

## Thermal Stress-Induced Release of CO<sub>2</sub> Inclusions in Olivine on Cooling from High Temperatures

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### Abstract

The previously observed phenomenon of CO<sub>2</sub>-release from inclusions when olivine cools from high temperatures was investigated. The observed rate of release of inclusions is shown to be directly proportional to the calculated temperature gradient across individual grains.

### Introduction

The presence of fluid micro-inclusions in olivine from olivine-bearing nodules has been known for more than one hundred years. Roedder (1965) has reported extensively on liquid and gaseous CO<sub>2</sub> inclusions in olivine nodules and phenocrysts from basalts from many locations throughout the world. In a previous paper (Killingley and Muenow, 1974) we have described a mass spectrometric procedure for the determination of the weight distribution of such micro-inclusions and found that, for Hawaiian olivines, an inverse relationship exists between the number and the size of inclusions. Using this procedure, which clearly distinguishes adsorbed CO<sub>2</sub> from inclusion CO<sub>2</sub>, we observed the phenomenon of the bursting of CO<sub>2</sub> from ruptured inclusions on cooling the olivine from high temperatures. We considered that this effect was a result of cracking caused by contractional stresses due to temperature gradients within the olivine grains. In the present paper we present inclusion-release curves obtained by cooling olivine from high temperature. Using a model based upon the unsteady heat conduction of olivine cooling to the temperature of the surrounding medium, we are able to construct theoretical curves which demonstrate the relationship between thermal strain within the cooling mineral grains and the CO<sub>2</sub>-inclusion release rate.

### Experimental

#### *Technique*

Our experimental procedure (Killingley and Muenow, 1974) involves heating small samples of

a mineral (less than 1 g) in a specially designed Knudsen cell which is interfaced with a high throughput vacuum system containing a mass analyzer. The released volatiles escape through a small orifice in the cell lid to form a molecular beam which enters the ionizer of a sensitive quadrupole mass filter, positioned a few inches from the cell. By continuously monitoring a major ion mass peak of the volatile in question, it is possible to observe rapid changes in the ion intensity as sharp spikes on a strip-chart pen recorder and oscilloscope. These signal-spikes correspond to vapor-release from individual ruptured fluid inclusions. For the quantitative measurement of CO<sub>2</sub>, an instrumental calibration is accomplished with the aid of small glass ampules containing known volumes of CO<sub>2</sub>. These ampules are heated in the Knudsen cell until they burst to release their contents. Recorder spike-heights corresponding to these standards are then plotted against CO<sub>2</sub> content. Unknown quantities are then determined by reference to these calibration graphs.

#### *Samples*

Olivine samples were obtained from dunitic nodules recovered from the 1801 Hualalai basalt flow on the island of Hawaii. They exhibit little evidence of magmatic reaction. Interior sections of the nodules were gently crushed to provide about a kilogram of material for sieving. The olivine was then sieved with standard U. S. series sieves. Samples containing 2 mm grains were hand-picked from appropriate sieve fractions. Each sample was ultra-

sonically washed with distilled water to remove dust particles.

### Results

The observed release of CO<sub>2</sub> micro-inclusions on cooling olivine from high temperatures is at first glance rather surprising (Fig. 1a). Quite evidently, this release must be associated with strains set up even at small grain sizes. It seems reasonable, however, that since brittle materials such as olivine fail in tension, surface cracks must be propagated inward on cooling due to the surface tensional forces from temperature gradients in each mineral grain, whereas, on heating, the unflawed interior of the grains is the only portion in tension (Roedder, private communication, 1974). In order to test this explanation we made the following measurements which are then compared with a theoretical model.

Samples containing approximately 0.5 g of 2 mm grain-size olivine were loaded into the Knudsen cell and the system slowly heated at a rate of 5°C/min to a high temperature and maintained there for 20 minutes to establish a uniform temperature throughout the grains. The  $m/e = 44$  mass peak was continuously monitored to observe inclusion bursts. During the heating cycle CO<sub>2</sub> inclusions were released when the temperature exceeded approximately 700°C and were detected as ion-current surges which were recorded as sharp spikes on a strip-chart pen recorder. The rate of release of CO<sub>2</sub> inclusions increased with temperature, particularly when temperatures of 1100°C were reached. As this is the approximate temperature of the erupting lava which transported the olivine nodules to the surface, a sharp increase in inclusion release is not unexpected. Such release presumably results from fracture of the olivine when internal pressures become higher than those previously experienced by the mineral while under an external pressure of one atmosphere, or less. When the heat input to the Knudsen cell was switched off, the rate of inclusion release initially decreased to zero. This was followed by a rapid increase in the release rate as the sample continued to cool. After reaching a maximum, the rate slowly decreased as cooling continued. The number of inclusions released per minute, per degree, was plotted as a function of time for three separate samples of the same material with different initial temperatures (Fig. 1a).

To explain these data we propose a model which

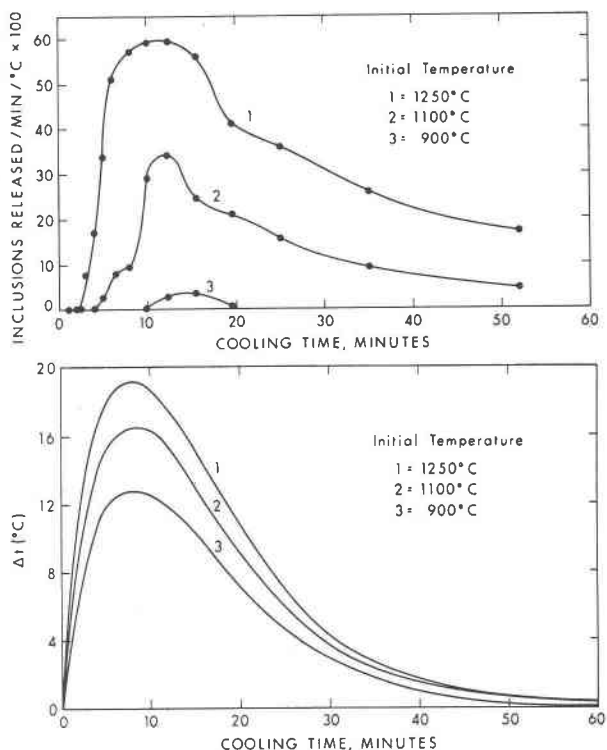


FIG. 1. (a) Experimental inclusion release rate as a function of cooling time of olivine grains. (b) Calculated differences,  $\Delta t$ , between center and surface temperatures of cooling 2 mm spheres of olivine as a function of time.

assumes that each mineral grain may be approximated by a uniform sphere with radius  $R_0$ . Initially, each sphere is at some high temperature ( $t_1$ ). The spheres are then imagined to be immersed into a medium of constant low temperature ( $t_0$ ) and cooled by unsteady heat conduction to the medium. The basic problem is then to calculate both the temperature at the center ( $t_c$ ) and at the surface ( $t_s$ ) of each olivine sphere as a function of the experimental cooling time. The treatment of this type of unsteady heat conduction is well established and may be found in standard texts on heat transfer (Heisler, 1947; Kutateladze, 1963; Kutateladze and Borishanskii, 1966). This is accomplished by referring to nomographs which relate a "dimensionless temperature" ( $\theta$ ) to a "dimensionless time" ( $Fo$ ) for various values of a Biot number ( $Bi$ ). According to this method,  $Fo$  (the Fourier number) characterizes the relationship between the rate of change of temperature and the physical properties and dimensions of the solid body in question. Thus,  $Fo = \lambda / c\gamma \cdot \tau / R_0^2$ , where  $\lambda$  is the thermal conductivity;

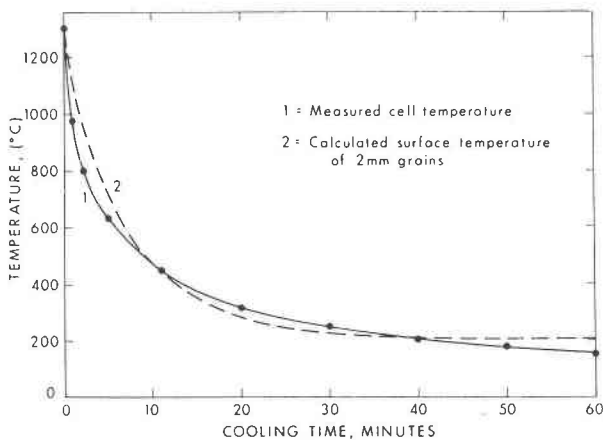


FIG. 2. Cooling curves for Knudsen cell and olivine grains.

$c$  is the specific heat;  $\gamma$ , is the specific weight;  $\tau$  is the cooling time. The Biot number characterizes the relationship between the temperature field in the solid and the heat transfer conditions at its surface. More specifically,  $B_1 = \alpha R_0 / \lambda$ , where  $\alpha$  is the heat transfer coefficient. The dimensionless temperature ( $\theta_c$ ) at the center of the sphere is given by  $t_s - t_0 / t_1 - t_0$ . To use the nomographs, one must select values for all the physical constants. At 500°C, which is the approximate midpoint temperature of the experimental cooling cycle, the specific heats of  $\text{Fe}_2\text{SiO}_4$  and  $\text{Mg}_2\text{SiO}_4$  are 0.20 cal/g/°C and 0.28 cal/g/°C, respectively (Touloukian and Buyco, 1970). We therefore chose a value of 0.24 cal/g/°C for the specific heat of olivine. The value  $6 \times 10^{-3}$  cal/cm/sec°C was obtained for  $\lambda$  from graphs constructed by Birch and Clark (1940) and  $3.4 \text{ g/cm}^3$  was assumed to be a suitable value for the specific weight of Hawaiian olivine (Tröger, 1959). To obtain an estimate for the value of  $B_1$ , an additional assumption had to be made. We assumed that the surface temperature of olivine grains (cooling in the Knudsen cell) would approximate the temperature of the Knudsen cell as measured by the Pt/Pt - 10% Rh thermocouple peened into the bottom of the cell. By selecting from the thermocouple cooling curve (Fig. 2, Curve 1) a temperature of 450°C which corresponds to a cooling time of 11 minutes, it was possible to calculate the corresponding values of  $\theta_s$  and  $F_0$  for 2 mm spheres. (A value of 200°C was arbitrarily chosen for  $t_0$ ). The value of  $B_1$  corresponding to these values of  $\theta_s$  and  $F_0$  was obtained from the appropriate nomograph and was found to be approximately 0.001.

Referring to the nomographs and using a Biot number of 0.001, we calculated the relationships between dimensionless temperature and dimensionless time for the center and for the surface of the given sphere to be:

$$\ln \theta_c = -3.0864 \times 10^{-3} F_0$$

$$\ln \theta_s = -3.0880 \times 10^{-3} F_0$$

For a series of values of  $\tau$ , and thus of  $F_0$ , we obtained a corresponding number of values of  $\theta_c$  and  $\theta_s$  and the corresponding temperatures  $t_c$  and  $t_s$ .

Curve 2 in Figure 2 is a plot of  $t_s$  versus time and is the calculated curve for the surface of a 2 mm olivine sphere cooling from 1250°C. The calculated curve has thus been approximately "fitted" to the thermocouple curve of the Knudsen cell (Curve 1). We next plotted the difference ( $\Delta t = t_c - t_s$ ) between center and surface temperatures as a function of cooling time. Curve 1 in Figure 1b is for an initial temperature ( $t_1$ ) of 1250°C; curve 2 for a ( $t_1$ ) of 1100°C and curve 3 for a ( $t_1$ ) of 900°C. Each curve has a maximum in  $\Delta t$  occurring after approximately 8 minutes cooling, and the level of the maximum decreases as the initial temperature ( $t_1$ ) decreases. By comparing the sets of curves in Figure 1b with those in Figure 1a, one indeed observes a positive correlation between the observed release rate of  $\text{CO}_2$  inclusions and the calculated temperature gradient in the mineral grains as they cool.

Finally, we made a rough estimate as to whether the differential expansion caused by  $\Delta t$  over the distances involved adds significantly to the internal stress in the walls of a hot  $\text{CO}_2$  inclusion in olivine. Using the expression,

$$S_r = 0.771 \frac{\alpha_t E}{2(1 - \nu)} (t_0 - t_1)$$

giving the maximum radial stress experienced by a sphere cooling from high temperatures (Grunberg, 1926) and values for Young's modulus, Poisson's ratio, and the coefficient of thermal expansion of olivine, we calculated a maximum stress of the order of 16,000 atmospheres for an olivine sphere cooling from 1250° to 200°C and 1,150 atmospheres for a sphere cooling from 900°C.

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