PARTIAL PRESSURE OF CO_2 AND IMPACT-INDUCED DEVOLATILIZATION OF CARBONATES: IMPLICATIONS FOR PLANETARY ACCRETION; J. A. Tyburczy and T. J. Ahrens, Seismological Laboratory 252-21, California Institute of Technology, Pasadena, CA 91125.

Introduction. Impact-induced devolatilization of hydrous and carbonate minerals plays a role in the evolution of terrestrial planetary atmospheres (1,2). Discrepancies exist among the several different types of experiments used to study the amount of CO_2 released from calcite as a function of impact velocity (2,3,4). Furthermore, the experimental determinations are not in agreement with predictions based on shock energy or shock entropy calculations (5,6,7,8). By considering the effect of the ambient partial pressure of CO_2 P_{CO_2} on the devolatilization process we can qualitatively account for the different experimental results and bring calculated devolatilization fractions into better agreement with the experiments. The improved calculations suggest that up to 20-25% of the carbon accreted onto the Earth by planetesimals may have initially been buried within the solid Earth with the remainder released to the atmosphere.

Discussion. Previous experimental results on calcite devolatilization were obtained by Lange and Ahrens (2), Boslough *et al.* (3), and Kotra *et al.* (4) (Figure 1). Lange and Ahrens (2) found significant decarbonation; as much as 30 per cent at pressures as low as 10-15 GPa, whereas the other two studies suggest very little decarbonation at pressures as high as 60 GPa. A major difference between the three studies is in the control of the ambient atmospheric conditions during the impact event. Lange and Ahrens employed chambers that were vented to the air (9); thus the ambient P_{CO_2} was 3.4×10^{-4} bar. Boslough *et al.* (3) captured the evolved CO_2 in an initially evacuated, confined chamber. Therefore P_{CO_2} changed during the course of the experiment and had a final value of between about 3×10^{-3} and 7×10^{-3} bars when the system had cooled to room temperature. In the experiments of Kotra *et al.* (4) the sample was exposed to the CO_2-rich muzzle gases from the gun barrel, thus creating a relatively high CO_2 pressure in the neighborhood of the sample. Thus, in experiments in which the ambient P_{CO_2} was low the devolatilization was much greater than in experiments in which P_{CO_2} was relatively high.

Post-shock energy and entropy calculations can be used to estimate the shock pressure required for incipient devolatilization and the fraction of material devolatilized for a given shock pressure (5,6). The post-shock entropy method is more widely used because information on the release path is not required, *i.e.* the release is assumed to be isentropic (10,11). The entropy increase in the shocked state, ΔS_H, is calculated using standard continuum relations and a knowledge of the adiabatic compression curve, the Gruneisen parameter γ, the heat capacity at constant volume C_v, and any phase transformations which may occur. ΔS_H is then compared to the entropy increase required for incipient devolatilization S_{IV} based on consideration of the equilibrium decomposition of calcite, $CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(gas)}$. This equilibrium is, of course, strongly dependent on P_{CO_2}. The hatched regions in Figure 1 show the shock-induced devolatilization calculated assuming that P_{CO_2} is equal to that of dry air at STP, the condition of the experiments of Lange and Ahrens (2), and assuming that $P_{CO_2} = 1$ bar, as has been assumed in previous applications of this method. The agreement with the experimental results is not perfect, but is significantly improved. Furthermore, the shape of the calculated curve is similar to that of the experimental curve, suggesting that this approach is valid. The remaining discrepancies between theory and experiment are probably caused by nonhydrodynamic effects such as localization of thermal energy (12,13,14).

Figure 2 shows the effect of ambient P_{CO_2} on the shock-induced CO_2 loss from calcite as a function of planetary mass for an accreting Earth. In constructing this figure, the incoming planetesimals were assumed to have density ρ_o, bulk modulus K and pressure derivative of the bulk modulus K′ equal to average Earth values, 5.5. g/cm^3, 100 GPa, and 5, respectively. The impact velocity is equal to the escape velocity. The target (growing planet) consists of .01 per cent calcite ($\rho_o = 2.7$ g/cm^3, K = 43 GPa, K′ = 4.28), a quantity sufficient to yield the total amount of CO_2 in the Earth's atmosphere and crust today (13). No direct heat effects or recondensation of atmospheric CO_2 are included in this calculation. The figure shows that the effect of mass balance on the devolatilization postpones the point at which complete devolatilization occurs until approximately 50% of the mass of the planet has been accreted. The evolution of atmospheric P_{CO_2} is shown in Figure 3. For the case of pressure sensitive devolatilization, the final atmospheric P_{CO_2} is about 15% lower than if impact induced volatile loss is independent of P_{CO_2}. It is significant that 20-25% of the incident CO_2 remains buried in the solid body in the case of P_{CO_2}-dependent volatile loss, whereas only about 10% of the incident CO_2 is buried in the case of P_{CO_2}-independent devolatilization.

Conclusions. Impact-induced devolatilization of carbonates is inhibited by an ambient CO_2 atmosphere, in accord with the law of mass action. Allowing for this effect brings several recent experimental and computational efforts into qualitative agreement. In an accreting Earth-like body, approximately 75%-80% of the CO_2 will be released to the atmosphere during impacts, with the remaining 20-25% remaining buried in the solid body.

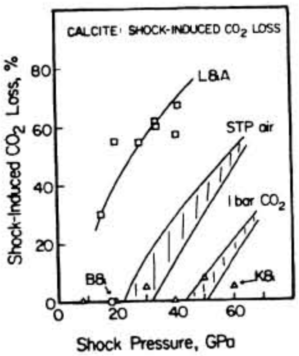

Fig. 1
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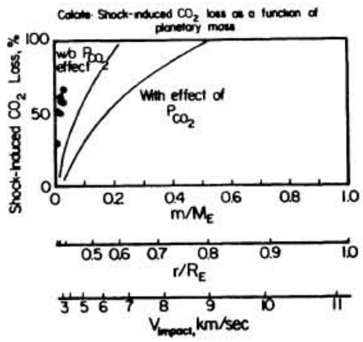

Fig. 2
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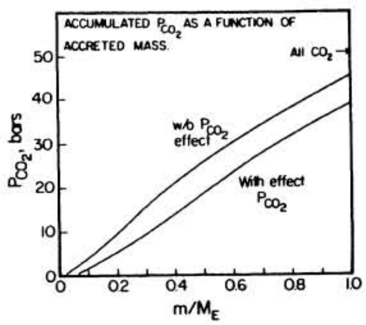

Fig. 3
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Figure 1. Impact-induced CO_2 loss from calcite versus peak (reverberated) shock pressure. Squares (2); hexagon (3); triangles (4). Hatched areas represent CO_2 loss under conditions of 1 bar CO_2 pressure and standard temperature and pressure (STP) air ($P_{CO_2} = 3.4\text{x}10^{-4}$ bars), respectively.

Figure 2. Impact-induced CO_2 loss in calcite as a function of planetary mass, calculated with and without effect of ambient P_{CO_2}. Projectile is assumed to be average Earth material, $\rho_o = 5.5 \text{g/cm}^3$, $K = 100$ GPa, $K' = 5$. The calcite portion of the target has the properties $\rho_o=2.7$ g/cm^3, $K = 43$ GPa, $K' = 4.28$. Impact velocity is equal to the escape velocity. Total CO_2 content in the system is equal to the total atmospheric and crustal CO_2 present in the Earth today.

Figure 3. Evolution of P_{CO_2} as a function of planetary mass for the system described in Figure 2. Arrow gives the value of P_{CO_2} if all the CO_2 present were released to the atmosphere. The difference between this point and each of the two curves represents the amount of CO_2 buried within the Earth during accretion according to the two models.

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