

EGU21-3547

<https://doi.org/10.5194/egusphere-egu21-3547>

EGU General Assembly 2021

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Nano-scale investigation of co-precipitated subglacial calcite and opal, antarctica

Silvia Frisia¹, Péter Németh², Andrea Borsato¹, John C. Hellstrom³, Attila Demény⁴, and Béla Pécz⁵

¹University of Newcastle Australia, Earth Sciences, CHALLAGAN, Australia (silvia.frisia@newcastle.edu.au)

²Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar tudósok körútja 2, 1117 Budapest, Hungary.

³School of Earth Sciences, The University of Melbourne, VIC 3010, Australia

⁴Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Budaörsi út 45, H-1112, Budapest, Hungary

⁵School of Environment, The University of Auckland, Auckland 1010, New Zealand.

Calcite crusts from the Elephant Hill Moraine (EHM) (76°17'35" S 157°20'05" E) collected during 1983-84 were interpreted as formed in subglacial environments influenced by hydrothermalism (Faure et al., 1988). More recently, ²³⁴U enrichment in these crusts was used to suggest that during the warm MIS 11 interglacial (ca. 400 ka), the ice sheet margin at the Wilkes Basin retreated about 700 km inland (Blackburn et al., 2020). Their ²³⁴U data from separate analyses of pure calcite and pure opal crusts suggested that "connate seawater would impart marine signatures to subglacial waters" (Blackburn et al., 2020), with the former associated with massive melting during MIS 11. However, robust U-series dating by Blackburn et al (2020) was only possible on pure end members of opal and calcite, whilst other EHM crusts did not yield reliable ages and were discarded. The inferred MIS11 ice-loss was then based on a model of ²³⁴U accumulation and on those carbonate ages that fit their hypothesis that connate seawater influenced the subglacial environment.

Here, we investigated the nanostructure of EMH samples that yielded unreliable U-Th ages, which were too old to fit into the ²³⁴U-based model of MIS11 connate seawater influencing subglacial waters. High-resolution transmission electron microscope images showed a complex history of precipitation, dissolution, re-precipitation, including the co-precipitation of nanocrystalline calcite and opal. Co-precipitation was documented by the inclusion of micrometre-scale opal spherules within calcite crystals whose lattice orientation does not change across the spherules and can be explained by the fluid being extremely enriched in silica. The calcite immediately surrounding the opal spherules was characterized by twins and likely a response to sub-ice sheet stress during their precipitation. The calcite-opal mixture partially replaced pre-existing calcite crystals, which appear broken, corroded and pre-date a final, pure calcite void-filling cement. Clearly, these EHM samples document several stages of crystallization, which imply repeated mobilization of chemical species. Preliminary Fluid Inclusion analyses of the crusts yielded a temperature of about 85°C, which inferred that at one stage calcite precipitation may have been influenced by

hydrothermalism associated with volcanism. Our identification of complex crystallization histories for the Elephant Moraine subglacial carbonates opens up alternative formation hypotheses to that proposed by Blackburn et al. (2020) such as the existence of multiple sources of aqueous solutions. Consequently, it is fraught to infer that all the EMH formed from connate marine waters generated 400 ka without dating of multiple phases of calcite precipitation from each sample.

References: Blackburn, T. et al. 2020, *Nature*, 583 (7817), pp.554-559. Faure, G. et al, 1988, *Nature*, 332(6162), pp.352-354.