Introduction: New shock wave recovery experiments carried out on single crystal calcite (CaCO₃) demonstrate that the onset of decarbonation occurs at dynamic pressures of <100 GPa (100 kbar) and complete loss of CO₂ requires shock pressures in excess of 50 and possibly as high as 70 GPa (700 kbar).

Calcite and other carbonate minerals are ubiquitous in all terrestrial shallow-marine, sedimentary basins. Carbonates store a substantial, if not most of the earth's CO₂ inventory. Shock loading results from meteorite impact upon carbonate bearing rocks. Because of shock heating, liberation of CO₂ occurs (1). Kieffer and Simonds (2) proposed that the absence, or near absence, of impact melt deposits around terrestrial impact structures in carbonate terranes can be explained by the action of liberated CO₂ gas which highly vesiculates and disperses the silicate melt produced. This widely distributed layer is then easily lost to erosion.

Although carbonate minerals are the major reservoir of CO₂ in carbonaceous meteorites (3), because carbonates are always a minor phase in meteorites, decarbonation upon impact of the planetesimals which formed the terrestrial planets did not give rise to the CO₂ in their proto-atmospheres. In previous papers we have developed models for a primary, impact-generated atmosphere/hydrosphere on the early Earth (4, 5, 6). These models are based on the premise that the volatiles contained in the planetesimals from which the planets are formed are released when the planetesimal impacts the surface and is accreted. Arrhenius et al. (8) qualitatively suggested this model and assume a proto-atmosphere/ocean would result from having the impact of planetesimals with compositions similar to various classes of meteorites. Carbonates are expected to form on an accreting planetary surface being bombarded by planetesimals via the following chain of reactions:

\[
\begin{align*}
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_2(X) + 2\text{H}_2\text{O} + \text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 & \quad \text{(1)} \\
2\text{H}_2 + \text{O}_2 & \quad \text{(2)} \\
\text{OH}_4(X) + 2\text{O}_2 + \text{CO}_2 + 2\text{H}_2\text{O} & \quad \text{(3)} \\
\text{Mg}_2\text{SiO}_4 + \text{CO}_2 + \text{CaCO}_3 + \text{SiO}_2 & \quad \text{(4)}
\end{align*}
\]

where \(X\) indicates the phase brought to the planet by the infalling planetesimals. The planetesimals would contain both phyllosilicates, as assumed in Eq(1), as well as, hydrocarbons represented by \(X\). In Eq(3) and under appropriate temperature conditions, the Urey-type reaction Eq(4), will produce carbonate reactions such as Eq(3) and impact upon carbonates formed on planetary crusts would then give rise to CO₂ atmospheres on Mars and Venus and probably produced a CO₂-rich primordial atmosphere on the earth (6). It is thus appropriate to examine models for the generation of a primary CO₂ atmosphere. This would occur via similar processes as those associated with the formation of an impact-generated terrestrial hydrosphere.

A parameter essential for all these problems is the threshold pressures which lead to incipient to complete CO₂ loss from carbonate. We determined the shock-induced CO₂-loss in calcite as a function of shock pressure. We also investigated structural and textural changes in the shock loaded samples by means of X-ray diffraction, infrared spectroscopy (not to be reported here) and SEM analysis.

Experimental details: Sample discs (diameter, 4 mm; thickness, 0.5 mm) were ground flat, polished and inserted into stainless steel target assemblies, similar to those described in (7). The targets were shock loaded by impact of disc-shaped metal flyer plates, accelerated by a 20 mm powder gun. Larger pieces of the recovered samples were examined in this section. Smaller fragments were analyzed by X-ray diffraction and infrared spectroscopy. The amount of post-shock CO₂ (i.e., CO₂ not released during shock loading) was quantitatively determined by thermogravimetry. Comparing the post-shock CO₂ with the initially present CO₂ yields the amount of shock-induced CO₂ loss for each sample as a function of shock pressure.

Results: The shock-induced loss of CO₂ as a function of shock pressure is given in Figure 1. Both the initial shock pressure reached upon entry of the first shock wave into the sample as well as the peak pressure obtained as a result of multiple reverberations of the shock wave between the walls of the target container are shown. Thus, our results for shock-induced CO₂ loss, versus, peak shock pressure represent minimum values for the liberation of CO₂ in shock loaded calcite when applied to a natural event.

Our data can be fit by a single line allowing specification of CO₂ loss as a function of shock pressure. Although the scatter in the data points is larger than that found for similar investigations in antigorite serpentine (7), the data are sufficiently consistent to allow prediction of a pressure range from ~10 to ~70 GPa for incipient to complete CO₂ loss in shock-loaded calcite. Based on the weight loss curves for each sample, obtained in the thermogravimetric analysis, we determined the temperature interval, AT, over which CO₂-loss took place (c.f., 7). Figure 2 gives AT as a function of shock pressure for our samples. The activation energy for CO₂ loss in the thermogravimetric analysis is directly proportional to AT and is given in...
Lange, M.A. and Ahrens, T.J.

Figure 3. The decrease in activation energy with increasing shock pressure indicates that the bond strength between CO₂ and CaO in the calcite lattice has been weakened as a result of the shock loading. Thus, shock loading of calcite not only leads to direct loss of CO₂ but also reduces the amount of energy which is required to remove the remaining CO₂. This result parallels findings in our investigation of shock-induced H₂O loss in antigorite-serpentine (7).

Optical microscopy and SEM analysis reveal textural changes in the shock-loaded calcite. The most remarkable features observed with the optical microscope are dark, vein-like structures which are randomly and nearly homogeneously distributed within the samples. Under the SEM these dark areas appear vesicular with the larger vesicles in part containing small, angular fragments. This is comparable to our findings in shocked antigorite-serpentine (8). We interpret these textures as regions of localized melting into which a gas phase has been injected. Even though we cannot at present prove the identity of the gas, we believe that most of it is liberated CO₂ which did not leave the sample (c.f., (9)).

Conclusions: Based on the present experiments we conclude that calcite loses its structural CO₂ when subjected to shock pressures from ~10 (incipient) to ~70 GPa (complete). Using equation of state data for calcite (10) shock pressures and impact velocities are easily related. If we assume that impact velocities of infalling planetesimals equal the escape velocities of the growing terrestrial planets, we can specify stages in the accretional sequences which correspond to a certain degree of CO₂ production from impact upon surface material. Figure 4 shows the shock-induced CO₂-generating function of the relative radius r/R (R = final planetary radius) and relative mass M/M (M = final mass of planet) for Earth, Venus and Mars. As can be seen, complete loss of CO₂ from calcite and thus the potential growth of a CO₂-rich atmosphere, occurs on Earth and Venus after both have grown to about 60% of their final size. Mars, because of its smaller size and lower mean density, never reaches this stage during its accretion.