

COMPLEXITIES IN CALCITE TEXTURES REVEALED: A COMBINED ELECTRON BACKSCATTER DIFFRACTION, X-RAY FLUORESCENCE, ELECTRON MICROSCOPY AND RAMAN SPECTROSCOPY STUDY OF STEEN RIVER IMPACTITES. E. L. Walton¹ and N. E. Timms², ¹ Department of Physical Sciences, MacEwan University, Edmonton, AB, T5J 4S2 (waltone5@macewan.ca). ²School of Earth and Planetary Sciences, The Institute for Geoscience Research, Curtin University, GPO Box U1987, Perth, WA, Australia.

Introduction: Impact into sedimentary rocks are thought to be more damaging to the atmosphere and biosphere compared to impacts of the same magnitude occurring in purely crystalline target. This increased destructiveness is due to the volatile-rich nature of sedimentary rocks and their ability to decompose, liberating climatically active gases such as CO₂ from carbonates, SO_x from sulfates or H₂O from phyllosilicates [1]. For example, calcite in limestone may decompose via the reaction $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)} \uparrow$ during adiabatic decompression from high shock pressures or due to post-impact thermal equilibration-related heating [2, 3]. Recent studies have emphasized the amount of impact melt that may be generated from carbonate rocks, which would significantly decrease the amount of atmospheric CO₂ released [4]. The relative importance of carbonate melting versus decomposition is actively debated [e.g., 5, 6]. In contrast to the obvious deleterious effects of hypervelocity impact events, they may also be regarded as conducive to life through creation of porous rocks and new hydrothermal systems [7]. The syn- and post-impact environment is therefore an extremely complex system, that can be unraveled through numerical and computer-based modeling, combined with field and laboratory studies; however, impacts into sedimentary targets are particularly difficult to model because of layering, pore space and volatiles. In this context, the mineralogy and microtextures of sedimentary-derived impactites are particularly useful, because they serve as physical markers of the physicochemical conditions in which they formed. Study of the texture, composition, chemistry and crystallography of a given mineral may be used to discriminate between those grains inherited from target rocks, impact-produced materials and hydrothermal precipitates.

This study focuses on calcite-bearing impactites from the crater fill deposits of the 25-km diameter Steen River impact structure in Alberta, Canada [8, 9]. The target stratigraphy comprised ~1.28 km of Devonian evaporites, variably dolomitized limestone and carbonaceous shales overlying Precambrian granitic rocks. Previous work on calcite in these breccias suggest several generations, distinguished by texture and minor element composition [9]. The distinct calcite varieties include: (1) cm-size lithic limestone clasts retaining primary sed-

imentary structures, (2) mm-size marble-textured calcite recrystallized from limestone clasts, (3) frothy calcite formed by incipient decomposition, (4) calcite quench-crystallized from impact melt, and (5) post-impact, hydrothermal calcite. In this study, we investigate calcite in these same breccias using non-destructive micro-X-ray Florescence (XRF) and electron diffraction backscatter diffraction (EBSD) mapping. XRF mapping is useful for simultaneous characterization of the distribution of major, minor, and trace elements over large areas, to a spatial resolution of ~10–30 μm. EBSD typically has a spatial resolution of ~50 nm, with the capability to identify crystalline phases, quantify grain size distribution, shapes and crystallographic preferred orientations of each phase, and characterize intragrain microstructures such as twins and crystal-plastic strain. EBSD can also be used to recognise amorphous (glassy) materials. Our results demonstrate how XRF and EBSD mapping may be combined with conventional methods to maximize the amount of information that may be gleaned from impactites containing minerals formed in the pre-, syn- and post-impact environment.

Samples and Methods: Thin sections and polished thin section offcuts of samples S3-703, S3-769.5, S1-921 from the calcite-bearing breccia at Steen River were examined. Sample numbers refer to the core identifier and the depth in feet (e.g., S1-921 is from core ST001 at a depth of 921 feet). EBSD mapping was done using a Tescan MIRA3 field emission SEM fitted with Oxford Instruments AZtec EDS/EBSD acquisition system and Nordlys Nano (S3-703A and S3-769.5) / Symmetry (S1-921) EBSD detectors at Curtin University. Data were processed via Channel 5.12 software to produce thematic maps and pole figures. XRF maps of the entire polished surfaces were obtained using a Bruker 2D micro-XRF Tornado system at CSIRO, Perth.

Results and Discussion: Calcite in all three samples were indexable using EBSD mapping, indicating that this phase is highly crystalline. EBSD quantified the grain size, shape and crystallographic orientation of calcite, which, when combined with compositional information from XRF and EDS maps, were used to gain insight into its formation conditions. The results reveal more complexity than described in our earlier combined SEM, EMPA and Raman spectroscopy study [9].

Sample S1-921: Impact melt occurs as groundmass-supported clasts, with calcite and plagioclase as the two

most abundant phases. Vugs and vesicles are filled by calcite and smectite group minerals. Portions of these clasts were mapped using EBSD with a 2 μm step size. The first area contains smectite-filled amygdales, with domains of banded calcite visible in SEM back-scattered electron (BSE) images. The flow-textured calcite is aligned with linear trains of vesicles and plagioclase laths. This calcite contains minor MgO, whereas the vug-fill calcite does not. EBSD demonstrates that both the vug-fill calcite and flow-textured calcite comprise extremely coarse, strain-free, highly crystalline calcite. This texture was expected for the vug-fill calcite, because hydrothermally-crystallized calcite can be coarse in this way. However, these are not textures expected for the impact melt domains. EBSD maps show that the grain boundaries of the large calcite crystals clearly cut across the flow texture, and so these grains must have formed via late stage replacement of a precursor phase. It is likely that the original material was unstable, possibly glassy impact melt. The distinct compositions determined from EDS and XRF mapping indicate that the recrystallization process did not significantly alter the calcite composition.

Sample S3-769.5: This breccia sample contains hydrothermal calcite, as well as entrained fragments of limestone rimmed by Ca-Fe-rich garnet (andradite). Two areas of S3-760.5 were mapped; the first, collected with a 4 μm step size, covers the boundary between an andradite-rimmed limestone clast and hydrothermal calcite. All calcite domains have random crystallographic orientations and distinct textures delineated by grain sizes quantified in the EBSD maps. A second, large area map, collected at a step size of $\sim 6 \mu\text{m}$, illustrates the range of carbonate textures, including coarse to very coarse hydrothermal calcite, a recrystallized limestone clast, a sulfide-rich limestone clast, and vug-fill calcite within silicate impact melt clasts. Twins, visible optically in the hydrothermal calcite, were indexed with EBSD. Grains within all calcite domains have random crystallographic orientations. XRF mapping shows that the limestone clasts, as well as the clasts that, based on texture, were mapped as carbonate impact melt, are both low in Sr and Mn-rich, whereas all textures identified as hydrothermal calcite are Sr-rich and Mn-poor.

Sample S3-703A: This sample contains a cm-size limestone clast containing recognizable fossils with a distinctly darkened rim. XRF mapping shows Mn-enrichment and Sr-depletion in the dark rim, compared with the clast center. Those grains in direct contact with the groundmass of the breccia are highly vesiculated (frothy). Within the breccia groundmass, impact melt is found as fluidal-textured clasts of silicate glass and calcite-bearing clasts. One fluidal calcite-rich clast contains a grain of reidite-bearing zircon, testifying to the

high shock provenance ($>30 \text{ GPa}$) of the breccia components [9]. Calcite in the reidite-bearing clast was mapped at 8 μm and 1 μm step sizes. The calcite grains are coarse, strain-free, twin-free and are shown to have grown across some of the vesicles. This texture is interpreted to represent late stage calcite grain growth, likely a hydrothermal replacement of precursor impact glass. EBSD maps acquired from frothy calcite areas show these grains comprise a single crystal orientation – even the frothy central region yields strong enough EBSD patterns to index. The Mn-rich vesicle-free rims yield stronger EBSD patterns and appear to be replacement rims. The crystallographic orientation of these domains is approximately syntaxial with the frothy cores. We interpret that this entire grain has recrystallized from melt, either calcite replacing impact glass or growing directly from melt, with the rim undergoing further recrystallization during a subsequent hydrothermal stage.

An additional EBSD and EDS map spanned the dark rim on the cm-size limestone clast, its unaltered interior, as well as a portion of the adjacent breccia groundmass. The clast margin comprises polygonal, low-Mn, crystalline calcite. This margin is surrounded by a very fine-grained high-Mn calcite domain, which appears dark in optical photomicrographs and that has an increase in secondary smectite group minerals that did not index with EBSD. The outermost rim (mid-grey in optical images) is coarser grained calcite compared with the black band, but not as coarse or even-textured compared with the clast center. The coarsest grain sizes are present in the impact melt clasts in the breccia groundmass, which comprise polygonal unstrained high-Mn calcite. The impact melt clasts have probably undergone significant recrystallization, probably during post-shock hydrothermal alteration, that still preserve the outlines of melt-related textures.

Conclusion: Our results demonstrate that the geological history read from calcite texture and composition may be even more complex than previously realized. Fluidal textures in BSE images, consistent with calcite crystallized from a molten state and therefore convincingly attributed to impact melting, may actually be replacement textures, revealed through EBSD mapping. This is likely due to the solubility of calcite in the post-impact hydrothermal environment, and that many impact products may be in metastable states that are susceptible to replacement.

References: [1] Pope et al. (1994) *EPSL* 128:719–725. [2] Kurosawa et al. (2012) *EPSL* 337:68–76. [3] Deutsch and Langenhorst (2007) *GFF* 129: 155–160. [4] Osinski et al. (2008) *GSA* 437:1–18. [5] Osinski et al. (2015) *EPSL* 432:283–292. [6] Hörz et al. (2015) *MAPS* 50:1050–1070. [7] Naumov (2005) *Geofluids* 5:165–184. [8] Grieve (2006) *Geol. Assoc. Canada* 157–160. [9] Walton et al. (2019) *EPSL* 515:173–186.