium. An aim of this research project was the formation of salt building blocks for later application in underground constructions.

This research examines the viscous property of naturally occurring rock salt samples using a sintering process, where the samples are heated closely to the melting point of halite and kept at this temperature for different time periods. The process for the formation of building block from naturally occurring rock salt was performed through compression followed by sintering.

Naturally occurring rock salt samples from evaporates of the Zechstein Lake were taken as a representative for a typical naturally occurring rock salt sample. The composition of the naturally occurring rock salt can vary as a result from the evaporation process and usually includes 1-2% anhydrite and 98-99% halite.

## Experimental

The main composition of naturally occurring rock salt is sodium chloride which is well known for its high thermal expansion coefficient. Natural rock salt samples were crushed and milled in a disc mill (Fritsch, Pulverisette 14) to obtain fine powders. After milling, the powders were dried at 35°C for 8 hours. Particle size distributions were determined by employing a Master Sizer instrument from Malvern UK. Well powdered samples were analyzed for their composition using PXRD. The mineral phases of the Zechstein samples are found as halite (98.3%) and anhydrite (1.7%).

Cylindrical powder compacts with a diameter of 5 mm and a height of 5 mm were prepared via uniaxial pressing. The pressure for different samples was varied set to 120 MPa for the compaction. The density of the obtained samples was determined by measuring their geometric volume and putting it in relation to their weight. The as-prepared powder compacts were sintered for further densification. Sintering was initially performed in a hot stage microscope (EM-201, Hesse Inst., Germany) up to maximum temperature of 810°C at a heating rate of 10°C/min. The hot stage microscope allowed the *in-situ* volumetric shrinkage to be determined during the sintering process by measuring the area of the samples projection in an optical setup by a CCD camera. Images were collected at a rate of 40 frames per minute. For chemical characterization and phase analysis of the starting material and final samples, ion chromatography (Metrohm Type 761 Compact IC) and powdered X-ray diffraction (PXRD PANalytical X'Pert PW3020) were employed. The structure of the samples was analyzed by scanning electron microscopy (FEI FESEM Quanta 200 + TSL-EDAX).

## Results and Discussion

The sinter experiments were performed with powdered rock salt samples at a pressure of 120 MPa and at a temperature of 700°C. The results presented in this manuscript origin from a series of experiments with varies temperature, pressure and time. We chose the change in time for the experiments to show the interesting findings. There are two powdered samples at two different time intervals, 30 min and 20 h.

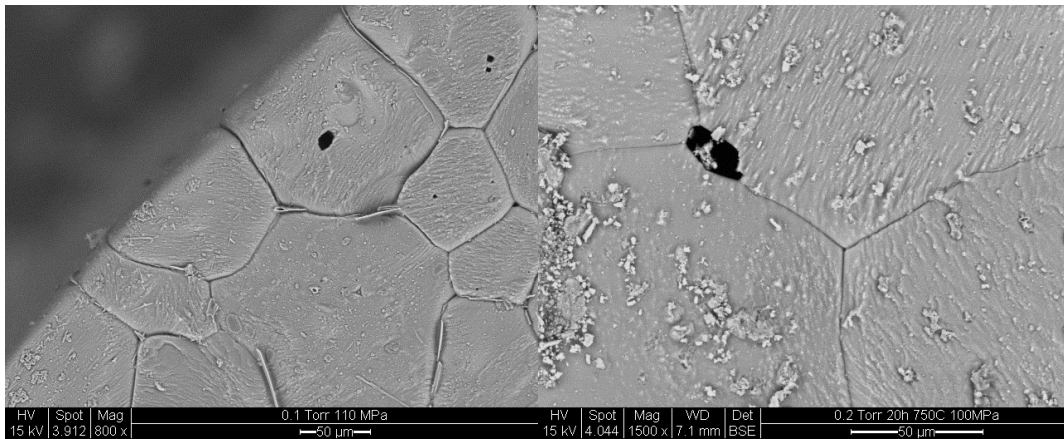
Figure 1 illustrates the microstructure of the samples surface after sintering at 700°C for the two different dwell times. Both images reveal large particles which are very well interconnected resulting in a closed outer surface of the sample. The sample sintered for 30 min shows elongated chip-like particles at the crystal grain boundaries. Those structures disappeared after sintering the sample for an extended period of 20 h. Figure 2 shows a detailed view of the chosen grain that was in a later procedure cut in the FESEM in order to examine the material around the grain boundary perpendicular to the surface of the material. More visible is the presence of the elongated grains between the grain boundaries of the larger gains.

FESEM images were taken to analyze these elongate particles. The surface was removed to result in a vertical cut at one of those particles between crystal boundaries. Figure 3 illustrates the vertical cut of the grain, where on the wedge is already visible. As the FESEM beam continued focusing the sample, the wedge changed its appearance, a sign of salts ductile property and explains that after 20 h sintering the elongate particles disappear (Figure 1).

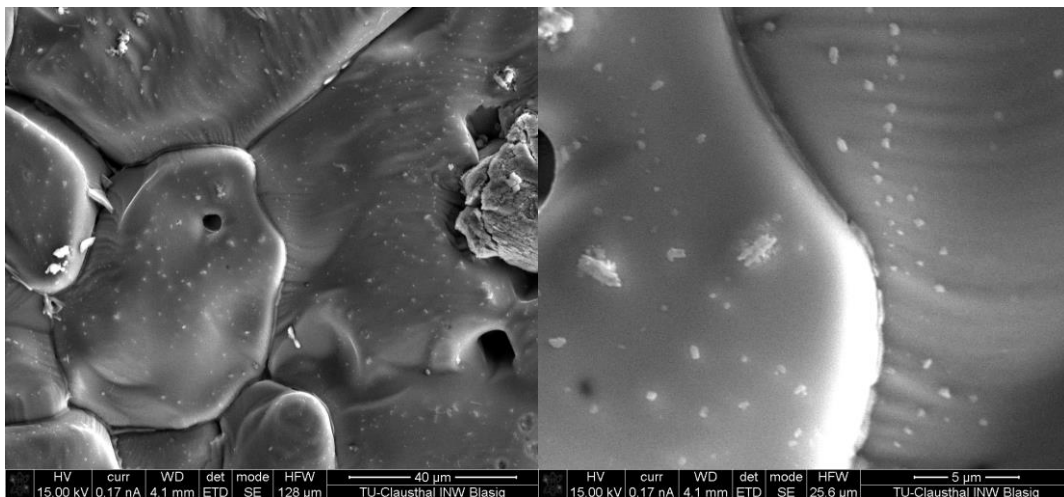
After having the cross-cut of the elongate particle between crystal boundaries, the material was examined for its composition and its crystalline structure. We found that the sintered samples contained the elongated arrangement formed wedges-like layouts into the rock salt and contained larger amounts of calcium sulfate compared to the main material. The powder compacts before sintering were thoroughly mixed and no calcium sulfate excess was observed anywhere. PXRD measurements were taken to prove the homogeneous mixture of the rock salt before sintering of the sample.

The sintering of the sample provoked a segregation of anhydrite from the homogenous mixture of naturally occurring rock salt. Adjusting the sinter process of it could lead to salt blocks of halite interiors and anhydrite outside. The solubility of anhydrite is much lower than halite and could also of advantage for the sintered building blocks.

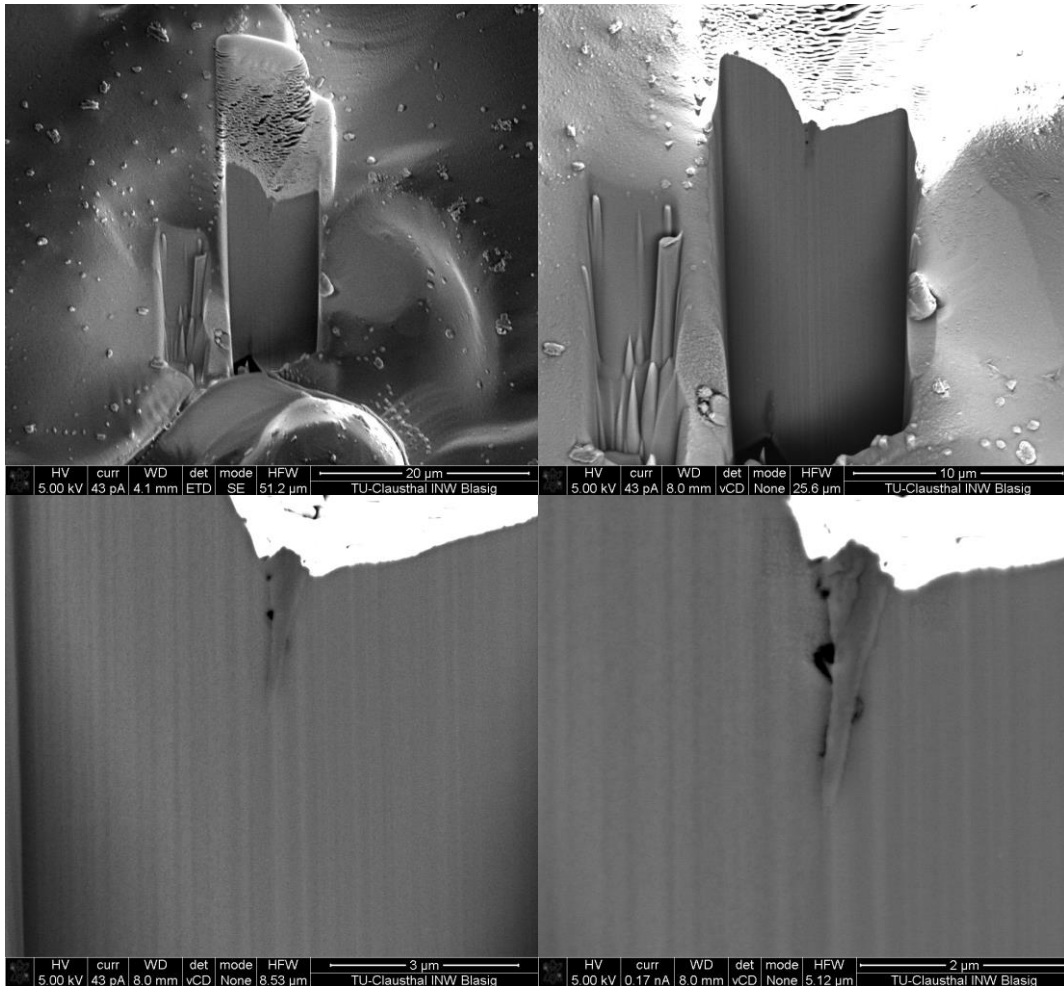
Reasons for the segregation of anhydrite could be related to its difference in solubility and to the difference in size of the ions calcium and sulfate from the ions sodium and chlorine. Other unknown different components might also have an influence on the segregation of anhydrite in halite.



**Figure 1: ESEM images of naturally occurring rock salt after different sinter times; 30 min (A) and 20 h (B).**



**Figure 2. FESEM images of sintered naturally occurring rock salt samples. Figure on the left shows the sintered grains of rock salt with needle-shaped lighter grains between the rock salt grains. Figure on the right shows detailed view of a grain and its captured different grain located in the grain boundary.**



**Figure 3: Detailed views of vertically cut sample along the grain boundary. Top images show the cut from the FESEM. Bottom images show zoomed-in images of the grain boundary, where two grains are separated by a wedge.**

### Conclusion

Sintering naturally occurring rock salt can result in phase separation of halite and anhydrite. This phase separation is time dependent and in our experiment had completely disappeared after 20 h. This opens a broad research branch as for sintering salt with different other compounds and observing their behavior for segregation. Chemical modelling on how the anhydrate first separates as the sample is heated and disappears after long time heating would be a great way of understanding the chemistry of naturally occurring rock salt better.

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