ON THE SHOCK BEHAVIOR OF CALCITE: RECENT RESULTS FROM MEMIN EXPERIMENTS.

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Introduction: The reaction of carbonates, *e.g.*, $CaCO_3$ (calcite) or $CaMg(CO_3)_2$ (dolomite), to hypervelocity impacts is still a matter of debate. Particularly, the question is whether carbonates released from high shock pressures will decompose and liberate CO_2 [1–4], or will be preserved as melt in impactites [5–6]. Considering the phase diagram of $CaCO_3$ [7], it has to be concluded that *both* processes can occur, depending on *P*–*T* conditions during impact. Specifically, post-shock temperatures and pressures of >1500 K and >0.1 GPa, respectively, should favor melting, whereas temperatures and pressures from 1500–3000 K and <0.1 GPa, respectively, should favor decomposition. Although calcite melts are known from impact experiments (*e.g.*, [8]), the record of carbonate melting *vs.* decomposition in natural impactites remains controversially discussed, with some authors favoring decomposition and others favoring melting.

Recently, we have reported first evidence of calcite melting in impact and laser melting experiments performed in the Multidisciplinary Experimental and Modeling Impact Research Network (MEMIN) [9]. Here, we extend the characterization of the calcite melts using a combination of optical microscopy, BSE imaging, FE-EMPA, and Raman spectroscopy; structural analysis of the material will be done with TEM.

Experimental Setup: We have performed a series of impact experiments with a two-stage light-gas gun at Fraunhofer Ernst-Mach-Institute, Freiburg. Experiment A30-5610 involved the impact of a 6.17 mm diameter basalt projectile onto a block of Carrara Marble (95 vol.% calcite ± dolomite ± apatite ± feldspar) at 4.94 km/s, resulting in ~51 GPa peak pressure. Ejecta particles were recovered with ejecta catchers and mounted in epoxy; hence, transmitted-light microscopy was not applicable in this case.

Additionally, we have performed a series of accompanying laser melting experiments at Technische Universität Berlin. A pulsed Nd:YAG laser with a wavelength of 1064 nm and adjustable settings for power, pulse energy, pulse frequency, and pulse duration has been used to quasi-instantaneously melt and subsequently quench the contact zones between blocks of basalt and Carrara Marble. Thin sections were made from the melt tracks and studied by the methods stated above. Although the laser experiments cannot exert the high pressures of hypervelocity impacts, they are capable of simulating typical conditions of rapid melting and quenching during decompression and, thus, impact melt genesis (cf. abstract by Ebert et al. [10]).

Results and Discussion: Calcite grains that show textures indicative of degassing and melting were detected in both types of experiments; the laser melting experiments, affecting larger amounts of Carrara Marble than the impact experiments, also yielded degassing of dolomite grains. It should be stressed that the term "calcite melt" does not refer to the existence of pure $CaCO_3$ *glass*, but rather to molten and subsequently (partly?) recrystallized material. Because of the ionic nature of $CaCO_3$, calcite glass is not expected to be stable (although carbonate glasses are known, *e.g.*, from the system $MgCO_3$–KCO_3 [11]).

Impact experiments. The impact experiments yielded calcite ejecta particles that mainly show low- to medium-grade shock effects, *i.e.*, intense twinning. We observed up to three sets of mechanical twins in individual grains, which most likely represent *e*, *r*, and *f* twins [8]. We also detected highly shocked calcite particles and composite particles composed of calcite and silicate melt from the basalt projectile. In these particles, calcite grains show textures indicative of melting, which are absent in the pre-impact calcite. Specifically, calcite melting is recognized by appearance of spherical or elongated vesicles in the material and loss of grain boundaries. Furthermore, Raman spectra obtained from the calcite melt are distinctly different to ones obtained from calcite grains next to the melt. They are characterized by a strong fluorescence signal and disappearance of the calcite bands at 155, 287, 714, 1087, and 1439 cm^{-1}. Compositionally, the melt is indistinguishable from the pre-impact calcite, indicating (partial) shock melting and boiling of the material as well. However, since we failed to detect residual CaO in the melt, it is unlikely that the gaseous species was CO_2. This indicates that the release path passed the field $CaCO_3$ (liquid) [7], with post-shock temperatures too low and/or post-shock pressures too high to reach the field CO_2 + CaO (solid) [7].

Laser melting experiments. In the laser melting experiments, melting of calcite is indicated along a zone between calcite and a large pool of basaltic melt. The contacts to calcite grains are sharp, with trails of vesicles and cracks extending from calcite into the optically isotropic melt (Fig. 1a), which shows the same Raman spectrum like the calcite melt from the impact experiments. On average, it is composed of 59.9 ± 7.5 wt.% CaO and 1.23 ± 0.51 wt.% MgO; the non-volatile total is 61.3 ± 7.9 wt.% (Table 1). Mixing with the adjacent basaltic melt was not observed, neither texturally in form of schlieren, nor compositionally in form of incorporation of elements that are absent in the pre-impact calcite (*e.g.*, SiO_2; Fig. 1c). This indicates that the melt contains variable, yet substantial, amounts of CO_2 (30.5–41.9 wt.%; Table 1).

Incipient degassing of calcite and dolomite is indicated by appearance of vesicles. Furthermore, calcite grain margins occasionally show foamy, highly porous zones, which in BSE images are brighter than the interiors of the grains (Fig. 1b), hence reflecting an increase in atomic number (Z) due to release of CO_2. An increase in Z is also observed in dolomite grains affected by degassing. Compositionally, incipient degassing is expressed in increasing CaO and MgO contents, increasing non-volatile element totals, and decreasing CO_2 contents (Table 1). Thus, CaO/CO_2 and MgO/CO_2 of the degassed material increase, whereas CaO/MgO usually reflects the initial ratio. Furthermore, we detected minor amounts of residual CaO close to the basaltic melt (Fig. 1c), indicating that this material must have passed the field CO_2 + CaO (solid) [7].

These observations indicate that pressure has passed a certain threshold in the laser pulses, which were continuously hitting the opening laser melt (and vapor?) zone—otherwise, the existence of calcite melt, which requires $P > 0.1$ GPa [7], is hard to explain. Moreover, the zoning shown in Fig. 1c (calcite–calcite melt– residual CaO–basaltic melt) indicates increasing pressures or decreasing temperatures from the point of laser irradiation, which coincides with the position of the basaltic melt pool.

Conclusions: We have experimentally demonstrated for the first time that both melting *and* decomposition of calcite can occur under *P*–*T* conditions commensurate with impact processes. An interesting step towards bridging the gap between experiment and nature would be to extend experimental investigations to natural carbonate-bearing lithologies, *e.g.*, Kaibab dolomite or mixtures of Kaibab dolomite and Coconino/Moenkopi sandstone from Meteor Crater [4].

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Table 1 Average CaO, MgO, and CO_2 contents of calcite (Cc), dolomite (Dol), and respective residues (melt/deg.).

	CaO	MgO	CO_2^*	Total†	CaO/ MgO	CaO/ CO_2
	wt.%					
Cc	55.3	0.80	43.8	56.2	70.0	1.3
n = 167	*0.04*	*0.17*	*0.4*	*0.4*	*14.4*	*0.1*
Cc melt	59.9	1.23	38.7	61.3	50.2	1.6
n = 24	*7.5*	*0.51*	*7.9*	*7.9*	*14.0*	*0.5*
Dol	30.8	22.5	46.6	53.4	1.4	0.6
n = 34	*0.6*	*0.6*	*0.7*	*0.7*	*0.1*	*0.1*
Dol deg.	34.4	23.4	42.1	57.9	1.5	0.8
n = 6	*5.6*	*3.1*	*4.5*	*4.5*	*0.4*	*0.2*

Avg. of *n* analyses; 2σ in italics. *Calculated by difference to 100. †Volatile-free including FeO, MnO, BaO, and SrO.

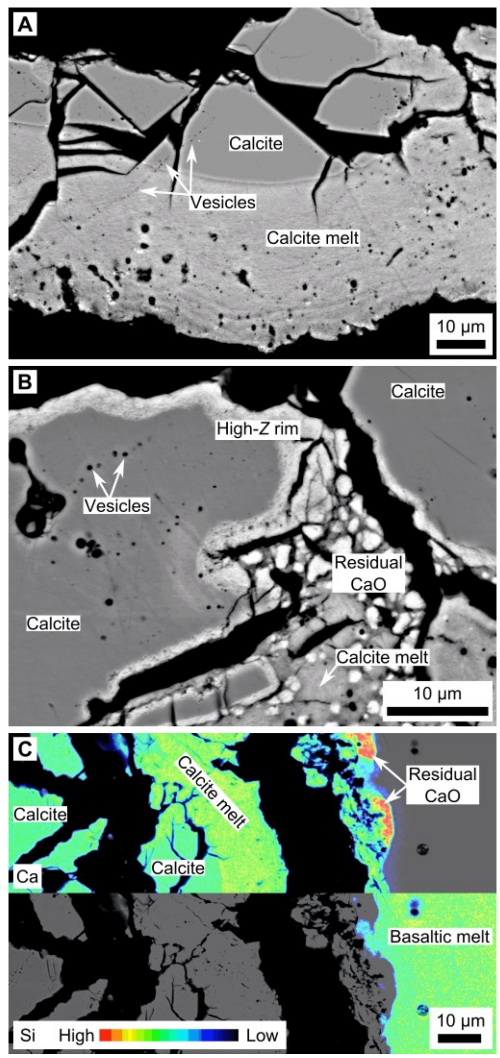

Fig. 1 Melting of calcite (a), degassing of calcite (b), and distribution of Ca and Si among the calcite melt zone (c).