A Mass Spectrometric Method for the Determination of the Size Distribution of CO_2 Inclusions in Olivine

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Abstract

A procedure is described for a mass spectrometric determination of the size distribution (by weight) of CO_2 inclusions in olivine. Samples are heated within a high temperature effusion-cell, and bursting of CO_2 from ruptured inclusions is detected by a quadrupole mass filter as ion-current signal-spikes. Intensities are calibrated from pressure spikes produced by the rupture of glass capillary ampules containing known amounts of CO_2.

The procedure was applied to samples of olivine, and an inverse relationship between the number and size of CO_2 inclusions was demonstrated. Inclusion sizes range from 2×10^{-9} g to smaller than 1×10^{-11} g of CO_2. No water was detected which could be associated with the bursting of CO_2. The technique clearly distinguishes adsorbed CO_2 from inclusion CO_2.

Introduction

Mass spectrometric techniques applied to the study of fluid inclusions in minerals have been reported by numerous workers and are summarized by Roedder (1972). In general, these methods have been concerned with the identification of the species present and the estimation of their relative or absolute amounts.

Release of volatiles from inclusions is usually achieved by grinding, crushing, or heating a mineral under vacuum. Analyses are then conducted on what is effectively a composite sample of the released contents of multiple inclusions. Experiments have also been described in which the fluid content of individual inclusions is investigated. Bratus, Stasiuk, and Panchishin (1968) recently described an omegatron mass spectrometer system in which they estimated quantities of gases in relatively large inclusions (in quartz) by piercing individual inclusions with a fine needle. In the procedure described here, a high temperature mass spectrometer is used, and the amount of CO_2 released from individual inclusions is measured to obtain a weight or size distribution. The technique has distinct advantages over microscopic methods since it is not limited to transparent minerals and eliminates many tedious visual measurements associated with the observation of a large number of inclusions. Microscopic techniques also require the preparation of special, doubly-polished, thick sections (Roedder, 1965).

Sample Description

The samples used for study were Hawaiian olivine and are from two sources: (1) Olivine separated from a dunitic nodule recovered from the 1801 Kaupulehu lava flow, Hualalai, Hawaii. The size of individual olivine grains is of the order of 1 mm. Richter and Murata (1961) describe crystals in these nodules as anhedral and forming a tightly interlocked, allotriomorphic, granular texture. (2) Olivine from a peridotitic nodule from Salt Lake Crater, Oahu, Hawaii (time since eruption estimated at 0.4 m.y.). Olivine separated from this nodule has a grain size of approximately 1 mm. Nodules from this location consist of olivine and pyroxene, with pink or brown garnet, and are considered possibly to be of mantle origin (Macdonald and Abbott, 1970).

Experimental

Samples were studied by decrepitation in a high temperature effusion-cell assembly capable of temperatures to 1600°C. The cell assembly contains a molybdenum crucible which is heated by radiation from a coiled tantalum resistance element. A set of four concentric molybdenum cylinders surrounds the cell and serves as a radiation shield. A molecular beam of released volatiles emerges through a 0.040″ diameter orifice in the cell lid and is directed through a moveable shutter-plate and into the ion source of a quadrupole mass filter (EAI, Quad 1110). The

shutter, attached to an external, linear-motion feed-thru, permits one to distinguish volatiles emitted directly from the crucible from those desorbed and back-scattered from the walls of the vacuum chamber or assembly components. Temperatures are measured with a Pt/Pt-10%-Rh thermocouple peened into the base of the cell. A detailed description of the apparatus has been given previously (Muenow, 1973). The entire assembly is mounted within a high through-put, fast-cycling, vacuum system containing sublimation and ion pumps (Varian, model VI-221).

Sample preparation consisted of gently crushing the nodule olivine and then sieving it to recover a 10-16 mesh (Tyler) fraction. This fraction, in the case of the Salt Lake olivine, contained some grains as large as 2 mm diameter but consisted mainly of intergranular pieces made up of several grains of 1 mm or less. The predominant grain size was 1 mm. The 10-16 mesh fraction of Hualalai olivine consisted of intergranular pieces containing several grains of various sizes, but with grains of size 0.5 mm to 1 mm predominating.

Each sample (0.2 g to 1 g) was placed in a Lucalox (crystalline, high temperature alumina) cell liner and loaded into the effusion crucible. Pressure within the apparatus was maintained at approximately 1×10^{-7} torr. The cell temperature was increased at the rate of 5°C/min. The CO_2^+-ion peak ($m/e = 44$) was monitored by the quadrupole mass filter and the amplified signal recorded on a fast-response, strip-chart, pen recorder and visually displayed with an oscilloscope. Release of CO_2 from inclusions on heating was observed as a series of sharp, ion-current, signal-spikes on the recorder chart. These recorder spikes were accompanied by corresponding deflections on a pressure-sensing ion gauge connected to the vacuum system. The intensity or peak-height of individual recorder spikes is proportional to the sizes of the corresponding inclusions so that by measuring a large number of such spikes a size-distribution can be obtained.

We verified that those spikes at $m/e = 44$ were due to CO_2 by observing the mass spectrum displayed on the oscilloscope. Mass peak 44 and the ion fragments of CO_2 ($m/e = 28, 16, 12$) were seen to burst in unison as decrepitation occurred. There was no evidence, either on the oscilloscope or in the recorded spectrum, of fragmentation patterns associated with other species having parent or fragment ions at mass 44.

As the crucible temperature was raised, it was found that appreciable amounts of CO_2 desorbed from the apparatus surfaces. This produced a continuously increasing background signal level, and it was therefore necessary to switch to higher attenuation positions on the recorder as the temperature increased. Since the recorder spike-heights at different recorder attenuations did not appear to be related to the simple ratios of the attenuation settings, a small and variable dc-voltage was connected in series with (and in opposition to) the recorder input to null out the background signal. Thereafter, a constant attenuation setting could be used at all temperatures, and the background signal was manually nulled from time to time (as the temperature increased) so that all spikes were recorded on scale.

Calibration of the quadrupole CO_2^+-ion spike-intensity was made by using small glass ampules containing known amounts of CO_2. The ampules (1.5 mm-2.0 mm i.d.; 2.0 mm-10.0 mm long) were made from standard melting point capillary tubes and were formed in the following manner. The end of a capillary tube was first sealed in an oxygen flame, and drawn out to a fine constriction at the required length. The tube was evacuated and refilled with air several times to ensure the removal of any CO_2 produced by combustion in the flame. The ampule was then sealed by touching the flame to the fine tube constriction, which caused it to break and seal instantaneously without heating the air in the tube. The CO_2 content of normal dry air was assumed to be 0.033 percent by volume (Weast, 1970).

To demonstrate the validity of using CO_2 in air as the standard for estimating essentially pure CO_2 from the sample, we made use of a fine-control, variable leak valve. Air was leaked into the apparatus to produce a relatively high pressure (10^{-4} torr) and the ion intensity of mass peak 44 was measured. After pumping out the air, we next leaked pure CO_2 into the system at a rate just sufficient to maintain the same pressure (within the system) as the partial pressure of CO_2 in the air leak. The ion intensity of mass peak 44 was again measured, and we found no sensible difference between the two ion intensity levels. This demonstrates that the presence of 3000 times as much other gas ($O_2 + N_2$) in air did not affect the quantitative ionization and detection of the CO_2 in the calibration standards. (It should be noted that the preparation of realistic standards of pure CO_2 for this dynamic system

would entail the construction of ampules about three orders of magnitude smaller than the air ampules used. This would be an extremely difficult task.)

The total volume of each ampule was calculated from its dimensions, which had previously been measured with a microscope. The ampules were then supported vertically in holes which were drilled into a small stainless steel cylindrical block and positioned inside the effusion-cell. The cell was heated, and between 750°C and 820°C the ampules burst to release their contents of nanogram amounts of atmospheric CO_2. Recorder spike-heights corresponding to these standards were then plotted against CO_2 content. An important consideration here is that when a set of calibration ampules is burst in the mass spectrometer system, the smallest recorder spikes are assumed to correspond to the bursting of the smallest ampules and the largest spikes are assumed to be due to the largest ampules. If, however, the results were random, with no linear relationship between observed spike size and ampule size, there would still be a chance of obtaining an approximately linear curve when plotting the two sets of numbers in the way described. To demonstrate that there is indeed a linear relation between the amount of released CO_2 and measured spike size, we prepared three sets of different sized ampules in which each set contained ampules of the same size. These three sets were then burst in three separate, consecutive, calibration runs using constant mass spectrometer sensitivity settings. The results are plotted in Figure 1 and indicate that a linear relationship does indeed exist.

Another potential problem arises if the calibration ampules are not supported vertically within the stainless steel holder. In this case, there is a tendency for the softened glass to collapse and to distribute the air into smaller sealed bubbles. These bubbles then burst independently of each other as the heating is continued.

Size Distribution

Data for the distribution curves were obtained by measuring the spike heights for approximately 1000 consecutive inclusion-bursts. The contribution of released-CO_2 from desorption from surfaces of the olivine was indicated by the behavior of mass peak 44 with increasing temperature, after subtracting the background contribution. This background contribution, due to desorption from the apparatus, was obtained on a separate heating run with no sample
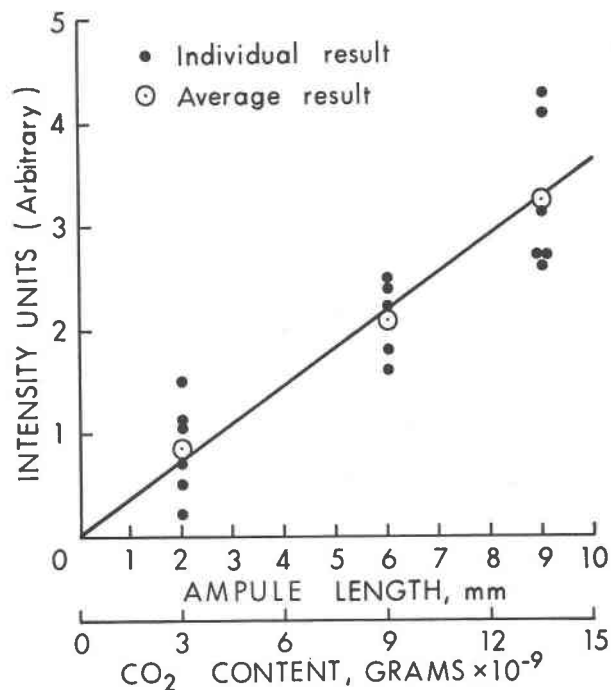

FIG. 1. Air ampule calibration curve.

present. The resultant desorption profile showed a peak maximum at 350°C, and was complete by 500°C. Release of CO_2 from inclusions, as evidenced by recorder spikes, did not commence until about 700°C. Although data could be taken from the spikes produced on heating, we found it possible to obtain similar results from spikes produced as the samples cooled from 1100°C. We observed that large numbers of inclusions ruptured as the olivine samples cooled, with a maximum burst rate near 500°C. The time taken for the sample to cool from 1100° to 500°C was about 8 minutes. Using data from inclusion release on cooling had the distinct advantage of a much lower instrumental noise level. Noise is manifest as rapid vibrations of the recorder pen, and the amplitude of these vibrations (noise level) was about five times greater at temperatures where inclusions were bursting on heating as that observed at temperatures where inclusions were bursting on cooling. The minimum detectable signal was consequently correspondingly smaller on cooling, but the weight-distribution curve was very similar to that obtained on heating.

The highest temperatures used were several hundred degrees below the olivine melting temperature (about 1500°C) so that not all inclusions were released on heating to 1100°C and cooling. When

repeating the cycle of heating and cooling on the same sample, we observed that comparatively few inclusions burst until the highest temperature recorded on the initial heating cycle was again reached. However, on cooling, the number and size distribution of inclusions released were similar to those released on the initial cooling cycle. (The phenomenon of inclusion release on cooling is thought to be due to contractional stresses and is being investigated further. It seems reasonable, however, that since brittle materials such as olivine fail in tension, surface cracks must be propagated inward on cooling due to surface tensional forces from the temperature differences, whereas on heating, the unflawed interior of the grains is the only part in tension.)

Weight distribution curves for two olivine samples (Fig. 2) were plotted from data obtained on cooling in each case. It is apparent that the number of inclusions is inversely related to inclusion size. The weight distribution of CO_2 inclusions in the Hualalai olivine (curve **A**) is similar to that for the Salt Lake olivine (curve **B**) although there appears to be a proportionately larger number of small inclusions in the Salt Lake sample. The steep increase in the number of small inclusions at the lowest level detected (1×10^{-11} g) suggests that there may be many more still smaller inclusions which we could not

detect. These results are in good agreement with Roedder's (1965) description of inclusions, studied microscopically. His selection of samples included olivine from Hualalai and Salt Lake, and he estimated medium inclusions to be of the order of 10^{-11} g. This weight corresponds to an inclusion size (assuming unit specific gravity) of 2–3 μm diameter, or 10 $(\mu m)^3$ volume. This is the smallest inclusion in which a liquid-gaseous CO_2 interface can be resolved optically. Although many inclusions smaller than this size can be seen, and probably contain CO_2, it has to remain a presumption that they do in fact contain CO_2 (Roedder, private communication).

Concluding Remarks

An important advantage of this technique is that it clearly distinguishes adsorbed species from those present within inclusions. An illustration of this may be seen in the following example: In a study of the contents of fluid inclusions, Roedder (1965) heated a sample of Hualalai olivine and concluded that about half as much water (approximately 0.01 percent) as CO_2 was evolved, yet neither water nor hydrous minerals were visibly present in the inclusions. He assumed that part of the water obtained may have been present in the inclusions as invisible films on the walls. Additional water could be present in basaltic glass inclusions and as firmly bonded, surface-held water (on the olivine) that was not removed by baking at 250°C. At high temperatures, where CO_2-release from inclusions was known to occur, we found that by monitoring mass peaks characteristic to water ($m/e = 17, 18$) no detectable amount was released as bursts. Since the detection limit of water was about 1×10^{-11} g per recorder spike, water (if present at all) could only be present to the extent of, at most, 2 percent of the CO_2 and certainly not of the order of 50 percent of the CO_2. This conclusion assumes that any decrepitative release of water from inclusions would produce H_2O molecules in the molecular beam, and that any adsorption on freshly exposed surfaces at these high temperatures would at least be no greater for H_2O than for CO_2. We further observed that the desorption profile for water was not complete until 500°C; this supports Roedder's suspicion that some of the water he found may have been strongly adsorbed on the olivine surfaces. At high temperatures (700°–1100°C) a plot of the ion intensity of mass 18 (H_2O^+) vs temperature was not noticeably
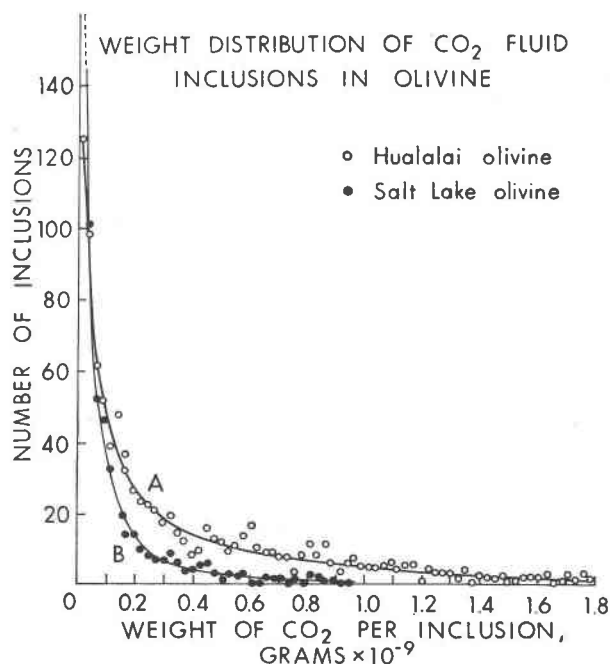

Fig. 2. Weight distribution of CO_2 fluid inclusions in olivine.

different between a sample and a blank run with no sample.

The fact that we found CO_2 desorption from olivine surfaces to be incomplete below 500°C suggests that errors may be inherent in methods which assumed quantitative removal of adsorbed species (in addition to water) after baking at relatively low temperatures. We suggest that for olivine, baking for several hours at 500°–600°C should be made before attempting measurements of volatiles released from inclusions. This preheating would certainly remove a substantial part of the original adsorbed gases. The surface adsorption of species subsequently released from fluid inclusions, however, remains a possibility which cannot be discounted, especially when making quantitative measurements.

Acknowledgments

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