

## SHOCK TEMPERATURES IN CALCITE ( $\text{CaCO}_3$ ): IMPLICATION FOR SHOCK INDUCED DECOMPOSITION

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**Abstract.** The temperatures induced in crystalline calcite upon planar shock compression (95-160 GPa) are reported from two-stage light gas-gun experiments. The temperatures are obtained fitting 6-channel optical pyrometer radiances in the 450 to 900 nm range, to a Planck radiation law temperature varied from 3300 to 5400 K. Calculations demonstrate that the temperatures are some 400 to 1350 K lower than if either shock-induced melting and/or disproportionation of calcite behind the shock front was not occurring. Here calcite is modeled as disproportionating into a molecular liquid, or a solid CaO plus  $\text{CO}_2$  gas. For temperature calculations, specific heat at constant volume for one mole of  $\text{CO}_2$  is taken to be 6.7R as compared to 9R in the solid state; whereas calcite and CaO have their solid state values (15R and 6R). Calculations also suggest that the onset of decomposition in calcite to CaO and  $\text{CO}_2$  during loading occurs at  $\sim 75 \pm 10$  GPa, along the Hugoniot whereas decomposition begins upon unloading from 18 GPa. The 18 GPa value is based on comparison of VISAR measurements of particle velocity profiles induced upon isentropic expansion with one-dimensional numerical simulation.

### INTRODUCTION

Research on the shock-induced devolatilization behavior of calcite is motivated by a need to understand the role the greenhouse gas  $\text{CO}_2$  played in the formation and evolution of atmosphere of Earth, Mars and Venus. These planets have long thought to contain substantial amount of carbonates in their crusts. In the case of Mars, definition of the shock pressure required to volatilize substantial quantities of  $\text{CO}_2$  from carbonates can be used to define the cratering rate and the period over which Mars operated an efficiently  $\text{CO}_2$  greenhouse, such that a liquid  $\text{H}_2\text{O}$  reservoir became available on the surface which might host early life.

Shock devolatilization is also important to evaluate the mechanisms of impact induced extinction of marine and terrestrial biota for example at the K/T boundary. The discovery of the Chicxulub crater as the impact site and studies that indicated  $\sim 70\%$  of the 3-km-thick section are

carbonates, raised possibility of an extinction mechanism involving a long duration ( $10^0$ - $10^4$  years) global greenhouse event with surface land temperature increasing by  $\sim 10$  degrees at K/T times due to injection of impact-induced  $\text{CO}_2$  into atmosphere [1].

Temperature measurements along the Hugoniot are useful for detecting and characterizing phase transitions including molecular dissociation [2]. In the present work, we measured shock temperatures in single-crystal calcite using optical pyrometry. A two-stage light gas-gun launched impactors shock compressed the samples. Comparison of measurements and calculations demonstrates that temperatures are lower than if either melting and/or devolatilization of calcite are not occurring. Since deficit we have is much more than that expected from melting suggests that shock-induced decomposition of calcite occurs behind the shock front.

## EXPERIMENTS

Experiments were performed on the two-stage light-gas gun at our laboratory. The projectile bearing flyer was accelerated to the velocities 5.0 to 6.9 km/s. The impact of the 0.5-mm-thick flyer plate induces a shock wave in the 0.5-mm-thick driver plate, which then propagates through the 3 mm thick, 12mm diameter sample (Fig. 1). The optical radiation from the shock-heated sample is directed into a six-channel (450 to 900 nm) optical pyrometer [3]. The photodiode (#1801, New Focus, Inc.) has a built in preamplifier with a 125 MHz bandwidth. Digital oscilloscopes recorded each channel on the optical bandwidth of ~5.0nm. Temperature and emissivity are determined by fitting the radiance at six wavelengths to the gray-body Planck spectrum. The results of the six experiments in the 95 to 160 GPa pressure range are shown in Fig. 2. Shock pressures were determined by performing impedance-match calculations employing measured flyer plate velocity and known equation of state of tantalum and calcite.

### MODEL TEMPERATURE CALCULATIONS

Calculations are presented below for two cases: one in which calcite does not decompose in the shocked state up to the highest shock pressure of the experiment, and other in which calcite decomposes according to the chemical reaction  $\text{CaCO}_3 \rightarrow \text{CaO}(s) + \text{CO}_2(g)$ .

#### No Decomposition of Calcite (Model -1)

Temperature increase upon shock compression in a material is calculated using the relation,

$$\int_{T_s}^{T_H} C_v dT = E_H - E_s - \Delta E_{tr} \quad (1)$$

where  $T_H$  and  $T_s$  are temperatures along Hugoniot and isentrope at the same compression and  $E_{tr}$  is phase transition energy. Temperature  $T_s$ , Hugoniot energy,  $E_H$ , and isentropic energy,  $E_s$ , are given by the following relations:

$$T_s = T_0 \exp[\Gamma(1 - V/V_0)]$$

$$E_H = \frac{1}{2} P_H (V_0 - V_H)$$

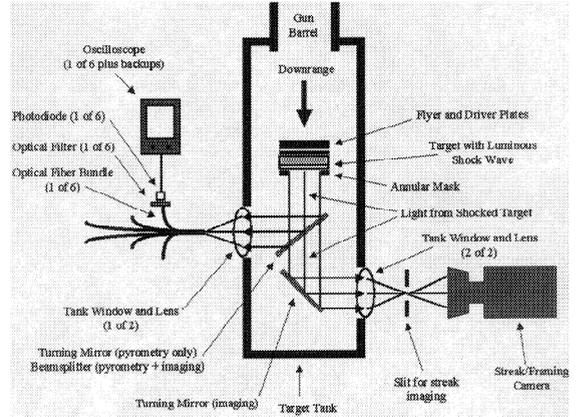


Figure 1. Schematic diagram of experimental setup for shock-temperature measurements.

$$E_s = -\int_{V_0}^{V_H} P_s dV$$

$$P_s = \frac{3K_0}{2} \left[ \left( \frac{V_r}{V} \right)^{7/3} - \left( \frac{V_r}{V} \right)^{5/3} \right] \left[ 1 + 3 \left( \frac{K'_0}{4} - 1 \right) \left\{ \left( \frac{V_r}{V} \right)^{2/3} - 1 \right\} \right]$$

where  $P_H$  and  $P_s$  are pressures along Hugoniot and isentrope at the same specific volume  $V_H$ ; the specific volumes  $V_0$  and  $V_r$  correspond to low pressure phase and high-pressure phase (on release) at ambient pressure;  $K_0$  and  $K'_0$  are the bulk modulus and its derivative. The analytic form assumed for the isentrope is the Birch-Murnaghan equation. The entropy increase along the Hugoniot has been determined using the relation,

$$\Delta S_H = \Delta S_{tr} + \int_{T_s}^{T_H} \frac{C_v}{T} dT \quad (2)$$

where  $\Delta S_{tr}$  is the entropy change of phase transition.

#### With Chemical Decomposition of Calcite

For chemical decomposition of calcite, the entropy criterion is employed. The decomposition begins at pressure for which shock-entropy equals  $S_I$ , entropy of incipient decomposition at normal pressure. The decomposition gets completed at pressure for which shock-entropy equals  $S_V$ , the entropy of complete decomposition at normal pressure. We have estimated the values of  $S_I$  and  $S_V$  for calcite to be  $1.47 \text{ kJ}(\text{kg.K})^{-1}$  and  $2.91 \text{ kJ}(\text{kg.K})^{-1}$  respectively, from the available thermodynamical data at normal pressure (Robie et al. [4]).

The shock-induced chemical decomposition of calcite is modeled in two ways. In Model-2, it is modeled to occur at constant shock temperature, and in Model-3, it is treated to occur over a range of temperatures.

*Decomposition Occurring at Constant Temperature (Model-2)*

Upon shock compressions down to specific volume  $V_0$ , for which  $\Delta S_H \leq S_I$  the material does not decompose. Temperature and entropy along the Hugoniot are calculated using equations 1 and 2, as in Model-1. At higher compressions, the decomposition of calcite is modeled to occur at constant temperature  $T_{H0}$ . The entropy in the compressed state is calculated using relation,

$$\Delta S_H = S_I + \frac{(E_H - E_S) - (E_{H0} - E_{S0})}{T_{H0}}$$

where  $E_{H0}$  and  $E_{S0}$  are Hugoniot energy and energy along isentrope at same specific volume  $V_0$ . At successively higher shock pressures, temperature remains constant but entropy increases, resulting in decomposition of additional material until compression to specific volume  $V_1$ , entropy value reaches  $S_V$ , and calcite is completely decomposed. At still higher shock pressures, the additional Hugoniot energy is used up in compressing and increasing temperature of the mixture of reaction products. Hugoniot temperature is given by

$$T_H = T_{H0} + T_S - T_{S1} + \frac{(E_H - E_S) - (E_{H1} - E_{S1})}{C_{V2}}$$

where  $T_{S1}$  is the isentropic temperature,  $E_{H1}$  is Hugoniot energy and  $E_{S1}$  is isentropic energy at specific volume  $V_1$ . The heat capacity,  $C_{V2}$ , of the mixture of the reaction products is assumed to be constant.

*Decomposition Over Range of Temperature (Model-3)*

Once decomposition of calcite sets in at shock-entropy  $S_I$ , upon higher compression, the fraction  $\alpha$  of decomposed calcite is determined from the entropy of shocked solid calcite using relation,

$$\alpha = (\Delta S_H - S_I) / (S_V - S_I).$$

In the shocked state, material consists of  $\alpha$  moles of each CaO and  $CO_2$  and  $(1 - \alpha)$  moles of calcite. The temperature for this mixture is given by

$$T_H = T_S + \frac{E_{H0} - E_{S0} - E_{tr}}{C_{V1}} + \frac{E_H - E_S - E_{H0} + E_{S0} - \alpha E_{sub}}{C_{V\alpha}}$$

where  $E_{sub}$  is the energy required for decomposing one mole of calcite.  $C_{V\alpha}$  is the mass weighted heat capacity of the mixture of calcite and reaction products, and it is given by,

$$C_{V\alpha} = (1 - \alpha)C_{V1} + \alpha C_{V2}.$$

These equations are applicable even when calcite is completely transformed to CaO and  $CaCO_2$ .

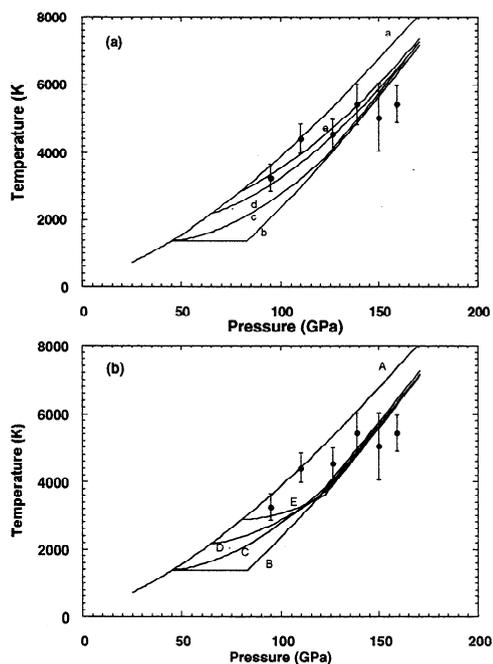
Material parameters assumed for calcite are taken from Tyburczy and Ahrens [5]. Since no specific heat  $C_V$  data is available on  $CaCO_3$  and CaO, the Dulong Petit values of 15R and 6R per mole of molecules have been used. For gaseous  $CO_2$  we have estimated it from the data of specific heat at constant pressure. The estimated value of 6.7R is smaller than solid state value of 9R.

**RESULTS AND DISCUSSIONS**

Experimental results and model calculations are plotted in Fig. 2. Comparison of measurements with calculations using Model-1 (curve a in Fig. 2a) indicates that the measured temperatures are some 400 to 1350 K lower than if shock-induced melting and/or decomposition is not occurring.

Melting of calcite has been observed in high pressure experiments [6]. We have assessed the influence of melting on shock temperatures. We estimated the entropy of fusion and assumed it is approximately equal to R per mole of atoms, the same as those of simple elements [7]. The value  $0.41 \text{ kJ}(\text{kg.K})^{-1}$  for calcite is about 28% of the value of entropy of vaporization. Temperature deficit estimated for calcite is ~450 K. This is too small to account for the observed temperature deficit.

In figure 2a, the curve b shows the calculations using Model-2 in which calcite decomposition begins at shock entropy  $S_I$  ( $1.47 \text{ kJ}(\text{kg.K})^{-1}$ ) and further decomposition at higher pressures occurs at constant temperature. The curve c displays calculation using Model-3 in which decomposition begins at shock entropy  $S_I$  but it occurs over a range of temperatures on further compression. The



**Figure 2.** Experimental and calculated shock-temperatures in calcite. Solid circles with error bars are measurements. Solid lines are calculations with different models: a- no decomposition; b-decomposition at constant temperature; c- decomposition over range of temperatures; d-with  $S_I=1.97$  and  $S_V=3.41$ ; e-with  $S_I=2.27$  and  $S_V=3.91$ ; A, B, C are same as a, b and c; D- with  $S_I=1.97$  and  $S_V=2.91$ , E- with  $S_I=2.27$  and  $S_V=2.91$ . All entropies are in units of  $\text{kJ}(\text{kg.K})^{-1}$

fact that these curves lie below the experimental data suggests that the decomposition does not begin when shock entropy equals the theoretical estimates of  $S_I$  but sets in when system is overdriven. Thus, the decomposition process shows hysteresis. Curves d and e indicate calculations done with Model-3 in which the values of  $S_I$  and  $S_V$  are increased by same amount keeping  $(S_V-S_I)$  constant. For calculation d,  $S_I$  is  $1.97 \text{ kJ}(\text{kg.K})^{-1}$  and  $S_V$  is  $3.41 \text{ kJ}(\text{kg.K})^{-1}$ , whereas for calculation e,  $S_I$  is  $2.27 \text{ kJ}(\text{kg.K})^{-1}$  and  $S_V$  is  $3.41 \text{ kJ}(\text{kg.K})^{-1}$ . The curves D and E of figure 2b show calculations using Model-3 where the value of  $S_I$  is increased but the value of  $S_V$  is kept constant. These curves correspond to  $S_I$  values of  $1.97 \text{ kJ}(\text{kg.K})^{-1}$  and  $2.27 \text{ kJ}(\text{kg.K})^{-1}$  respectively.

Considering the uncertainty in the experimental data, the comparison through visual inspection of all the calculations with these show that the

calculation d and e are much closer to the measurements. This suggests that the chemical decomposition of calcite behind the shock front begins around  $75 \pm 10$  GPa. This is higher than 18 GPa pressure at which calcite begins to decompose on unloading. The 18 GPa value is based on the comparison of VISAR measurements of particle velocity profile induced upon isentropic expansion with numerical simulation [8]. The higher pressure for the onset of chemical decomposition at the shock front could be due to kinetic effects, as the time available for the reaction to occur at shock front is much smaller than in experiments involving isentropic release subsequent to loading.

## CONCLUSIONS

Shock temperatures in single crystal calcite have been measured at 95 to 160 GPa in two-stage light-gas gun using optical pyrometry. Model calculations have been performed for shock temperatures in this material. Comparison of the measured and calculated temperatures suggests that the onset of decomposition in calcite to solid CaO and gaseous  $\text{CO}_2$  occurs at the shock front around  $75 \pm 10$  GPa. This decomposition pressure is higher than 18GPa from which pressure calcite begins decomposing upon unloading.

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