## Solid Inclusion Piezothermometry I: Comparison Dilatometry

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#### Abstract

Solid inclusion piezothermometry is a technique for determining the pressure and temperature of inclusion of one mineral in a host mineral. Application of the technique requires knowing the pressure-temperature curves of constant difference in natural strain between two crystallographically oriented mineral rods. For this purpose, two different kinds of comparison dilatometer, designed for use in an internally-heated high pressure gas apparatus, have been developed and are described in detail. Each design offers advantages and disadvantages in fabrication, demand upon size of sample material, and versatility.

The comparison dilatometers have been used at pressures up to 7 kbar simultaneously with temperatures up to that of the low-high quartz transition. Data obtained have been cross-checked successfully between the two kinds of comparison dilatometer and between results from them and previously-determined physical properties of synthetic periclase, synthetic halite, and quartz. As a test of accuracy, results from one design of comparison dilatometer were compared with predictions for periclase vs halite for the pressure range up to 7 kbar and temperatures up to  $\sim 600^{\circ}$ C. The maximum deviation between experimental results and prediction was  $\sim 6^{\circ}$ C at any pressure. Such accuracy is more than sufficient for developing data for use in solid inclusion piezothermometry and may be of value in determining equations of state.

#### Introduction

In reconstructing and analyzing the geologic history of an area, a frequent need has been data on the pressure and temperature of an igneous or metamorphic process. Solid inclusion piezothermometry is a procedure for determination of a pressure and temperature of crystallization of a rock by taking advantage of elastic effects in host minerals around mineral inclusions (Rosenfeld and Chase, 1961; Rosenfeld, 1969; Adams, 1971; Cohen, Rosenfeld, and Adams, 1972) or in the inclusions themselves (Harris *et al*, 1970). As currently pursued by us, the method, stripped of details, uses the following strategy:

(1) From a thin section of a given rock, small portions containing appropriately-oriented host inclusion pairs are separated from the slide and subjected to adjustment of pressure (P) and temperature (T) using experimental apparatus; a P and T is found for each pair that just causes the disappearance of the optical effect in the host due to deviatoric stress.

(2) The investigator then refers to sets of *isomekes* (Gr. "equal" + "length"), curves previously determined using separate pieces of host and inclusion minerals. Isomekes are P - T curves along each of which the distance between two reference points

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embedded in the host mineral remains equal to that between two reference points embedded in the inclusion mineral. In Part II of this series (Adams *et al.* 1975), isomekes are shown to be equivalent to curves of constant difference in natural strain between the two minerals in specific crystallographic directions. For each mineral pair, that particular isomeke is selected which incorporates values of the variables determined in the first operation. Barring complications, that isomeke will pass through the *P* and *T* at which the inclusion was incorporated in the host. The intersection of independent isomekes for two or more different pairs should be  $T_f$  and  $P_f$ , the temperature and pressure of crystallization, respectively.

In this first of two related papers, we detail the design, testing, and limitations of the comparison dilatometers that were built to yield direct determination of isomekes. The second paper of this series gives a theoretical treatment of solid inclusion piezothermometry, the calibration for quartz included in garnets (or the converse), and application of this calibration to conditions of crystallization in selected metamorphic terrains with particular reference to the  $Al_2SiO_5$  triple point.

#### **Comparison Dilatometry**

We have developed two basically different types of comparison dilatometer. Both monitor isomekes in an internally heated argon apparatus and are designed in such a way that completion of an electrical circuit indicates presence on the isomeke. Our designs differ from that of Bridgman (1949, p. 194) and many others in that no slidewire or equivalent electrical system is used.

#### **One-Contact** Dilatometers

These dilatometers are formed by clamping together pieces of the two minerals to be compared so that the effects of suitable change in P and T will cause a small, preset gap to close. Electrically conductive coatings on the two minerals allow current to flow upon contact and this indicates presence on a particular isomeke. Electrical contact can be broken only by returning to the *same side* of the isomeke as that of the starting condition.

Description of "J" Dilatometer. This dilatometer (Fig. 1), developed by Adams (1971, p. 26-28), was used in the work reported by Adams, Cohen, and Rosenfeld (1970). Even though superseded by the more easily constructed "opposed rods" dilatometer discussed later, it is illustrated here because it is the first dilatometer used to determine isomekes and because five experiments by Adams *et al* (1975) were carried out with it. The "J" dilatometer consists of two elongate pieces machined from oriented samples of the crystals to be compared. The upper crystal, or "rod", is clamped to the lower riser of a crystal shaped into a vertically flattened "J", the "base". The device is converted into an electrical switch by evaporating a thin metal coating onto the top and free end of the rod and onto the base along one side and opposite the free end of the rod. Attachment of electrical leads from a monitor outside the argon apparatus to the coating on top of the rod and on the side of the base completes the circuit.

The rod, which has the cross-sectional shape of an isosceles right triangle, is guided by a complementarily shaped right angle groove in two supports. The rod is clamped to the base by a U-shaped spring of tungsten wire constrained by a centered longitudinal groove in the bottom of the base. So that one of these supports will serve as a fiducial marker for subsquent strains of rod and base, the clamping force of the tungsten spring is positioned near that support. Thus the relatively high frictional force prevents sliding of the rod relative to that support. Motion of the free end of the rod relative to the base thus is only a function of strain of the rod along its length between the free end and the clamped position.

One electrical lead is attached to the tungsten clamp. The clamp, in turn, makes electrical contact with the metal coating atop the rod by means of a conductive paint or by a roller bearing made of stainless steel hypodermic tubing. The other electric lead terminates in a groove on the side of the base



FIG. 1. Scale drawing of "J" dilatometer. 1. Side view. Electrical lead to clamp (C) and insulation not shown. II. View from clamp end of dilatometer. III. View from top showing base (B) only. Letters designate the following components: A, roller bearing that is in electrical contact with metallic coating atop rod; B, base, one of minerals being investigated; C, tungsten wire that clamps rod to fiducial ridge in base; D, electrical contact, formed when metal coating at end of rod touches similar coating on upright part of base opposite; F, fiducial ridge; G, guiding support; R, rod, other mineral being investigated; W, other electrical lead, bonded with metallic contact cement to metallic coating on side of base. and makes electrical contact with the metal coating on the base via conductive paint.

Description of "Opposed Rods" Dilatometer. To eliminate some of the difficulties associated with the "J" dilatometer, a variant, the "opposed rods" dilatometer (Fig. 2) was developed. The longitudinal 90° groove in the "opposed rods" dilatometer is through-going and is easily ground with a shaped grinding wheel. This permitted construction of narrower but simultaneously less fragile fiducial ridges for the rods by using an Airbrasive® tool and masking technique. Narrowness of fiducial ridges ( $\approx 100$  $\mu$ m) contributes to precision, but this improvement is partly offset by error associated with the presence of the fiducial ridge for the second rod. The electrical circuit is similar to that of the "J" device.

This device also has the virtue of utilizing more readily available smaller pieces of mineral for both the rods and the base. Although vacuum-deposited conductive coatings are still necessary on the tops and contacting parts of rods, this design eliminates dependence on conductive paint, at best a somewhat unreliable component of electrical circuitry. A roller bearing is kept near each fiducial ridge so as to maintain high frictional resistance to sliding between rod and fiducial ridge but low frictional resistance at the free end.

*Experimental Procedure.* An isomeke is determined for a particular setting of the gap by noting the set of P-T points for which a voltage source just causes a detectable current to pass through the device (that is, the switch is closed). Normally an isomeke is determined with this type of device by slowly changing, say, temperature until the circuit is just closed, then *immediately* reversing the sense of temperature change so as to break the circuit before force builds up at the electrical contact and causes a rod to reset by sliding at the clamped support(s). The pressure is then changed and the previous operation repeated to locate another point on the isomeke, and so on. Figure 3 is part of a strip chart record that shows a typical example of isomeke determination.

Distinction is made between data points obtained on the P-T path going away from starting conditions and those obtained on the return path. Reproducibility is necessary for a run to be accepted. This test was applied to all dilatometers described here.

For this kind of dilatometer, the quality of coating and its adhesion to mineral surfaces is critical. For example, experimental data for "make contact" and "break contact" had to be treated separately until improved coating techniques rendered the distinction unnecessary.

The dilatometer is reset to determine a new isomeke by changing the gap width  $\gamma$  between the free end of the rod (r) and the corresponding part of the base (b) in the "J" device, or between the free



FIG. 2. Scale drawing of "opposed rods" dilatometer. I. Side view. Two insulated electrical leads, not shown, are attached to clamps (C). II. End view. III. View from top showing base (B) only. Letters designate the following components: A, roller bearings that are in electrical contact with metallic coatings atop rods: B, base, one of minerals being investigated; C, tungsten wires that clamp rods to fiducial ridges in base; D, electrical contact, formed between coatings at ends of rods; F, fiducial ridges; R, rods, other mineral being investigated. Thermocouple (not shown) is placed near dilatometer during experiment.

ends of the rods in the "opposed rods" device. This adjustment of the position of the rod(s) is normally done under a microscope at room conditions (designated by subscript o).  $\gamma$  is estimated from

$$\gamma \equiv l_{\rm bo} - l_{\rm ro} \approx [(\beta_{\rm bo} - \beta_{\rm ro})]$$

 $(P_1 - P_o) - (\alpha_{bo} - \alpha_{ro})(T_1 - T_o)]/_{bo}$  (1) where  $l_{bo}$  and  $l_{ro}$  are the lengths of mineral being compared,  $\alpha$  is the linear coefficient of thermal expansion,  $\beta$  is the linear coefficient of compressibility, and  $P_1$ and  $T_1$  are the *P* and *T* at which one desires to intercept the new isomeke.

It is evident from the nature of devices of this type, their convenient adjustment at ambient conditions, and the necessity that  $\gamma \ge 0$  (compare Equation 1 above) that they permit determination of isomekes only in that part of *P*-*T* space on one side of the isomeke passing through ambient *P* and *T*. Isomekes in the other part of *P*-*T* space are attainable by construction of a congruent device in which the oriented material of rod(s) and base are interchanged.

Accuracy. As a check on accuracy of this type of dilatometer, a "J" device was made of quartz with the base oriented || c and the rod  $\perp c$ . This combination was selected because of the existence of accurate data on  $\alpha$  and  $\beta$  for quartz (McSkimin *et al*, 1965). Figure 4 shows data for runs projecting to the temperature axis\_at 31°C and 65°C.

The points for both runs conform rather closely to straight lines having a slope of 0.0360°C/bar below approximately 3 kbar. Using equation (7-II),<sup>3</sup> this slope almost exactly equals the 0.03605°C/bar calculated for 25°C and 1 bar using data for quartz from McSkimin et al (1965). Lines bracketing the calculated slope in Figure 4 represent a standard deviation of 0.0076°C/bar, calculated from analysis of error propagation (Bevington, 1969, p. 56-65) assuming conservatively estimated standard deviations  $\sigma_{\beta}$ =  $10^{-9}$  bar<sup>-1</sup> and  $\sigma_{\alpha} = 10^{-7}$  °C<sup>-1</sup>. An estimate of the precision with which thermal expansion or compressibility in one direction, say || c, could be determined is obtained by combining the above estimate of standard deviation in slope with the same conservative assumptions for  $\sigma_{\beta \perp c}$  and  $\sigma_{\alpha \perp c}$ . We obtain  $\sigma_{\alpha \parallel c} = 0.18 \times 10^{-6} \, {}^{\circ}\mathrm{C}^{-1}$  and  $\sigma_{\beta \parallel c} = 0.0074 \times 10^{-6}$ bar-1.

*Critique*. These devices have the great advantage of simplicity of design; and some excellent data, such as those in Figure 3, have been obtained with them.



FIG. 3. Part of 2-pen strip chart record for determination of an isomeke between quartz (48° from c) and almandine using the "J" dilatometer. Corrected for offset of pens.

Their designs do not make strong demands on precision of machining. Unlike the design of Bridgman (1949, p. 194) and in common with our other dilatometers, possibility of hysteresis and other error due to "stick-slip" of sliding parts is reduced essentially to nonexistence. There are also difficulties. Construction of the base of the "J" dilatometer requires a rather large homogeneous crystal—a major objection when dealing with natural materials in which zoning and inclusions are commonly present.



FIG. 4. Data points obtained with "J" dilatometer for determination of two isomekes between quartz  $\perp c$  and quartz  $\parallel c$ . The intermediate straight line associated with the set of experimental points denoted by circles was determined using Equation (7-II) and data at 25°C and atmospheric pressure from McSkimin *et al* (1965). Straddling lines indicate standard deviation of slope based on estimated standard deviations of properties used in Equation (7-II).

<sup>&</sup>lt;sup>3</sup> Equations so labeled are from Part II of this series (Adams et al, 1975).

That dilatometer is not easy to construct, since the 90° groove in the supports, even though not demanding precision, is obtained by hand-lapping with a very short stroke. The fundamental asymmetry in the "J" dilatometer might also be increased by any temperature inhomogeneity within the high pressure apparatus. Scanning electron microscope examination shows that vacuum-evaporated metal coatings crumple when scratched, tear from pressure welding, and occasionally buckle after high temperature runs due to differential strain between coating and substrate or expansion of gas beneath the coating; such damage may cause nonrandom errors that are difficult to detect or evaluate. The lesser problem of resetting of the devices can be offset by careful experimental procedure. The earlier-mentioned necessity of making two devices of this type, interchanging materials of rod(s) and base, to explore all of P-Tspace is an added difficulty.

## Two-Contact ('Gate') Dilatometer (Figure 5)

This dilatometer is formed by clamping rods of the two minerals to be investigated side-by-side to a nonreactive base. Only when both rods are of equal length do the two simultaneously make contact with a spring-loaded, hinged gate. Such contact completes a series electric circuit, and the flow of current indicates presence on a particular isomeke. Electric contact can be broken by *any P-T* change away from the isomeke.

Description. In the "gate" dilatometer, any condition of equidistance  $l_x = l_y$  between fiducial ridges  $F_1$  and  $F_2$  in the base B, and the free ends of the rods  $R_1$  and  $R_2$ , is indicated by completion of an electrical circuit. When the circuit (Fig. 7) is completed, *i.e.*, when on an isomeke, the electrical path from the voltage source is: strip chart recorder; chromel lead through closure piston to chromel terminal; gold wire



FIG. 5. Stereoscopic photograph of "gate"-type comparison dilatometer. Units on scale are millimeters. See Figure 6 for identification of parts.

#### SOLID INCLUSION PIEZOTHERMOMETRY-I.



FIG. 6. Scale drawing of "gate" dilatometer. I. Side view, supports (S) removed for clarity. II. View from gate end with gate removed. III. View from top; some components removed for clarity. IV. Gate. Letters designate the following components:  $A_1$ ,  $A_2$ -roller bearings; B-base;  $C_1$ ,  $C_2$ -tungsten wires that clamp rods to fiducial ridge in base;  $E_1$ ,  $E_2$ -electrical contact ball bearings;  $F_1$ ,  $F_2$ -fiducial ridges; G-gate;  $H_1$ ,  $H_2$ -hinge ball bearings; J-connection between gate and gate spring;  $R_1$ ,  $R_2$ -rods of minerals being investigated; S-supports for dilatometer; T-thermocouple;  $U_1$ ,  $U_2$ -spring clamps that keep electrical contact balls,  $E_1$  in contact with rods, R, and also serve as part of the electric switch circuit;  $W_2$ -electrical lead from closure piece to electrical contact ball,  $E_2$  (note:  $W_1$  not shown);  $W_g$ -electrical lead, when connected, from gate to ground; Y-gate spring.

 $W_1$  to clamped end of rod  $R_1$ ; through W-Re alloy spring clamp U<sub>1</sub> to coated 0.7938 mm (0.03125  $\pm$ 0.00001 inch) stainless steel ball bearing E1 that was welded to U<sub>1</sub> before coating; through polished, optically flat, tungsten carbide gate G; and then back to the voltage source along a path on the other side of the device, symmetrically equivalent except for absence of the recorder. The chromel-alumel thermocouple T (Figs. 6, 7) is placed in a longitudinal central groove in the base with the junction located symmetrically in the plane of the rods. The voltage developed by the thermocouple is charted by one pen of a two-channel recorder, and current through the electrical contact circuit is charted by the other pen. Lead W<sub>g</sub> from the gate to ground via J and the gate spring Y is useful primarily for trouble-shooting malfunctions in electrical contacts.

Certain design features of this dilatometer merit attention. The position at which the gate is loaded by J lies just beneath the intersection of two hypothetical lines connecting the points of contact between  $E_2$  and  $H_1$ , and  $E_1$  and  $H_2$ . Except for the small deformation of rods, balls, and gate under the slight spring forces used, the method of loading the gate assures that there will be an electrical signal only when the centers of the four balls are coplanar. Under this circumstance, presence on an isomeke is assured, given sufficiently precise shaping of base, balls, and gate.

The five straight lengths of 0.508 mm diam. tungsten wire, S and C, support the dilatometer. Supports S terminate on both ends in segments of fired pyrophyllite rod that simultaneously hold the device, conduct electrical wires to the dilatometer, fill space inside the cylindrical furnace, and center an encapsulating cylinder of stainless steel with internally nested cylinder of gold. The high thermal conductivity of the last reduces thermal gradients in the vicinity of the dilatometer to negligible values. Springs C cause roller bearings A to pin the mineral rods to fiducial ridges F and also hold the dilatometer in place. The roller bearings are an important feature, since they also effectively decouple the dilatometer from flexural motions of the supporting assembly.

The base was machined from annealed, stoichio-



FIG. 7. Schematic diagram of electrical circuitry for the "gate"type dilatometer. I is the ice bath for the cold thermocouple junction. Other lettered parts are same as in Figure 6.

metric spinel (MgAl<sub>2</sub>O<sub>4</sub>), manufactured using the Czochralski process by Union Carbide. It proved very satisfactory. Spinel was selected because of its high crystal symmetry, homogeneity, absence of any easily cleaved direction, high electrical resistivity. hardness, strength, low coefficient of thermal expansion, high density of packing of oxygens (to preclude possible problems from diffusion of argon at high pressure), and highly annealed character corresponding to maximum deviatoric stress  $\approx 10^2$  bars (maximum birefringence  $\approx 10^{-5}$ ). Wires of tungsten and various tungsten-rhenium alloys maintained their elasticity to the highest temperatures employed (~800°C in a dry argon atmosphere) and therefore proved satisfactory in construction of the supports and springs. Supports S and spring clamps C are made of pure tungsten wire, whereas slightly more ductile wire of W<sub>95</sub>Re<sub>5</sub> or W<sub>74</sub>Re<sub>26</sub> is used for parts that must be bent or welded-U, J, Y, and wire welded to H<sub>1</sub> and H<sub>2</sub>. The stainless steel (440C) balls are manufactured by Winsted Precision Ball Company for ball point pens. To enhance durability under experimental conditions, the electrical contact balls E are coated on the contact side at 600°C in a vacuum evaporator, first with chromium, and next

with  $Pt_{80}Pd_{20}$  alloy. In spite of the coating, electrical contacts on the balls become pitted at higher temperatures; generally, a new set of electrical contact balls is used for each experimental run. In order to minimize deterioration of electrical contacts, the DC signal current is kept low, ~1.4  $\mu$ A. Deterioration of electrical contacts presently limits the temperature range of accurate experimentation to approximately 650°C, although useful experiments have been performed to 800°C.

The contact side of the gate is optically flat, and the gate itself must be conducting, stiff, hard, not subject to warping, capable of taking and keeping a polish, and of low corrosivity. Gates of antimony-doped single crystal silicon yielded good results, but they rapidly decrease in their already low electrical conductivity during the course of experiments. We therefore employ very fine-grained tungsten carbide (Carmet 310) which, although it behaves well during a single run, must be polished and checked against an optical flat before starting each new run, since a fine powder forms on its polished surface upon removal to air.

*Experimental Procedure.* With the gate dilatometer the necessary and *sufficient* condition for presence on an isomeke is completion of the electrical circuit through the dilatometer. It is not necessary to be alert at the controls of the argon apparatus, as presence of the free-swinging gate normally precludes resetting. Figure 8 shows 10 minutes of recording from a run using this dilatometer. The finite, but small, width of the signal probably indicates a slight departure from rigidity within the dilatometer. This is perhaps due primarily to elastic flattening of balls rather than torsion of the gate, because variation in thickness of the gate does not noticeably affect the signal width. The signal width corresponds to a strain



FIG. 8. Part of 2-pen strip chart record for determination of an isomeke between quartz  $\perp c$  and spessartitic almandine using the "gate" dilatometer (WC gate). Corrected for offset of pens.

difference of the rods between  $25 \times 10^{-6}$  and  $50 \times 10^{-6}$ . In assessing precision, it is probably more significant to pay attention to the signal edge, where the "noise" indicates sensitivity to strain differences of  $\sim 10^{-6}$ , *i.e.*, length difference of  $\sim 100$  Å. The "true" isomeke is presumably the *P*-*T* curve for which the two balls are equally flattened. This would probably be a curve intermediate between, and parallel to, the *P*-*T* curves for each of the signal edges. Since these curves are essentially parallel, there is little trouble in inferring the position of the "true" isomeke.

In each determination of an isomeke, the earliest *P-T* points are redetermined at the end of the run as a check against resetting or deterioration of electrical contacts. An important check before starting a run was to ascertain that the balls E were seated in the 90° grooves. Setting of the gap  $\gamma$  between one ball and the gate is based on Equation (1). The magnitude of  $\gamma$  determines  $\delta_{x-y}$ , the natural strain difference, in conformity with (5-II):

$$\delta_{\mathbf{x}-\mathbf{y}} = \ln\left(1+\frac{\gamma}{l_{\mathbf{x}\mathbf{o}}}\right) \approx \frac{\gamma}{l_{\mathbf{x}\mathbf{o}}}.$$
 (2)

In contrast with the "J" and "opposed rods" devices,  $\gamma$  may be either positive or negative, depending only upon arbitrary assignment of the labels "x" and "y" to the rods. Thus *all* of *P*-*T* space is accessible by mere adjustment of the rods. Setting gap widths of 0  $\mu$ m to 20 $\mu$ m, using a machinist's microscope at ambient conditions, is not too difficult, since the permitted fractional error in setting is rather large. We were able to set gaps with a precision of 2  $\mu$ m or better.

Accuracy. To give accurate results, the gate dilatometer makes greater demand on precision machining than do the "J" and "opposed rods" dilatometers, both of which adhere more closely to the principles of kinematic design (Wilson, 1952, p. 104). As well as having a number of parts, a basic reason for this demand is the dependence upon a longitudinal vertical plane of symmetry that maintains itself during experimentation. During development of the "gate" device, data from both kinds of devices were cross-checked, with results becoming concordant for the latest models.

For a test of accuracy of the "gate" device, we used independent standards whose relevant properties had been studied over a range of simultaneously elevated P and T. Figure 9 shows data for four isomekes for single crystal rods of synthetic periclase (MgO) and synthetic halite (NaCl). The solid lines are from numerical integration of Equation (7-II) using the  $\alpha$ 's and  $\beta$ 's from second degree trend surfaces fitted to the values of these quantities for MgO (Spetzler, 1969, p. 151–171) and NaCl (Spetzler, Sammis, and O'Connell 1972, p. 1735–1737). Below 1 kbar the data points forming the curve having a 45°C intercept at 1 bar lie essentially on a straight line having a slope equal to that calculated from  $\alpha$ 's and  $\beta$ 's at 25°C and 1 bar, using Equation (7-II). At 7 kbar the maximum departure in temperature is only ~6°C. The agreement between the two approaches is good. It thus appears that, given sufficient care, both kinds of comparison dilatometer can give isomekes that accord with those determined by independent means.

Although it is not the primary purpose of this paper to explore the suitability of comparison dilatometers for work on equations of state of solids, it is obvious that they may prove useful in this regard. To check further on accuracy, we determined isomekes for synthetic stoichiometric spinel (subscript s) against "standards" NaCl (subscript h) and MgO (subscript p) in order to determine  $\alpha_s$  and  $\beta_s$  at 25°C and 1 bar. Synthetic spinel is currently undergoing investigation by R. J. O'Connell (personal communication), and preliminary information is available. Solution of two simultaneous equations of the form of (7-II) for m, the derivative of an isomeke, yields:

$$\alpha_{s} = \frac{(\beta_{h} - m_{h-s}\alpha_{h}) - (\beta_{p} - m_{p-s}\alpha_{p})}{m_{p-s} - m_{h-s}}$$
(3a)

and

$$\beta_{s} = \frac{m_{p-s}(\beta_{h} - m_{h-s}\alpha_{h}) - m_{h-s}(\beta_{p} - m_{p-s}\alpha_{p})}{m_{p-s} - m_{h-s}}$$
(3b)

From Equation (3) and expressions for error propagation based on estimated standard deviations, we get

$$\alpha_s = (5.86 \pm 0.17) \times 10^{-6} \,^{\circ}\mathrm{C}^{-1}$$
  
 $\beta_s = (0.1708 \pm 0.0022) \times 10^{-6} \,\mathrm{bar}^{-1}$ 

O'Connell (personal communication), from ultrasonic measurements, obtains

 $\beta_s = (0.1689 \pm 0.0005) \times 10^{-6} \text{ bar}^{-1}.$ 

If we use O'Connell's value of  $\beta_s$  as given and solve equations like (7-II) and (3) for  $\alpha_s$  and  $\sigma_{\alpha s}$ , first using  $m_{h-s}$  and then  $m_{p-s}$ , we obtain, respectively,

$$\alpha_s = (5.80 \pm 0.11) \times 10^{-6} \, ^{\circ}\mathrm{C}^{-1}$$

$$\alpha_s = (5.62 \pm 0.10) \times 10^{-6} \, ^{\circ}\mathrm{C}^{-1}$$

There is no satisfactory value in the literature for  $\alpha_s$ ,



FIG. 9. Data obtained with "gate" dilatometer (WC gate) for four isomekes between synthetic periclase and synthetic halite. Solid lines are isomekes calculated from results of ultrasonic measurements by Spetzler (1969) and Spetzler *et al* (1972).

and it will be interesting to obtain an independent value for it. The success in determining  $\beta_s$  and the independent replication of  $\alpha_s$  using two different isomekes suggests that the "gate" dilatometer provides accuracy that is, perhaps, sufficient for study of equations of state of solids. This is a task whose demands for experimental accuracy considerably exceed those of solid inclusion piezothermometry.

Critique. The most important reasons for adoption of the "gate" over the "J" and "opposed rods" devices are: (1) The difficult machining is concentrated into one base that is used for all experiments. Only the rods of minerals to be compared need separate machining, a task easily accomplished with conventional equipment. (2) It is unnecessary to coat the mineral rods to form an electrical circuit. (3) All of P-T space is accessible to isomeke determinations with only one experimental assembly, merely by appropriate adjustment of the gap between one or the other ball contacts and gate. (4) The mineral rods used are much less demanding of large single crystals. (5) The gate device, with sensitivity to strain

differences  $\approx 10^{-6}$ , appears to be more precise by about an order of magnitude. (6) The symmetrical design and better thermocouple placement probably improve accuracy. (7) Because of the hinged gate, there is no resetting by sliding of rods on the fiducial ridges if care is taken in adusting forces of the spring clamps relative to that of the gate spring. (8) The guiding channels for electrical leads in the base and the supports S and clamps C greatly reduce the likelihood of short circuits due to movement of components. (9) The gap that determines location of an isomeke can, with practice, be more precisely set because of doubling of the apparent gap due to reflection by the polished gate. (10) Once assembly is completed, the gate device permits convenient and rapid switching of rods.

Some disadvantages of the "gate" device are: (1) The many more components than those of the other devices require considerable time, care, effort, and complicated procedure for their manufacture. This is especially true of the spinel base. (2) *Initial* assembly of the "gate" device takes considerably longer than

assembly of the other devices and requires patience, care, and steadiness-of hand. (3) There is a possibility that the balls E will rotate during an experiment and therefore travel slightly across the ends of the rods as a result of differential strain of the wires U and the rods. This is an uncontrolled variable and conceivably could cause a slight experimental inaccuracy. (4) The small longitudinal compressive stresses on the rods, resulting from forces of springs U and Y, are approximately equivalent on both rods and probably have negligible effect.

One minor source of inaccuracy is common to both kinds of dilatometer—the finite width ( $\sim 1\%$  of rod length) of the fiducial ridge. It is conceivable that, within the width of the ridge, the "pinning" position of a rod may vary reversibly or irreversibly during the course of an experiment.

If the more demanding needs of determination of equations of state are to be satisfied, it should be possible to modify the "gate" dilatometer to eliminate some of the deficiencies cited. Work is in progress on some of these improvements.

## **High Pressure Apparatus**

Experiments were performed in the internally heated argon high pressure apparatus described by Goldsmith and Heard (1961). Pressure was determined using a 7 kbar Heise Bourdon tube gauge, and temperature was determined with chromel-alumel thermocouples. Electrical and thermocouple leads pass through an axial hole in the closure piston (Goldsmith and Heard, Fig. 1), to two chromel and one alumel thermocouple leads, introduced in the same manner as described by Goldsmith and Heard (1961). Signal power was supplied from a 1-1/2 volt battery through a resistor across the input of a potentiometric millivolt recorder. Closing the circuit allowed a  $\sim 1.4 \ \mu A$  current to flow, the presence or absence of which was recorded on the strip chart simultaneously with the thermocouple millivoltage (Figs. 3, 8). Pressure is noted with a precision of better than  $\pm$  5 bar on the strip chart from visual readings of the Heise gauge.

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# Solid Inclusion Piezothermometry II: Geometric Basis, Calibration for the Association Quartz—Garnet, and Application to Some Pelitic Schists

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#### Abstract

A procedure that enables determination of a pressure-temperature curve containing the pressure and temperature of incorporation of one mineral into a crystallizing host mineral consists of two steps. One step is determination of any experimentally-determined pressure and temperature for which a piezobirefringent halo in the host around the inclusion just vanishes. The second step uses a set of pressure-temperature curves, each of which indicates constant difference in natural strain between the two minerals as obtained by comparison dilatometry (Part I of this series). Barring complications, especially plastic creep, the curve that passes through the pressure and temperature at which the halo vanishes contains the pressure and temperature of incorporation. The intersection of two independently-determined curves of this type is the pressure and temperature of incorporation.

We report calibration of the association, quartz in three different orientations and garnet having a variety of compositions, to 7 kbar between 25°C and just below the low-high quartz transition. Extreme compositional variation within the solid solution (Fe<sup>2+</sup>,Mg, Ca, Mn<sup>2+</sup>)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> has little effect on calibration. An implication of our work is that the linear coefficient of thermal expansion of almandine-type garnet near standard conditions is ~7.58  $\times 10^{-6}$  °C<sup>-1</sup>, considerably higher than previously accepted.

Tight pressure-temperature restrictions on the  $Al_2SiO_5$  triple point, consistent with the determinations of Newton and of Holdaway, result from applications of solid inclusion piezothermometry and other petrological information to occurrences in New England and an Alpine occurrence. The inferred denudation rate of  $0.5 \pm 0.1$  mm/year at the Alpine occurrence lies within the range of values obtained by Clark and Jäger from data on heat flow and geochronology at the nearly Gotthard Tunnel.

## Introduction

Some years ago Rosenfeld and Chase (1961, p. 528–535) and Rosenfeld (1969, p. 320–331, 345–347) discussed application of comparison dilatometry to solid inclusion piezothermometry, a procedure for

determination of the pressure and temperature at which a mineral inclusion was incorporated into a host mineral. In the previous paper of this series (Adams, Cohen, and Rosenfeld, 1975; hereafter referred to as Part I), we have detailed techniques of comparison dilatometry that were petrologically motivated.

In this paper we pursue further petrological goals by (1) elaboration of the general qualitative

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<sup>&</sup>lt;sup>2</sup> The authors consider themselves equal partners in carrying out the work described herein.

geometric basis for solid inclusion piezothermometry, previously treated extensively and quantitatively for the special case of the host-inclusion pair, almandine-quartz (Rosenfeld, 1969, p. 320-328); (2) presentation of results of comparison dilatometry between garnet of various compositions and quartz in three orientations, extending the work of Adams et al (1970) to higher pressures; (3) correction, based upon experiments, of precalibration petrological inferences of Rosenfeld (1969, p. 335-345); and (4) addition of new observations on metamorphic rocks in western New England and the central Alps. We also briefly call attention to the discordance of our comparison dilatometry with previous X-ray diffraction work on synthetic almandine (Skinner, 1956).

#### **Basis for Solid Inclusion Piezothermometry**

#### Relationship of Geometry to Method

Assumptions of our model are that: (1) at the condition of envelopment (designated by subscript f) by the host, the inclusion is

- (a) congruent to its cavity in the host;
- (b) at the same temperature  $(T_f)$  as that of the host;
- (c) at the same pressure  $(P_t)$  as that of the host; and that pressure is, for all practical purposes, hydrostatic;

and (2) after envelopment,

- (d) host and inclusion are of such strength and stability that, within the lifetime of the combination and the conditions affecting it, all strains are solely elastic and thus not the consequence of plastic flow, phase transition, or radioactive damage;
- (e) no tensile stress is maintainable across the interface between inclusion and host; and
- (f) the inclusion does not shift irreversibly to a new position in the cavity.

The outline of the inclusion at  $P_f$  and  $T_f$  is the reference state for subsequently developed strains of inclusion and host.

For the purposes of analysis of ensuing strains and their implications, conceive the inclusion to be removed from the host without rotation and its outline to be superposed on the outline of the cavity in the host. Further, let host and inclusion, considered in this way, undergo identical changes in homogeneously distributed temperature and hydrostatic pressure.

If this assemblage, as imagined above, is subjected

to a sufficiently wide range of pressure-temperature conditions, two regions in P-T space will logically arise if host and inclusion have different equations of state. Region I will be characterized by the presence of at least one direction in the inclusion for which its strain ( $\equiv$  fractional change in length) is greater than the strain of the cavity in the same direction. Region II will be characterized by the absence of any direction for which the strain of the inclusion is as great as that of the cavity in the same direction. These two regions will be separated by a boundary along which, at each point, (1) there will be at least one direction in the inclusion for which the strain in the inclusion is equal to that in the host in the same direction; and (2) there will be no other direction for which the strain in the inclusion exceeds that of the host. That boundary will, of course, include  $P_f$  and  $T_f$  if the stated restrictions apply.

Now consider the inclusion within the host. By some procedure, permit access of a pressure medium of low viscosity to the host-inclusion interface. There will be a region of the P-T diagram within which the strains of both inclusion and host are governed by the second-rank tensor properties, thermal expansion and compressibility, which relate strain to the scalars, respectively temperature and hydrostatic pressure (Nye, 1957, p. 290). This region is characterized by those conditions for which all strains in the inclusion are less than those in the host in the same directions (i.e., region II). This would not necessarily have been so if the pressure medium had not been permitted access to the host-inclusion interface.<sup>3</sup> Within region I. on the contrary, the situation is more complicated. There the strains of both inclusion and adjacent host are governed by second-rank thermal expansion tensors and fourth-rank compliance tensors, relating strain to nonhydrostatic stress. Accommodation of an inclusion, which in the model has at least one direction in which strain of the inclusion exceeds that of the host in the same direction, results in a halo of inhomogeneously distributed nonhydrostatic stress in the host around the inclusion.

In the absence of relaxational phenomena within or around the *in situ* inclusion, the boundary between regions I and II must pass through  $P_t$  and  $T_t$ . Further, that boundary can be located because nonhydrostatic stress in the host around the inclusion in

<sup>&</sup>lt;sup>3</sup> The preceding sentences of this paragraph state the essential "trick" that allows avoidance of difficult problems in elasticity and permits use of hydrostatic pressure apparatus in our system of piezothermometry.

region I causes a stress-optical effect that is visible under the petrographic microscope. If a polished thick or thin section of the assemblage is made parallel to a section of zero birefringence in the host away from the influence of the inclusion, this effect, due to a field of deviatoric stress, expresses itself between crossed polars as a piezobirefringent halo. The boundary is then recognizable as the limiting P-T line for disappearance of the piezobirefringent halo.

Although it is more nearly precise to consider the assemblage in three dimensions, it is also useful in many cases to reduce the conceptual model to one that is approximately two dimensional rather than three dimensional (Rosenfeld, 1969, p. 318-329, 338). This particularly applies to thin sections in which a host-inclusion combination is cut so thin and in such an orientation as to have the cavity boundary penetrate the section essentially perpendicularly. The same analysis as in the previous paragraph applies, except that only strains parallel to the section are considered. The comparable subdivisions of the P-Tdiagram in this case will, in general, be different from that for the three-dimensional case except for highly symmetric combinations in which both host and inclusion are cubic. The boundaries, in either case, include  $P_{\rm f}$  and  $T_{\rm f}$ .

The principal advantages of the two-dimensional simplification over the three-dimensional approach are: (1) ease of laboratory observation: thin sections readily permit laboratory identification of conditions of equal strains in host and inclusion; (2) the fact that the direction of equal strains is very nearly restricted to the plane of the section; (3) the fact that sectioning permits access of a fluid medium of low viscosity and thus the operating pressure of the system to the region between host and inclusion;<sup>4</sup> and (4) the fact that the piezobirefringent halo becomes sensitive not only to P and T but also to the angular relations among the host, inclusion, and thin section.<sup>5</sup>

As defined in Part I, an *isomeke* is any *P*-*T* curve along which the distance between two reference points embedded in the hydrostatically stressed host mineral remains equal to that between two reference points embedded in the hydrostatically stressed inclusion mineral. The boundary between regions *I* and *II*, mentioned above, is an isomeke.

Determination of any isomeke, passing through  $P_{\rm f}$ ,  $T_{\rm f}$ , is a two-step procedure. First, a comparison dilatometer (see Part I) is constructed using pieces of the host and inclusion minerals being studied. This device is designed to monitor a set of isomekes passing through a P-T region that is sufficiently large to include any possible values of  $P_f$  and  $T_f$ . Each isomeke, by definition, shares the property that it is a P-T trajectory for which the length of an appropriately oriented line segment between two points of reference<sup>6</sup> embedded in a piece of the inclusion mineral equals that between similarly defined points in a piece of the host mineral. Secondly, let some laboratory pressure  $(P_n)$  and temperature  $(T_n)$  be found for which the piezobirefringent halo around the inclusion in the host is observed to vanish. The isomeke passing through  $P_f, T_f$  is then that particular isomeke passing through  $P_n, T_n$ . The intersection of that isomeke with another, independently determined for some other host-inclusion combination in the specimen, uniquely specifies  $P_f, T_f$ , assuming that both combinations formed under the same conditions.

## Relationship of Solid Inclusion Piezothermometry to Equations of State

Because equations of state provide an alternate means for the determination of isomekes, it is desirable to clarify their interrelationship.

Let the *natural strain* (Nadai, 1950, p. 73-74)  $\bar{\epsilon}$  between two points of reference embedded in a given solid be defined as

$$\tilde{\epsilon} \equiv \ln\left(\frac{l}{l_0}\right) = \ln\left(1 + \epsilon\right)$$
 (1)

where

 $l \equiv$  distance between the points at some P and T

o  $\equiv$  subscript indicating standard conditions, P = 1 bar and  $T = 25^{\circ}$ C, not necessarily on a desired isomeke.

<sup>&</sup>lt;sup>4</sup> Rosenfeld (1969, p. 320–326, 330) makes applications based on the two-dimensional approach, which entails relaxation by thinsectioning of some or all of the elastic strain due to deviatoric stress. Determination of the angular relations for elimination of that strain is an essential feature of the method. That this approach can only be approximate when dealing with noncubic minerals results from the necessarily finite thickness of the thin section, the irregular shapes of real inclusions, and the possible presence of shear stresses parallel to the host-inclusion contact.

<sup>&</sup>lt;sup>5</sup> As an example, let  $\theta$  be the angle between the section normal and c of a uniaxial inclusion (e.g., quartz) in an optically isotropic host (e.g., garnet). A *P*-*T* region will exist for which the condition of appearance of a piezobirefringent halo at a particular *P* and *T* is  $\theta > \theta_c$ , where  $\theta_c$  is the limiting value of  $\theta$  for which a halo appears (Rosenfeld, 1969, p. 320–323).

<sup>&</sup>lt;sup>6</sup> The line segments connecting the reference points in each piece also must parallel the crystallographic directions within host and inclusion for which the strains are equal in the conceptual model. While it is simple to identify these directions for minerals of high symmetry (see, for example, Rosenfeld, 1969, p. 318-327), a general procedure that is also applicable to minerals of the least symmetric crystal systems has not yet been developed.

$$\epsilon \equiv \frac{l-l_0}{l_0} \equiv$$
 the conventional strain.

Then the natural strain difference,  $\delta_{x-y}$ , between the line segments connecting two reference points embedded in solid x and two reference points embedded in solid y at some arbitrary P and T is

$$\delta_{x-y} \equiv \bar{\epsilon}_x - \bar{\epsilon}_y \tag{2}$$

Now an isomeke, by definition, is a curve in P and T along which two reference points embedded in x remain the same distance apart,  $l_x$ , as that between two reference points embedded in y,  $l_y$ , or

$$l_x = l_y \tag{3}$$

The location of the isomeke is uniquely determined by the ratio of  $l_y$  to  $l_x$  at standard conditions,  $l_{y0}/l_{x0}$ , which is a constant, not necessarily equal to unity, for a given isomeke. To see this, from Equation (1) we obtain

$$\ln l_x = \bar{\epsilon}_x - \ln l_{x0} \tag{4a}$$

$$\ln l_y = \bar{\epsilon}_y - \ln l_{y_0} \tag{4b}$$

Subtracting Equation (4b) from (4a) and using Equations (2) and (3), we find

$$\delta_{x-y} = \ln\left(\frac{l_{y0}}{l_{x0}}\right)$$
 (5)

 $\delta_{x-y}$  is thus constant along a given isomeke and can, in principle, be determined at standard conditions by measuring  $l_{x0}$  and  $l_{y0}$ . From Equation (2) the relationship between an isomeke and the equations of state of two solids is also evident. An isomeke is found to be any curve in P and T along which the difference in natural strain is constant. Thus a good graphical way to see the functional relationship between isomekes and equations of state is a P-T diagram with contours of constant natural strain. The superposition of such diagrams for x and yallows determination of isomekes by a simple procedure. Each isomeke is a contour of constant difference,  $\delta_{x-y}$ , in natural strain.<sup>7</sup> If, eventually, an accurate way for measuring  $\delta_{x-y}$  can be incorporated into our system of comparison dilatometry and the equation of state of x is known, it follows from Equation (2) that  $\bar{\epsilon}_{y}$  can be determined all along the isomeke characterized by that  $\delta_{x-y}$  by subtraction of  $\delta_{x-y}$  from  $\bar{\epsilon}_x$ . The equation of state of y could thereby

be determined by generation of suitably spaced isomekes.

The differential equation of an isomeke also follows from Equation (2). The total differential of  $\delta_{x-y}$  is

$$d \delta_{x-y} = \left(\frac{\partial \delta_{x-y}}{\partial T}\right)_{P} dT + \left(\frac{\partial \delta_{x-y}}{\partial P}\right)_{T} dP \qquad (6)$$

At constant  $\delta_{x-y}$ ,

$$m_{x-y} \equiv \left(\frac{\partial T}{\partial P}\right)_{\delta_{x-y}} = -\frac{(\partial \delta_{x-y}/\partial P)_T}{(\partial \delta_{x-y}/\partial T)_P}$$
$$= \frac{-[(\partial \bar{\epsilon}_x/\partial P)_T - (\partial \bar{\epsilon}_y/\partial P)_T]}{(\partial \bar{\epsilon}_x/\partial T)_P - (\partial \bar{\epsilon}_y/\partial T)_P} = \frac{\beta_x - \beta_y}{\alpha_x - \alpha_y}$$
(7)

where  $\beta$  and  $\alpha$  are, respectively, the isothermal linear compressibility and isobaric linear coefficient of thermal expansion, both simply defined as partial derivatives of  $\overline{\epsilon}$ .

There is ample reason, therefore, to use  $\bar{\epsilon}$ -P-T diagrams in analyzing data from comparison dilatometry.

## Calibration for Association Quartz-Garnet

The previous calculation of families of isomekes (Rosenfeld, 1969, p. 327-334; there called "integral null curves" or "isogons") for almandine-quartz was based on the very scant data on  $\alpha$ 's and  $\beta$ 's and on long-range extrapolation using more-or-less reasonable boundary conditions.

We present here the experimental calibration of the association quartz (q)-garnet (g), emphasizing garnet of the almandine type (garnet #1, in Table 1 and Fig. 1). Limited experiments on other garnets, whose compositions are also shown in Table 1 and Figure 1, allow some generalization about the effect of solid solution on the almandine-quartz isomekes. All garnets were analyzed by electron microprobe.

#### **Experimental Results**

# Results for Pair: Quartz-Almandine-Type Garnet

Figures 2, 3, and 4 show data points within the region bounded by the low-high quartz transition and 7 kbar for isomekes of almandine-type garnet (garnet #1) relative to quartz. In Figure 2 the quartz rod is oriented  $\perp c$ ; in Figure 3 it is oriented at an angle of 45° relative to c; and in Figure 4 it is oriented || c. The curves in these figures are derived as described in a section below. For convenience in petrographic utilization (Rosenfeld, 1969, p. 327-328), the curves are identified by  $\sin^2\theta$ , where  $\theta$  is the angle between

<sup>&</sup>lt;sup>7</sup> The method of plotting isomekes is identical to that used by geologists in plotting convergence maps, maps showing contours of constant vertical component of thickness of a stratigraphic unit (Lahee, 1941, p. 649-654).

## ADAMS, COHEN, AND ROSENFELD

TABLE 1. Compositions of Garnets Studied

	1		2	3	4	5	6	
				Weight percent oxi	des			
SiO2 TiO2 A1203 Cr203 FeO MnO MgO CaO Total	37.77 0.00 21.11 0.00 35.11 2.24 4.53 0.39 101.15		38.25 0.00 21.55 0.04 26.09 2.32 9.47 1.92 99.64	43.04 0.38 22.94 0.18 10.17 0.30 19.02 4.87 100.90	42.30 0.14 22.19 1.89 8.84 0.35 19.03 5.16 99.90	36.43 0.00 20.64 0.00 18.65 24.29 0.00 0.32 100.33	39.23 0.19 21.80 0.00 1.84 0.45 0.00 34.76 98.27	
Si Al Cr Ti Mg Fe2+ Mn Ca	3.00 1.97 0.00 0.00 0.54 2.33 0.15 0.03	3.05	Number 2.97 1.97 0.00 0.00 1.10 1.69 0.15 0.16	of ions on the basis 3.04 1.91 0.01 0.02 2.00 3.10 0.60 0.02 0.37 2.99	of 12 oxygens 3.02 1.87 0.11 0.01 2.03 0.53 0.02 0.40 2.9	3.00 2.00 0.00 0.00 1.28 1.69 0.03 3.00	$\begin{array}{c} 3.01 \\ 1.97 \\ 0.00 \\ 0.01 \\ 0.00 \\ 0.12 \\ 0.03 \\ 2.86 \end{array} $ 3.	01
				Mol. percent compon	ents			
Fe3A12Si3O12 Ca3A12Si3O12 Mg3A12Si3O12 Mn3A12Si3O12 Ca3Cr2Si3O12	76.39 0.98 17.70 4.92 0.00		54.52 5.16 35.48 4.84 0.00	20.23 11.40 67.43 0.60 0.34	19.16 2.71 73.49 0.77 3.87	42.67 1.00 0.00 56.33 0.00	3.99 95.02 0.00 1.00 0.00	
		1. 2. 3.	Almandi Pyropic Pyrope	ne Source : F. Bir Almandine U.S.N.M U.S.N.M. #107062,	ch; locality un . #120315, Fort Alice Springs,	known Defiance, Arizona Australia		2

Cr-Pyrope -- UCLA Museum 3227D, Arizona

5. Spessartitic Almandine -- Verma #1 (Verma, 1960)

6. Grossular -- Asbestos, Quebec (J. Arem, Collector)



FIG. 1. Compositional tetrahedron for garnets used in comparison dilatometry. Numbers correspond to chemical analyses listed in Table 1.

the axis of the rod and the  $\perp$  to c (*i.e.*, for quartz  $\perp$  c  $\sin^2\theta = 0$ ). It is easily seen that, in applying these results to thin sections,  $\theta$  is the same angle as  $\theta$  in the comparison dilatometry (see footnote 5).

# Results for Pairs: Quartz and Pyropic, Spessartitic, and Grossularitic Garnet

Figures 5, 6, and 7 show data points for isomekes of quartz in the two principal orientations relative to pyropic (Table 1, #3), spessartitic (#5), and grossularitic (#6) garnets. Similar determinations, not illustrated because they are concordant, were made for garnets #2 and #4 of Figure 1 and Table 1. The solid curves in Figures 5, 6, and 7 are derived from interpolation equations presented below for isomekes of quartz-almandine-type garnet and are placed in the figures for purposes of comparison.

# **Discussion and Synthesis**

The most useful results to petrology that stem from this comparison dilatometry are: (1) experimentally-



FiG. 2. Data for isomekes between almandine-type garnet (No. 1 in Table 1) and quartz in a direction  $\perp c$ . Solid lines based on numerical analysis discussed in text. Type of dilatometer (see Part I) used: 1, 2, 4, 5-"gate" (antimony-doped silicon gate); 3-"gate" (gate of chrome-coated synthetic sapphire); 6-"gate" (WC gate).



FIG. 3. Data for isomekes between almandine-type garnet (No. 1 in Table 1) and quartz in a direction 45° from c. Solid lines based on numerical analysis discussed in text. Type of dilatometer used: 1, 2, 5-"gate" (WC gate); 3, 4-"J".



FIG. 4. Data for isomekes between almandine-type garnet (No. 1 in Table 1) and quartz || c. Solid lines based on numerical analysis discussed in text. Type of dilatometer used: 1, 5-"gate" (antimony-doped silicon gate); 2, 3, 4-"J"; 6-"gate" (WC gate).



FIG. 5. Data for isomekes between pyropic garnet (No. 3 in Table 1) and quartz  $\perp c$  and ||c| using "gate" dilatometer (WC gate). Solid lines for comparison are derived from interpolative equations for quartz and almandine-type garnet.



FIG. 6. Data for isomekes between spessartitic almandine (No. 5 in Table 1) and quartz  $\perp c$  and ||c using "gate" dilatometer (WC gate). Solid lines for comparison are derived from interpolative equations for quartz and almandine-type garnet.



FIG. 7. Data for isomekes between grossular (No. 6 in Table 1) and quartz  $\perp c$  and ||c| using "opposed rods" dilatometer. Solid lines for comparison are derived from interpolative equations for quartz and almandine-type garnet.

determined isomekes for the almandine-quartz combination; and (2) the demonstration that extreme variations in composition of garnet cause only small variations in the trajectories of the isomekes. Referring to Equation (7), the minor effect of major compostional departures probably reflects the fact that the changes, respectively, in  $\alpha_g$  and  $\beta_g$  due to compositional variation at any P and T are small relative to  $(\alpha_q - \alpha_g)$  and  $(\beta_q - \beta_g)$  at the same P and T. This contrast in the properties of garnet and quartz, besides increasing sensitivity, thus becomes another asset of this pair of minerals for solid inclusion piezothermometry. The petrologist using the pair garnetquartz will, for most occurrences, be working with garnets much closer to almandine than to the other garnets considered. It should therefore be justifiable for him to use isomekes derived for quartz and almandine-type garnet with only approximate determination that he is dealing with this type of garnet.

One additional conclusion from this work is the large difference between coefficients of thermal expansion of garnet, deduced below, and those obtained by X-ray diffraction on synthetic garnets (Skinner, 1956). Near 25°C and 1 bar, the data for one isomeke in Figure 4 very nearly parallel the temperature axis. Using the known properties of quartz referred to in Part I and the compressibility of almandine-type garnet (designated by *a*),  $\beta_a = 0.189 \times 10^{-6} \text{bar}^{-1}$  (Soga, 1967), Equation (7) suggests that, near 25°C and 1 bar,

$$\alpha_{\alpha\parallel c} \approx \alpha_a \approx 7.56 \times 10^{-6} \,^{\circ}\mathrm{C}^{-1}.$$

Using this same equation, the compressibility of spinel (s),  $\beta_s$  mentioned in Part I, our calculated value of  $\alpha_{so} = 5.72 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ , and the slope of an isomeke for the same garnet relative to spinel at its intercept with the temperature axis (60°C instead of 25°C), we obtain  $\alpha_{ao} = (7.58 \pm 0.14) \times 10^{-6} \,^{\circ}\text{C}^{-1}$ . There is close agreement between our two independently determined values, which are ~39 percent larger than thermal expansions derived from the X-ray work of Skinner (1956) on synthetic almandine.

The differences between the previous data on thermal expansion for garnet and values inferred above account for the marked discordance between the calculated isomekes of Rosenfeld (1969) and those presented in this paper. Revised geological interpretations based upon the correct measurements are discussed below.

# Representation and Interpolation of Experimental Results

Were satisfactory equations of state for almandine and low quartz available, smoothing of experimental data and presentation of results would be easily accomplished utilizing these equations in the manner previously discussed. No such equations of state, valid throughout the pressure and temperature region of our experimentation, have been advanced. Much of the theoretical problem lies with changes in physical properties which are precursors to the lowhigh transition of quartz; some of these precursory phenomena are readily detected more than 75°C below the transition (Klement and Cohen, 1968).

Empirical methods were thus used to smooth and present the quartz-almandine data. The technique presented here yielded a relatively simple representation which, although suitable for geological applications, is not suitable for accurate equations of state.

The empirical equation is an excellent fit to the data for quartz  $\perp c$ -almandine and quartz 45° to c-almandine; the empirical equation fits the quartz ||c-almandine data with less precision, although suitably for petrological purposes, to within 75° of the low-high transition. Progressive deviation of the empirical equation from the experimental data within ~75°C of the transition undoubtedly is an artifact of the mathematical form and simplicity of the equations.

The desired equation should generate isomekes as a function of temperature, pressure, and orientation of quartz. No single integrated equation was found to do this, although a differential equation was. The calculated quartz-almandine isomekes were thus obtained by numerical integration of

$$\frac{dP}{dT} = a_1 + a_2 P + (a_3 + a_4 P) \ln (T_\lambda - T)$$
(8)

where

$$a_1 = 56.391 + 13.323 \quad \sin^2\theta - 23.646 \quad \sin^4\theta$$
(9a)

$$a_{2} = -9.241 \times 10^{-4} - 4.881 \times 10^{-3} \sin^{2}\theta + 7.718 \times 10^{-3} \sin^{4}\theta$$
 (9b)

$$s_3 = -7.948 - 3.011 \sin^2 \theta + 3.526 \sin^4 \theta$$
(9c)

$$a_4 = 2.147 \times 10^{-4} + 7.634 \times 10^{-4} \sin^2 \theta$$
$$-1.333 \times 10^{-3} \sin^4 \theta \qquad (9d)$$

and

# $T_{\lambda} = 573.2 + 0.02683P - 0.1435 \times 10^{-6}P^2 \quad (10)^{6}$

P is in bars and T in °C.

Briefly, coefficients in Equation (8) were obtained by numerical techniques as follows: The experimental data for one isomeke were ordered in ascending temperature or pressure, depending upon the slope of the isomeke. An arbitrary interval of 25°C was chosen, and data points which are separated by a distance greater than or equal to this arbitrary interval were selected by the computer starting from the lowest temperature or pressure. This ordered set was the basis of all succeeding calculations.

Next, the derivative of the isomeke,  $dP/dT_i$ , was found at each point  $T_i$  in succession by the Lagrangian interpolation polynomial of degree 2. Except at the end points,  $dP/dT_i$  was obtained using  $T_i$  and the adjacent higher and lower temperature points. The derivatives at the end points were found from the first three and last three points.

Each experimental determination of an isomeke was processed in this manner. All dP/dT values for isomekes involving a specific orientation of quartz were then grouped together and a smooth surface of the form of Equation (8) best fit by least squares analysis. For each of the three orientations of quartz utilized in the experiments, values of  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$ were found. Thus 12 coefficients were determined. Finally, a quadratic equation was fitted to each coefficient a as a function of the orientation of the quartz,  $\theta$ . These quadratics are given in Equations (9a-9d).

The isomekes for almandine together with any arbitrary orientation of quartz were then obtained by standard numerical integration techniques using Equation (8). These curves, spaced at intervals of 0.2 in  $\sin^2\theta$ , are given in Figure 8. Also, Figure 9 is a "fan" of isomekes emanating from P = 1 bar and  $T = 25^{\circ}$ C at intervals of 0.1 in  $\sin^2\theta$  for petrographic convenience (see footnote 5; also *cf* Rosenfeld, 1969, p. 334–345).

A number of equations other than Equation (8) were examined to obtain a representation of all the data. Some utilized functions other than  $\ln (T_{\lambda} - T)$ ; others utilized additional terms. No consistently

better representation was found to fit *all* the data, although some may have yielded better representations in limited regions. Some equations with more coefficients may have fit the data just as well, but the simpler equation was chosen for presentation here. The  $\ln(T_{\lambda} - T)$  term allows presentation of an equation of simple form that approximates our data. This logarithmic term, however, has no particular theoretical basis and its behavior may cause deviations from a good fit to the quartz ||c-almandine data. Caution should be used in applying Equation 8 outside the region within which which we have applied it.

## **Geological Applications**

Ideally one should be able to use solid inclusion piezothermometry alone to determine P - T conditions of metamorphism; the most precise such determinations would employ location of isomekes crossing at relatively high angles. For example, using thin sections of garnets with quartz inclusions in conjunction with Figure 8, such high-angle intersections would require finding conditions for elimination of birefringent halos around quartz grains having both low and high inclinations,  $\theta$ , of the c axis to the section normal. When applying solid inclusion piezothermometry to location of the Al<sub>2</sub>SiO<sub>5</sub> triple point, commercially available heating stages are suitable for determining such null conditions for quartz grains with low  $\theta$ . To obtain null conditions with quartz grains having high  $\theta$ , however, requires use of a high aperture window bomb. Thus, pending completion of such an optical high pressure device, we have not been able to investigate null conditions of halos for grains with values of  $\theta$  sufficiently far apart to give accurate "triangulation" in P - Tspace.

Instead of using piezobirefringent halos around quartz inclusions in garnet alone, we have thus been forced to combine their use with additional petrological data as was done by Rosenfeld (1969, p. 335-345) to infer pressures and temperatures of crystallization. In that paper isomekes were generated using the limited information on coefficients of compressibility and thermal expansion then available. For any particular temperature, the pressures implied in Figure 8 of that paper are higher than they would be using the isomekes of Figure 9 in this paper. The discrepancies, though not large (~1.5 kbar), result largely from coefficients of thermal expansion previously available for garnet, coefficients

<sup>&</sup>lt;sup>8</sup> From preliminary work on the low-high quartz transition. More extensive work (Cohen, Klement, and Adams, 1974) suggests that the coefficient of the  $P^2$  term may be negligible and that slight alteration in the coefficient of the P term may be appropriate. Such modifications have no significant effect on our results.



FIG. 8. Calculated sets of isomekes at intervals of 0.2 in  $\sin^2\theta$ : almandine-type garnet and quartz.

that we now believe are too low as a result of experiments reported above. Figure 10 updates the most critical parts of his illustration for localities in New England and includes new information from the southern Gotthard Region in Switzerland.

Figure 10 applies the data presented here to garnetquartz combinations from areas selected to yield information bearing on  $Al_2SiO_5$  polymorphism. Restrictions on the location of the andalusitekyanite-sillimanite triple point are inferred as follows:

(1) Specimen Gar. 1 is a kyanite-bearing paragonite schist from the well-known locality of Gassetts, Vermont, that (a) is located in the kyanite zone many miles from any known contemporaneous sillimanite (Thompson and Norton, 1968, p. 320); (b) shows, using the two-dimensional approach, weak piezobirefringent halos in almandine around quartz inclusions having  $\theta = 0^{\circ}$ ; (c) is isogradic with marble, cropping out 4.13 km to the north in Duttonsville Gulf (Thompson and Norton, 1968, p. 320), that consists mostly of dolomite with minor calcite having 5.8 mole percent MgCO<sub>3</sub> <sup>9</sup>(Rosenfeld, 1969, p. 343); (d)

<sup>&</sup>lt;sup>9</sup> This composition includes thin dolomite lenses that show evidence of exsolution because they are oriented normal to *c* of the host calcite, they extinguish under crossed polars parallel to the host calcite, and they have a graded range of coarseness that is of finer grain than that of the dolomite of the matrix.



FIG. 9. Calculated "fan" of isomekes between almandine-type garnet and quartz, emanating from P = 1 bar and  $T = 25^{\circ}$ C at intervals of 0.1 in sin<sup>2</sup> $\theta$ .

has, in an adjacent sample, the following  $\Delta$  O<sup>18</sup>/O<sup>16</sup> values (Garlick and Epstein, 1967, p. 192–193, 212) between quartz and the minerals indicated: 3.0 (muscovite), 4.3 (garnet), 5.0‰ (biotite). Utilization of (a), (b), (c), Figure 9, and interpolated isopleths for MgCO<sub>3</sub> solubility in calcite obtained from the experimental data of Goldsmith and Newton (1968) places kyanite in a small P - T region above 5.6 kbar at a temperature of 545 ± 20°C. This temperature, in turn, calibrates facts (d)<sup>10</sup>, to be used below.

(2) Specimen A57d is from the Silurian Clough quartzite in the eastern highlands of Connecticut (Garlick and Epstein, 1967, p. 214). Specimen A57d (e) is very near the kyanite-sillimanite isograd 0.44 km northeast of an outcrop of kyanite schist and 0.43 km north-northwest of one of sillimanite-bearing schist; (f) indicates recrystallization temperature very nearly the same, within the precision of measurement, as that of specimen Gar. 1, because the following  $\Delta 0^{18}/0^{16}$  values (Garlick and Epstein, 1967, p. 214) between quartz and the minerals indicated are close to those of specimen Gar. 1:3.0 (muscovite), 4.4



FIG. 10. Geological application of solid inclusion piezothermometry using the garnet-quartz combination. See text for specimen locations and discussion. Dotted isomekes are from Figure 9. Heavy lines indicate range of uncertainty for each specimen. Steep lines attached to heavy lines represent geochemically determined information on temperature of crystallization. Dashed lines are subdivisions of the Al<sub>2</sub>SiO<sub>6</sub> diagram after Holdaway (1971). Triple point determinations within that diagram: H = Holdaway (1971); N = Newton (1966); RGB = Richardson *et al* (1969).

<sup>&</sup>lt;sup>10</sup> The work of Clayton, O'Neill, and Mayeda (1972, p. 3064) leaves the earlier experimental calibrations of the O<sup>18</sup>/O<sup>16</sup> geothermometer based on fractionation between quartz and muscovite in a very uncertain state.

(garnet), 5.9‰ (biotite); (g) has values of  $\sin^2\theta_c$ , at atmospheric pressure, of 0.2 to 0.32 at 25°C and 0.06 at 90 ± 15°C (new values from Adams, 1971, p. 87-90). Utilization of (e), (f), (g), and Figure 9 indicates that kyanite crystallized near the sillimanite field in a small P - T region near 5 kbar and 545 ± 20°C, in quite good accord with placement of the kyanite-sillimanite boundary by both Newton (1966) and Holdaway (1971, p. 115). Thus we infer that the triple point should lie at a temperature below 545°C along a curve governed by the Clapeyron equation that emanates from  $T \sim 545°C$  and  $P \sim 5$  kbar.

(3) Specimens  $\alpha$  39 and AG4 are from the vicinity of the south border of the Gotthard Massif near Lukmanier Pass, Tessin, Switzerland.  $\alpha$  39 is from the Triassic Quartenschiefer near the small hamlet of Brönich; and AG4 is from pre-Triassic schist of the Lukmanier-Decke immediately south of Passo del Sole, about 5 km west of Brönich. Specimen  $\alpha$ 39, a quartz-bearing paragonite schist, (h) shows, by abundant porphyroblasts of kyanite and oligoclase  $(\sim An_{18})$ , that the reaction leading to production of kyanite was: paragonite + quartz  $\rightarrow$  kyanite + plagioclase + H<sub>2</sub>O; (i) indicates, by the relationship of trains of inclusions inside porphyroblasts to their continuation outside, that the porphyroblasts formed late in the last major deformation that accompanied the metamorphism; (j) has some kyanite porphyroblasts that are bent up to 60° and have reac-



FIG. 11. Bent kyanite porphyroblast surrounded by selvage of sillimanite needles in paragonite schist from vicinity of Brönich in the Lukmanier Pass region, Switzerland. Minerals: K = kyanite; S =sillimanite; O = oligoclase; M = white mica; R = rutile.

tion selvages of sillimanite needles that are also bent, but to a lesser degree, about the same axis (Fig. 11); (k) was located near a paragonite-muscovite schist in which  $d_{002 \text{ muscovite}} = 9.929 \text{ Å}$  (Frey, 1969, p. 126). We infer from (i) and (j) that the incomplete reaction kyanite  $\rightarrow$  sillimanite occurred after dehydration reaction (h) that produced the kyanite porphyroblasts and therefore after the thermal maximum. If the reaction kyanite  $\rightarrow$  sillimanite had taken place before the thermal maximum, dispersed and relatively coarse sillimanite should have been formed by the dehydration reaction instead of kyanite. Inasmuch as this is not the case, we infer that sillimanite formed primarily as a result of unloading and not as a result of rising temperature. Based on Rosenfeld et al (1958), we infer that the solid solution between muscovite and paragonite, reflected in basal spacings, indicates the maximum temperature of metamorphism. For that association, Rosenfeld (1969, p. 343-344) calibrated  $d_{002, \text{ muscovite}}$  against MgCO<sub>3</sub> concentrations in calcite of closely juxtaposed dolomitic marbles. This enables use of fact (k) above to select the correct isopleth for MgCO<sub>3</sub> solubility in calcite from the experimental work of Goldsmith and Newton (1968), in this case 4.9 percent. Intersection of this isopleth with an isomeke obtained from isogradic specimen AG4 (see metamorphic map of Niggli, 1970, p. 18-19), yields the temperature and pressure of crystallization. Observation shows that isomeke to have a value of  $\sin^2\theta_c$  between 0.14 and 0.35 using Figure 9. The intersection (Fig. 10) lies in a small P - T region near 4.3 kbar near 515  $\pm$  25°C.

(4) The discussion of specimen  $\gamma 612$  from Gap Mountain, New Hampshire, is unchanged from Rosenfeld (1969, p. 340-343) except for recalibration of isomekes. In  $\gamma 612$ , which has  $\sin^2\theta_c$  between 0.6 and 0.7, there is evidence of the reaction and alusite  $\rightarrow$  sillimanite. This is consistent with the results of Holdaway in that those isomekes intersect his andalusite-sillimanite boundary. The data for  $\gamma 612$  are not so restrictive as the combined results for specimen A57d and the alpine specimens.

In summary, the information from the Alps not only is consistent with location of a pressure and temperature on the kyanite-sillimanite boundary in New England but is probably more restrictive on the temperature of the triple point. What makes the Alpine information of most interest is the above inference that the reaction kyanite  $\rightarrow$  sillimanite took place at or below approximately 515°C. The sillimanite in the southern Gotthard area is 25 km from

the nearest point on the sillimanite isograd to the southeast (Niggli, 1970, plate 2). Its occurrence is probably a result of a curious set of circumstances: activation of recrystallization by strain energy of deformation coupled with relatively rapid unloading due to denudation that accompanied the formation of the central Alps as a range of high mountains after the Eocene (Niggli, 1970, p. 18). The rapidity of unloading relative to cooling by thermal conduction apparently maintained temperatures sufficiently high for the reaction to take place when the P - T path of the rock entered the sillimanite field on its way to the lower P and T at the earth's surface.<sup>11</sup> Assuming that there are no problems with metastable crystallization of sillimanite relative to andalusite in the geological time intervals involved, the triple point must lie at  $T < (515 \pm 25^{\circ}\text{C})$ . Examination of Figure 10 shows that the experimentally inferred triple points of Newton (1966) and of Holdaway (1971, p. 115) lie within the P - T region below 515°C between temperatures on the isomekes for specimens A57d and AG4 or  $\alpha$ 39 on the high-P side and specimen  $\gamma 612$  on the low-P side. This is consistent with the above inferences from solid inclusion piezothermometry and geochemistry. The triple point of Richardson, Gilbert, and Bell (1969, p. 266) lies at too high a temperature to be consistent with the above interpretations.

The information from specimens  $\alpha 39$  and AG4 in Figure 10 also provides information on the average denudation rate since the thermal maximum in the area. Clark and Jäger (1969, p. 1149) place the thermal maximum in the area at (30 ± 5) m.y., consistent with the work of Steiger (1964). Denudation of ~16 km of material (inferred from the 4.3 kbar pressure of crystallization) during that interval leads to a mean denudation rate of  $0.5 \pm 0.1$  mm/year. This rate is closely comparable with inferred denudation rates of Clark and Jäger (1969, p. 1154) for the area of the Gotthard Tunnel a few kilometers to the west of Passo del Sole along the structural trend. They interpreted a relatively high heat flow there as a transient effect of denudation.

## Epilogue

Full application of solid inclusion piezothermometry awaits completion of a high aperture window bomb to complement a heating stage in finding conditions for halo elimination. Using the heating stage and window bomb, it should become possible to cross-check answers obtained totally by solid inclusion piezothermometry against those obtained by other means.

The possibility of plastic deformation around or in an inclusion must be considered. Carstens (1971) has demonstrated creep around inclusions in mantlederived garnet xenocrysts that must have followed a P - T path which, at high temperature, greatly and rapidly departed from the relevant isomekes (cf Rosenfeld and Chase, 1961, p. 538). It remains to be seen whether such plastic deformation is important in regionally metamorphosed crustal rocks that recrystallized at much lower temperatures and that probably followed P - T paths having much lower departures from relevant isomekes over much longer time intervals. It is even possible that quantitative experimental and theoretical analysis of dislocation halos, such as those noted by Carstens, might yield information on original conditions of formation and/or unroofing history.

The work we report here is thus somewhat in the nature of a progress report. Further experimental determinations of isomekes are needed—e.g., sillimanite-garnet, diamond and its inclusions—and some are in progress. Further instrumentation will have to be developed—e.g., the window bomb—and this is also in progress; and further work will be necessary on dislocation creep and the theoretical foundations of solid inclusion piezothermometry.

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<sup>&</sup>lt;sup>11</sup> That this phenomenon is not unique in the region is indicated by the textural evidence in a specimen collected 12 km to the south. There, in a specimen of the higher temperature paragonitemuscovite ( $d_{002} = 9.888$  Å) schist near Alp Sponda on Pizzo Forno (collector: J. B. Thompson, Jr.), we have observed in thin section a selvage of sillimanite needles, coarser than those in  $\alpha$ 39, adjacent to unbent kyanite. This occurrence is in the same area where Keller (1968, p. 41-47) found kyanite and andalusite in lenses ("Knauer") in textural relationships that suggest that the latter recrystallized from the former. He called on a falling P and T path at a T below that of the triple point to explain the sequential relationship. Other possibilities at Pizzo Forno are that the P-T path passed out of the kyanite field into the sillimanite field and then into the andalusite field and that the good expression of these later phases is a consequence of rapid unloading with a broad loop in the P-T path extending to considerably higher temperatures than those of  $\alpha 39$ . Given the negative dP/dT of the andalusite-sillimanite reaction boundary, a larger P-T loop would give a higher T of entry into the andalusite field, thereby facilitating the crystallization of that mineral. Presumably specimen  $\alpha$ 39 also passed through the andalusite field, but at too low a temperature for reaction in the available time.

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