

SHOCK BEHAVIOR OF CALCITE, ANHYDRITE, AND GYPSUM D.D.Badjukov¹, Yu. P. Dikov², T.L. Petrova³, and S.V.Pershin⁴; 1 - Vernadsky Institute, Kosygin St., 19, Moscow, 117975, Russia, 2 - IGEM, Moscow, Russia; 3- Institute of Lithosphere, Moscow, Russia; 4 - Insitute of Chemical Physics, Chernogolovka, Russia

Impact-induced outgassing of carbonate or sulfite rich targets of giant impact craters is thought to influence on the evolution of the Earth's atmosphere[1,2]. In particularly, the outgassing of an anhydrite caused by the Chixulub impact can play an important role in the K/T event [3-5]. Estimations of amount of sulfur released to the atmosphere have been based on numerical simulation of formation of the Chixulub crater [6]. Results of this calculations and similar ones depend on a set of parameters including a degree of the outgassing as a function of shock pressures. Previous experiments on carbonate and sulfate have shown in contrast to the calculations that the minerals are rather stable in shock waves [2,7-11]. In order to evaluate the problem of the partial outgassing we have carried out shock recovery experiments on calcite, anhydrite, gypsum and mixtures of quartz with calcite and anhydrite by high parameters in closed containers. A degree of outgassing of the material by various shock pressures have been calculated too.

Experiments. Cylindrical samples located in steel containers were used for the shock recovery experiments. A geometry of the experiments provided a passage of a shock wave configuration along sample axis with the velocity of detonation of explosive charge (ca. 7.9 km/s) [12]. A pressure distribution along a radius of the sample cylinder is not uniform because a diameter of the shock configuration is less than a diameter of the specimens. Shock parameters were estimated using experimental [7,13] or calculated Hugoniot curves. It should be noted that real post-shock temperatures in the specimens can be higher than equilibrium post shock temperatures due to an intensive plastic flow. Only material located near the central axe of the samples and, hence, loaded at a maximum pressure was studied by optical, X-ray, and in some cases microprobe, and X-ray photoelectron spectroscopy (XPS) methods.

Results. Calcite loaded at 61 GPa demonstrates a recrystallization only. No traces of a presence of CaO or Ca(OH)₂ were identified by X-ray diffractometry data. New-formed calcite grains are presented by euhedral crystals with dimensions in the range of 20-40 μm. This calcite contains small areas of very fine-grained carbonate matter. Therefore it can be suggested that initial calcite was melted after the shock loading. It is confirmed also by a presence of steel spherules in the carbonate matrix at a contact with the steel container and, hence, the new-formed calcite grains should be a product of a melt crystallization. On the other hand, the calcite recrystallization may occur in a solid state. The fine-grained carbonate areas can be a result of a back reaction of CO₂ with CaO. An anhydrite sample loaded at 63 GPa shows neither recrystallization nor decomposition. Intensive plastic deformations in anhydrite crystals are observed only. Gypsum loaded at 56 GPa is converted to anhydrite. The XPS spectrum of the sample demonstrates a presence of some amount of H₂SO₄ and SO₂. However, according to X-ray data CaO is not presented. We suggest that the desulfurization of gypsum is a result of its reaction with a minor silicate component to be contained in the sample. Equimolar mixtures of quartz with calcite and anhydrite loaded at GPa and GPa respectively demonstrate a passage of a reaction between the components. Products of the experiments consist of a glass embedded in a calcite or anhydrite matrix. In some cases the glass forms drops and spherules with vesicles filled by anhydrite or calcite. This is an evidence for a molten state of the specimens after their release. The glass from a shot with anhydrite demonstrates a presence of S (3.5 wt %). Contents of CaO in the glass lie in a range of 27 - 32 wt.%. XPS spectra indicate two structural states of [SiO₄] tetrahedra in the glass. Namely there are isolated tetrahedra and polymerized to chain tetrahedra with [SiO₄]⁻⁴/[SiO₄]⁻² ratio of 0.25. Also a presence of SO₂ is established in the anhydrite-quartz target. A calculated mole part of calcite and anhydrite which take place in a reaction with quartz is about 0.5. This estimate can be obtained on the basis of Ca contents in the glasses.

Calculations. Gains of the specific internal energy after decompression (ΔE) in the specimens were calculated using experimental and calculated Hugoniot curves and the Mie-Gruneisen equations of state. If outgassing reactions pass after decompression at a temperature (TR) and an ambient pressure (P), then partial outgassing due to shock heating can be expressed as: $X = (\Delta E - \int_{238}^{TR} C_p dT) / (\Delta H^{TR} + PV)$, where X is a mole part of reaction products, ΔH^{TR} is the enthalpy of the reaction at the temperature of TR, C_p is the specific heat of a sample matter by constant pressure, and V is the molar volume of the gaseous phase at P and TR. Results of the calculations together with experimental pressures are plotted on Fig.1 and 2. There is some discrepancy between our calculations and

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the calculations performed earlier [7,10,11]. The main reason for the discrepancy can be an estimation of ΔE . Using equilibrium release adiabats without taking into account phase transformations in the calculations can lead to lower ΔE and X values when compared to those computed using a direct integration along the Hugoniot curve or experimentally determined release adiabats.

Discussion. The experiments and calculations demonstrate that outgassing of quartz-calcite and quartz-anhydrite mixtures occurs by lower pressures relatively to pure calcite and anhydrite. Hence a more effective impact-induced outgassing of crater targets should be due to reactions between carbonate or/and sulfate and silicate components of crater target rocks. The reactions should lead to formation of Ca-rich impact glasses. Some impact glasses of the Kara crater can be considered as a product of mixing of carbonate and quartz-rich rocks in various proportions [14]. K/T yellow Ca-rich glasses are believed to form also by the impact melting of the carbonate- and evaporite-rich target of the Chixulub crater [15]. Our preliminary rough estimation of the SO_3 mass produced by the Chixulub impact is $8 \cdot 10^{17}$ g. The estimation based on the mass of the yellow glass and contents of S and Ca in this glass [15-17].

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Fig.1. Degree of devolatilization as a function of shock pressure.

Partial pressures of SO_3 and CO_2 are taken to be 1 bar. Arrows represent shock pressures in our experiments on gypsum(1), calcite(2), and anhydrite(3).

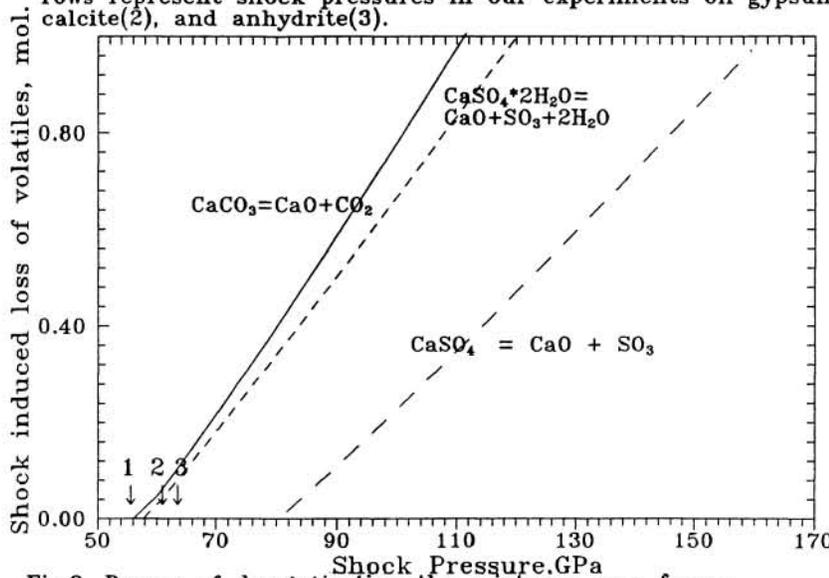
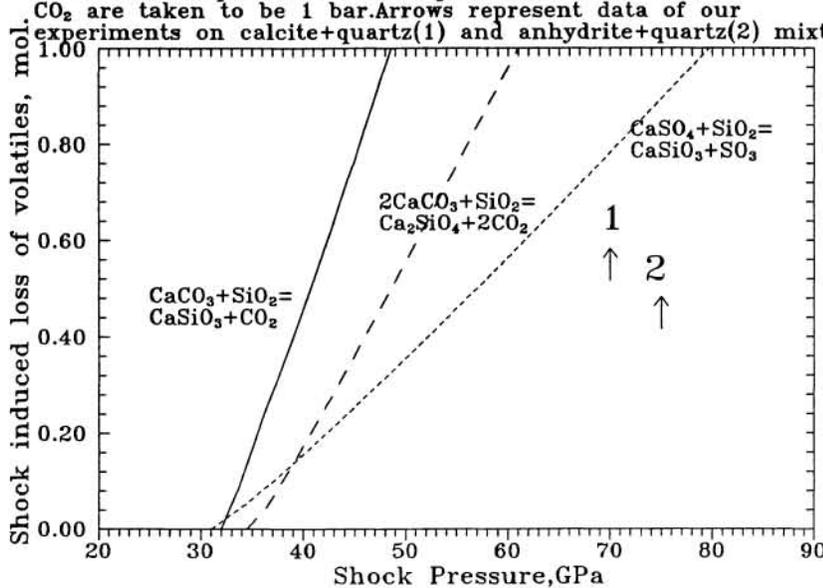


Fig.2. Degree of devolatilization the mixtures as a function of shock pressure. Partial pressures of SO_3 and CO_2 are taken to be 1 bar. Arrows represent data of our experiments on calcite+quartz(1) and anhydrite+quartz(2) mixtures.



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