

RAPID, IMPACT-INDUCED DEHYDRATION, MELTING, AND RECRYSTALLIZATION OF $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ (GYPSUM, BASSANITE, ANHYDRITE) INFERRED FROM LASER-IRRADIATION EXPERIMENTS. C. Hamann¹, L. Hecht^{1,2}, S. Schäffer³, K. Born¹, R. Luther¹, D. Heunoske³, and J. Osterholz³, ¹Museum für Naturkunde Berlin, Invalidenstr. 43, 10115 Berlin, Germany (christopher.hamann@mfn.berlin), ²Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74–100, 12249 Berlin, Germany, ³Fraunhofer-Institut für Kurzezeitdynamik, Ernst-Mach-Institut, Ernst-Zermelo-Str. 4, 79104 Freiburg, Germany.

Introduction: Understanding the shock behavior of the calcium sulfates 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 (CaSO_4) is essential for understanding the outcomes of hypervelocity impacts into evaporates, which are widespread on Earth and increasingly often discovered on Mars [1]. Since sulfates contain structurally bound volatiles such as SO_2/SO_3 and H_2O , most interest focuses on quantification of the shock-induced release of these volatiles to assess its role in the modification or generation of planetary atmospheres. For instance, the mass extinction at the end of the Cretaceous has been shown to be causatively related to the Chicxulub impact event and the global climatic effects caused by shock-induced release of SO_2/SO_3 from CaSO_4 into the Earth's atmosphere [2,3]. In addition, impact events as well as volcanic activity may trigger release of H_2O from calcium sulfates into the Martian atmosphere [4] and, thus, could assist with generating habitable conditions.

Quantification of the amount of volatiles released from sulfates in hypervelocity impact scenarios rely on assignment of the shock-pressure and entropy thresholds for incipient and complete devolatilization and vaporization. However, these thresholds are poorly constrained for the calcium sulfates [2,5], and many studies produced inconsistent to even contrasting results. Furthermore, reports of sulfate impact melts in terrestrial impactites [6,7] suggest that the shock behavior of the calcium sulfates is more complex than traditionally thought and possibly involves melting and interaction with coexisting silicate impact melts. Based on our previous study on the interaction between carbonates and laser-generated melts [8], we report here on the fate of gypsum and anhydrite in laser-irradiation experiments. We investigate transformation of hydrated to anhydrous forms of calcium sulfate; decomposition and melting of gypsum and anhydrite; and chemical interactions between calcium sulfates and silicates in impact-related contexts relevant for Earth and Mars.

Methods: We used a continuous-wave fiber laser of 1.07 μm wavelength at Fraunhofer-Institut für Kurzezeitdynamik in Freiburg, Germany to irradiate a gypsum plate (experiments L1130 and L1131; Fig. 1a,b) and a pulverized anhydrite–granite (experiment L1132; Fig. 1c) mixture in ambient air at 1 bar and room

temperature. The laser emitted a power of 2 or 5 kW for 2 or 5 s, and $1/e^2$ beam diameters of 6 or 17 mm were used, respectively, for the two different target setups. The average laser intensity in the $1/e^2$ region varied between 7.6×10^2 and $1.5 \times 10^4 \text{ W/cm}^2$ and the laser–matter interaction zone was observed using the setup described in [8]. Textural and compositional characterization of the irradiated samples employed light microscopy, Raman spectroscopy, scanning electron microscopy, and electron microprobe analysis.

Results and Discussion: Surface temperature measurements during laser irradiation show that peak temperatures on the sample surfaces of 1000–1200 K for the gypsum experiment (Fig. 1b) and of 2200 K for the anhydrite–granite experiment (Fig. 1c) were reached within milliseconds. Cooling of the samples back to room temperature was complete within ~ 30 s and ~ 90 s, respectively, and followed exponential cooling curves. We anticipate generally similar cooling profiles for centimeter to decimeter-sized impact ejecta (cf. [8]).

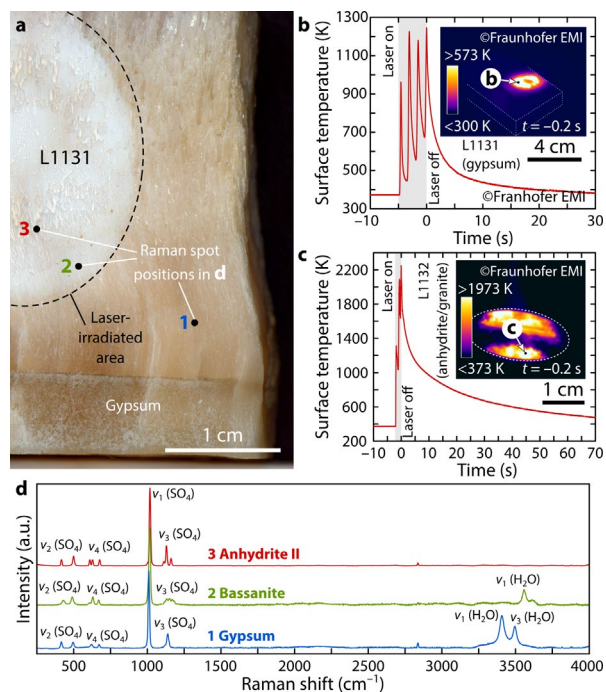


Fig. 1 a The laser-irradiated gypsum plate. b, c Exemplary surface temperature profiles of L1131 and L1132. d Raman spectra collected from the surface of the gypsum plate (cf. a).

Dehydration and Melting of Gypsum. Laser irradiation of the gypsum plate resulted in dehydration of gypsum and successive transformation of gypsum to anhydrite via bassanite (Fig. 1a). This transformation is evident in the 3250 to 3750 cm^{-1} region of Raman spectra collected from the gypsum plate after laser irradiation (Fig. 1d). In this region, the Raman bands corresponding to the stretch vibration modes of water are positioned. The gypsum \rightarrow anhydrite transformation is accompanied by a slight upshift of the Raman band associated with the ν_1 symmetric stretch vibration modes of the SO_4 tetrahedra (i.e., from 1010 cm^{-1} in gypsum to 1017 cm^{-1} in bassanite to 1018 cm^{-1} in anhydrite). In addition, dehydration of gypsum is also evident from back-scattered electron (BSE) images obtained from the irradiation zones by an increase in brightness and by the presence of cracks in individual bassanite and anhydrite crystals that are absent in gypsum of the starting material (Fig. 2a). Furthermore, textures and compositions indicative of complete water loss as well as melting and recrystallization of the remaining anhydrous CaSO_4 component (e.g., existence of round vesicles; filling of original cleavage space by flow-textured material of anhydrite composition; presence of 120° triple junctions between newly formed anhydrite crystals) are present in the high-temperature parts of the laser-irradiated regions (Fig. 2b). These features are absent in the original gypsum and those parts of the sample that experienced lower temperatures.

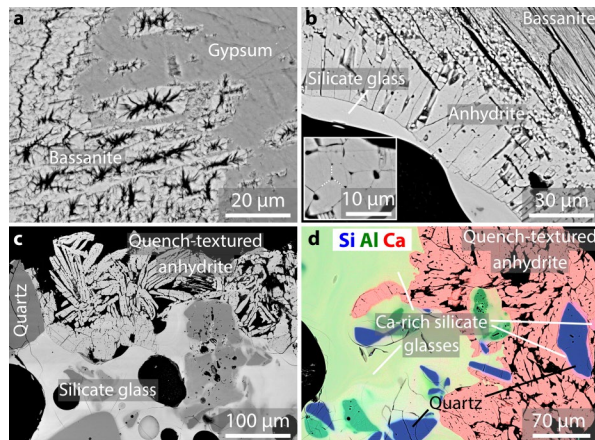


Fig. 2 Exemplary BSE images of **a** dehydration of gypsum; **b**, **c** dehydration, melting, and recrystallization of gypsum and anhydrite; and **d** silicate–sulfate interaction (element map).

Melting of Anhydrite and Chemical Interaction with Silicate Melts. Laser irradiation of the anhydrite–granite experiment produced clast-bearing melt droplets that quenched to highly vesicular silicate glasses of variable texture and composition (Fig. 2c). In addition, blebs and droplets of quench-textured anhydrite that contain inclusions of silicate melt droplets and granite-

derived silicate mineral grains with textures indicative of partial melting are disseminated in the silicate glasses (Fig. 2c,d). Compared to both the bulk composition of the granite as well as to individual Ca-rich mineral phases (e.g., plagioclase) of the granite, the silicate glasses are typically strongly enriched in CaO (up to 30 wt% CaO; Fig. 2d). In addition, most silicate glasses contain detectable amounts of SO_3 (up to 2 wt% SO_3), suggesting complete devolatilization of anhydrite (i.e., release of SO_2/SO_3) and incorporation of residual CaO as well as minor amounts of SO_3 into the silicate melts. However, quench-textured, vesicular anhydrite with lath-shaped crystals and/or 120° triple junctions (inset of Fig. 2b; cf. [7]) between individual crystals (both absent in the original anhydrite), and compositionally and texturally sharp interfaces to the surrounding silicate glass (reminiscent of menisci formed by liquid immiscibility [8]) suggest that melting of anhydrite and recrystallization of the sulfate melt also took place. Limited amounts of SiO_2 (up to 1 wt%) and K_2O (up to 0.6 wt%) were detected in the quench anhydrite, suggesting in keeping with previous observations on terrestrial impactites [6] that sulfate and silicate melts indeed exchange chemical components during the brief time scales (seconds to tens of seconds) in which both materials were in the liquid state here. These observations strengthen hypotheses of [6,7] and suggest that melting of anhydrite and chemical interaction between silicate and sulfate impact melts is a viable process during crater formation in sedimentary targets.

Conclusions: Our results suggest that the thermally triggered dehydration of gypsum and transformation of gypsum to anhydrite via bassanite can be exceptionally fast (seconds to tens of seconds) and will be readily triggered by flash-heating events such as hypervelocity impacts or magmatic activity. The presented Raman spectra and microtextures may be useful for future interpretation of similar reaction products observed on Mars [1]. Furthermore, our results confirm previous observations on shock-melted sulfates [6,7] and suggest that impact melting of sulfates should be indeed more prevalent than previously thought. Specifically, our results illustrate that silicate and sulfate impact melts will readily interact, resulting in Ca-enriched silicate melts and Si-enriched, recrystallized sulfate melts.

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