

OCCURRENCE OF THE SODIUM CARBONATE SHORTITE IN THE FLENSBURG C1 CHONDRITE.

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Introduction: The Flensburg C1 chondrite was recovered one day after a bright daylight fireball was witnessed on 12 September 2019 across northern central Europe. The single stone of 24.5 g mass consists of a unique, highly altered, clast-bearing C1 lithology with abundant Mg-rich serpentine, hydrothermally grown sulfide laths and abundant Ca and Ca-Mg carbonates [1]. Similar lithologies with no or very low modal abundances of carbonates have only been described as clasts within the Kaidun chondritic micro-breccia [2, 3].

During the initial study of Flensburg, Bischoff et al. [1] encountered a sodium-bearing Ca carbonate mineral that eluded immediate identification. This was mainly due to decomposition during SEM-EDX analysis. Using careful Raman spectroscopic study, the mineral was identified as the anhydrous Na-Ca carbonate shortite, $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$, which here is reported for the first time to occur in an extraterrestrial material.

Sample and Analysis: Raman analysis was conducted on thin section PL19173 (WWU Münster) of Flensburg using a WiTec alpha300 confocal micro-spectrometer at FSU Jena. Laser excitation used a wavelength of 532 nm and coupling to the sample was accomplished with 10×/0.25 and 100×/0.90 Carl Zeiss Epiplan objectives. The laser power was adjusted to <12 mW. Raman shifts were calibrated using a silicon reference (521.2 cm^{-1}), which was calibrated against a Ne gas discharge lamp and cyclohexane.

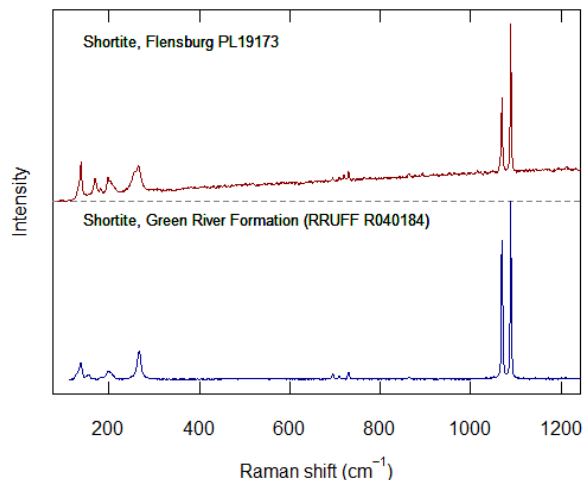


Fig. 1: Raman spectra of shortite in Flensburg and a terrestrial reference sample from the RRUFF database (ruff.info/R040184).

Results: Raman spectra of the Na-Ca carbonate show two ν_1 symmetric CO_3 stretching bands at 1069.1

and 1088.7 cm^{-1} (Fig. 1). These agree with terrestrial shortite and are characteristic of the two symmetrically distinct coordination environments of its carbonate groups. At higher laser power or lower numerical aperture, the doublet rapidly merges into a broad peak at intermediate frequency, possibly due to laser-induced heating of the surrounding opaque minerals. Accompanying grains of calcite and dolomite show single ν_1 bands at 1085.5 and 1094.6 cm^{-1} , respectively.

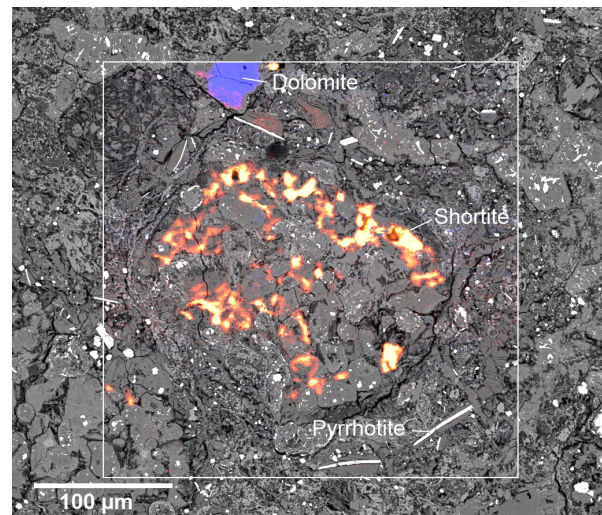


Fig. 2: Raman map of shortite (warm colors) in a relic chondrule of Flensburg (over BSE image). Calcite is present just outside the Raman-mapped area.

Spatial mapping of the shortite ν_1 doublet shows that the mineral typically fills interstitial spaces of former mesostasis within individual, highly altered chondrules (Fig. 2). It occurs in association with calcite and dolomite but rather seldom in direct contact with these.

Thermodynamic modelling. Currently, there is no comprehensive set of thermodynamic properties of shortite available. Jagiecki et al. [4] studied the equilibrium of the reaction $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} + \text{CaCO}_3$, in which shortite forms pirssonite and calcite. Their work provides two equilibrium temperatures of $55 \pm 2\text{ }^\circ\text{C}$ and $52 \pm 2\text{ }^\circ\text{C}$ at water activities of 0.94 and 0.70, respectively. From these values and the van 't Hoff equation an approximate reaction enthalpy of -174 kJ/mol can be obtained. Utilizing van 't Hoff extrapolation I derived dissolution equilibrium constants of shortite and included them into the pitzer.dat thermodynamic database of PHREEQC [5] to allow assessing the stability of shortite relative to other phases and aqueous

solution. This used the Pitzer specific interaction method appropriate to obtain activities in brines of high ionic strength. Due to the linear extrapolation of the two close datapoints of [4] and the high ionic strength of the solutions involved the results have estimative character until better thermodynamic data for shortite becomes available.

As established by [4], the formation of shortite instead of the hydrated phases pirssonite and gaylussite, $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, requires elevated temperatures or low water activities in the coexisting fluid. At $a(\text{H}_2\text{O}) = 1$ shortite is not stable below $\sim 56^\circ\text{C}$. This is independent of pH as long as calcite is the predominantly coexisting Ca species. Lower water activity shifts the shortite-pirssonite-calcite equilibrium towards lower temperatures, therefore stabilizing shortite in brine solutions with high concentrations of dissolved Na_2CO_3 (e.g., 1.1 molal at 55°C , [4]).

Based on Flensburg's sulfide mineralogy and the comparison to the similar C1 lithologies of Kaidun, the alteration temperature of Flensburg was $>100^\circ\text{C}$. It possibly reached up to 400°C as indicated by thermal models and old carbonate Mn-Cr ages [1].

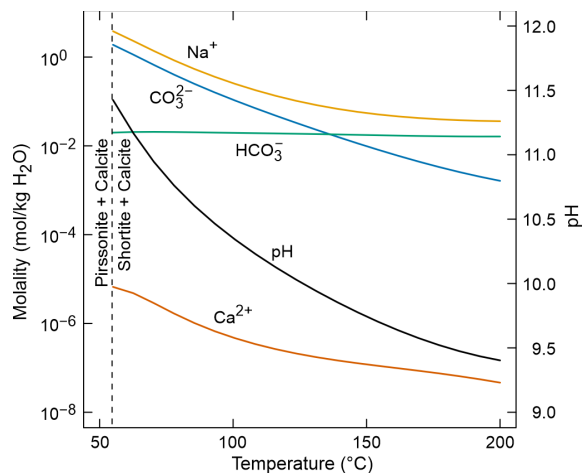


Fig. 3: Molalities and pH of an aqueous solution saturated in shortite and calcite calculated using PHREEQC; no other phases, solutes, or external CO_2 buffering were considered to be present.

Using the PHREEQC/Pitzer model, equilibrium compositions of a brine coexisting with shortite and calcite were calculated up to 200°C . With increasing temperature, the brine's alkalinity, ionic strength and pH steadily decreases (Fig. 3). Above 100°C the molality of Na_2CO_3 is below 0.1 mol/kg and the activity of water becomes larger than 0.99 . Hence, if shortite formed together with calcite and the sulfide assemblage, which are often closely intergrown, then the coexisting fluid was a Na-rich, alkaline, but not highly concentrated solution (less than half the ionic strength

of sea water). This is consistent with the absence of evaporitic phases such as Ca-free Na carbonates, although those might have been dissolved during the few hours when the Flensburg meteorite was exposed to humid weather.

An origin of shortite by late-stage desiccation of pirssonite seems rather unlikely, because owing to their different stoichiometries, this requires the addition of CaCO_3 . Thus, shortite is most likely a primary mineral that precipitated during fluid-driven alteration.

The sodium enrichment of the parent fluid is quite remarkable, because also the coexisting Mg-rich serpentine contains an unusually large Na component (1-2 wt.% Na_2O , charge-coupled to substitution of Al^{3+} into the structure [1]). Similar lithologies within the polymict Kaidun micro-breccia lack sodium enrichment in serpentine and some of these clasts do not contain carbonates at all [2, 3].

The characteristic morphology of acicular or lath-shaped pyrrhotite crystals sheathed by serpentine and the occurrence of Si-bearing magnetite in Flensburg and the Kaidun clasts strongly suggests that both originated in close vicinity and likely on the same parent body. This suggests that the parent lithology experienced heterogeneous alteration conditions in terms of fluid composition, probably at a low water/rock ratio. The latter is also indicated by the presence of serpentine veinlets and Flensburg's bulk oxygen isotopic composition [1]. The localized occurrence of shortite in individual, highly altered chondrules suggests that fluid transport was quite restricted and Na released from chondrule mesostasis remained near its source region or that precipitation was strongly controlled by porosity (due to dissolved mesostasis). A low water/rock ratio is quite surprising given the essentially complete alteration of the precursor – this still needs answering. The many similarities but also distinct differences between Flensburg and the Kaidun clasts render these lithologies important witnesses of intense and complex hydrothermal alteration in the early Solar System.

References: [1] Bischoff A. et al. (2021) *GCA*, 293, 142–186. [2] Zolensky M. E. et al. (1996) *Meteoritics & Planet. Sci.*, 31, 484–493 [3] Harries D. and Zolensky M. E. (2016) *Meteoritics & Planet. Sci.*, 51, 1096–1109. [4] Jagniecki E. A. et al. (2013) *GCA*, 115, 31–45. [5] Charlton S. R. and Parkhurst D. L. (2011) *Computers & Geosciences*, 37, 1653–1663.

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