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LIQUID CO_2 INCLUSIONS IN OLIVINE-BEARING NODULES AND PHENOCRYSTS FROM BASALTS[1]

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ABSTRACT

Inclusions of highly compressed, generally liquefied, nearly pure CO_2, usually with glass (presumably basaltic), were found in the minerals of every occurrence of olivine-bearing nodules in basalts studied, from 72 localities throughout the world. They were found in olivine, clinopyroxene, orthopyroxene, and plagioclase, from dunitic, peridotitic, pyroxenitic and gabbroic nodules. Large numbers of these inclusions are secondary in origin, trapped during the healing of fractures, but many are found that appear to be primary; both types require the existence of immiscible globules of a dense, supercritical CO_2 fluid in the basaltic liquid, at high pressures. Under ordinary microscope examination, they appear as opaque dust grains, usually $<5\ \mu$ in size. A cool microscope stage, high magnification, and strong, convergent light, free of infrared, are needed to recognize them. Their composition was established by five methods. Similar CO_2 inclusions were also found in phenocrysts of olivine, titanaugite and oxyhornblende in basalts from 19 occurrences, in some eclogite xenoliths and in kimberlite from a diamond pipe. Thirty-one other ultramafic igneous rocks showed evidence of gas inclusions under pressure, but no visible liquid CO_2.

The primary inclusions permit the estimation of the pressure at the time of formation of the enclosing minerals. The secondary inclusions record the ambient pressures at the time of breaking and rehealing of the host mineral. Many inclusions of both types in the nodules show a density of filling corresponding to the pressure of 10–15 km of basalt liquid, but inclusions formed at greater depths may have decrepitated on eruption. The fact that many inclusions did not decrepitate upon eruption (or subsequent laboratory heating in air to 1200° C) indicates that olivine has a surprisingly high tensile strength at high temperature. The saturation of basalt magmas with respect to CO_2 on a world-wide basis, as evidenced by these inclusions, has considerable significance to a variety of petrologic problems such as vesiculation, the composition of volcanic gases, and the origin of phenocrysts, carbonatites, and perhaps diamonds.

INTRODUCTION

In November of 1962 Professor D. S. Coombs of the University of Otago, New Zealand, called my attention to some two-phase (liquid plus gas) fluid inclusions, in which the bubble exhibited Brownian movement, in the olivine of peridotitic nodules from the 1801 Hualalai basalt flow in Hawaii. These inclusions, and others like them from nodule occurrences throughout the world, proved to consist of liquid and gaseous CO_2 under high pressure, in a completely unexpected and novel occurrence.

Liquid carbon dioxide inclusions in minerals are not uncommon. Inclusions in pegmatite and alpine-type vein minerals frequently show various amounts of liquid CO_2, along with water (Roedder, 1963), and

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[1] Publication authorized by the Director, U. S. Geological Survey.

they have been reported in the major rock-forming minerals in some granitic rocks (Smith, 1953). Relatively high pressures are required for their formation, as liquid CO_2 needs >1000 psi to contain it at the critical point (31° C.); very much higher pressures are needed at higher temperatures. The common occurrence of such inclusions in the nodules in basaltic lavas, erupted under high temperature–low pressure conditions, thus presents us with a valuable relict of another, very different, high pressure environment, saturated with respect to CO_2. We also have the fascinating problem of why the inclusions did not decrepitate upon eruption.

I am particularly indebted to John Creel for much of the sample preparation and many homogenization temperature runs, and for long hours of searching for inclusions in obstinate samples. I also wish to acknowledge the help of many people in supplying samples, as listed in Table 3, especially R. N. Brothers, K. A. Rodgers, J. F. Lovering, D. S. Coombs, D. Galligher, J. J. Reed, H. Kuno, R. L. Smith, H. G. Wilshire, and C. S. Ross. I want to thank E. Dale Jackson, G. C. Kennedy, and D. S. Coombs for reading the manuscript. As this report is the direct result of Professor Coombs' original observation, I wish to express my appreciation of his generosity in turning the investigation over to me.

GENERAL OCCURRENCE AND DESCRIPTION

Lack of previous recognition. Of the 72 occurrences of olivine-bearing nodules that were examined, from many parts of the world, liquid CO_2 inclusions were recognized in 64 and their presence in the other 8 was inferred from several lines of evidence detailed below.[1] No nodule occurrence was found that did not show some evidence of them. As nodules have been studied intensively for many years without a single report of such inclusions,[2] some explanation is in order.

Most of the inclusions studied appear, at first glance, to be merely opaque specks (solid inclusions) in the enclosing mineral, and hence are easily overlooked. During ordinary petrographic examinations of either thin sections or grain mounts, they would normally be seen as bothersome dust and ignored. They differ from the common opaque solid in-

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[1] Throughout this report the "nodules," "inclusions" and "xenoliths" of peridotite, dunite or similar rock types in basalt are all arbitrarily called "nodules" or "olivine nodules" for simplicity, with no genetic connotation intended.

[2] One early paper presents an interesting vignette of science. In checking the older literature on nodule occurrences in connection with this paper, I found that Vogelsang (1869) and Zirkel (1870) reported the occurrence of liquid CO_2 inclusions in the olivine *phenocrysts* (xenocrysts?) of basalts from Eifel, Saxony and Hesse. The first of these occurrences was verified by Deicha (1955, p. 95) and the present study (sample ER 64–123).

clusions of spinel or magnetite, however, in that even in ordinary lighting at moderate magnification, the larger ones usually show a pinpoint of light coming through the center of the otherwise dark mass. The low index of refraction of CO_2 (well under 1.2, Quinn and Jones, 1936), causes a rounded inclusion of it in a high index mineral to act as a strong negative lens. Strongly convergent light, as from the normal high-power substage condenser, will counteract this, but unless used with a good infrared filter, it will cause the two CO_2 phases to homogenize, making the inclusion appear empty. Even with optimum conditions of observation detailed below, and knowledge of what to look for, most of the CO_2 inclusions in the samples studied are unsuited for positive identification, and hence the earlier failure to recognize the CO_2 is understandable.

Description of the CO_2 inclusions. The inclusions are generally rounded to almost spherical, although some samples of both pyroxene and olivine show sharply faceted negative crystals containing CO_2. Many show a dark border of unknown nature (Fig. 6). Only rarely are they flattened, permitting good delineation of the inclusion contents; many of the photomicrographs are of such flattened, *atypical* inclusions. Most are small, rarely $>30\ \mu$, and usually $<5\ \mu$; many are well under $1\ \mu$. Where the gas bubble is relatively small and free from the walls, it may be in constant Brownian movement. Large numbers of small inclusions occur closely spaced, roughly outlining crystallographically oriented planes, or curving surfaces through the crystal. Not infrequently such healed cracks die out within a single mineral grain as shown by the gradual decrease of inclusion size down to an abrupt cutoff at $\sim 0.3\ \mu$. Rarely, such healed cracks cross grain boundaries. Larger inclusions are randomly distributed, or widely spaced in crystallographically controlled planes. Additional details on mode of occurrence are given below, in a discussion of the evidence for primary *vs* secondary origin.

The volume per cent of CO_2 inclusions varies widely, even from grain to grain in the same sample. Some large (25-cm^2) thick sections show only a few tiny inclusions, (corresponding to a few parts CO_2 per trillion of rock), yet individual grains of olivine have been found with an estimated 3 volume per cent CO_2 (corresponding to about 0.5 weight per cent CO_2; see Fig. 10); such material may be responsible for the small amounts of CO_2 reported in some analyses of nodules. Most of the nodules studied contain only about one part CO_2 per billion.

Other phases present in CO_2 inclusions. In addition to CO_2 liquid plus CO_2 gas, *glass* is a highly variable but major constituent of many of the inclusions, and may well occur as an invisible film on the walls of the remainder. This is presumably basaltic in composition, as indicated by its brownish color and several crude determinations of the index of refraction (about 1.61; see Stewart, 1962). These were made by crushing selected olivine grains in index liquid on the microscope crushing stage.

Ordinary glass inclusions in the minerals of volcanic rocks normally show an immobile "gas" bubble formed on cooling as a result of greater shrinkage of the glass (magma) than of the surrounding host mineral. Such bubbles are usually found to be nearly a vacuum, and show a relatively constant and small volume ratio to the glass; they were seen in most of the samples investigated (*e.g.* Figs. 3, 5, 6). The CO_2-bearing inclusions do not show a uniform gas/glass ratio, and nearly always show much higher gas/glass ratios than could be obtained by shrinkage of the glass on cooling.[1] Non-uniformity of gas/glass ratios is an ambiguous criterion for CO_2 in the inclusions, and must be used with care, as the necking down of flat or elongate glass inclusions with recrystallization of the host mineral can yield variable ratios.

Some samples show abundant isotropic cubic crystals, presumably of *spinel*, partially oriented in an epitaxial array in the olivine (cube faces parallel to the olivine crystal axes), each with a bleb of glass attached, and some with a "bubble" of CO_2 (now liquid plus gas) in the glass. Many CO_2 inclusions appear to be attached to an *opaque platelet*, also presumed to be spinel (Fig. 23). Crystal facets are sometimes seen on the edges of these platelets, under asymmetric dark-field illumination.

The glass in some CO_2-glass inclusions includes one or more *birefringent* crystals. In a few samples, these birefringent crystals are regular in their occurrence and volume ratio to glass in a series of inclusions, and hence are definitely daughter minerals, formed from the glass after the inclusion was trapped. Generally their occurrence is random, indicating either accidental trapping of solid crystals present in the melt, or accidental nucleation of daughter minerals in the glass of the inclusion after trapping.

Negative crystal inclusions of CO_2 frequently have irregular *dark masses* filling the space between the large rounded central bubble of CO_2 and the sharply faceted exterior (Fig. 17); this material may be glass that has crystallized to a granular opaque mass after trapping, or may even be graphite (see section "Other constituents present").

Sample preparation for microscopy. Although many of the samples examined in this study were available only as ordinary petrographic thin sections, these are difficult to work with for several reasons. First, the

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[1] Glass inclusions and gas inclusions have been obtained in synthetic olivine in the laboratory (Fouqué and Michel-Lévy, 1881; Jordan and Naughton, 1964).

normal preparation of thin sections causes complete loss of the liquid CO_2 from most of the larger inclusions that are so much easier to identify. Second, the ground upper surface of high index minerals such as olivine interferes with the clarity of the image obtained at high magnification (1000X), making the sometimes rather faint meniscus between CO_2 liquid and gas more difficult to recognize.

Much more useful for this work are doubly polished plates about 1 mm thick, although it is difficult to distinguish between pyroxenes and olivines in such plates. Clear epoxy resins are best for impregnating, but can form rather peculiar and bothersome multifluid-phase "inclusions" in pores in the rock. Crushed fragments can be mounted for observation in an index liquid closely matching the mineral, but the degree of mismatch due to anisotropy of the mineral, even in correctly oriented, plane-polarized light, generally makes the resolution poor.

IDENTIFICATION CRITERIA

Five different methods were used to identify the CO_2, depending upon the nature of the individual samples. As much of the widely scattered literature on this subject is over 100 years old and not readily available (see annotated bibliography by Smith, 1953), the methods will be described.

Gas evolution on crushing. Deicha (1950) has developed a method for the detection of gases under pressure in inclusions. In essence, the inclusion-bearing material is crushed in a drop of fluid between glass plates, on the microscope stage, whereupon any gas under pressure will expand to form a bubble.[1] As one volume of liquid CO_2 will expand to approximately 350 volumes of gas, and as bubbles a few microns in size are easily visible, the method is very sensitive. Most of the specimens listed were checked for gas evolution on crushing, simply using a metal point to press on the coverglass near each grain. As olivine is very tough, thick coverglasses are needed; 5–10 mm squares cut out of ordinary microscope slides are generally adequate.[2] A comparatively few grains of mineral of similar size are most satisfactory. They should be kept away from the edge of the cover, as the violent movement of the grains upon breaking sometimes pulls in air bubbles from the edge of the mount, causing confusion. Occasionally this violent movement may also cause momentary bubbles from cavitation, but these are easily distinguished

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[1] A crushing stage designed by Deicha is available from Microscopes Nachet, 17, Rue Saint Severin, Paris V^e, France.

[2] A new crushing stage, permitting better control in the crushing of hard, tough minerals, was used on a number of the samples; it will be described separately.

from the bubbles from gas inclusions, particularly in those grains in which a crack can be seen to advance slowly up to the inclusion as pressure is applied.

Crushing in oil has shown that all specimens believed to contain liquid CO_2 inclusions showed voluminous evolution of gas, in amounts roughly proportional to the amount of inclusion fluid present. The evolution is usually instantaneous (Fig. 24), as would be expected for gas under 1000 psi pressure.[1] In those grains having large isolated regular inclusions, it is possible to obtain a measure of the volume expansion of the inclusion contents upon crushing. This is done by measuring the total volume of the inclusion and its degree of filling before crushing, and the diameter of the gas bubble(s) evolved. These are crude measurements at best, but do serve to indicate that each volume of liquid in the inclusions expands to several hundred volumes of gas (*i.e.*, approximately 6-fold or 7-fold increase in diameter). One of the major sources of error here lies in the difficulty of finding a satisfactory mounting medium. Ideally, it should match the index of the mineral, be able to wet it, be easy to free of bubbles during mounting, be transparent, and not absorb even very minute quantities of CO_2. The mass of the emitted gas bubble is so small relative to the mass of the surrounding liquid that even a very low solubility for CO_2 will permit the bubble to be dissolved in a relatively few seconds.[2] Quantitative measures of volume per cent expansion are best made with glycerine but it is difficult to use. For most work, ordinary index liquids matching the grain were the best compromise.

The process of solution of the evolved bubbles in index liquids gave evidence for the presence of small amounts of at least one other gas in the inclusions. The rate of this solution is complicated by the progressive increase in the ratio of surface to volume and by the increasing distance to be traversed by diffusing gas molecules (including the increase due to collapse of the bubble). For a given gas, however, the rate of shrinkage of bubble diameter increases rather uniformly until finally, at diameters less than a few microns, the exponential rise in surface tension results in a sudden "blinking out" of the remaining bubble. Some of the bubbles evolved on crushing these samples were found, however, to dissolve in the oil rather rapidly down to a given point, and then much more slowly, down to the point where surface tension effects suddenly took over.

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[1] In a few samples strain polarization is visible in the olivine surrounding CO_2 inclusions when viewed in polarized light at the normal extinction positions.

[2] Most of the medium-sized inclusions crushed in this work contain about 1×10^{-11} grams of CO_2. The mass of fluid within a zone only one bubble radius in width, surrounding the bubble, is approximately 4000 times greater than the mass of the CO_2. This fluid can be reached by diffusion through an average distance of only 5 μ.

In most of these, the volume decreased to about 1 per cent of its former value in about 10 seconds, and then an equal or longer length of time was needed for the solution of the remaining small bubble. An acid $BaCl_2$ solution gave similar results, but alkaline $BaCl_2$ solution—a good solvent for CO_2—showed almost instantaneous shrinkage of the bubble ($\sim$0.1 seconds) to the small, less-soluble residue, as would be expected for a CO_2-rich gas.

Some of the samples showed inclusions that appeared empty. Upon crushing in oil, many of these emitted large volumes of gas, indicating that they contained gas under pressure, or that they were completely liquefied gas. Unfortunately, it is not always possible to relate evolved gas bubbles to specific inclusions. This is particularly true for small inclusions, that are usually very numerous, and for hard minerals, that jump about upon crushing. In a few samples, gas bubbles were evolved from apparently opaque inclusions of unknown nature. Many of the samples that showed only a weak evolution of gas had no specific features that could be designated as the source of the gas; these small gas bubbles apparently come from inclusions too close to the limit of resolution of the microscope to be distinguished from the minute solid specks visible in most minerals at magnifications of 1000 or more. High-pressure gas inclusions should liquefy upon cooling, and this has been shown to occur in some suitably shaped inclusions. However, a small amount of low-index liquid in a cavity in a high-index mineral generally is not visible, unless there is a sharp corner that is clearly illuminated (Fig. 20). Conversely, an inclusion of liquid CO_2 without a gas bubble will also appear empty, but will evolve even more gas on crushing.

Chemical analysis of evolved gases. This is the most obvious method, but unfortunately it is the least readily applicable, and the results are ambiguous. The amount of CO_2 present in most nodules, estimated optically from the volume of the inclusions, is so small that large samples must be used. Furthermore, a truly satisfactory extraction procedure has not been found. Most of the attempts at extraction and chemical analysis were made on several dunitic nodules from one Hawaiian sample that showed relatively large numbers of inclusions (ER 63-33a). All adhering basalt was removed, and the nodules were gently crushed to <1 cm. The friable, saccharoidal texture so characteristic of these nodules resulted in the formation of about 30 per cent of fines <1 mm. A 20-gram sample of this mixed material was then further crushed in an iron mortar in a stream of clean dry air under positive pressure. The stream passed through weighing tubes of $MgClO_4$ (for H_2O), and then "Caroxite" and $MgClO_4$ (for CO_2), both before and after the mortar.

Approximately 20 mg of CO_2 was recovered, but a high blank, from several sources, made the analysis suspect. Furthermore, when the crushed sample (mostly <1 mm) was examined in oils, many of the grains were found to contain numerous unopened inclusions.

Preliminary experiments had shown that grains <1 mm, heated in air at 1000° for one day, lost some of the larger inclusions by decrepitation; similar runs for 30 minutes at 1200° C. showed extensive oxidation of the iron in the olivine (unless mixed with graphite dust), but the smaller CO_2 inclusions were still intact, and showed no evidence of leakage. As a result, a series of analytical determinations of the CO_2 evolved on decrepitation in a slow stream of air were made, at temperatures above 1200° C. (Table 1). Pure nitrogen was used in place of air for some runs to preclude oxidation of any form of carbon.[1] A preliminary 1-minute wash with dilute, room-temperature HCl, followed by electrolytic cleaning (Roedder, 1958) was used to eliminate possible carbonate, but appeared to be unnecessary. The samples were held in long fused silica or mullite tubes with fused silica wool plugs, and were heated in a platinum-wound furnace. Small amounts of reaction with the tubes occurred. In each run, the sample was first baked for one or more hours

TABLE 1. ANALYSES OF GASES EVOLVED ON DECREPITATION OF SAMPLE ER 63-33a

Sample weight, grams	Flush gas	Baking temp. °C	Run temp. °C	Estimated decrepitation efficiency per cent	Weight per cent, corrected for decrepitation efficiency	
					H_2O	CO_2
50	Air	180	$\sim$1000	25	0.015	0.035
50	N_2	235	$\sim$1300	50	0.01	0.02
200	N_2	190	$\sim$1300	50	0.01	0.03
50	N_2	270	1530	100[1]	0.015	0.024

[1] Sample was baked at 150° for 1 hour; heated up to 230° over 1 hour; and then held at 230–270° for ½ hour before the run. During this last ½ hour 0.0014 per cent H_2O and 0.0006 per cent CO_2 was evolved (*not* included in the figures above). Of the total amounts shown, 0.008 per cent H_2O and 0.016 per cent CO_2 was evolved in the range 270°–1030°, and the remainder between 1030° and 1530°, at which temperature the sample was liquefied. (Compositions approaching these in the system MgO-FeO-SiO_2 have a liquidus around 1750° C, but the other constituents present, presumably about 10% of the total, lower this greatly.)

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[1] No differences were recognized in the results with the two flushing gases, even though carbon has been reported in such rocks. Craig (1953, p. 80) reports 0.030 per cent C in an Hawaiian olivine basalt, and Hoefs (1965, p. 413) found 0.022 per cent C (and 0.050 per cent CO_2) in a split of nodule sample ER 63-33.

at the indicated temperatures, with continous flushing at 150 cc/min.

Examination under the microscope after the runs showed that even 20 minutes at 1300° C. (measured with Pt/Pt-10Rh thermocouples) did not cause complete decrepitation of the smaller inclusions. Hence the analytical results must be corrected to obtain the true total CO_2 (and H_2O) in the inclusions. This correction is based on the crude optical estimate of the efficiency of decrepitation. In the last analysis shown in Table 1, the sample melted and dissolved a portion of the mullite tube, so a 100 per cent extraction efficiency is assumed. Considering the apparent volume per cent of inclusions in this sample, the amount of CO_2 found by analysis is of the right order of magnitude.

Other than complete fusion, vacuum ball milling to a very fine grain size (Goguel, 1963) is perhaps the only valid procedure for extraction. Using this method, Goguel (1965) found 0.0050 per cent CO_2 in a nodule from Kassel, Germany (the same locality as ER 64-27), and he reports 0.00024 and 0.00026 per cent CO_2 in two other nodules (1963), but with the ratio H_2O/CO_2 several orders of magnitude higher than that of Table 1.

Water is rather insoluble in liquid CO_2 (Stone, 1943), and if present in the inclusions it would be expected to form a separate liquid phase. Since water is a polar liquid, the liquid CO_2 is not, when both phases are present in an inclusion the water phase clings to the mineral walls, and the CO_2 liquid surrounds the central gas bubble. Only one sample was found in which liquid water could be seen in the inclusions (Figs. 13,14).

As the analyses (Table 1) show that about one half as much water as CO_2 is evolved, yet neither liquid water nor hydrous minerals of any sort were visible in these particular nodules, it is presumed that a part of the water obtained may be present in the inclusions as invisible films on the walls (Roedder, 1963, p. 187). Additional water may be present in the basaltic glass inclusions, and as firmly bonded surface water on the olivine that is not removed by baking at 250° C. Such adsorbed surface water may be very difficult to remove. Kunkel (1950) found that well-cleaned quartz surfaces normally have one or two layers of water molecules that are not released by heating under 500° C. These ambiguities in the water analysis may be resolved by extraction with vacuum crushing of carefully prepared grains in a mass spectrometer system.

Thermal expansion. Ever since the careful work of Brewster (1823) on the thermal expansion of a "remarkable new fluid found in the cavities of rocks" (later shown to be liquid CO_2), it has been known that this liquid has a very high coefficient of thermal expansion. By measuring the gas/liquid ratios in these inclusions at several temperatures, using a vernier micrometer ocular, a crude value can be obtained for the coefficient of expansion. The precision of this calculation depends strongly on the inclusion shape and optical quality, and is seldom good, but a few very regular inclusions did permit fair approximations to be made. Thus sample ER 63–119, from Gila County, Arizona, showed a large inclusion with liquid exhibiting an expansion of over 9 per cent in volume on changing from +4° C. to +18.2° C., in fair agreement with published data on CO_2 (Quinn and Jones, 1936, p. 58).

This high thermal expansion of CO_2 liquid can also make the recognition of CO_2 liquid more difficult. In a number of the samples studied, nothing but apparently empty "gas" inclusions were seen. On checking a few of these "gas" inclusions by cooling to below room temperature, some were found to develop a shrinkage vapor bubble, *i.e.*, the "gas" was really CO_2 liquid. This occurred at temperatures as low as $+3.24° \pm 0.08°$ C. (ER 63–144 from Derbyshire).

Although the microscope freezing stage (Roedder, 1962) was used for much of the work, this temperature range can be obtained and controlled easily by much simpler means. The thin section (or even liquid immersion oil mount) is merely hung on a wire sling just under the surface of water in a flat-bottomed glass dish on the stage. Temperatures, read on a thermometer, are controlled by small additions of hot water or ice. Equilibration is obtained rapidly by pumping the water with a rubber ear syringe. Surface waves from vibration are minimized by a shallow ring placed over the slide.

Phenomena on cooling can also be observed, qualitatively, by evaporating a drop of acetone on the slide. For lower temperatures one may hold against the slide a thin washer of copper with blotting paper on its upper surface. The blotter is wet periodically with a few drops of ethyl chloride from a normal medical spray dispenser and observations are made through the hole in the washer. Lower temperatures may be obtained by a direct ethyl chloride spray, or contact with dry ice, but the film of acetone needed to minimize frosting prevents good visibility.

Critical phenomena. Carbon dioxide has a critical point at 31.0° C., and the available data on the two-phase field show it to be very broad and flat on top (Fig. 1). As a result, inclusions of CO_2 with a fairly wide range of filling densities will exhibit "critical" phenomena experimentally indistinguishable from true critical phenomena obtainable only with inclusions having the critical filling density (0.468 g/cm^3, Kobe and Lynn, 1953). The inclusions in the minerals of the nodules show a range of properties consistent with the assumption that they are essentially pure CO_2. Some were cooled to known temperatures in a range where the

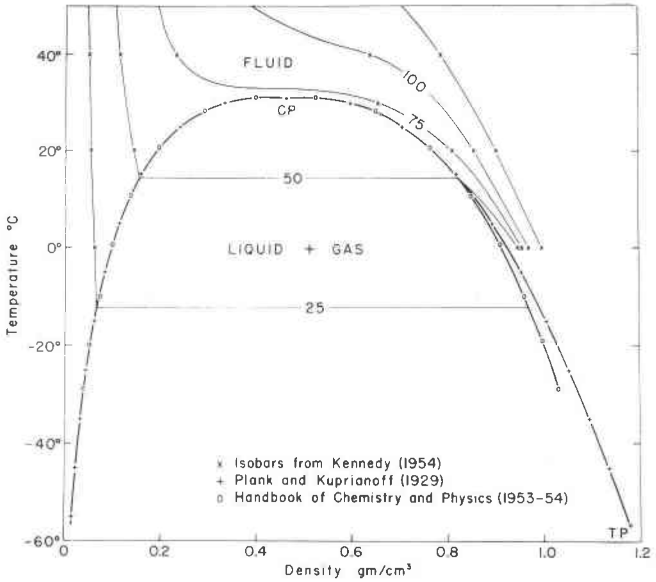

FIG. 1. Two-phase field in the system CO_2.

densities of the phases are relatively insensitive to temperature (*e.g.*, $<20°$ C.) and the volumes of the two phases were measured. The total (average) density was then calculated, assuming both the liquid and gas to be pure CO_2. Those inclusions with a density well under 0.468 g/cm³ homogenized, on heating, in the vapor phase—all the liquid evaporated to form gas—at temperatures less than but near to 31°;[1] those with filling densities well over 0.468 homogenized in the liquid phase—the liquid expanded to eliminate the gas phase—at similar temperatures. Those inclusions near to 0.468 in filling density homogenized with apparent critical behavior, at temperatures within 0.1° of 31° C. The specific behavior of individual inclusions in this third group was erratic, as is to be expected from the very slight curvature of the top of the two phase field, and the problems of precision temperature control (see following section). This critical temperature is very specific for CO_2. Among common substances, only acetylene (36°), ethane (32.1°), and nitrous oxide (36.5°) are near it. Other gases, that might be found in a volcanic environment, are either far below or far above it (*e.g.*, $N_2-147°$; $CO-139°$; $CH_4-82.5°$; and $HCl+51.4°$; $H_2S+100.4°$; $SO_2+157.2°$; and $H_2O+374°$ C.). Mixtures of any of these with CO_2 would generally exhibit critical phenomena at tem-

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[1] Only one exception was noted: ER 63-138a, from Hoher Hagen, Germany, homogenized at 31.65±0.05° C. (Fig. 8).

peratures intermediate between those for the constituents. Although liquid water may be present in these inclusions, it is not very soluble in liquid CO_2 (Stone, 1943, reports about 0.1 per cent at 22°), and hence should have little effect. H_2S, HCl and SO_2 all have strong odors, but no odors were detected on crushing large samples of the nodules in air.

Infrared absorption. Although CO_2 liquid and gas are both transparent and colorless in the visible spectrum, they show strong absorption in the infrared (see Plass and Stull, 1963). It was found that two-phase CO_2 inclusions could be made to homogenize in two ways, either by simple warming of the slide, or by increasing the intensity of the microscope lighting.[1] In fact, it was possible to adjust the size of the bubble rather closely by adjusting either a substage diaphragm or the voltage to the light source. When adjusted so that the inclusion just stays homogeneous, an interruption of the light beam for as little as 0.1 second will cause momentary heterogenization. When an infrared-absorbing ("heat-absorbing") filter was placed in the light path, a much higher intensity light was needed to cause homogenization. Olivine is rather transparent in the infrared (Duke and Stevens, 1964), and hence heating of the whole mineral plate by the light is probably not significant. This is corroborated by the fact that inclusions in 3 mm thick polished plates seemed to react just as fast as those in 0.030 mm thin sections.

Infrared absorption in the inclusions has some significance in the practical problem of searching for them. In order to see detail inside most CO_2 inclusions in olivine, rather bright light, a high-power sub-stage condenser, and a magnification of at least 300 are needed. Under these conditions, unless the stage of the microscope is rather cool and an efficient infrared filter is used, the inclusions will appear gas-filled. It also has significance in any accurate filling (homogenization) temperature determinations. By absorption the inclusion is warmed slightly relative to the surrounding mineral, and the circulating bath. Thus normal illumination, without filters, may give an apparent homogenization temperature that is several tenths of a degree low, and intense illumination gave homogenization temperatures as much as 1.28° lower than was obtained with low illumination, plus effective infrared filters. The temperature differences vary with the size of the inclusion. If a reasonably good filter is used, the light intensity is significant only in precise determinations in the vicinity of the critical point, where very minor differences in the thermal regime in the neighborhood of the inclusion may have considerable effects. Thus individual inclusions have been found, with near to critical density of

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[1] This was first reported, for CO_2 inclusions in pegmatitic beryl, by Cameron *et al.*, 1953.

filling, that homogenize in the gas phase *or* by fading of the meniscus, depending on how the heating with the light is applied. In addition, absorption of all light by an opaque grain in a CO_2 inclusion can cause localized boiling of the CO_2 liquid.

SPECIFIC OCCURRENCES EXAMINED

Samples, mainly nodules, containing recognizable liquid CO_2 inclusions. Recognizable liquid CO_2 inclusions were found in nodules from 64 localities summarized in Table 2; details on each sample, including available information on specific location, source, nature of the occurrence, rock type, appearance of the inclusions, mineral host, and homogenization behavior and temperatures are given in Table 3A.[1] Inclusions of liquid CO_2 were also found in apparent phenocrysts of olivine, titanaugite, and oxyhornblende in the basalt of nine of the samples listed in Table 3A.

Olivine-bearing nodule samples possibly containing CO_2 inclusions. In addition to the 64 localities mentioned above, the nature of the available sample material from 8 other nodule localities, listed in Table 4, precluded positive identification of CO_2 inclusions. In each of these, however, the presence of high-pressure gas inclusions, presumably also CO_2, is inferred from (1) the presence of glass inclusions with large and highly variable glass/gas ratios; (2) the presence of apparently all-gas inclusions; and/or (3) the evolution of gas bubbles on crushing in the microscope crushing stage. Details on the evidence found in samples from these localities, plus additional samples in this same category from localities identical or nearly identical with those listed in Tables 2 and 3A, are given in Table 3B.

The presence of even a single liquid CO_2 inclusion a few microns in diameter is just as significant, in terms of its chemical and physical environment of formation, as a large number of them. On the other hand, the inclusions are so irregularly distributed and rare in some of the nodules that completely negative results on the search of a single slide or plate cannot be considered to be valid proof of their absence at that locality. The frequency of occurrence of recognizable CO_2 inclusions in the

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[1] In order to save space, the bulk of the supporting data for this paper, assembled as Tables 3A, 3B, 3C, and 3D, consisting of 20 pages, has been deposited as Document No 8547 with the American Documentation Institute Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C.

A copy may be secured by citing the Document number and remitting $2.50 for photoprints, or $1.75 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress, Washington 25, D. C., U. S. A.

TABLE 2. OLIVINE OCCURRENCES CONTAINING RECOGNIZABLE LIQUID CO_2 INCLUSIONS. ALL ARE OLIVINE-BEARING NODULES EXCEPT AS NOTED. DETAILS IN TABLE 3A

Hawaii	1801 Kaupulehu flow, Hualalai; cinder cone near Halepohaku, and cinder cone high on Mauna Kea, and 1950 Ohia Lodge flow, Mauna Loa, Hawaii. Koloa lavas, Hanapepe stream; and Kapohakukilomanu stream, Kauai. Salt Lake Crater, Oahu.
Germany	Hoher Hagen, Göttingen; Westberges, near Hofgeismar; Hirzstein, Kassel; Dreiser Weiher, Eifel; Mosenberg, near Manderscheid (phenocrysts?); Unkel, Prussia.
Austria	Kapfenstein, Styria.
New Zealand	Tokatoka, N. Auckland; Todd's quarry, Arapohue, Northland; Ngatutura Point, Ohuka; Port Waikato; Roose's quarry, Bombay; Kirikiripu, Raglan; Waterbox quarry, Raglan; Stevenson's quarry, Auckland; Lake Pupuke, North Shore, Auckland; Smale's quarry, Onepoto Basin; and Shoal Bay. Dunedin; Lake Waihola, E. Otago; Mt. Dasher; Swinburn Survey District; Wilkinson's Hill, Nenthorn Valley, E. Otago; Kakanui; and Kokonga, Otago.
Japan	Taka-sima, N. Kyushu; Ichinome-gata, Akita.
Antarctica	Mt. Bird region, Ross Island; Hut Point, McMurdo Sound (xenocrysts (?) of olivine; phenocrysts of titanaguite); Mount Marajupu; Peaks 118 and 118A, Raymond Fosdick Range.
Pacific	Isla de Guadalupe, NE Pacific
Virginia	Mole Hill, Harrisonburg (xenocrysts?)
Texas	Knippa quarry, Uvalde.
New Mexico	Kilbourn's Hole, 30 miles NW of El Paso, Texas.
Arizona	Rice Station, and Globe City, Gila County; Mount Trumbull, Mohave County.
Nevada	Black Rock Summit, Nye County.
Montana	Bearpaw Mtns.
California	Ludlow, and Bagdad, San Bernardino County.
Mexico	Camargo, Chihuahua.
Ethiopia	Mega.
Australia	Delegate, Armidale, MacAlister Trig. Sta., Drogheda Trig. Sta. Oberon, Rawdon, Bulli, Nandewar Mountains, and Dundas quarry, Sydney, N. S. W.; Camperdown, and Mt. Leura, Victoria.

Table 2—(*continued*)

Canada	Timothy Mountain, B. C.
Nigeria	Durumi, Ropp Hills.
Morocco	Timahdit, Azrou.
England	Calton Hill, Derbyshire.
South Africa	Wesselton diamond mine (kimberlite pipe).
Indian Ocean	Kerguelen Archipelago.
Tasman Sea	Lord Howe Island.

various minerals gave no useful guidelines in this search. In some the pyroxenes had abundant inclusions and the olivine had few; in others this was reversed. CO_2 inclusions were seen in plagioclase from only a few localities, but comparatively little plagioclase was found in the samples examined. Although a few dark inclusions, possibly gaseous, were seen in some spinel grains, the still higher index of refraction, and the much smaller *volume* of spinel studied (as much thinner plates are needed for transparency) would make the discovery of recognizable CO_2 inclusions unlikely. Similar possibly gaseous inclusions were seen in the garnets of the eclogite nodules examined.

Table 4. Additional Olivine-Bearing Nodule Occurrences Possibly Containing CO_2 Inclusions. Details in Table 3B

Morocco	Timahdit, Azrou.
Austria	Kapfenstein, Styria.
Iceland	Lake Graenavatn
Australia	Bombo quarry, Wallabadah, and Sherbrook, New South Wales.
New Zealand	The Hummock, Mt. Stoker district; Kokonga, Central Otago; Saddle Hill, E. Otago; and Trig. L, Swinburn S. D., E. Otago.
Texas	Knippa quarry, Uvalde.
Alaska	Imuruk Lake, Seward Peninsula.

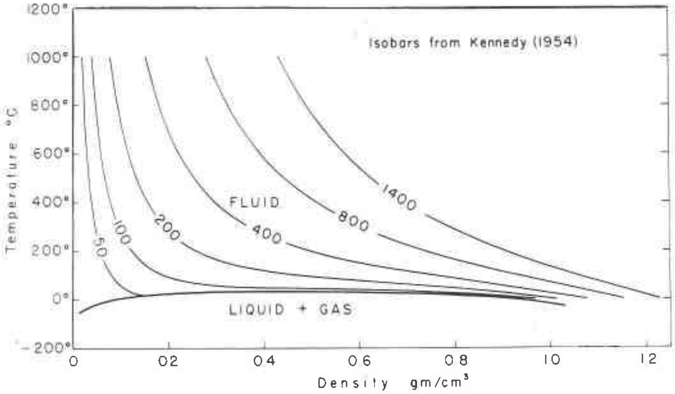
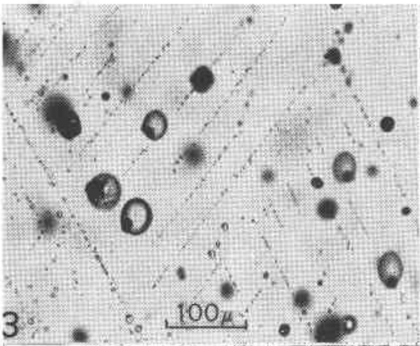


FIG. 2. High-temperature P-T data on the system CO_2.

Other igneous rock occurrences possibly containing CO_2 inclusions. In addition to the occurrences of olivine nodules, a series of olivine-rich and ultramafic rocks from a variety of occurrences were examined for CO_2 inclusions. Samples from 31 localities, summarized in Table 5 and detailed in Table 3C, showed evidence, similar to that described above, of high pressure gas inclusions. Ten other localities (Tables 3D and 6) showed no evidence of CO_2 inclusions, but such negative evidence is not conclusive. This work indicates merely that gas inclusions are present in many mafic igneous rocks, but does not prove that the gas is CO_2 or that the rocks are related genetically. The volumes of gas released on crushing were generally small.

INTERPRETATION AND SPECULATION

Origin of the inclusions—primary vs secondary. There is little doubt as to the secondary origin of the inclusions that occur on curving surfaces through grains, particularly where their size grades downward from the surface of the grain to the end of the healed crack (Fig. 6, 8, 9). Also, those planes of inclusions that cut across grain boundaries obviously are secondary. Planes of vermicular glass plus CO_2 inclusions outlining fractures (Fig. 8) may be the precursors of the planes of sharply euhedral inclusions (Figs. 9, 17). It is difficult to visualize an environment surrounding the crystal at the time of fracturing that will result in the trapping of a mixture of dense CO_2 and silicate melt such as Fig. 8, or almost all CO_2 (Fig. 9), but this is a fairly common phenomenon in the minerals of nodules. Very similar arrays of two-phase secondary inclusions occur in southern Illinois fluorite crystals which fractured while immersed in an immiscible mixture of droplets of oil in brine (Roedder, 1965, Fig. 19).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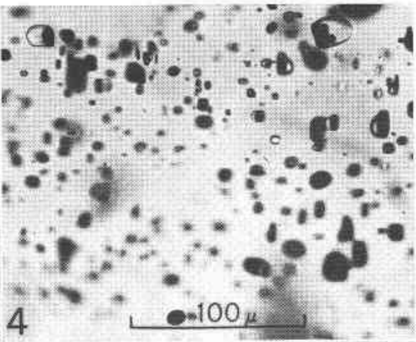
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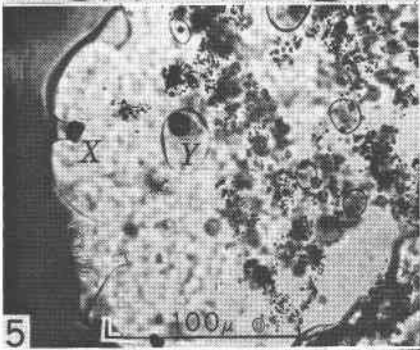
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X
Y
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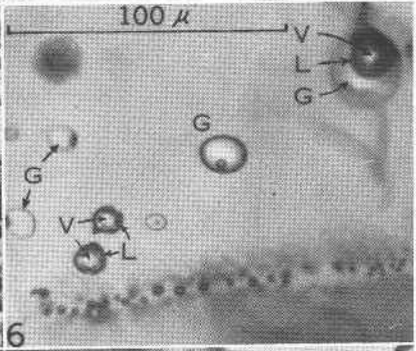
6
100 μ
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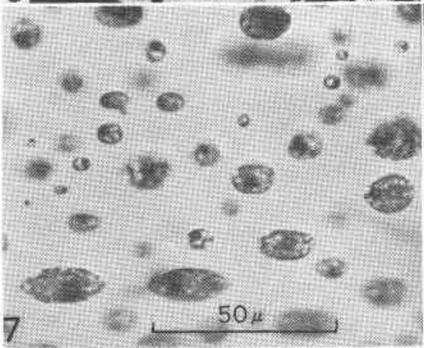
L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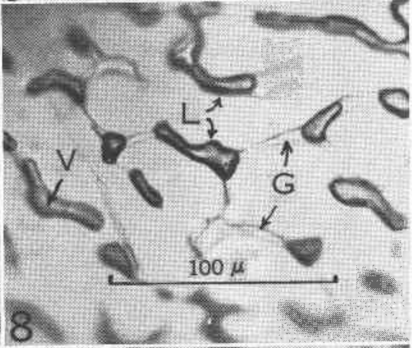
50μ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V
G
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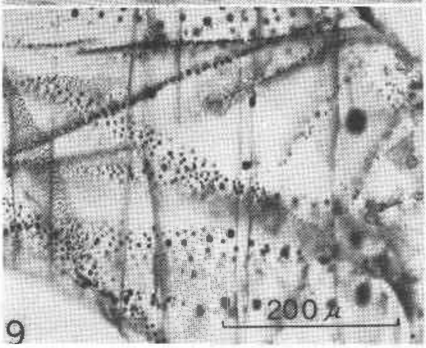
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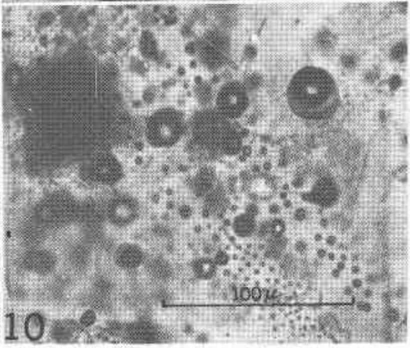
200μ


10
100μ

Although most of them are apparently secondary, the features of some CO_2 inclusions almost completely preclude any origin other than primary. Apparently at one stage in the growth of some of these olivine crystals, spinel (?) crystals nucleated and grew on their surfaces in a partially epitaxial array (Figs. 4, 5, 13, 19, 23). Growth of the olivine covered some of these spinel crystals, enclosing them perfectly. Others were enclosed imperfectly, trapping some of the surrounding silicate fluid, and additional growth irregularities in some crystals trapped silicate fluid without spinel. Any inclusion that had enough silicate fluid ($>\sim 4\ \mu$), and cooled slowly enough to nucleate a "gas" phase, now has a small bubble in the glass. The volume of this bubble is a measure of the differential shrinkage between the glass and the olivine, over some unknown temperature interval between the temperature of trapping and the temperature at which the glass would no longer flow enough to permit further expansion of the bubble under the particular cooling history involved.[1] Available data

[1] These bubbles apparently form during eruption, as they seem to be random in distribution within their inclusions. If they formed during slow cooling under static conditions, they would be expected to show a preferential positioning in response to gravity.

FIG. 3. Primary glass inclusions arranged as a "ghost" inside olivine phenocryst[1] from basaltic cinder cone, South Point, Hawaii (ER 63-79).

FIG. 4. "Ghost" of crystals, presumably spinel, in epitaxial array on former growth surface inside olivine phenocryst; many have caused the entrapment of primary glass inclusions. Same locality as Fig. 3.

FIG. 5. Portion of phenocryst of olivine in dark, partly crystallized glassy submarine basalt flow near Hawaii, from depth of 9700 feet (ER 63-14). Shows many spinel (?) inclusions (dark specks), one of which is about to be enclosed (X), and several glass inclusions, one of which has a large gas/glass ratio (Y), indicating trapping of primary gas bubble.

FIG. 6. Isolated, presumably primary inclusions of glass (G) with small shrinkage bubble and opaque daughter mineral, and two liquid CO_2 inclusions (L) showing characteristic dark borders and large, faint, rapidly-moving vapor bubble (V). Inclusion in upper right shows all 3 phases; CO_2 in it homogenizes in the gas phase at $30.91\pm0.02°$ C. Plane of secondary CO_2 inclusions across bottom. 1801 flow of Hualalai, Kaupulehu, Hawaii (ER 63-33a).

FIG. 7. Plane of secondary glass inclusions crystalized to granular mass. Small shrinkage bubble in each. Nodule from 1950 lava of Mauna Loa, Hawaii (ER 63-89).

FIG. 8. Typical partially healed fracture containing glass (G)+CO_2 (L), in process of necking down to form individual secondary inclusions. One faint CO_2 gas bubble is visible (V); this inclusion homogenizes in the gas phase at $31.65\pm0.05°$ C., indicating that constituents other than just CO_2 are present. Hoher Hagen, Göttingen, Germany (ER63-138a).

FIG. 9. Grain, mounted in resin of n-1.67, showing numerous planes of sharply-faceted secondary CO_2 inclusions. See also Fig. 17. Same sample as Fig. 6.

FIG. 10. High concentration of CO_2 inclusions, up to 3 volume per cent. Some also contain glass. Same sample as Fig. 6.

[1] All photomicrographs are of single crystals of olivine from nodules, unless otherwise noted.

TABLE 5. OTHER IGNEOUS ROCK OCCURRENCES POSSIBLY CONTAINING CO_2 INCLUSIONS. ALL PHENOCRYSTS ARE OF OLIVINE, EXCEPT AS STATED. DETAILS IN TABLE 3C

Cyprus	Troödos massif (phenocrysts? in basalt).
Australia	Stony Creek, N. S. W. (phenocrysts in basalt).
New Zealand	Dun Mountain (dunite).
Arkansas	Murfreesboro (kimberlite).
North Carolina	Webster (dunite, websterite, and enstatite).
New Mexico	Cabezon (phenocrysts in basalt).
Washington	Twin Sisters Mountains (dunite).
Hawaii	Kilauea Iki lava pond (phenocrysts), submarine flow from 9700 feet depth (phenocrysts), South Point (cinder cone).
Kentucky	Ison Creek (kimberlite diatreme).
Montana	Shonkin Sag laccolith (olivine and pyroxene phenocrysts); Stillwater Complex (olivine).
Maine	Greenville (troctolite).
Idaho	Snake River basalts.
California	S. California batholith (olivine norite).
Belgian Congo	Lueshe carbonatite.
South Africa	Bushveld complex, dunite and pyroxenite from Mooihoek, Zwartfontein, and Forest Hill platinum mines; kimberlite from DeBeers, DuToitspan, and Wesselton diamond mines.
Atlantic Ocean	St. Paul Rock.

(Birch *et al.*, 1942) on the thermal expansion of basalt liquid and olivine, and the opposing but lesser difference in the compressibilities of the two, indicate that this bubble should be on the order of a few volume per cent, in agreement with a number of measurements of actual inclusions.

During the trapping of both primary and secondary glass inclusions, however, there were small droplets of another, immiscible fluid in the silicate fluid—microscopic globules of dense, supercritical CO_2. Some of these attached themselves to the olivine surface; others seemed to adhere preferentially to the spinel plates. In both, later growth of the olivine

TABLE 6. OTHER IGNEOUS ROCK OCCURRENCES APPARENTLY FREE OF CO_2 INCLUSIONS. DETAILS IN TABLE 3D

Italy	Vesuvius 1944 and 1858 leucite basalt flows.
Idaho	Snake River basalts.
North Carolina	Addie (dunite).
California	Siskiyou County (dunite).
Oregon	Elk Creek (picrite basalt).
South Africa	Kimberley mine (kimberlite); and Bushveld complex, Onverwacht platinum mine (dunite).
Hawaii	Kilauea (plagioclase phenocrysts in pumice; olivine phenocrysts in Pele's tears).
Germany	Fichtegebirge, and Silberbach (eclogite).

covered them, also trapping much silicate fluid inside some, and only a film in others. Thus the variable ratio of gas bubble to glass to spinel depends upon the existence and size of CO_2 bubbles that were trapped along with the silicate liquid and spinel. The enclosure of minerals other than spinel by olivine or pyroxene, either growing epitaxically or incidentally trapped, also led to the simultaneous trapping of primary CO_2 inclusions (Figures 11 and 12).

The shape of some primary all-CO_2 inclusions (*e.g.*, USNM 96584, Nigeria) appears to be as originally trapped, and it may well be that all rounded CO_2 inclusions (*e.g.*, Fig. 23) have maintained their original droplet shape.[1] With time, the walls of some of the CO_2 inclusions recrystallized, presumably via the enclosed silicate fluid, to form sharply euhedral negative crystals, either primary or secondary (Fig. 17). On cooling to temperatures below 31°, those inclusions with a sufficiently dense fluid CO_2 phase separated into liquid and gas.

One problem in the assignment of a primary origin to those CO_2 inclusions attached to opaque spinel(?) plates is the occurrence of apparently similar oriented opaque plates along part of the walls of some secondary inclusions (*e.g.*, Figs. 9, 17). Such plates must be daughter minerals that grew in an oriented array on the walls of the fracture, and were part of the

(Text continued on page 1768)

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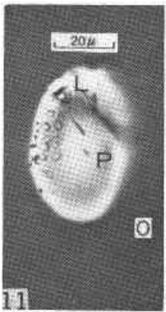
[1] A number of apparently primary CO_2 inclusions from several localities show peculiar spines (*e.g.*, Fig. 21). These spines are of unknown origin and composition; they may be merely thin plate-like or tubular extensions of CO_2. They are generally elongated $\perp$ {100} of the enclosing olivine.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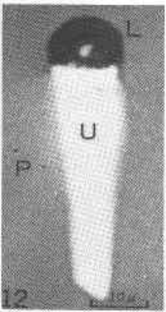
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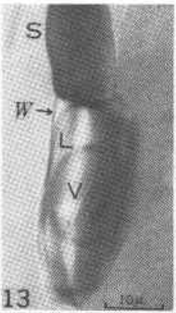
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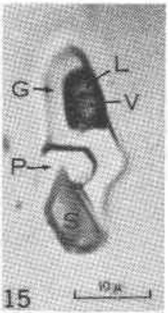
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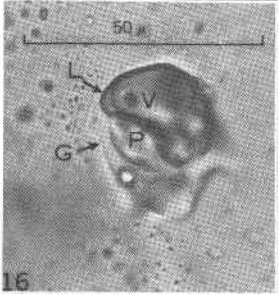
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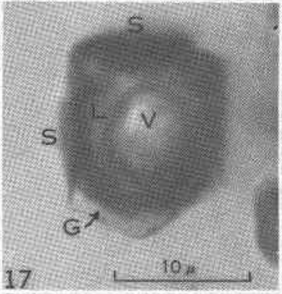
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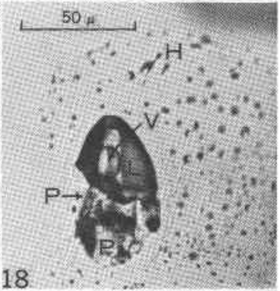
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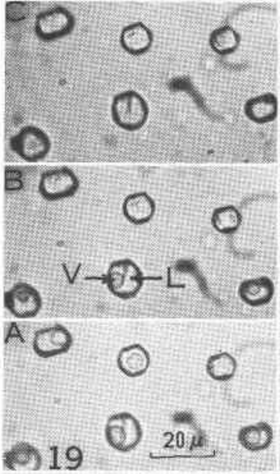
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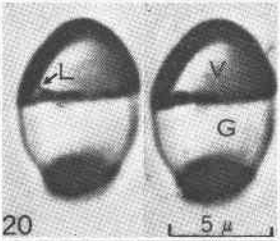
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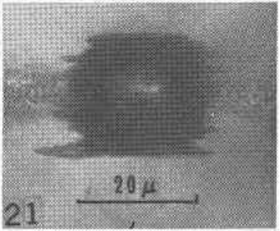
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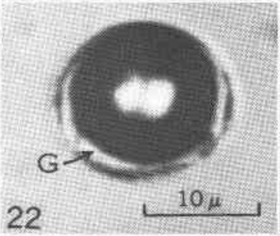
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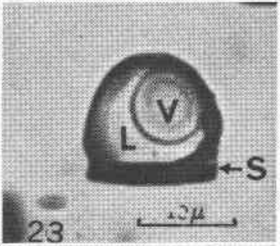
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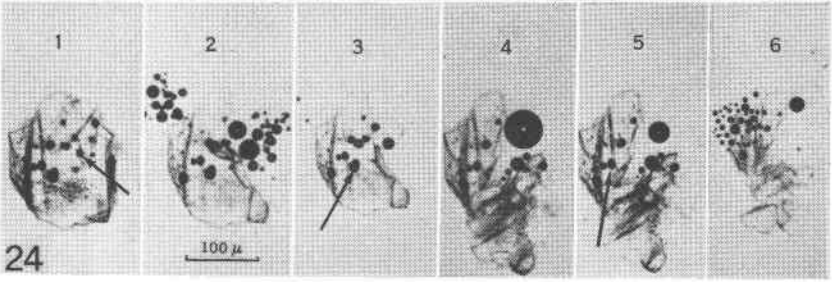
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FIG. 11. Primary CO_2 inclusions trapped at interface between embedded crystal of pyroxene? (P) and surrounding olivine (O). The largest inclusion (L) shows a circular bubble of vapor in liquid CO_2; its homogenizes in liquid phase. Partially crossed nichols. Ngatutura Point, Ohuka, N. Zealand (ER 64-171).

FIG. 12. CO_2 inclusion (L) attached to end of unknown crystal (U) embedded in pyroxene (P). A number of these embedded crystals, many with such CO_2 inclusions covering their larger ends, are arranged in parallel throughout the pyroxene, and although unconnected, exhibit uniform, inclined extinction. Their index of refraction is only slightly greater than the host, hence partially crossed nichols were used for this photograph. Presumably the embedded crystals grew simultaneously with the host, but their growth was stopped by preferential adherence of CO_2 blebs to their exposed terminations. Isla de Guadalupe, NE Pacific (ER 63-128).

FIG. 13. CO_2 inclusion attached to spinel grain (S) in orthopyroxene from olivine nodule from Ichinome-gata, Japan (ER 65-8). Many elongated spinel crystals lie parallel to an extinction direction of the pryroxene, and such CO_2 inclusions are attached to many. V—gaseous CO_2; L—liquid CO_2; W—liquid water. This sample contains the only recognized water in all the nodules examined. The high CO_2/H_2O ratio is apparently constant throughout the sample (See also Fig. 14).

FIG. 14. Same grain as Fig. 13. This CO_2-H_2O inclusion was trapped apparently without a spinel crystal. On the freezing stage the H_2O and CO_2 reacted to form the hydrate $CO_2 \cdot 5\frac{3}{4}H_2O$ (Roedder, 1963, p. 188); it melted at $+10.1 \pm 0.2°$ C.

FIG. 15. Inclusion containing isotropic high index brown spinel crystal (S); birefringent colorless crystal, presumably of pyroxene, with *n* about equal to enclosing olivine, (P); glass (G); liquid CO_2 (L); and gaseous CO_2 (V). Homogenizes in the liquid phase. From an olivine phenocryst (xenocryst?) in olivine leucite nephelinite, Mosenberg, West-eifel, Germany (ER 64-123).

FIG. 16. Large inclusion (32 μ) of glass (G) in olivine, containing at least three birefringent crystals (only one, P, is in focus), and a large low-density CO_2 bubble, now containing only a little liquid CO_2 (L) in gaseous CO_2 (V). Homogenizes in the gas phase. Brewsters Road Quarry, Bombay Hills, New Zealand (ER 64-161).

FIG. 17. Faceted secondary inclusion from grain in same sample as Figure 6. This inclusion was one of a series outlining a healed fracture similar to those shown in Figure 9. Opaque plates, possibly of spinel (S) line cavity, but the recrystallization has occurred through the glass (G). Most of the inclusion is filled with liquid (L) and gaseous (V) CO_2.

FIG. 18. Presumed primary inclusion of numerous birefringent crystals (P), possibly with glass, and liquid (L) and gaseous (V) CO_2, homogenizing in the liquid phase. A halo of tiny inclusions (H) surrounds the central inclusion, presumably indicating fracturing and partial leakage during pressure drop on ascent. From an olivine phenocryst (xenocryst?) in olivine leucite nephelinite. Same sample Fig. 15.

FIG. 19. Serial pictures during homogenization run, showing appearance of flat CO_2 inclusions at various temperatures: A, +30.50°; B, +30.70°; C, +30.72°. Just below the homogenization temperature (B) the vapor bubbles (V) in each are only slightly different in indexes of refraction than the liquid CO_2 (L), and exhibit very rapid Brownian movement. The straight, parallel sides of the inclusions may consist of tiny plates like Figs. 17 and 23. Same sample as Fig. 6.

FIG. 20. Inclusion of glass (G, with opaque bleb) and low-density CO_2 gas (V) at two temperatures. On cooling, (at left) a small fillet of liquid CO_2 forms (L). Ludlow, California (ER 63-73).

FIG. 21. CO_2 inclusion with unexplained "spines." Although this is in a pyroxene

fluid that entered it. This would not invalidate the other criteria for primary origin, applied to other inclusions.

Pressure at the time of formation. The present phase ratio of liquid CO_2 to gaseous CO_2 can be estimated, from vernier micrometer ocular measurements on flat or geometrically regular inclusions, at known temperatures. The density of filling of the cavity can then be calculated from the available data on phase densities in the system CO_2 (Fig. 1), neglecting the apparently small amount of other gas or gases present. Many of the inclusions studied showed filling densities of 0.7 to 0.8 gm/cm^3 and some were as high as 0.89 gm/cm^3. The homogenization behavior provides a check on these calculated densities. Thus inclusions with a calculated filling density of 0.77 homogenized in the liquid phase at about +20°, and the most dense one found, in sample ER 63–144, from Calton Hill, Derbyshire, homogenized at $+3.24 \pm 9.08°$ C.[1]

Once the density is obtained, the approximate pressure at the time of trapping can be determined. Data on densities in the system CO_2 are known up to 1000° C. and 1400 bars (Kennedy, 1954; see Fig. 2). As the majority of basaltic lava temperatures are probably between 1100° and 1200° (as measured on tholeiites at Hawaii), and as it is unlikely that gross changes in temperature either way occurred during ascent and eruption, the probable temperature of trapping of these inclusions was also about this same range. Although the intersection of the measured densities of inclusions with the 1200° line on Fig. 2 lies well beyond

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[1] At room temperature this looked like an empty "gas" inclusion. Most of the samples were not examined at such low temperatures, so there may well be other such high-density all-liquid CO_2 inclusions.

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crystal from an nodule, many similar inclusions are seen in olivine. Camargo, Mexico (ER 63-55).

FIG. 22. Gas inclusion with thin film of glass (G), in olivine phenocryst from basalt surface crust of Kilauea Iki lava lake, Hawaii. Most but not all of these show a vacuum on crushing (ER 63-86).

FIG. 23 Typical hemispherical inclusion of CO_2 liquid (L) and vapor (V), attached to flat opaque plate, presumably of spinel (S), crystallographically oriented in the enclosing olivine. Homogenizes in the liquid phase at $30.40 \pm 0.02°$ C. Same locality as Fig. 6 (ER 63-32Z).

FIG. 24. Serial photographs of an olivine grain, embedded in oil of *n*-1.64, on the crushing stage. Pressure was applied, causing cracking, between frames 1 and 2, 3 and 4, and 5 and 6. The explosively evolved bubbles come from the inclusions indicated in frames 1, 3, and 5. One minute elapsed between taking frames 2 and 3, and between 4 and 5. Same locality as Fig. 6.

Kennedy's experimental data, it seems reasonable to extrapolate, graphically, to obtain at least the order of magnitude of the pressures at the time of trapping. The pressures obtained in this manner, 2500 to 5000 bars, require approximately 8 to 16 kilometers of overlying magma or rock column. As long as the assumption as to temperature is valid, the pressure for each inclusion, *at the time of its trapping*, could not have been greater *or* lesser, unless partial leakage occurred later.

There is considerable evidence that leakage of some inclusions has occurred: (1) the nodules are usually very friable, and many planes of empty inclusions that probably contained CO_2 originally are now transected by visible fractures; (2) some large primary inclusions still containing CO_2 show a short crack out into the olivine, into which part of the contents of the inclusion (glass, etc.) has been pushed, without rupturing the surrounding crystal (Figs. 16, 18);[1] (3) the largest inclusions ($>30\ \mu$) are frequently empty; and (4) commonly, the lava surrounding the nodule is partially separated from it by a layer of gas vesicles. As olivine phenocrysts in the same lavas generally do not have attached gas bubbles, it is assumed that these vesicles represent gas evolved from the nodules, rather than merely collected from the lava. Gas bubbles were found to be attached to olivine crystals in the basalt of only one sample, ER 63–169 from Antarctica. These olivines have other indications of xenocrystic origin, however, so this gas also may have come from inclusions in the olivine. Gas evolution from nodules may be of considerable help in disaggregating and dispersing the nodules during the ascent of the lava.

Individual presumably primary CO_2 inclusions occurring in groups normally give rather consistent homogenization temperatures, corresponding to a uniform density of fill and hence pressure of trapping, but secondary ones are not consistent. There is an indication that secondary inclusions may have a lower degree of fill than primary inclusions in the same sample, but so few inclusions can be proven to be primary that this relationship is not certain. It is very possible that the secondary inclusions formed *during* the ascent. At that time the pores of the nodules were filled with basalt melt and bubbles of CO_2 evolved from the decrepitation of inclusions formed at greater depths. The bubbles would be under the ambient hydrostatic pressure, and any healing of a new fracture in the nodule minerals would trap such a mixture. Since the pressure in any inclusion at constant temperature (after enclosure) remains essentially constant during the ascent, it is probable that the CO_2 inclusions we see now, both primary and secondary, are a biased sample of those originally

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[1] Apparently the fracture propagates only far enough to relieve the internal pressure, by placing more olivine under maximum compression, thus increasing the cavity volume.

present, as those with higher filling densities, formed at greater depths, would be the first to decrepitate. Thus the pressure estimates made may be correct for the sealing of those inclusions, but are minimum values for the sample as a whole.

It is also obvious that the higher pressure inclusions would be the first to be opened by deformation. Ernst (1935) has shown that nodules from a number of European localities (including two represented in the present study, Dreiser Weiher and Hoher Hagen, Germany) are strongly deformed. Visible liquid CO_2 inclusions were generally not found in the sheared portions of the nodules. A series of dunite and other ultramafic igneous rocks were found to contain gas inclusions (presumably CO_2) under pressure (Tables 3C and 5), but the tectonic fabrics of such rocks (Turner, 1942; Thayer, 1963) suggest that if CO_2 had been present, much of it would have been lost during shearing deformation. As expected, very little gas was evolved from the sheared rock samples.

High-temperature tensile strength of silicates. Those inclusions that do not decrepitate on eruption at the surface (at about 1200° C.) have been exposed to one atmosphere external pressure while holding 2500–5000 atmospheres internal pressure. This fact, plus the verification by laboratory heating experiments described above, can be used to place a crude minimum on the ultimate high-temperature tensile strength of the enclosing minerals. With the assumption that these small "pressure vessels" behave as infinitely thick walled containers, the tensile stress in the walls should be approximately equal to the internal pressure, *i.e.*, up to 70,000 psi at 1200° C. Although room temperature tensile strengths over 1,000,000 psi have been determined for silica glass and single crystals of alumina, graphite and other materials (Kelly, 1965), and graphite has been made with a tensile strength of 50,000 psi at over 3000° C. (Anonymous, 1964), the tensile strength exhibited by olivine is far in excess of that for most materials at 1200° C. Young (1965) has found that at high temperatures, the deformation of olivine is related to the dislocation density. Only a very small volume of the olivine crystal surrounding an inclusion is under maximum stress, and it probably has few if any major dislocations, as those inclusions with weaker walls probably decrepitated on eruption. It should be noted, however, that many of the inclusions that do withstand eruption—and subsequent reheating to 1200° or more —occur as planes of secondaries along healed fractures. Thus not only is their stress somewhat additive, but the olivine holding the two parts together has grown as a fracture healing, presumably with many dislocations and even discontinuities, yet it can stand the tension. Data for olivine at room-temperature are available on the compressibility (Adams,

1951) and the shear strength as a function of confining pressure (Riecker and Seifert, 1964). If the high temperature tensile strength is measured, along with an extension of the experimental study of the CO_2 system to higher pressures, the CO_2 inclusions may permit more quantitative limitations to be placed on the conditions of origin of nodules. It might also be noted that since these inclusions (in olivine, pyroxene, and plagioclase) have withstood heating to about 1200° over their filling temperature without decrepitation, a "decrepigram" of such material would have a minimum correction of 1200° for "overshoot."

Other constituents present. Regardless of whether the olivine-rich nodules represent the accumulation of crystals formed from basaltic magmas, or these magmas represent partial melting of olivine-rich nodule material, it seems logical to assume a genetic relation between the gases in the inclusions in nodules and those evolved during the basaltic volcanism that brought the nodules to the surface. It would be highly desirable to know what other gases such as He, Ar, and Xe might have collected in the inclusions, and some attempts at analysis are in progress, but unambiguous gas extraction is a problem.[1]

The equilibria between CO_2, H_2O, and ferrous silicates at high temperatures should result in the formation of some CO, H_2 and CH_4 in the inclusions, but their behavior at the critical point indicates that only very small quantities, if any, are now present. The nodules have generally been cooled rather fast, and some even come from volcanic bombs, but at the high pressures involved, internal gas reactions upon cooling might still be significant. Heald *et al.* (1963) have calculated that the gas evolved from Halemaumau, Hawaii, should have a CO_2/CO ratio of about 12 at 1500° K.[2] This much CO cannot be present in the inclusions now, as it would certainly affect the critical phenomena. It is probable that at least part of any CO present at high temperatures has dissociated on cooling, according to the well-known reaction: $2CO = CO_2 + C$. The gases inside inclusions in olivine could thus precipitate carbon, and it is possible that the dark borders seen in some CO_2 inclusions (Fig. 6), and even some of

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[1] S. R. Hart of the Dept. of Terrestrial Magnetism, Carnegie Institution of Washington (personal communication) found 5.5×10^{-7} cc STP of radiogenic Ar per gram in sample ER 63-33a, from Hualalai, and Butler *et al.* (1963) found 4×10^{-11} cc STP of Xe per gram in a Bavarian eclogite. It is possible that part of the excess argon reported in pyroxene from some xenoliths and eclogites (Lovering and Richards, 1964; McDougall and Green, 1964) may come from CO_2 inclusions, as it is not rare to find far more inclusions in pyroxene than the other minerals.

[2] Calculations by Kennedy (1948) showed only 0.163 volume per cent hydrogen at 1200° C., but Heald *et al.*, calculated about ten times as much.

the opaque plates tentatively called spinel (?), may be graphite (French and Eugster, 1965).

It has been proposed that the carbon dioxide in Hawaiian volcanism may come from assimilation of coral reef carbonates, and Lessing and Catanzaro (1964) found Sr and Rb isotopic evidence suggesting such contamination. The presence of a separate CO_2 phase during crystallization of Hawaiian samples at depths believed to be beyond the effects of such contamination, and in other localities where such carbonate sediments are probably not available, indicates that at least some and possibly all of this CO_2 is juvenile.

The problem of the relative amounts of water and of carbon dioxide in volcanic gases is of considerable interest. Rubey (1951) proposed a ratio of about 20 during the degassing of the earth, and similar high ratios are found for the gases from basaltic volcanoes. Moore (1965) presents evidence that Hawaiian tholeiite magma contains about 0.45% magmatic water. As a result of a study of the Hessian Tertiary basalt province, Wedepohl (1964) feels that the major primary gas in these melts was CO_2, and that most of their water content was taken up near the earth's surface. CO_2 is essentially insoluble in granitic melts (Wyllie and Tuttle, 1959), but should dissolve to some extent in basaltic ones. Even so, it is probably much less soluble than H_2O in basaltic melts, and could form a separate, immiscible phase, to be trapped in the growing crystals, while the bulk of the water stayed in the liquid melt. Obviously, the CO_2 inclusions must not be considered to be a "sample" of the volatiles *present* in the magma, but only of those *evolved as a separate phase* under those conditions, perhaps modified by internal reactions on cooling.

This early saturation with respect to CO_2 suggests that later deuteric and even ore fluids from these magmas or their differentiates should also be high in CO_2. The late-stage carbonation of mafic igneous rocks and their contact aureoles (*e.g.*, Wilshire, 1958) is an indication of such CO_2.

Vesiculation and volcanism. The CO_2 we see in the inclusions described constitutes only an extremely small portion of the total volatiles erupted from any given vent, which have been estimated to be as much as 1 per cent by weight (Macdonald, 1961). It represents, however, only that small portion of the separate immiscible CO_2 phase at depth that happened to become trapped in sufficiently strong olivine "pressure vessels" to hold it upon eruption. A larger portion of these minute globules presumably stayed suspended in the saturated liquid basalt which carried the nodules up to the surface. These globules represent incipient vesiculation, even at >10 km depth, and should act as nuclei to minimize any supersaturation with respect to gases, and the resultant explosive action.

Macdonald (1961, p. 678) feels that it is unlikely that magmas at depth are often saturated. One seemingly conclusive line of field evidence for this is the lack of vesicles in basalt dikes 2000 feet or less below the surface, where now cut by deep canyons (Macdonald, 1963, p. 1076). Even if the magmas forming these dikes had been saturated with respect to a CO_2 fluid, several factors tend to minimize the significance of this evidence: (1) unless formed by second boiling, upon crystallization, the vesicles we see in a dike are only those that were accidentally trapped during their ascent, and the entire dike-filling may have been rather effectively degassed earlier; (2) in glassy dikes, at least some of the gases evolved on pressure decrease at essentially constant temperature during ascent may be resorbed by temperature decrease at constant pressure during solidification in place (although the solubility of CO_2 in basalt magma is probably low, considerable water may move between magma and vesicle); and (3) "vesiculation" on a scale as indicated by the primary CO_2 inclusions in olivine would be difficult to recognize, as a CO_2 globule 10 μ in diameter at 16 km depth would expand to only 25 μ radius at 2000 feet (0.6 km) depth. Moore (1965, p. 51) has shown that Hawaiian submarine basalt magmas apparently do not become saturated with respect to water until they reach very low pressures, equivalent to <300 meters of lava, yet they do show vesiculation at greater pressures, possibly due to CO_2.

During eruption, 20 μ-diameter globules would have a negligible rate of ascent relative to the enclosing magma, but as the pressure decreases during ascent, their radius will increase, from simple expansion and from further outgassing of the saturated magma with pressure drop. The rate of rise of such bubbles, according to Stokes law, is a direct function of the *square* of the radius. Thus the processes of expansion (resulting in both a lower bulk density, which controls the ambient pressure, and in an expulsion upward of an equal volume of magma), and of bubble rise through the magma, become self reinforcing, and presumably result in vigorous lava fountaining and other volcanic phenomena.

Cooling rates. Nucleation phenomena in the inclusions provide two indications, both qualitative at present, of the cooling rates involved in the lavas in which the nodules are found. First, the general lack of shrinkage bubbles in the smaller glass inclusions (<4 μ) would indicate rapid cooling for these samples. Much smaller glass inclusions, down to <1 μ diameter, in leucite phenocrysts from Vesuvius (sample ER 62–131, Table 3D) were found to have tiny shrinkage bubbles. Second, although many samples show some cloudiness or daughter mineral crystallization, in only one sample, ER 63–89, from Hawaii, was consistent evidence found for crystallization of the bulk of the glass (Fig. 7). Basaltic glass exhibits relatively high rates of nucleation and crystallization, but it must be noted that glass inclusions in the minerals of volcanic rocks frequently are not devitrified even though the glassy ground mass is full of dendritic or spherulitic crystals (*e.g.*, Fig. 5, and Drever and Johnston, 1957).

As with many nucleation phenomena, these two rate processes—nucleation of a gas bubble, and of crystals—are volume dependent, and the inclusions provide very small volumes, beautifully isolated from spurious seeding.

One other nucleation phenomenon is worthy of note. In sample ER 63–138a, from Hoher Hagen, Germany, a large group of glass inclusions in a pyroxene crystal in the olivine-rich nodule all show a large daughter mineral (>25 volume per cent) believed to be olivine on the basis of its birefringence and index relative to the host. Presumably this much olivine also crystallized out invisibly on the walls of similar glass inclusions in olivine.

Origin of phenocrysts. CO_2 inclusions in phenocrysts, either primary or secondary, can be used to establish a minimum depth for their crystallization. At least nine of the samples listed in Table 3A showed definite liquid CO_2 inclusions in single coarse crystals of olivine, titanaugite and oxyhornblende that occurred in the finer grained basaltic matrix, and ten other samples, in Tables 3A and 3B, showed evidence suggestive of such CO_2 inclusions. Although many of these are probably xenocrysts from the disaggregation of nodules, certainly some of them are actual phenocrysts. The large (10 mm) sharply euhedral titanaugite phenocrysts in basalt from Antarctica (ER 63–169) showed definite planes of secondary liquid CO_2 inclusions,[1] and hence must have formed at considerable depth. A few sharply euhedral olivine phenocrysts were also found to contain CO_2 inclusions. Although these were undeformed (Talbot *et al.*, 1963), there is still a possibility of xenocrystic origin by overgrowth on a xenocrystic core. Figures 15 and 18 are of presumably primary multiphase CO_2 inclusions in euhedral olivine crystals from one of these samples.

Some of the glass plus gas inclusions in the olivine phenocrysts in the lavas of the Kilauea Iki eruption of 1959 (ER 63–86, Table 3C and Fig. 22) contain gas under pressure, and others contain essentially a vacuum bubble. The latter are common in volcanic samples and presumably have formed by the condensation of steam-rich gas bubbles trapped at very

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[1] This sample also showed one plane of several dozen secondary inclusions in a large xenocrystic(?) olivine crystal, each with a birefringent crystal, glass, and liquid and gaseous CO_2, all in apparently *uniform* ratios, implying that a homogeneous fluid was trapped. This observation has not been reconciled with laboratory data indicating low solubilities for CO_2 in basic melts.

near the surface, but as the hydrostatic pressure increases at about one atmosphere per 3 meters depth, noncondensable gas inclusions with moderate pressures at room temperature can form at comparatively few meters depth. From Fig. 1 it is apparent, however, that an inclusion that shows even a trace of liquid CO_2 at 20° C. would have a filling density of about 0.2. This would require about 600 atmospheres at 1200° (Fig. 2), corresponding to about 2 kilometers depth. A careful search should be made for liquid CO_2 in inclusions in the phenocrysts of the tholeiitic basalts, where the possibility of a xenocrystic origin (from nodules) is more remote.

Megapetrological ramifications. The CO_2-saturation of the presumed basaltic environment from which the minerals of the olivine-rich nodules crystallized throughout the world has so many interesting consequences that a little additional speculation seems apropos.

First, it might be suggested that the mineral assemblage we now see in at least some of the nodules, particularly the gabbroic ones, may be the result of solid transformations from earlier, high-pressure assemblages (*e.g.*, eclogitic) characteristic of the mantle. Such transitions may occur at relatively shallow depths (Lovering, 1958; Kennedy, 1959). The primary inclusions in the gabbroic nodules examined here, both glass and CO_2, would seem to preclude this inversion having occurred in these samples, as it is difficult to envisage an inversion process whereby such inclusions would be left intact. It also seems unlikely that glassy pyroxene and feldspar could form as the result of solid transformations, yet many of the grains in the nodules are glassy. The olivine in many nodules is also glassy ("peridot"), but it would not be involved in the solid transformations. Although it is true that glass inclusions might represent melting, at lower pressures, of former high-pressure solid inclusions, the all-CO_2 inclusions pose a problem, except for the remote possibility that magnesite is present at very high pressures. If complete recrystallization occurred during the transition, it would have to preserve the mineralogical and textural evidence of gravitational settling described by Brothers (1960) for at least one of the localities studied (Raglan, New Zealand, ER 64-4). Several eclogite nodules from similar occurrences showed small but plainly visible CO_2 inclusions (ER 64–195, 196, 198, and 202, from Australia and Hawaii). From this it seems necessary to conclude that the gabbroic nodules have crystallized above the Mohorovicic discontinuity, and that the others, regardless of their source, still have the same gross mineral assemblage in which they crystallized.[1]

[1] One sample from Ichinome-gata, Japan (ER 65-9A), provided by Professor Kuno, showed intergrowths of spinel in clinopyroxene from the breakdown of garnet, and several planes of presumably secondary inclusions of both pure CO_2 and of a CO_2-H_2O mixture.

Second, there is a rather extensive literature on the origin of the nodules, and many geologists consider at least part of them to be fragments of the mantle, from below the Mohorovicic discontinuity (*e.g.*, Turner and Verhoogen, 1960, p. 201; Lovering and Morgan, 1963); the primary CO_2 inclusions seem to preclude this, but raise new questions as well. Although the Mohorovicic discontinuity is very shallow in the vicinity of Hawaii (Lovering, 1958, assumes it to be 5 km below the ocean floor), and only about 17 km below the island itself (Eaton and Murata, 1960), most of the primary CO_2 inclusions in nodule samples from Hawaii have filling densities indicating formation at even shallower depths. The Mohorovicic discontinuity is presumably deeper at most of the other localities. Decrepitation of those inclusions with higher filling densities, formed at greater depths, does not influence the significance of these data. Partial (but invisible) leakage of *all* primary inclusions, or a non-primary origin, must be invoked if these nodules are to be mantle material. On the other hand, the inclusions do permit us to state with some certainty that these particular host mineral grains could not have crystallized at *less* than the depths calculated. At Kilauea, Eaton and Murata (1960) have proposed the existence of a shallow, inflatable chamber, high in the volcanic pile, with its roof <5 km depth. As the pressures at 5 km depth would be inadequate to maintain CO_2 at the densities found in many of the inclusions (both primary and secondary), the minerals of the nodules must have formed at greater depths. They could conceivably have *accumulated* in a shallower chamber to form the source rock for the nodules.

No attempt was made in this brief investigation to correlate the inclusion data in detail with the available petrologic and petrographic studies such as the mineral assemblage, the aluminum content of the pyroxenes, or the enclosing rock types. It should be noted that CO_2 inclusions were found in all types of nodules examined—peridotite, pyroxenite, dunite, eclogite, and gabbro. It is hoped, however, that this report will encourage others to look for these inclusions in the course of their work, and explore at least some of the many fascinating avenues that they present. One such suggestion is that the CO_2-saturation of the alkali basalt magmas is but another indication of the differentiation process, in agreement with the accumulating evidence (Moore and Peck, 1965) that the alkali basalts represent a late stage in the development of tholeiitic basalt volcanoes.

Third, there is an interesting possibility that the CO_2 may have been involved in the origin of the diamond. Although unconfirmed by later work, Bauer and Spencer (1904, p. 119) reported the occurrence of liquid CO_2 inclusions in diamond, and suggest that they may be pertinent to the problem of genesis (p. 236). Diamond pipes and diatremes frequently are associated with alkali-rich rocks and carbonatites, and show evidence of explosive, gas-rich emplacement, perhaps even as a fluidized gas-solid system (Dawson, 1962; Davidson, 1964; see also kimberlite-carbonatite symposium, 4th general meeting of the Int. Mineralogical Assoc., New Delhi, India, Dec. 1964). Birch (1963) and Boyd and England (1965) present evidence that the kimberlite pipes have come up at least 100 km. In view of this, several samples of kimberlite were examined for CO_2 inclusions. Evidence of high pressure gas was found in samples from the DuToitspan, Wesselton, and DeBeers pipes, South Africa, and one sample from the Wesselton pipe showed a group of liquid CO_2 inclusions up to 3 μ in diameter. Although these inclusions could not be called primary, a more extensive study of such inclusions should be undertaken, and if possible, C^{12}/C^{13} measurements should be made on them for comparison with available data on diamonds and carbonatites (Taylor *et al.*, 1965).

Last, there is considerable field evidence of an association of alkalic (frequently high potassium) rock types with carbonatites the world over (Pecora, 1956). Included among these alkalic rock types are a wide variety of ultramafic rocks (Strauss and Truter, 1951; Franz and Wyllie, 1964), and the alkali basalts in which practically all olivine-rich nodule occurrences fall (Kuno, 1959). CO_2 inclusions have been reported in the calcite of the carbonatites at Alnö (von Eckermann, 1948, footnote, p. 154) and at Sukulu (Williams, 1956, p. 22). Roedder (1963, p. 195) has found liquid CO_2 in feldspar from a carbonatite vein-dike in the Bearpaw Mountains, Montana, as well as gas inclusions under pressure in calcite from the Lueshe deposit in the Belgian Congo (present study, sample ER 63–168). Strontium isotope data on carbonatites and associated basalts by Powell *et al.* (1962) indicate that at least some carbonatites are magmatic in origin, and that the CO_2 in them must be juvenile. Pecora has placed the source for the CO_2 and the alkalic magmas deep in the crust (1956, p. 1551), but he shows that there is considerable field evidence of explosive volcanism associated with carbonatites, to the extent that a fluidized gas-solid system has been proposed as a mode of eruption for them also (Bailey, 1960). This all suggests that during the presumed deep-seated evolution from the alkali basalts to the highly alkalic suites characteristic of many carbonatite areas, a simultaneous separation and enrichment of the carbon dioxide phase (either by the rising of bubbles or by expulsion on partial crystallization in place) provided the carbon dioxide and the motive power for the gas-rich eruptions, and could have caused the formation of a low-melting carbonatitic lava (Wyllie and Tuttle, 1962). Such processes may also have influenced the early atmosphere of the earth, and might even have affected the face of the moon.

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Note: Most of the samples studied have been deposited at the U. S. National Museum.