IS   CARBON   DIOXIDE

AN   ORE - FORMING   FLUID   UNDER

SHALLOW   EARTH   CONDITIONS?

By R. M. Garrels and D. H. Richter

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
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Dr. T. H. Johnson, Director
Division of Research
U. S. Atomic Energy Commission
16th Street and Constitution Avenue, N. W.
Washington 25, D. C.

Dear Dr. Johnson:

Transmitted herewith is one copy of TEI-472, "Is carbon

dioxide an ore-forming fluid under shallow earth conditions?" by

R. M. Garrels and D. H. Richter, December 1954.

We plan to submit this report for publication in Economic

Geology.

Sincerely yours,

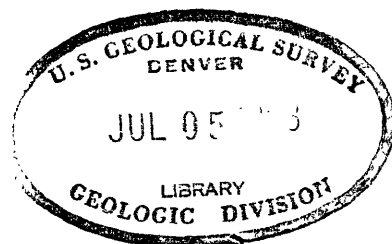for W. H. Bradley
Chief Geologist

Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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IS CARBON DIOXIDE AN ORE-FORMING FLUID UNDER

SHALLOW EARTH CONDITIONS?

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ABSTRACT

A review of some of the physical chemical properties of CO_2 and of the system CO_2-H_2O indicates that under some shallow earth conditions CO_2 can exist as a separate phase with a density approximately that of water. The effect of dissolved neutral or acid salts on the solubility of CO_2 in H_2O is negligible. Carbonates, oxides, and silicates, through reactions with a CO_2-saturated water phase, will eventually cause the disappearance of a CO_2 phase. The prevalence of CO_2 in the earth's crust is attested by its abundance in natural gases and fluid inclusions in minerals.

Some of the characteristics of uranium ores of the Colorado Plateau are compatible with the assumption that deposition was from a fluid CO_2 phase.

INTRODUCTION

During the course of some speculations regarding the origin of the sandstone-type uranium deposits, we were led to consider the possibility that a non-aqueous phase might be the agent of metal transport and deposition. Because of the prevalence of carbon dioxide in earth materials of all kinds, a review of the properties of carbon dioxide under shallow earth conditions seemed warranted. Although we do not have the temerity to advocate carbon dioxide as

the ore-forming medium in such deposits, the results of the review were so opposed to our preconceived ideas concerning the nature of this gas that we are impelled to present them for general consumption.

Among the questions that occurred to us at the start of the investigation were:

Do water and carbon dioxide exist as separate phases in rocks? If so, what is the concentration of water in the carbon dioxide phase, and vice versa? What is the density of carbon dioxide under shallow earth conditions? What is known about the solvent properties of carbon dioxide?

PART I - THE SOLID PHASE

P-V-T relations for CO_2

The pressure-volume-temperature relations for CO_2 are shown in figure 1 (Michels and others, 1935, 1935a; and Kennedy, 1954). Superimposed on the diagram are lines showing high, "normal", and low thermal gradients under hydrostatic pressure conditions, and the same gradients for lithostatic conditions. As an example, let us briefly examine some of the properties of CO_2 along a "normal" thermal gradient ($1^{\circ}C/100$ ft.) under lithostatic pressures as shown on the P-V-T diagram. At a temperature of $110^{\circ}C$ and pressure of 800 atmospheres, corresponding to a depth of 10,000 feet, CO_2 has a specific volume of 1.08, or in other words, a density of 0.93. At decreasing temperatures and pressures, the CO_2 volume slowly increases, concomitant with a slow decrease in density, until near surface conditions are reached. Here at $15^{\circ}C$ and 50 atmospheres (750 feet below the

Depth, ft.

Pressure, atmospheres

Temperature, °C

Hydrostatic Lithostatic

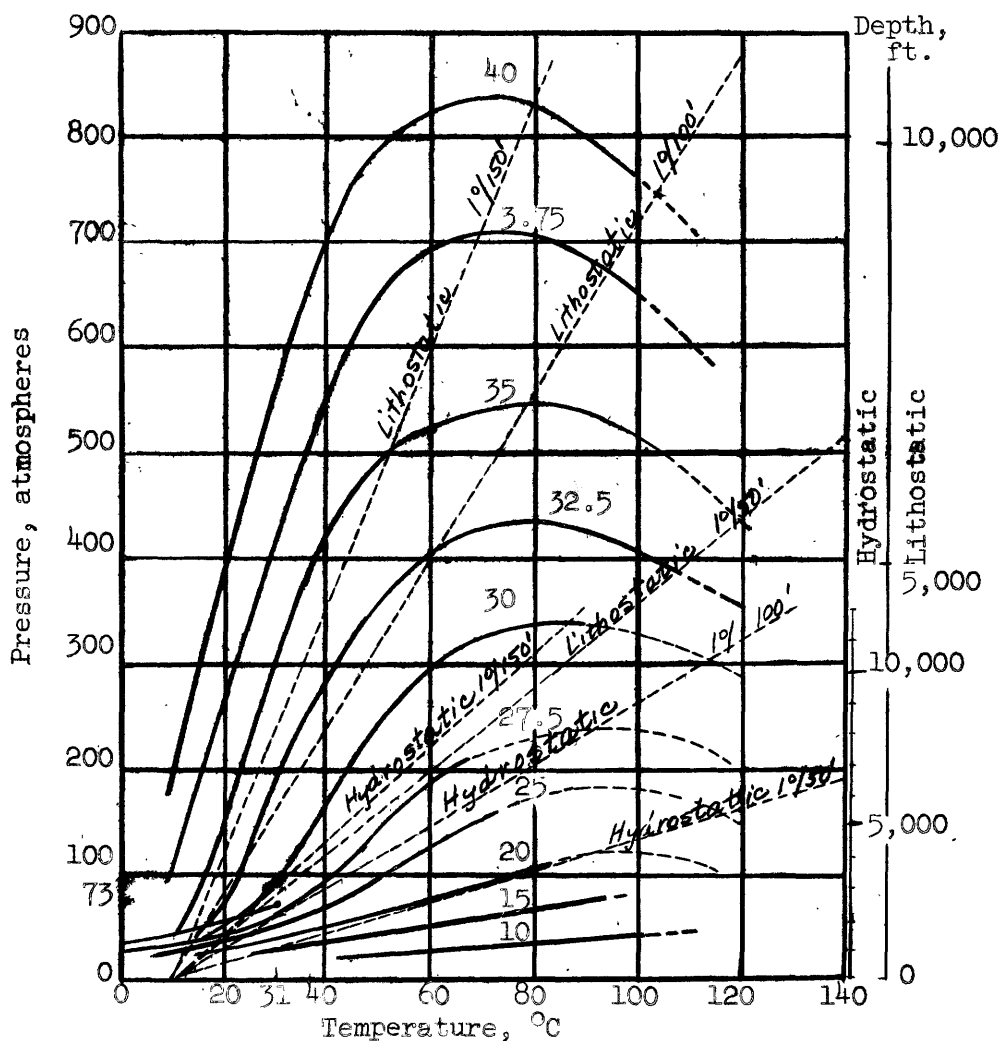Figure 1.--P-V-T diagram for CO_2 with superimposed high, "normal", and low thermal gradients under lithostatic and hydrostatic pressures. Specific volumes (sloping solid lines) are expressed in cc/g. Greatest density is reached under a high pressure-low temperature gradient (left hand dashed line), least density under hydrostatic pressure and a high temperature gradient (right hand dashed line).

surface), equivalent to the intersection of the earth gradient and
CO_2 vapor pressure curve, CO_2 rapidly expands filling a volume eight
times that of its original size. With further decrease in temperature
and pressure CO_2 continues to expand rapidly until equilibrium is
established with atmospheric conditions. The lithostatic pressure
gradient must represent roughly the maximum that can exist for
appreciable time intervals. Gas or fluid pressures, built up from
below, are greater than the hydrostatic pressure by the amount neces-
sary to overcome the frictional resistance of the enclosing rocks.
In unfractured and slightly permeable rocks the pressure must exceed
the rock load if the fluid is to move at an appreciable rate. That
such conditions do exist is shown by measured pressures in drill holes;
in fact, Pinfold (1954, p. 1660) reports bottom hole pressures in
excess of the lithostatic load. The temperature gradients chosen are
well within the observed range (Lindgren, 1919, p. 80-84, and Van
Orstrand, 1934). The lithostatic pressure is computed on the assump-
tion that the average rock density is 2.7.

CO_2-H_2O solubility relations

The solubility of CO_2 in water has been determined by Wiebe and
Gaddy (1939, 1940); the solubility of H_2O in gaseous CO_2 should be
roughly proportional to the partial pressure of H_2O. On this basis
the weight ratio of water to CO_2, for a given pair of P-T values, is
taken as proportional to the ratio of the vapor pressure of water to
the total pressure on the system (P_{CO_2} + P_{H_2O}). For actual calcula-
tion of the mole percent water in the gaseous CO_2, the Gas Law was
used.

Some question may arise as to the validity of the assumption that CO_2 at high density acts as a gaseous solvent, or that water vapor itself under such high total pressure obeys the Gas Law. However, determinations of the solubility of water in liquid CO_2 (Stone, 1943) suggest that serious error in the order of magnitude of the calculated solubilities is not likely. At $22.5^{\circ}C$, and under the vapor pressure of CO_2 (60 atmospheres), the solubility of water in liquid CO_2 is only 0.954 weight percent. Furthermore, the data at temperatures up to 22.5° indicate that the solubility of water in liquid CO_2 increases with temperature at a decreasing rate under the equilibrium vapor pressure. Because earth gradients have linear increase in pressure, whereas the vapor pressure curve of CO_2 is exponential, it appears very likely that no great error is involved in the calculated solubility.

Figure 2 shows the composition of the water phase and the carbon dioxide phase for a mixture of carbon dioxide and water, transported down a thermal gradient of $1^{\circ}C$ per 100 feet under lithostatic conditions. The low mutual solubility is apparent.

Figure 3 shows iso-solubility curves for CO_2 in water on a P-T graph. The nearly constant solubility at low temperatures and pressures along all the gradients chosen, as well as the marked increase at the higher ranges, are noteworthy features. In other words, a saturated solution of CO_2 in water, if it moves upward from depth, will separate a nearly pure fluid CO_2 phase. This deduced behavior is substantiated by observations on certain three-phase fluid inclusions in many minerals. The three phases are two liquids and a gas at room temperature. If the inclusions are heated one of the liquid
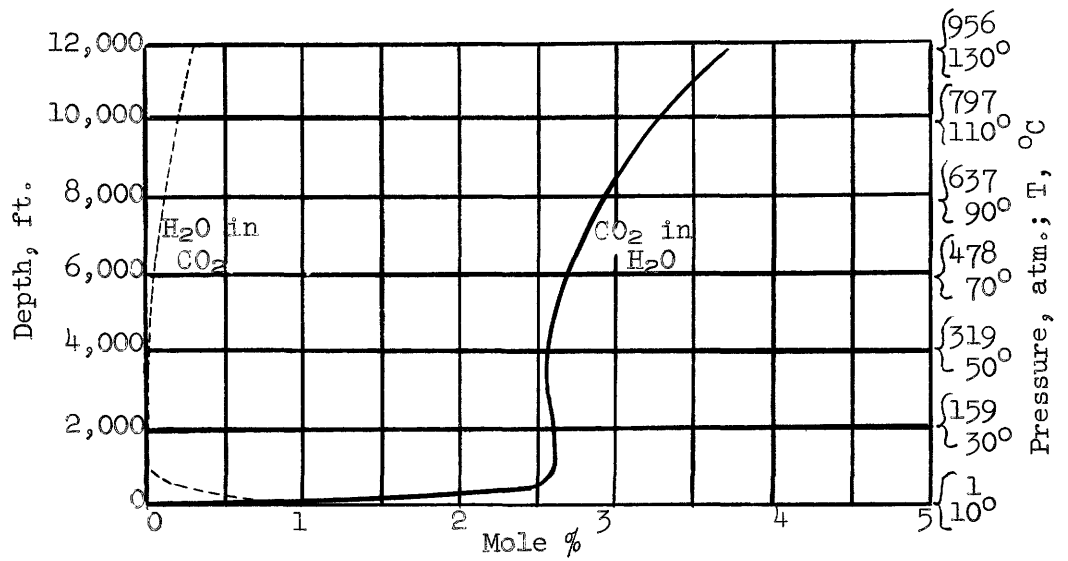
Figure 2.--Solubility relations of CO_2-H_2O along a " normal" thermal gradient and under a lithostatic load.
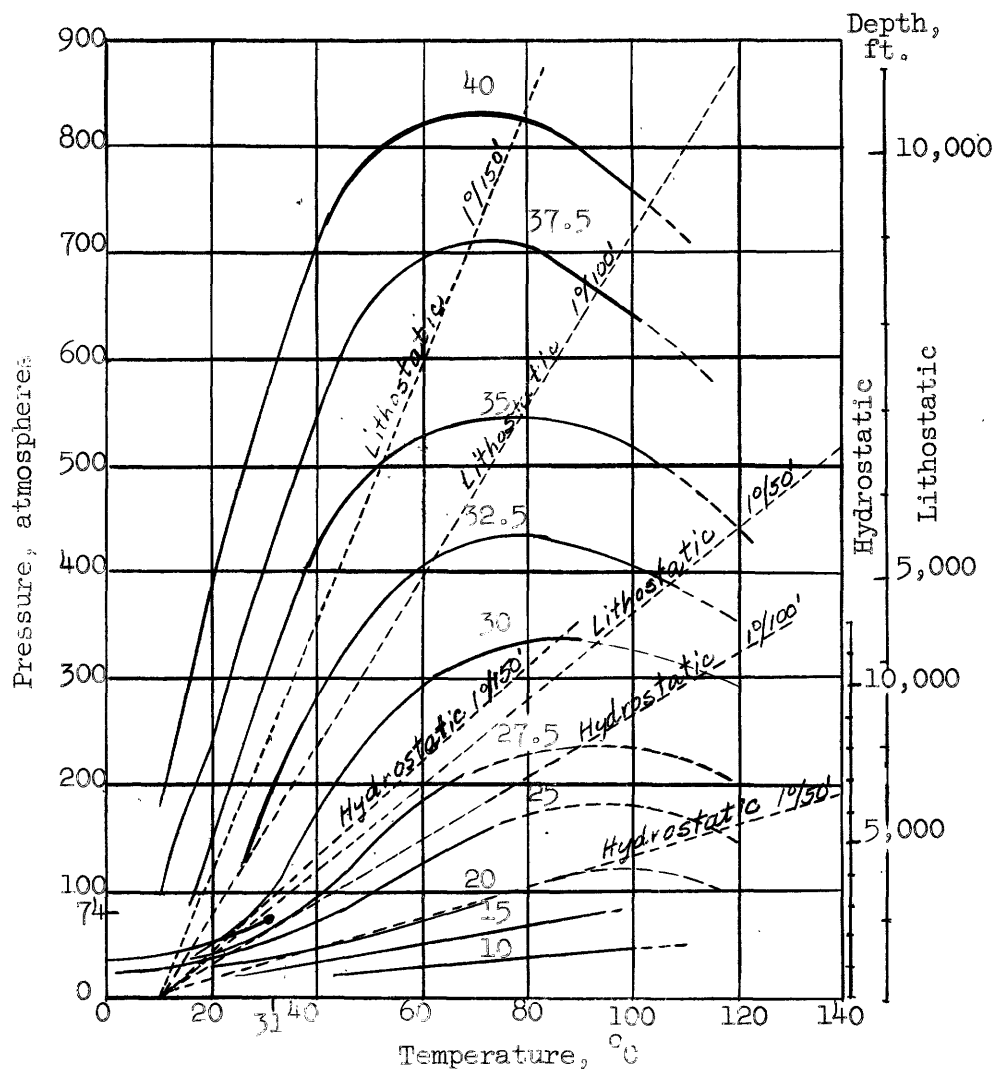
Figure 3.--P-T diagram for CO_2 with iso-solubility lines for CO_2 in H_2O. The figures are expressed in cc/gram at STP. (After Wiebe and Gaddy). Also shown are high, "normal", and low thermal gradients under lithostatic and hydrostatic pressures. Note that the solubility relations are such that there is very little change with depth, irrespective of the specific earth gradient. For example, under lithostatic pressure, and under a temperature gradient of $1^o/150'$ (left hand dashed line), the solubility is essentially constant from 50 to 500 atmospheres pressure, and increases only from 35 cc CO_2/gram H_2O at 500 atmospheres to 40 cc/gram at 830 atmospheres.

phases disappears at $31^{\circ}C$, the critical temperature of carbon dioxide.
The remaining gas and liquid phase commonly persist to temperatures
about $200^{\circ}C$; then the gas phase disappears and the inclusions fill
with liquid (Cameron and others, 1953). On cooling, the sequence of
events is reversed. The disappearance of the vapor phase, on heating,
is by no means entirely attributable to the expansion of the liquid
phase but must also indicate a high solubility of CO_2 in H_2O at
temperatures above $200^{\circ}C$ and high pressures. Further evidence of the
existence of a nearly pure dense gaseous CO_2 phase under earth condi-
tions is shown by numerous fluid inclusions that exhibit only a gas
phase above the critical temperature of CO_2 and a liquid phase with
a small gas bubble below the critical temperature. The absence of
appreciable water in the CO_2 phase is shown by the disappearance of
liquid CO_2 at the critical temperature for pure CO_2. Appreciable water
in solution would raise the critical point.

Density relations

To illustrate density changes it is instructive to take a mixture
of one mole of CO_2 and one mole of water from the earth's surface down
various earth gradients. At the surface the volume discrepancy of the
two phases is huge; 18 cc. for the liquid water and 23,100 cc. for the
gaseous CO_2, but the descent into the earth changes the picture con-
siderably.

In figure 4 the changes are shown diagrammatically. CO_2 shrinks
as pressure is applied and reaches a density approaching that of water
at depths of a few thousand feet, depending upon the specific earth
gradient. Thus under natural conditions it is probable that at rela-
tively shallow depths a fluid CO_2 phase may exist with a density equal

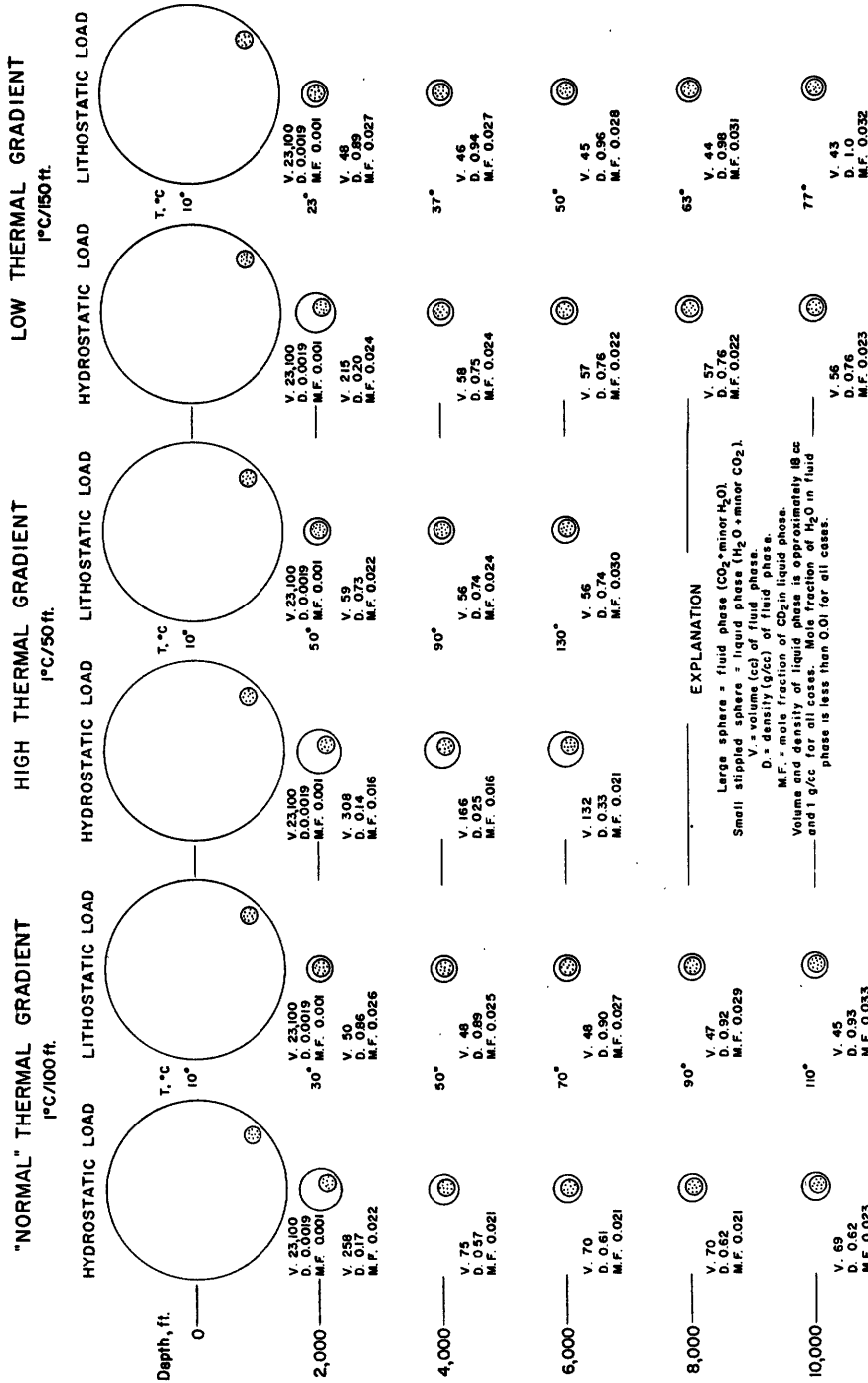Figure 4.--Diagrammatic representation of the history of an equimolar mixture of CO_2 and H_2O down various temperature-pressure gradients. The circles are sections of spheres representing the relative volume of the CO_2-rich phase and the H_2O-rich phase. The change from a "dense liquid-rare gas" system at the surface to a "dense liquid-dense gas" system takes place at shallow depths under all gradients shown.

to or slightly greater than that of water! In fact, in moderate to high latitudes, where the near-surface temperature is low, liquid CO_2 may form.

In figure 5 the density of CO_2 as a function of depth is shown graphically, to emphasize the high density that is reached at relatively shallow depths.

CO_2, under most earth conditions, has a density greater than that of liquid CO_2 at room temperature. There is no change in solvent properties of a liquid phase as it changes to a gas, if there is no change in density, so dense gaseous CO_2 can be expected to behave like the liquid (cf Hannay and Hogarth, 1879; Ingerson, 1934, pp. 457-458; Smith, 1943, p. 34). The fact that in many environments, it is not only denser, but hotter than the liquid, indicates that it probably is considerably more effective as a solvent. The density of liquid CO_2 at $31^O C$, under its vapor pressure of 73 atmospheres, is 0.47, whereas at 100° and 1000 atmospheres, the density of the fluid is about 1.0.

<center>

Effect of dissolved material on

CO_2 solubility in water

</center>

So far the discussion has been concerned only with the system CO_2-H_2O. The question arises as to the effect of other dissolved materials on the CO_2 solubility in water. Most dissolved salts reduce gas solubility, if no chemical reaction between the dissolved gas and the solutes occurs (Mellor, 1925, p. 53). Such reaction by dissolved CO_2 with neutral or acid salts is not to be expected; a long list of
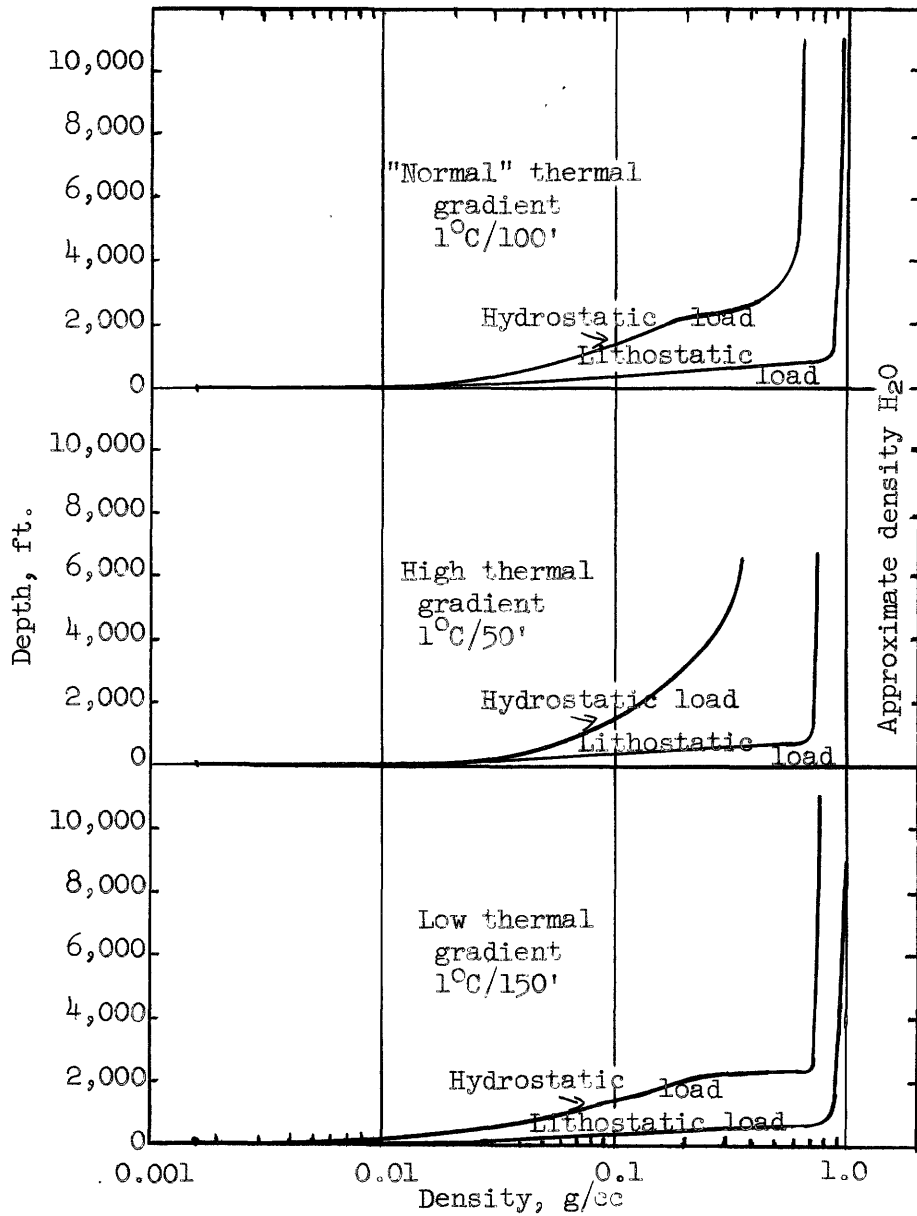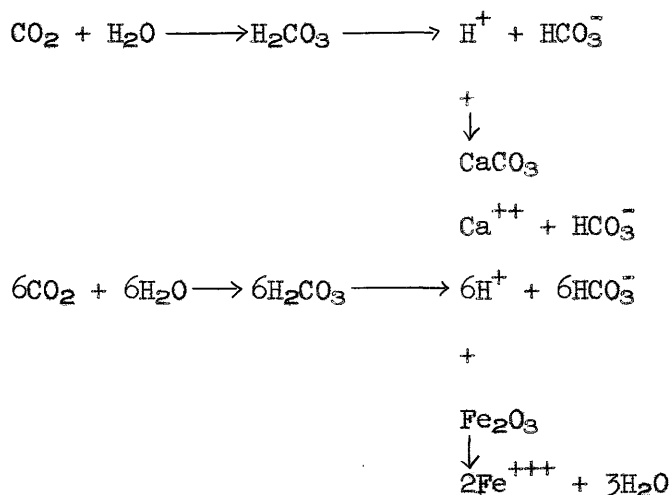
Figure 5.--Density of CO_2 under various shallow earth conditions.

determinations of CO_2 solubilities in a variety of such salt solutions (Seidell, 1940, pp. 225-230) shows remarkably uniform behavior and a relatively small salt effect.

Dissolved CO_2 will react with dissolved basic salts, such as sodium carbonate, but the solubility is probably most affected by the reaction of the CO_2-H_2O system with rock minerals susceptible to acid attack. If a "bubble" of dense CO_2 were injected into a water-saturated sandstone that had a calcite or an iron oxide cement, CO_2 would dissolve in the water and then react with the iron oxide and calcite. As a result of the reactions, the bubble would eventually disappear. The reactions would be:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

$$+ \\ \downarrow \\ CaCO_3$$

$$Ca^{++} + HCO_3^-$$

$$6CO_2 + 6H_2O \longrightarrow 6H_2CO_3 \longrightarrow 6H^+ + 6HCO_3^-$$

$$+$$

$$Fe_2O_3 \\ \downarrow \\ 2Fe^{+++} + 3H_2O$$

The same type of reaction would take place with silicate minerals but at a much slower rate.

In general, then, in a low temperature system of CO_2 and H_2O, a separate CO_2 phase will exist even if the weight percent CO_2 is small; but, if the system is placed in contact with rocks containing carbonates or oxides, the CO_2 phase will gradually disappear as it dissolves into the water to replace that used up by reaction.

A separate CO_2 fluid phase would thus not be expected to persist indefinitely if it were moving through water-saturated rocks, unless they were pure quartz sandstones, or perhaps certain acid resistant clays. Certainly it would tend to disappear in limestones, or from oxide or calcium carbonate cemented sandstones, siltstones, or shales.

The rate of disappearance would be a complex variable, depending on the rate of reaction of the solids and the rate of diffusion of CO_2 into the water phase. The second variable would in turn depend on whether or not the CO_2 was moving relative to the water phase.

The persistence of gaseous CO_2 as a separate phase in nature is shown by its presence in the exhalations of many volcanoes and hot springs, as well as by its occurrence as a major constituent in some natural gases from stratigraphic or structural traps (table 1). Concerning its ubiquitous nature in fluid inclusions in minerals Lindgren (1919, p. 95) eloquently states: "The presence of liquid carbon dioxide in cavities in minerals of igneous rocks is proof of its occurrence in the molten magma consolidated in depth. Every eruption brings new evidence of exhalations from magmas congealing near the surface; and almost every volcanic district of recently closed igneous activity testifies to the persistence of this gas in escaping from the cooling lavas below."

SUMMARY

In summary, CO_2 can exist as a separate phase under shallow earth conditions. At depths below 1,000 feet, under a "normal" temperature gradient and a lithostatic load, its density is equal to that of liquid CO_2 at the critical point. Under high pressure gradients and

Table 1.--The CO_2 content of some earth gases.

Locality	Percent CO_2	References
Volcanoes and fumaroles		
Iceland, average of 5 analyses	44	Clarke (1924, p. 262) after Bunsen
West Indies, average of 3 analyses	48	Clarke (1924, p. 269) after Moissan
Kilauea, Hawaii, average of 5 analyses	57	Day and Shepherd (1913, p. 588)
Hot springs		
Lassen National Park, Calif., average of 26 analyses	93	Day and Allen (1925, p. 131-133)
Yellowstone National Park, Wyo., average of 40 analyses	85	Allen and Day (1935, p. 86)
Oil and gas fields		
Tampico, Mexico	10.7 - 97.9	Muir (1935, p. 1000-1003)
Walden, Colo.	92	Dobbin (1935, p. 1065)
Jaritas Dome, N. Mex.	67.2	Dobbin (1935, p. 1065)
San Rafael swell, Utah	91.2	Ley (1935, p. 1124)

low temperature gradients its density approximates that of water at
depths between one and two miles. Dense fluid CO_2 probably has sol-
vent properties more nearly comparable to a liquid than to those
generally attributed to a gas. Unfortunately, little is known of
the solvent properties of liquid CO_2. In most rocks a separate CO_2
phase probably would disappear over a long period of time as a result
of reaction of the CO_2-saturated water phase with rock minerals
susceptible to acid attack.

PART II - THE GASEOUS PHASE

CO_2 and uranium deposits

The relatively common occurrence of fairly pure gaseous CO_2 in
nature, plus the fact that its density, even under shallow earth con-
ditions, is greater than that of liquid CO_2 at room temperature, leads
naturally to the possibility that CO_2 may play an important role in
the transportation and deposition of other compounds. Present knowl-
edge of the solvent properties of dense gaseous CO_2, or even of liquid
CO_2, is very limited and certainly merits extensive investigation.

To show the part that dense CO_2 might play as a transporting
agent, it is intriguing to consider to what extent it would fit the
characteristics required of the fluid that deposited the uranium ores
of the Colorado Plateau. Rather than attempt any coherent reconstruc-
tion of the details of the processes of deposition, we prefer to
assemble a somewhat disconnected group of arguments, explanations, and
generalizations, which we hope will prove provocative, and may lead
others to more detailed examination of some of the aspects considered.

First, the best reconstruction of the conditions of deposition of the ores indicates that CO_2 would have an appropriate density. According to Stieff and Stern (1952, p. 708), the ores were deposited in early Tertiary or Late Cretaceous time. At the end of Cretaceous, the ore-bearing Triassic or Jurassic beds were buried by about 10,000 feet of sediment, so that, on the basis of a "normal" geothermal gradient, and a hydrostatic load, the temperature would have been about $110^{O}C$, and the pressure about 300 atmospheres. The density of CO_2, under these conditions, is about 0.6, roughly that of liquid CO_2 at room temperature under its equilibrium vapor pressure. If it is considered that the geothermal gradient would probably be a little lower in a basin of sinking sediments, and that the pressure on ascending CO_2, held back by the frictional resistance of the nearly impermeable shales of the Chinle, Brushy Basin, and Mancos formations, might well be lithostatic, the density of CO_2 would be about that of the pore waters of the mineralized sediments. The relation of the ores to the containing beds suggests strongly that the density of the ore fluid was equal to or greater than the pore waters; in the Shinarump conglomerate, ore is characteristically in channels at the base of the formation, whereas in the Salt Wash sandstones of the Morrison formation, it commonly "floats" in the middle of an apparently homogeneous sandstone layer. Elsewhere in the Salt Wash, the ore may "hang" against a shale split for long distances, and then abruptly cut down across bedding planes. In still other places it hugs the base of a sandy layer.

The "bleached" shales that so often underlie or overlie ore bodies might be the result of the slow solution of CO_2 in the pore waters of the rock, with concomitant removal of hematite cement and solution and

recrystallization of calcite. The effect of CO_2 dissolving in pore waters might also account for the occurrence of ore in light-colored sandstones, often with disseminated pyrite. The CO_2 dissolved in the pore waters would react with the iron oxide of originally red sediments, and the resulting ferric iron would be reduced and precipitated as pyrite by a small amount of H_2S in the CO_2, or could even be adsorbed by, or taken up in the structure of clay minerals (Gruner, 1953, p. 28-34).

The rhythmic precipitation that is so common in the ores, and has led some workers (Fischer, 1942, p. 389) to postulate a ground-water origin, might be rhythmic precipitation at the shrinking boundary of the dissolving CO_2 phase.

The very sharp, sometimes undulating margins of many ores, suggest deposition at a phase boundary, perhaps between pore waters and the dense gaseous CO_2.

The fact that the ores represent additions of an unusual suite of elements, which are deposited interstitially in the rocks, suggests transportation by an unusual solvent, which has very little effect, except addition, on the rocks within the ore itself. Because the added elements resemble the trace element suite in petroleum, it has been postulated by some as the ore fluid (Erickson and others, 1953). Liquid CO_2 has been characterized as a non-polar, or weakly polar solvent (Mellor, p. 58) and conceivably might be a solvent for a similar suite of metals, as well as for organic materials. Furthermore, recent laboratory experiments indicate that the solubility of certain crude oils in liquid CO_2 is great enough to warrant its use in secondary oil recovery. (Johnson and others, 1952).

The natural gases of the Colorado Plateau are well known as tending to run very high in CO_2 (table 1). In reading an account of the distribution of CO_2-rich gas wells in the United States, one is struck by the number of occurrences in southwestern Colorado, northwestern New Mexico, and southeastern Utah. By coincidence, perhaps, a dry ice plant was planned in Grand Junction to utilize CO_2-rich gas from the Morrison formation.

In summary, we have felt for some time that there is a "gimmick" in the vexing problem of the origin of the ores of the Colorado Plateau. From the little we know, CO_2 is just sufficiently common and unusual to lead us to the suspicion that it will bear a good hard look as a candidate for ore depositing honors.

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