

# Calcium Sulphates of the Atacama Desert – The Gypsum-Anhydrite Phase Transition Revisited

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## Introduction

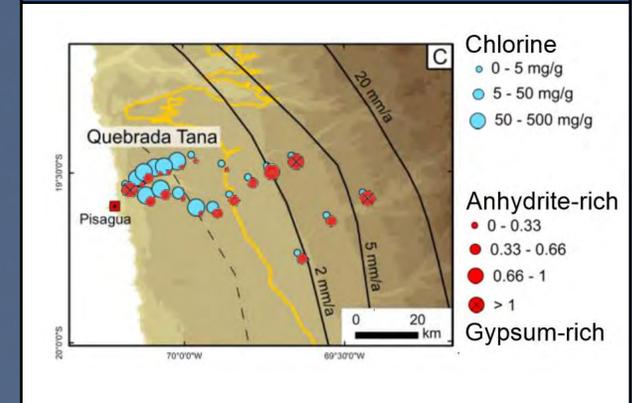
Present as *gypsum* ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), *bassanite* ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) and *anhydrite* ( $\text{CaSO}_4$ ), calcium sulphates comprise a significant fraction of evaporite minerals in the Atacama Desert, as well as, on Mars. Field observation suggest a **secondary formation process for the dehydrated sulphates** (Figs. 1 & 2). However, previous studies ruled out phase transitions by simple heating under the ambient conditions of the Atacama Desert [1]. Based on recent experiments by Dixon et al. [2] and subsequently Miller [3], we plan to perform **flow-through experiments** on synthetic and natural gypsum samples **with salt brines to control and lower the activity of water** necessary for the phase transitions to occur at the relevant environmental conditions (Fig. 2).

## Gypsum replacement by anhydrite



← Figure 1: Subsurface evaporite clast from SE of Salar Grande, Chile. Anhydrite has precipitated into fractures of gypsum dominated rock. Arrows demark fractures filled with anhydrite. Image by Benedikt Ritter.

## Correlation of chloride and anhydrite



← Figure 2: Spatial correlation of near surface chlorine and anhydrite abundances. Modified after [4].

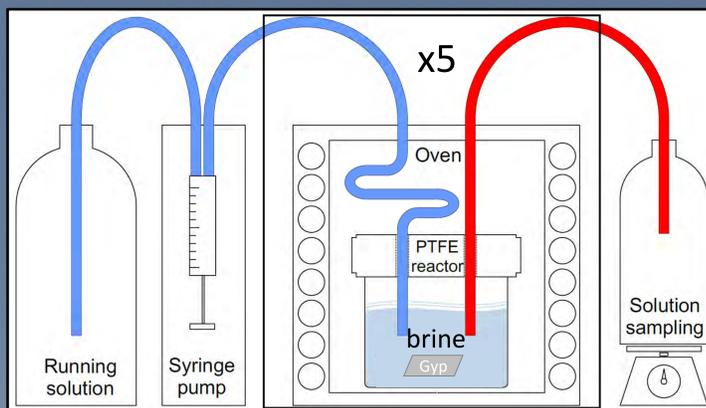
## Methods

### Experimental set-up

- ➔ 1ml-syringe pump
- ➔ Distributing head allows 5 experiments simultaneously with independent flow rate control
- ➔ Separate ovens with independent T-control
- ➔ Out-flow brine collected for later analysis

### Analytical set-up

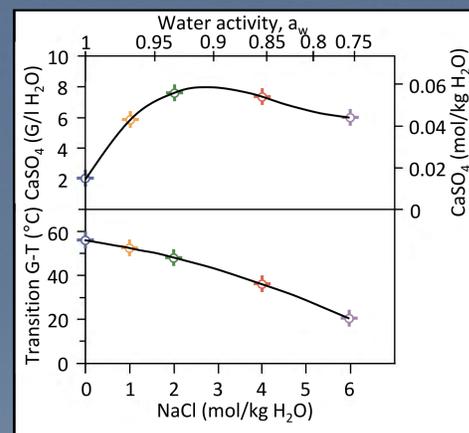
- ➔ Raman spectroscopy for point-measurements / mapping
- ➔ XRPD for bulk measurements
- ➔ SEM for crystal habit characterization
- ➔ Potential further chemical analysis



↑ Figure 3: Schematic depiction of the experimental setup. Modified after [5].

## Questions

- ➔ Can primary anhydrite form under the conditions of the Atacama Desert, or is it a secondary product?
- ➔ If so, is secondary anhydrite formation the result of phase transformation, dissolution-re-precipitation within highly saline brines, or a combination of both?



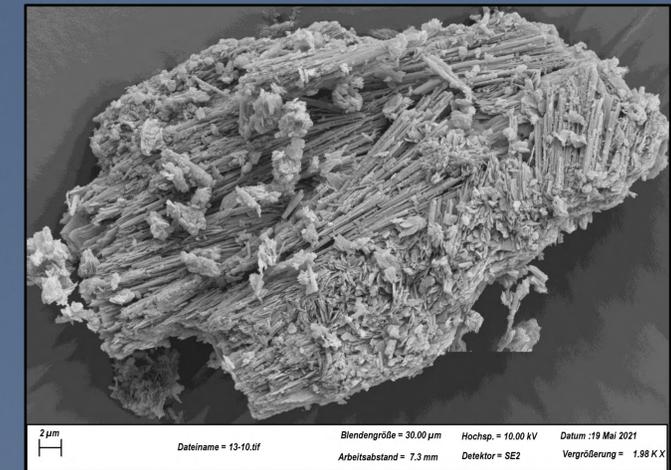
↑ Figure 4: Gypsum to anhydrite transition temperature and gypsum solubility as a function of  $M_{\text{NaCl}}$ . Modified after [6].

## Preliminary results

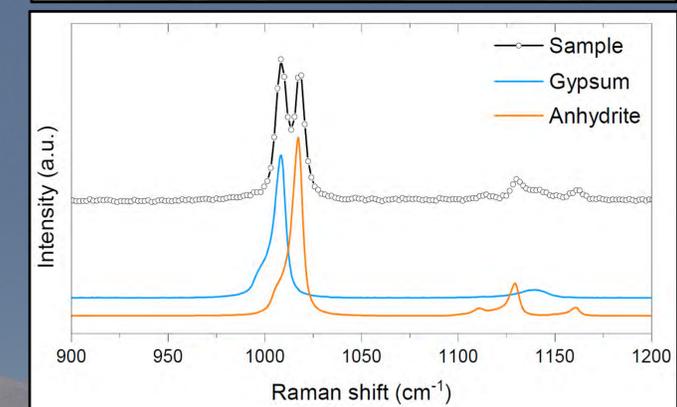
Preliminary **batch experiments at 50°C** on optical grade crystalline gypsum and gypsum powder in **8-12M  $\text{CaCl}_2$  brine** confirm a significant **dependence of the rate of conversion on crystal size**.

- ➔ Gypsum powder converted to **~80% anhydrite / ~20% Bassanite within 2 weeks** (Fig. 4)
- ➔ Crystalline samples showed significant surface conversion to **anhydrite (bassanite) only after 4 weeks** (Fig. 5)
- ➔ These preliminary results, namely the formation of bassanite from gypsum, seem to oppose the work of Miller [3], who suspected trace amounts of bassanite in only a single experiment

**In all cases, further analysis is ongoing.**



← Figure 5: SEM image of calcium sulphate powder after 2 weeks of reacting. Note small aggregates of likely bassanite on longer prismatic aggregates of likely anhydrite.



← Figure 6: Raman spectrum of crystalline sample surface after 2 weeks of reacting. Anhydrite is beginning to appear.

## References

- [1] Ritterbach, Laura, and Petra Becker. "Temperature and humidity dependent formation of  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  ( $x=0 \dots 2$ ) phases." *Global and Planetary Change* 187 (2020): 103132.
- [2] Dixon, Emily M., et al. "Assessing hydrodynamic effects on jarosite dissolution rates, reaction products, and preservation on Mars." *Journal of Geophysical Research: Planets* 120.4 (2015): 625-642.
- [3] Miller, Kayla. "Anhydrite nucleation and growth at low temperatures: Effects of flow rate, activity of water, and mineral substrates." (2017).
- [4] Voigt, Claudia, et al. "The spatial distribution of soluble salts in the surface soil of the Atacama Desert and their relationship to hyperaridity." *Global and Planetary Change* 184 (2020): 103077.
- [5] Lenting, Christoph. "Glass corrosion." (2019).
- [6] Berdugo, I., E. Romero, M. Saalnik & M. Albi: On the behaviour of the  $\text{Ca-SO}_4\text{-H}_2\text{O}$  system. *Rev. Acad. Colomb. Cienc.* 32(125): 545-557, 2008. ISSN 0370-3908.