INFRARED AND ELECTRON SPIN RESONANCE SPECTROSCOPIC STUDIES ON EXPERIMENTALLY SHOCKED CALCITE

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Introduction. Carbonates are major constituents of the earth's sedimentary crust. Of the approximately 145 currently known impact structures, some 30 involve carbonate rocks [1]. Although experimental calibration data for a wide pressure range are not available, shock effects in carbonate minerals may be used on an empirical basis for shock classification. These shock effects include: anomalous extinction, microfractures, shock-induced twinning [2,3], shock-induced plastic deformation, as indicated by asterism and line-broadening in X-ray patterns [4], and also, degradation of electron spin resonance (ESR) spectra [5]. In order to calibrate these shock effects, we have started a series of shock recovery experiments on single crystal calcite, sampled from Eskifjord in Iceland.

Experimental methods. Shock recovery experiments were performed at room temperature on 0.5 mm thick disks (Ø 15 mm) with the shock wave travelling parallel to the (0001)-plane of calcite. Peak pressures of 2.8, 6.2, 8.2, 9.8, 15, 30, 45, and 64 GPa were reached by reverberation of the shock wave [6]. A compressed air gun accelerator similar to that described by [7] was used for the pressure range below 10 GPa. An experimental set-up with an high-explosive driven flyer plate as described by [8] was used for the experiments in the 15-64 GPa range. Due to these techniques, the duration of the peak-pressure was short, being 1.8 μs for the 2.8-9.8 GPa range, and 0.63 μs for 15 GPa, 0.5 μs for 30 GPa, 0.3 μs for 45 GPa and 0.45 μs for 64 GPa.

The recovered samples were investigated by microscopic, infrared (IR) and ESR spectroscopic techniques. For the spectroscopic techniques, calcite samples were ground into a coarse powder. Spectra were taken at room temperature. IR transmission spectra (KBr-technique) were obtained with a Bruker IFS 48 FTIR-spectrometer from 4000 to 400 cm^{-1}. ESR spectra were recorded on a Bruker ESP 300 spectrometer operating at X-band frequency (9.78 GHz). The spectrometer was set at a modulation amplitude of 0.1 T and operated in the first derivative mode.

Results. Compared to the unshocked reference calcite, the shocked samples show an increasing fragmentation with increasing shock pressure. Undulatory extinction appears at 6.2 GPa. Planar microfractures and shock induced twinning appear at 8.2 GPa. Decrease of birefingence, beginning of amorphization or formation of high pressure polymorphs, however, could not be substantiated on the microscopic scale. The IR spectrum of the reference calcite shows characteristical absorption bands at 876 cm^{-1} (= υ_2 out-of-plane bend of CO_3^{2-}), 1425 cm^{-1} (= υ_3 antisymmetrical stretch of C-O), 713 cm^{-1} (= υ_4 in-plane bend), 1799 cm^{-1} (= combination of υ_1 and υ_3) and 848 cm^{-1} (= υ_2 lattice mode). The positions and relative intensities of these bands remain unchanged with increasing shock pressure. At a pressure of 9.8 GPa, a band at 1097 cm^{-1} clearly becomes active (Fig. 1), which is due to υ_1 symmetrical stretch of C-O. The Mn^{2+} feature (Mn^{2+} is present as a trace constituent in calcite) occurs from approximately 300 to 400 mT, and is centered near 350 mT. The first derivative spectrum of Mn^{2+} shows six prominent hyperfine split peaks due to the central transitions $M_s=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m_I=0$, and intervening lower intensity absorptions of the forbidden transitions $M_s=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m_I=\pm1$. Hyperfine components, due to non-central transitions, appear at the low and high field ends of the spectrum. With increasing shock pressure, spacings between the hyperfine peaks of the central transition $M_s=+\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m_I=0$ remain unchanged. Spectra of the shocked samples show decreasing peak intensities of the non-central transitions at low and high field (Fig. 2). Peaks of the non-central transitions $M_s=\pm5/2\leftrightarrow\pm3/2$, $m_I=\pm5/2\leftrightarrow\pm3/2$ and $M_s=\pm3/2\leftrightarrow\pm1/2$, $m_I=\pm5/2\leftrightarrow\pm3/2$ are not detectable at pressures ≥ 9.8 GPa and ≥ 30 GPa, respectively.

Discussion. The activation of the IR absorption band υ_1 suggests a deviation of the D_3 site symmetry selection roules of CO_3^{2-} [9]. This could be interpreted as a deformation of the calcite structure by shear-waves at 9.8 GPa. The structure looses its centro-symmetry. Formation of a high-pressure polymorph like aragonite however, could not be detected by IR. In the ESR spectra, the disappearance of non-central transitions $M_s=\pm5/2\leftrightarrow\pm3/2$, $m_I=\pm5/2\leftrightarrow\pm3/2$ at 9.8 GPa and $M_s=\pm3/2\leftrightarrow\pm1/2$, $m_I=\pm5/2\leftrightarrow\pm3/2$ at 30 GPa indicates a decrease of zero field splitting with increasing pressure. The decrease of zero field splitting indicates changes of the Ca^{2+} polyhedra site symmetry with shock loading and corroborates the IR findings. ESR and IR spectroscopy complement one another. The ESR findings confirm and expand the investigation of [10], who compared shock metamorphism of calcite from coralline limestone samples retrieved from the Cactus nuclear explosion crater, and shock experiments up to 10.62 GPa.

A combination of optical, IR and ESR spectroscopic methods may yield a reasonable estimate of the shock metamorphic overprint of calcite from natural impact lithologies. As optical, IR and ESR spectroscopic findings, however, are dependent of the pre-shock stage, such results can not serve as an "absolute" shock barometer.

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In addition, it is inherent in the reverberation method, that the duration of the pressure pulse is short and the post-shock temperature is low in comparison to the natural case.

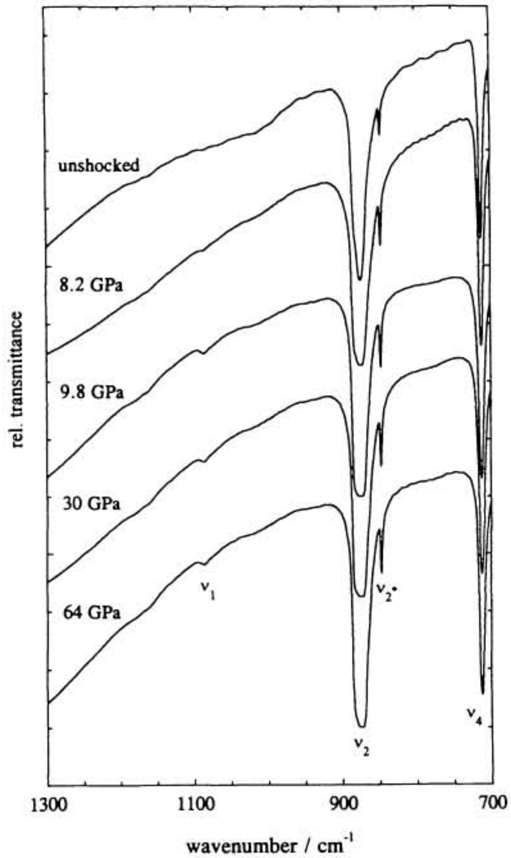

Fig. 1: Comparison of IR absorption bands in a selected wavenumber-range of unshocked calcite (Iceland spar) and samples experimentally shocked parallel (0001). At 9.8 GPa a band at 1097 cm^{-1} becomes active, due to υ_1 symmetrical stretch of C-O (υ_2^* = lattice mode).

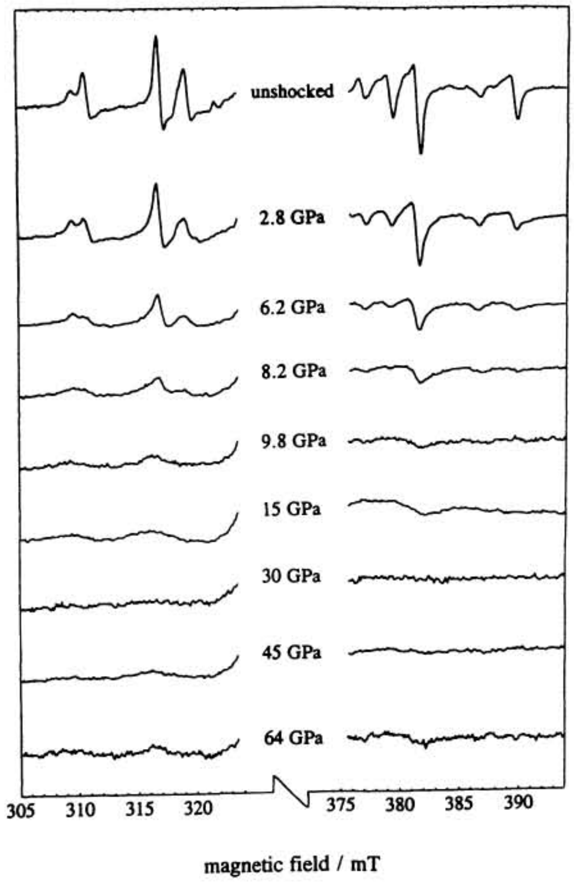

Fig. 2: Comparison of ESR spectra in first derivative mode at low and high field of unshocked calcite and samples shocked parallel (0001). Peaks of the non-central transitions $M_s=\pm^5/_2\leftrightarrow\pm^3/_2$, $m_I=\pm^5/_2\leftrightarrow\pm^3/_2$ and $M_s=\pm^3/_2\leftrightarrow\pm^1/_2$, $m_I=\pm^5/_2\leftrightarrow \pm^3/_2$ are not detectable at pressures ≥ 9.8 GPa and ≥ 30 GPa, respectively.

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References. [1] GRIEVE, R.A.F. (1994) personal communication. [2] RODDY, D.J. (1968) in FRENCH, B.M. & SHORT, N.M. (eds.) *Shock Metamorphism of Natural Materials*, 291-322. [3] SHORT, N.M: & BUNCH, T.E. (1968) in FRENCH, B.M. & SHORT, N.M. (eds.) *Shock Metamorphism of Natural Materials*, 255-266. [4] DACHILLE et al. (1968) in FRENCH, B.M. & SHORT, N.M. (eds.) *Shock Metamorphism of Natural Materials*, 555-569. [5] POLANSKEY, C.A. & AHRENS, T.J. (1994) *J. Geophys. Res.*, **99**, 5621-5638. [6] RICE et al. (1959) in SEITZ, F. & TURNBULL, D. (eds.) *Solid State Physics*, 1-63. [7] REIMOLD, W.U. & STÖFFLER, D. (1978) *Proc. Lunar Planet. Sci. Conf.*, **9th**, 2805-2824. [8] MÜLLER, W.F. & HORNEMANN, U. (1969) *EPSL*, **7**, 251-264. [9] CIFRULAK, S.D. (1970) *The American Mineralogist*, **55**, 815-824. [10] VIZGIRDA, J. & AHRENS T.J. (1980) *Geochim. et Cosmochim. Acta*, **44**, 1059-1069.