

FIG. 8. Unequal depth of reaction envelope of $\text{Ca}(\text{OH})_2$ developed on cleavage rhombohedron of optical calcite. Experimental conditions: 665°C ; 10,000 psi (H_2); 4 hours. The unreacted calcite core was cleanly plucked from the $\text{Ca}(\text{OH})_2$ rim during grinding and for illustrative purposes the calcite void was filled with plastic.

were immediately imbedded in quick-setting plastic, and flats were carefully ground normal to the side cleavage surfaces. If the samples were not potted, spontaneous spalling of the reaction film and shattering of the core generally occurred on standing. In addition to normal cleavage, conchoidal fracture was sometimes observed on the shattered calcite. The depth of alteration was measured optically and found to be very anisotropic and crystallographically similar for all crystals. The average ratio of maximum to minimum depth of the anisotropic reaction rim (for 29 samples) is 2.1.

The crystallographic orientation of several specimens was determined by using thin sections, a petrographic microscope, and a universal stage. The reaction rims and crystallographic orientation are shown in Figure 5. In a sense, the reaction rims may be compared to etch figures. Under normal conditions, the calcite I crystal system and class are given as: trigonal, $\bar{3}2/m$. Honess and Jones (1937) in their investigation of etch figures in carbonate minerals by optically active solvents, noted

that the six sides of a cleavage rhombohedron of calcite always showed the same figures and solubility rates, whereas dolomite showed unlike solubility of the rhombohedral cleavage faces. The crystallographic orientation of the unequal reaction rims, as determined optically on the remaining calcite core of our specimens, shows that the *c* axis does not pass through the intersection of the three similarly reacted faces. The crystallographic anisotropy of the reaction implies more than a loss of the symmetry center.

DOLOMITE AND HYDROGEN

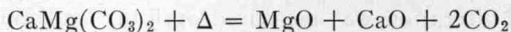
Dolomite and hydrogen were reacted under the following conditions: (1) fragment size 40–60 mesh; (2) 520°C to 835°C; (3) 2000 to 5000 psi initial hydrogen pressure; and (4) experiments lasting between 2 and 12 hours. Solid reactants observed include: CaCO₃(calcite); Ca(OH)₂; CaO; non-crystalline Mg(OH)₂; elemental carbon or graphite, and "soot". Gas analyses show: CH₄; C₂H₆; CO; and CO₂. Water is the oxygenated product from all of the experiments.

The experimental results are summarized in Table 4 and plotted in Figures 9 and 10. The weight percent CO₂ remaining in the solid and the mole percent CH₄ formed are again plotted against time at 5000 psi for 620°C, and against temperature at 5000 psi for 4-hour runs.

In the thermal dissociation of dolomite under the vapor pressure of the system, the reaction occurs in two stages. The first dissociation, stoichiometrically simplified, is given as follows:



With increasing temperature, the remaining calcite decomposes to lime and carbon dioxide with the exact dissociation temperature determined by the carbon dioxide pressure. If the P_{CO_2} never exceeds 100 mm, dolomite decomposes in a single stage dissociation as follows:



In the dolomite-hydrogen reaction CO₂ is not a reaction product under most of the experimental conditions and appears only as a minor component of the reaction gases at lower hydrogen pressures (Table 4). It likely is incidental to the main reaction of direct methanation. The basis for this statement is found in the dolomite-hydrogen gas analyses and the reasoning previously used in discussing the calcite-hydrogen system.

The dolomite-hydrogen reaction occurs in two steps. The first stage is represented by the following equation: