Synthesis of Graphite and Hydrocarbons by Reaction between Calcite and Hydrogen

Abstract. *The reaction of calcite with hydrogen was investigated over a range of pressure, temperature, and time. The reaction initiates at about 500°C. Its primarily temperature-dependent rate proceeds in a crystallographically anisotropic manner, and reaction products are CaO, $Ca(OH)_2$, H_2O, CO, CH_4, C_2H_6, and C (graphite), plus a black solid residue that may be hydrocarbon.*

Equilibrium calculations, based on standard thermodynamic data, indicate that hydrogen can be an important species in a gas phase in equilibrium with rock material at elevated temperatures. If carbon is available at low pressures of oxygen, methane is thermodynamically stable.

Studies of meteoritic minerals show that, if gases existed within disrupted parent bodies, they must have been highly reducing in character. Hydrogen and hydrogen compounds are assumed to be dominant species. Similar gases probably exist within Earth and have been observed in surface and near-surface exposures of intrusive rocks (*1*).

We now report the following observations concerning the hydrogen-calcite reaction: (i) the reaction initiates at about 500°C; (ii) the reaction rate is strongly temperature-dependent and, within the range investigated, secondarily pressure- and time-dependent; (iii) methane and water are ubiquitous reaction products; ethane and carbon monoxide appear under certain conditions; carbon dioxide was not observed; (iv) carbon as graphite, and possibly solid hydrocarbons, formed in some reactions; (v) the reaction rate is crystallographically anisotropic.

Freshly cleaved rhombohedrons of optical-grade calcite were reacted with electrolytic-grade hydrogen in a 25-cm^3 "cold seal"–type pressure vessel (*2*). Specimens loosely housed in platinum foil were placed in the externally heated lower end of the vessel and were kept under helium until experimental temperatures were reached. Reaction-gas samples were extracted from the cool upper end of the vessel and were vented after each experiment; the system was then flushed and charged with helium, and the vessel was removed from the furnace and allowed to cool. Most samples were opened in air and placed in argon-filled containers, but some were opened in a dry glove box filled with argon, and samples were sealed in glass capillaries for x-ray analysis. The depths of the reaction surfaces on the calcite rhombs were measured by optical microscopy.

The temperature range investigated was 420° ± 5° to 970° ± 10°C, and the pressure (initially entirely hydrogen) ranged from 100 to 11,700 psi (lb/in.^{2}; 1 psi, 0.068 atm); durations were from a few minutes to 64 hours.

Experimental data on the temperature-, pressure-, and time-dependent nature of the reaction appear in Fig. 1, a, b, and c, respectively. Results of five mass-spectrographic analyses of the reaction gases are given in Table 1. Water is not included in the analyses, but it was present.

As a guide to interpretation of these preliminary results it is helpful to consider the free-energy change for the principal calcite-hydrogen reactions (Fig. 2); these equilibrium values (*3*) do not rigorously apply to our experiments but they provide useful approximations. The mass-spectrographic analyses have been used for estimation of the free-energy change for reaction-A, with the pressure of H_2O assumed to be the same as that of methane. The calculated values are shown in Fig. 2 by numbers corresponding to the experiments of Table 1. These results indicate that the observed initiation of the calcite-hydrogen reaction at about 500°C occurs not because the free-energy change becomes negative with increasing temperature, but rather because the temperature must reach at least 500°C for the reaction to proceed at a measurable rate. It appears that experiments 37 and 44 approached equilibrium.

Eck *et al.* (*4*) have calculated the limited equilibrium distribution of gaseous organic compounds for various mixtures of carbon, hydrogen, and oxygen. The very low free energy of formation of the CaO results in its effective removal from our system, and the reaction should and does follow the predictions for the C–H–O system.

Graphite and a dispersed dark solid, possibly hydrocarbon, also formed during certain of our experiments; graphite was confirmed by strong x-ray diffraction patterns. Other dark material was sometimes present on the reaction surface as minute lustrous black particles similar in size to the graphite particles; it did not yield an x-ray diffraction pattern.

Our experimental conditions for formation of graphite are in agreement with the graphite phase boundary predicted by Eck *et al.* (*4*), who consid-

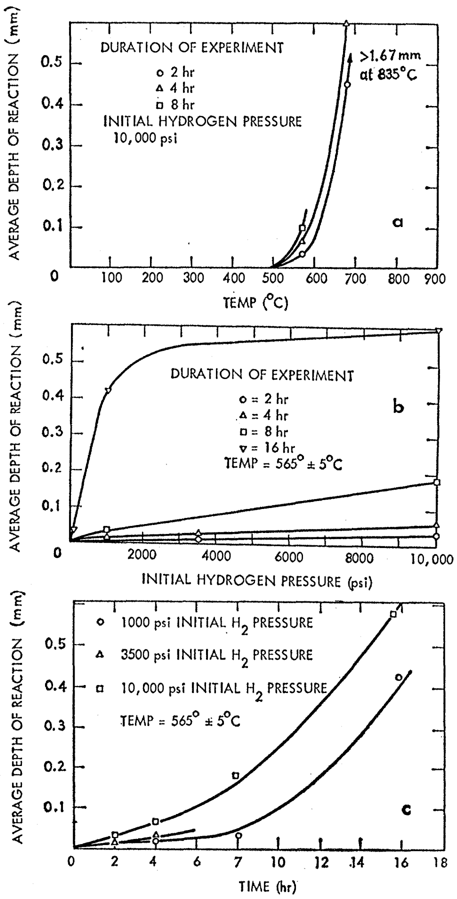

Fig. 1. (a) Average depth of reaction versus temperature for 2, 4, and 8 hours at constant pressure. (b) Average depth of reaction versus initial hydrogen pressure at constant temperature. (c) Average depth of reaction versus time for three initial hydrogen pressures at constant temperature.

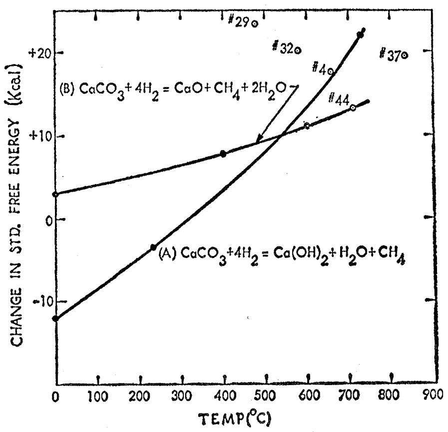

Fig. 2. Free energy versus temperature for the calcium carbonate plus hydrogen reaction.

Table 1. Mass-spectrographic analyses of reaction gases calculated on a water-free basis. The detection limit was 0.01 mole percent. The starting hydrogen contained < 5 parts per million (ppm) N_2, < 0.5 ppm CO_2, and < 0.5 ppm CO. Residual He (< 0.05 percent) was common to most experiments, and 0.11 percent N_2 and 0.02 percent O_2 were found in experiment 32; H_2 values include HD and D_2.

Exp. (No.)	Pressure, total (psi)	Temp. (°C)	Time (hr)	Percentage			
				H_2	CH_4	C_2H_6	CO
29	9800	480	18	99.88	0.04		
32	9900	580	20	99.56	.26		
4	11,700	660	4.5	99.01	.88	0.08	0.03
44	8900	715	15	96.75	3.20		
37	9800	835	3	98.90	1.10		

ered that the absence of graphite from their experimental system reflected the high activation energy necessary for its direct formation from methane and other simple organic compounds. Urey and Lewis (*5*) objected to an equilibrium origin for the hydrocarbons in carbonaceous chondrites in the absence of graphite, as was proposed by Studier *et al.* (*6*). The appearance of graphite in experiment 4 after only 4.5 hours at 660°C indicates that in the calcite-hydrogen system the absence of graphite cannot be attributed solely to a high activation-energy barrier.

It is not known whether CO_2 ever formed in our experiments; if so, it must have converted immediately to H_2O and CO or CH_4; none of the analyzed gases contained CO_2 in detectable amounts (less than 0.01 percent).

The thermal dissociation of calcite and its dependence on surface area have been studied in detail (*7*). The surface dependence of our calcite-hydrogen reaction is substantiated by the observation that calcite powder reacts much more rapidly than does a single rhomb of equal weight.

Electron photomicrographs of unreacted calcite surfaces showed many defects, mainly pits that in part appear to perforate the surface; products of incipient reaction localized about these defects. Optical examination showed that the reacted areas about defects enlarged along crystallographic directions.

In many runs, a core of unreacted calcite enveloped by a cohesive rim of $Ca(OH)_2$ was recovered. If samples were allowed to stand unconfined, spontaneous spalling of the reaction film and shattering of the core generally occurred. In addition to rupture by rhombohedral cleavage, conchoidal fractures were observed on some of the shattered pieces of calcite.

Samples from most experiments were quickly embedded in plastic, and a flat surface was ground perpendicular to four rhombohedral faces. Reaction depths measured on the crystallographically similar rhombohedral faces $(\bar{1}101)$,$(1\bar{1}0\bar{1})$ and (0111),$(01\bar{1}\bar{1})$ were unequal, whereas the adjoining pairs $(1\bar{1}0\bar{1})$,$(0\bar{1}11)$ and $(\bar{1}101)$,$(01\bar{1}1)$ were reacted to similar depths. The average ratio of the difference in reaction depth between the two pairs for 29 measured samples was 2 : 1. The crystallographic orientation of the reaction surfaces was determined on three samples and found to be consistent. The observed anisotropy implies more than a loss of the center of symmetry.

The reaction film consisted of either CaO or $Ca(OH)_2$; CaO was identified in samples when the bomb was opened in a dry glove box and the solid reaction product was sealed in a glass capillary. All samples opened in air yielded strong $Ca(OH)_2$ patterns; for some a weak CaO pattern also appeared. It is likely that in all the higher-temperature experiments CaO was the principal solid product.

The idea must be considered that planetary atmospheres and hydrospheres may not represent unaltered solar nebula gas nor result from simple outgassing of unaltered occluded gas, but may result from a complex gas-solid reaction within the solid before liberation of the gas at the surface. If hydrogen is the major gas released from the compressed solid, it will have an affinity for the highly electronegative elements that form volatile hydrides, with the thermal stability of the hydrides rapidly decreasing down the series. If only the first one or two elements in each series are considered, the list includes all the elements needed to form the observed planetary atmospheres, Earth's hydrosphere, and much of the main framework of Earth's crust. The bond energies X–H (kilocalories per mole) are as follows: BH_3 (93); CH_4 (99.3), SiH_4 (76); NH_3 (93.4), PH_3 (77); H_2O (110.6), H_2S (83); HF (135), HCl (103.1). It is interesting to note that these elements also constitute the elemental components of common volcanic gases.

The proposed process could also provide the source of carbon, hydrogen, and sulfur believed necessary to convert the iron-rich group of chondrites into carbonaceous chondrites (*8*). Addition of hydrogen to diopside converts diopside to tremolite in a matter of hours (*9*). In part the hydrated carbonaceous chondrite minerals could have originated from hydrogen-silicate reaction, or more likely have formed nearer to the surface by a reaction between the original anhydrous chondrite minerals and juvenile water formed by a deeper hydrogen-solid reaction. The carbonaceous material under this scheme would be abiotic hydrocarbons, of low volatility, localized within the crust in their migration to the surface. This origin would satisfy the requirement that subsequent to their formation the carbonaceous chondrites were never heated above 300°C for any length of time (*10*). Support for this scheme is the observation that the vacuoles of carbonaceous chondritic minerals contain hydrogen, methane, and carbon monoxide.

The surface temperature would have a considerable influence on the outgassing process: if it were low enough to freeze water but above the melting temperature of many hydrocarbons, a hydrocarbon atmosphere and liquid might develop, with the water entrapped in a zone below the surface as a solid.

Hydrocarbons and graphite in igneous rocks (*1*) could have formed by this process. Hydrogen is reported to be 0.4 percent by volume of the Kilauea gases (*11*). The enigmatic graphite veins may have formed by similar reactions, and some graphite in graphitic marbles and schists also may have an abiotic origin.

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13. Part of the work was performed under the auspices of the AEC. We thank Richard and Patricia Crawford for mass-spectrographic analyses, Vernon Silveira and Carl Meyers for x-ray diffraction analyses, and R. W. Taylor for helpful discussions of the thermodynamics.

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Ethanol-1-C^{14} Metabolism in Alcoholics and Nonalcoholics

Abstract. *Metabolism of ethanol-1-C^{14} was assessed in a group of alcoholic and nonalcoholic male subjects. All subjects were screened for absence of physical derangement. Subjects were also carefully matched by dietary, social, and environmental criteria. No differences in rate of output of $C^{14}CO_2$ were detected after ingestion of alcohol which produced concentrations of 50 to 60 milligrams of alcohol per 100 milliliters of blood. These data do not support the hypothesis that alcoholics metabolize ethanol more rapidly than nonalcoholics do.*

The rate of ethanol metabolism is a variable which has been postulated to differentiate alcoholics from nonalcoholics, both in the alcoholic's behavioral tolerance for large quantities of alcohol and as a potentially important factor which may account for differences in susceptibility to alcoholism (*1, 2*). Alcoholics who drink up to 900 ml of beverage alcohol a day for several weeks can function well on a variety of perceptual-motor tasks (*3*). This finding suggests that behavioral tolerance may be related to an induced or innate metabolic efficiency with respect to alcohol. If it could be clearly demonstrated that the rate of ethanol metabolism differentiates alcoholic from nonalcoholic individuals, such data would facilitate the search for a biological mechanism upon which such differences could be based.

An induced increase in the rate of ethanol metabolism after prolonged ingestion of ethanol has been demonstrated in man (*4*). Also, studies with experimental animals have shown that increased rates of ethanol metabolism occur after forced ingestion of alcohol and that this enhanced metabolic rate may be correlated with an increase in activity of alcohol dehydrogenase in the liver (*5*). There have been no studies (with C^{14}-labeling techniques) of alcohol metabolism in alcoholics or nonalcoholics who had taken an acute dose. Although many studies have indicated that there are no significant differences in the rate of ethanol metabolism in alcoholics and nonalcoholics (*6*), two major difficulties related to the method of study prompt a further examination of this problem.

First, most studies have been concerned with the rate of disappearance of ethanol in the blood after acute oral or intravenous administration of ethanol. Because alcohol dehydrogenase acts as a rate-limiting factor in the metabolic degradation of ethanol, it has been assumed that serial measurements of alcohol concentrations in the blood would adequately reflect the overall rate of ethanol metabolism. However, it has been shown that differences in the specific activity of alcohol dehydrogenase (*7*) do not account for the observed interspecies differences in ethanol metabolism. Other factors, such as the rate of regeneration of nicotinamide-adenine dinucleotide from its reduced form in hepatic tissue, appear to be significant in limiting the rate of alcohol metabolism. Therefore, a comprehensive assessment of ethanol metabolism in man should include not only measurement of oxidation of alcohol to acetaldehyde, but also a study of the metabolism of intermediates to carbon dioxide and water.

Second, there has often been inadequate screening and matching of subjects and inadequate detail concerning effects of intercurrent illness and nutritional disorders. For example, many alcoholics have a variety of illnesses (associated with problem drinking) which may affect the rate of alcohol metabolism; these include hepatic, gastrointestinal, and nutritional disorders. Consequently, it is crucial to select subjects who are without evidence of any of these disorders.

In our experiment, alcoholics and nonalcoholic subjects were screened and matched to permit assessment of alcohol metabolism with minimum variables. In addition, the techniques for measurement of ethanol metabolism provide data concerning the total rate in vivo for all intermediates in man. More than 90 percent of the radioactive substance of C^{14}-labeled alcohol can be recovered as $C^{14}O_2$ (*8*). Forsander and Räihä (*9*) found that, after administration of C^{14}-labeled ethanol to intact rats or its addition to an isolated perfused rat-liver system, the label was also present in acetate, acetoacetate, β-hydroxybutyrate, and pyruvate. Goodman and Deykin (*10*) reported that alcohol is also a precursor of the ethyl esters of fatty acids.

Twelve adult male volunteers were selected from a group of inmates in a correctional institution; they had been in the institution for at least 3 weeks before the study and had ingested no alcoholic beverages during that period of time. They were given physical examinations and radiological and laboratory tests to rule out the presence of pulmonary, gastrointestinal (including hepatic), neurological, cardiovascular, or nutritional disease. All subjects received an identical diet and had the same opportunity for physical activity in a similar social milieu for 3 weeks prior to the study.

Six of the subjects were nonalcoholic individuals who had been incarcerated for offenses associated with sexual deviance. The six alcoholic subjects who had been incarcerated for offenses associated with disorderly conduct and alcohol intoxication had a history of at least 5 years of alcoholism and were classified as "gamma alcoholics" according to Jellinek's criteria (*1*). Gamma alcoholism is characterized by (i) recurrent ingestion of large quantities of alcoholic beverages; (ii) loss of control over drinking behavior; (iii) loss of social, family, and occupational resources because of drinking problems; and (iv) occurrence of withdrawal signs and symptoms after cessation of drinking.

The mean age of the alcoholic subjects was 39 years (range, 33 to 45 years); the mean age of the nonalcoholic subjects was 33 (range, 30 to 39 years). None had a history of drug addiction or had received any medication for at least 3 weeks prior to this study. All were of normal intelligence, and none showed evidence of a psychotic disorder.

Subjects did not ingest any food or water for 6 hours before the experiment. At zero time, subjects drank a 43-percent ethanol solution, the dose