FREEZING-INDUCED FRACTIONATION OF ICE, GLASS AND SALTS FROM SIMULATED ENCELADUS OCEAN FLUIDS. M. G. Fox-Powell[1,2] and C. R. Cousins[1]. 1School of Earth and Environmental Sciences, University of St Andrews, Irvine Building, North Street, St Andrews, UK (mgfp@st-andrews.ac.uk), [2]Open University, Walton Hall, Milton Keynes, UK

Introduction: The Saturnian moon Enceladus exhibits large cryovolcanic plumes sourced from a subsurface ocean [1], which contain evidence of endogenic organic chemistry and ongoing hydrothermal activity at the core-ocean boundary [1-3]. Salt-rich ice particles observed in the plumes by the Cassini spacecraft are interpreted as rapidly frozen ocean spray [4] thus studying them provides a means of probing the chemistry, habitability and potential biology of an extraterrestrial ocean. However, little is known about how ocean constituents evolve as they are transported towards the extreme cold at the Enceladan surface. We investigated the partitioning of ice and non-ice materials and the pH-dependence of cryogenic mineral formation using simulated Enceladus ocean fluids. As thermal conditions inside the vents are not well constrained, we investigated two end-member scenarios of ice particle production: flash-freezing (≥ 100 Ks^{-1}), and slow freezing (~1 $Kmin^{-1}$), to provide new understanding of the range of possible products of cryovolcanism at Enceladus.

Approach: Our simulated Enceladus ocean fluids were designed based on up-to-date constraints provided by Cassini data and modelling efforts [1-3, 5]. Fluids bore a $Na-K-Cl-HCO_3-CO_3-NH_4-NH_3-Si$ chemistry and were synthesized spanning the estimated pH range of 9-11 [1,5]. Flash freezing experiments were performed by dripping ~4 µl aliquots of room-temperature Enceladus ocean simulants into liquid N_2. Slow freezing experiments were performed by placing aliquots of Enceladus ocean simulant into a 233 K chiller. Cooling rates were compared with physical models of plausible cooling rates in the Enceladus vents. Samples were imaged by cryo-Scanning Electron Microscopy (SEM) at 123 K. For bulk analyses, cryogenic precipitates were extracted from ice via sublimation.

Findings: *Glass formation and ice templating.* We show for the first time that fluids with Enceladus ocean composition form ice-templated aqueous glass when rapidly flash-frozen. In the interior of frozen droplets, a solidified brine-vein network was observed, which had formed despite the extremely rapid cooling rate (Fig. 1A). Bubbles of gases exsolved at the glass transition were incorporated into the glass, further indicating the vitreous nature of the ice-templaed solid phase. As cooling rate is a function of droplet size, closer to the droplet edge, or in droplets with smaller radii, cooling rates

could feasibly be orders of magnitude higher. However, even at the droplet surface, a vein network was established. If plume particles result from a flash-freezing mechanism, the production of cryovolcanic glass at Enceladus should be expected.
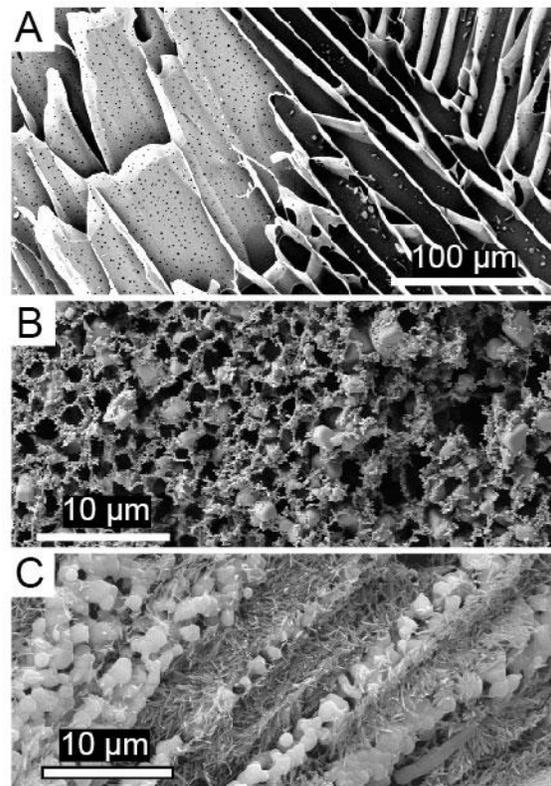

Fig. 1. A. Vitrified brine vein network interior of flash-frozen droplet, showing ice (dark regions) and glass (lighter material). Imaged at 123 K. **B.** Crystals formed through re-warming flash-frozen glass. **C.** Crystals formed through slow freezing.

Mineralisation via direct crystallisation versus devitrification. We found that crystallisation of salt minerals occurred either directly, by precipitating from brine during gradual freezing, or growing from glass upon re-warming of flash-frozen samples. These contrasting mechanisms were reflected in the distribution of crystals. Flash-frozen samples exhibited random crystal distributions whereas crystals produced by slow freezing were arranged in lamellar or globular clusters of locally distinct crystal types (Fig. 1B,C). These latter textures

are similar to those observed following eutectic solidification in igneous and metallic systems [6], and are explained by relative solubility, which we investigated using the program FREZCHEM [7]. As more soluble minerals (such as chlorides) form late in the precipitation sequence, they force less soluble minerals (such as carbonates) into aggregates. The growth of crystals from glass requires nucleation points, hence we consider the rapid formation and incorporation of micro-crystals and/or silica nanoparticles into glass during flash-freezing as likely, where they can template crystal growth when increased temperatures permit.

At pH 9, amorphous silica was supersaturated prior to freezing, a precondition for forming the silica nanoparticles observed originating from Enceladus [3]. Above pH 10.5 the solubility of amorphous silica increases exponentially. Although colloidal opal-a is not seen in our experimental precipitates under SEM for either freezing rate, Si is observed by energy dispersive X-ray spectroscopy to associate preferentially with the small Na-carbonates. Even at pH 11 therefore, silica must form early during freezing, nucleating or becoming incorporated into carbonates.

Mineralogy of cryogenic salts. Measurements of bulk mineralogy using X-ray diffraction showed that carbonate mineral assemblages differed between upper and lower pH estimates for Enceladus's ocean. From pH 11 fluids, carbonate assemblages were dominated by thermonatrite ($Na_2CO_3 \cdot H_2O$), whereas at pH 9 trona ($Na_3H(CO_3)2 \cdot 2H_2O$) and nahcolite ($NaHCO_3$) were the major phases (Fig. 2). This demonstrates that carbonate mineral assemblages can function as an independent pH probe for Enceladus's ocean.

At pH 11, the mineralogy produced by slow-freezing is strikingly similar to that produced by flash-freezing, despite the latter crystallising via secondary devitrification (Fig. 2). By contrast, at pH 9, flash-frozen samples lack the nahcolite present in the slow-frozen samples. This suggests that the flash-freezing process kinetically inhibits $NaHCO_3$ precipitation. Hence for lower pH fluids, the presence of nahcolite is an indicator of more gradual freezing, while its absence might implicate a flash-freezing devitrification process. These results provide a strong rationale for non-destructive plume particle measurements. Moreover, given that Na-carbonate minerals, interpreted as cryovolcanic in origin, have been remotely detected on the dwarf planet Ceres, the lessons learned here could be applied alongside modelling efforts to unravel the volcanic history of this body.

Our experiments show that different cryovolcanic products are possible in Enceladus plume particles, including vitrified glass and crystalline material. If crystalline material exists within plume particles,
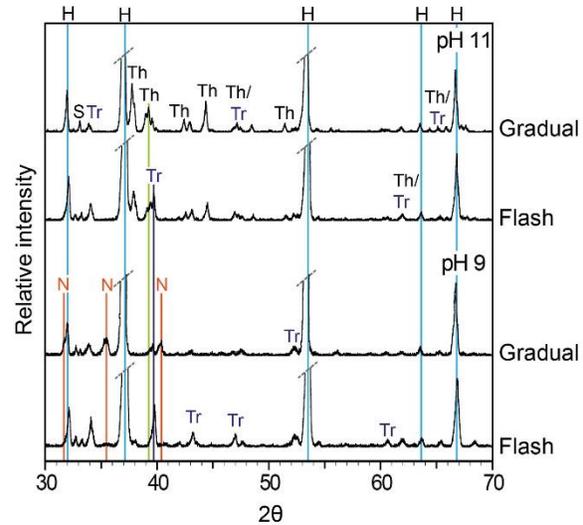

Fig. 2. X-ray diffraction patterns collected from crystalline cryogenic salts at both pH levels following endmember freezing scenarios. Identified peaks are: H, Halite (NaCl); S, Sylvite (KCl); Tr, Trona ($NaH_3(CO_3)_2 \cdot 2H_2O$); Th, Thermonatrite ($Na_2CO_3 \cdot H_2O$); N, Nahcolite ($NaHCO_3$). Note largest halite peaks at 37.0 and 53.5° (2θ) are truncated for clarity.

crystallization textures can delineate between primary precipitates (i.e. slow-frozen) versus secondary devitrification (i.e. flash-frozen, followed by increased temperatures). Whether Cassini encountered glass-bearing particles at Enceladus depends on the specific thermal histories of the particles, which are currently unknown. The production of cryovolcanic glass at Enceladus would be highly significant, as vitrification captures ocean constituents in their last liquid-phase abundances and can perfectly preserve microorganisms, further raising the significance of the plumes for astrobiology. Proposals for future missions also centre around plume particle analysis [8]. Based on our results, non-destructive measurements of plume particles could open powerful new avenues of investigation at Enceladus, and at other bodies with potential cryovolcanism, such as Jupiter's moon Europa.

References: [1] Waite, J. H. et al. *Science* 356, 155–159 (2017) [2] Postberg, F. et al. *Nature* 558, 564–568 (2018) [3] Hsu, H.-W. et al *Nature* 558, 564–568 (2018) [4] Porco, C. C. et al. *Science* 311, 1393–401 (2006) [5] Glein et al. *Geochim. Cosmochim. Acta* 162, 202–219 (2015) [6] Akamatsu, S. & Plapp, M. *Curr. Opin. Solid State Mater. Sci.* 20, 46–54 (2016) [7] Marion, G. M. et al. *Comput. Geosci.* 36, 10–15 (2010) [8] Reh, K. et al *IEEE Aerosp. Conf. Proc.* (2016)