

OXYGEN ISOTOPIC COMPOSITION OF
FISSURE-GROWN QUARTZ, ADULARIA, AND CALCITE
FROM BROADLANDS GEOTHERMAL FIELD,
NEW ZEALAND

with an appendix on

QUARTZ-K-FELDSPAR-CALCITE-MUSCOVITE
OXYGEN ISOTOPE GEOTHERMOMETERS*

PETER BLATTNER

New Zealand Geological Survey, P.O. Box 30368, and D.S.I.R. Institute
of Nuclear Sciences, Private Bag, Lower Hutt, New Zealand

ABSTRACT. Oxygen isotope analyses of well developed, fissure-grown quartz, adularia, and calcite crystals are related to downhole temperatures and other data from the Ohaki-Broadlands geothermal field. The bore no. BR 7 profile shows how oxygen isotope analyses of geothermal minerals provide quantitative evidence on subsurface hydrology, particularly with regard to zones of boiling, and on the past stability of a geothermal system. The lower part of this profile permits correlation of a temperature of 275°C with

$$10^3 \ln [(O^{18}/O^{16})_{\text{quartz}} / (O^{18}/O^{16})_{\text{K-feldspar}}] = 3.3$$

Based on the constraints gained from Broadlands, on the 600°C quartz-K-feldspar fractionation from Blattner and Bird (1974), and on earlier data of O'Neil and Taylor (1967, 1969) and O'Neil, Clayton, and Mayeda (1969), quartz-feldspar, quartz-calcite, and quartz-muscovite oxygen isotope geothermometers may be calibrated independently of isotopic analyses of solutions. The corresponding new equations are

$$10^3 \ln \alpha (\text{quartz-K-feldspar}) = 0.82 + 0.74 \cdot 10^3 \text{ K}^{-2}$$

$$10^3 \ln \alpha (\text{quartz-muscovite}) = 1.30 + 1.27 \cdot 10^3 \text{ K}^{-2}$$

$$10^3 \ln \alpha (\text{quartz-calcite}) = 0.37 + 0.88 \cdot 10^3 \text{ K}^{-2} \text{ [NBS-28} \approx 9.8/\text{PDB} = 30.36]$$

The constant of the quartz-calcite equation depends directly on the scales of reporting used for silicates and carbonates respectively.

There lies the rock and we must let it lie
Even having thought ourselves to rack and ruin
Mephistopheles (Goethe, Faust, pt. II, l. 10114-10115)

INTRODUCTION

In active geothermal areas pressures, temperatures, and solution compositions of geological systems are accessible to direct measurement. Attempts have been made to use such areas as natural laboratories, with reaction times much longer than and control, hopefully, almost as good as in laboratory experiments (Helgeson, 1967; Clayton, Muffler, and White, 1968; Muffler and White, 1969; Browne and Ellis, 1970; Eslinger and Savin, 1973; Clayton and Steiner, 1975).

Problems with the experimental calibration of mineral pair oxygen isotope geothermometers and with the isotopic equilibration of quartz were reviewed by Blattner and Bird (1974), who obtained a quartz-K-feldspar calibration point at 600°C. To cover the full geological temperature range at least one additional calibration point at a substantially higher $1/T^2$ value is required (see app.). Because of low reaction rates,

* Institute of Nuclear Sciences Contribution No. 463.

TABLE I
Isotopic compositions of quartz, adularia, and calcite from Broadlands geothermal fields

Depth below surface (m)	Material analyzed	Quartz*	$\delta O^{18}_{SMOW}(\text{‰})$ Adularia*	Calcite**	$\delta C^{13}_{PBD}(\text{‰})$ Calcite***
Drillhole BR7					
160.9	Bulk cuttings, dust removed			4.8	
194.4	Bulk cuttings, dust removed			4.2	- 8.9
	Bulk cuttings fraction <1mm removed			3.9	
310.3	Quartz crystals <3mm, milky	12.3			
313.3	Quartz crystals <3mm, clear	17.9 ± 0.3(2)			
316.4	Quartz crystals, ~3mm, clear	11.5			
319.4	Top 1/3 of clear, 5mm long quartz prism	8.7			
	Bottom 2/3 of same	8.7			
343.2	Quartz crystals <3mm, clear (from core)	9.3			
429.5-	A. calcite fragments (from core)			7.9	- 5.7
431.0	B. clear quartz crystals <3mm, intergrown) with calcite (from core)	10.2		7.2	
528.2	Calcite fragments			8.1 ± 0.1(3)	- 5.4
708.1	Bulk cuttings, fraction <1mm removed			2.5	
747.7	Calcite crystals (from core)			2.4	
813.2	Adularia crystals <2mm (from core)		2.1		
834.5	a. Tabular calcite crystal about 1×5×5mm			2.4	- 8.9
	b. Adularia crystal, 3mm, clear		2.5		
	c. Adularia crystals <2mm		1.7		
	d. Adularia crystals		2.0		
	e. Part of adularia crystal		2.2		
	f. Quartz prism, ~3mm, clear	5.8			
837.6	Part of clear quartz crystal	5.9			
840.6	Adularia crystals, ~2mm, clear, and quartz crystals <3mm, clear	5.5 ± 0.2(2)	2.12 ± 0.08(3)		

837.6	e. Part of adularia crystal	5.8	2.2	
	f. Quartz prism, ~3mm, clear	5.9		
840.6	Adularia crystals, ~2mm, clear, and quartz crystals <3mm, clear	5.5 ± 0.2(2)	2.12 ± 0.08(3)	
841.2	Calcite fragments			
849.7	Tabular calcite		2.50 ± 0.1(2)	-10.2
865.0-868.1	Tabular calcite		2.10 ± 0.05(2)	- 8.5
886.4	Quartz prism, 10mm		1.6	-10.1
	Center of base, clouded, and base including clouded zone	5.73 ± 0.15(4)		
	Discrete overgrowth, clear (3 samples)	4.4 ± 0.1		
892.5	Quartz crystals <3mm, clear†	6.05 ± 0.15(2)		
893	Part of clear quartz crystal	5.7		
1096.7	Clear quartz crystals <3mm, and tabular calcite	4.7 ± 0.1(2)	0.77 ± 0.12(2)	- 9.9
1102.8	Clear quartz crystals <3mm, and tabular calcite	4.2 ± 0.15(2)	1.0	
	Drillhole BR1			
1235	A. Clear quartz prism, 10mm, no visible overgrowth			
	base	9.9		
	side of prism	8.2		
	top	6.8		
	B. Tabular calcite		1.9	
	Drillhole BR13			
850	Tabular calcite		2.9	- 8.0
905	Tabular calcite		1.6	- 9.4
957	Tabular calcite		2.1	- 8.7

§ Unless marked "bulk cuttings" or "from core", samples are fissure-grown crystals, picked from cuttings.

* NBS28 = 9.8‰ on same scale.

** Te Kuiti Limestone (Craig, 1957) = 26.06‰; PDB1 (Craig, 1957) = 30.36‰ on same scale.

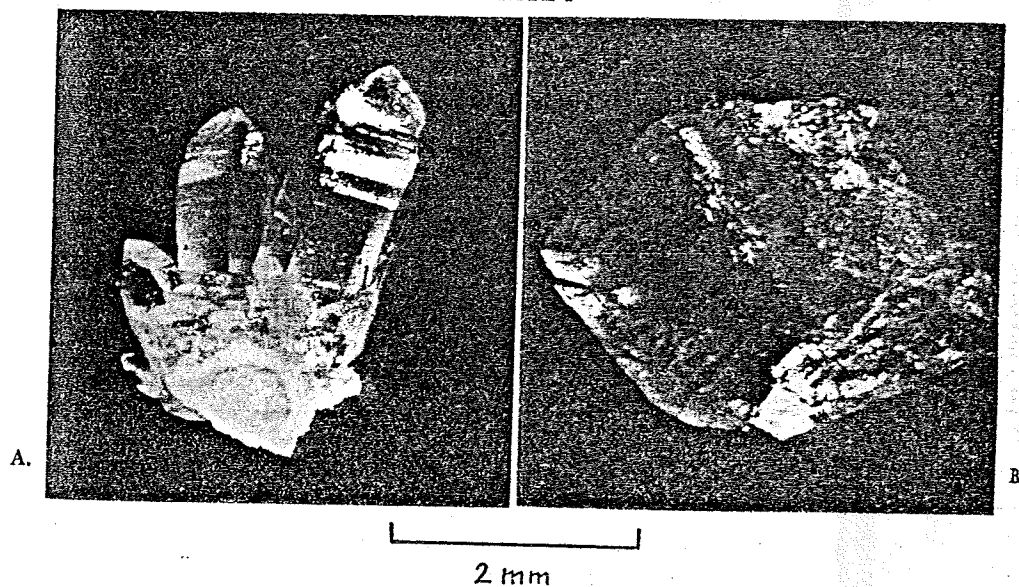
*** Te Kuiti Limestone (Craig, 1957) = -1.67‰ on same scale.

† This sample from fluid inclusion study of Browne, Roedder, and Wodzicki (1974).

adularia, and calcite from Broadlands geothermal field, N.Z.

787

PLATE I



A. Typical fissure-grown quartz from drillhole BR7 (314 m).
B. Typical fissure-grown adularia from drillhole BR7 (817 m). Horizontal edge at left corner runs backward. Note quartz prism at lower right.
Photos D. L. Homer

such a result is not likely to come forth soon from a laboratory, and geothermal minerals provide a much needed opportunity to estimate isotopic fractionations at temperatures below 300°C. In the discussion of the Broadlands data, potential uses of mineral isotopic analyses for geothermal exploration will also become obvious.

PROCEDURES AND RESULTS

Samples (table 1) were mainly fissure-grown geothermal minerals, obtained from the collection of the Ministry of Works and Development, Wairakei. Crystals of quartz and adularia were clear except where noted, colorless, and generally of simple habit (pl. 1). Total impurities in quartz and andularia were less than 1 percent. The oxygen of these minerals was extracted by reaction with bromine pentafluoride and converted quantitatively to carbon dioxide by a modification of the technique of Clayton and Mayeda (1963). Calcite crystals were similar in size, clear, and frequently had a pronounced tabular habit. Carbon dioxide gas was extracted from calcite and some carbonate bearing bulk rocks by 100 percent H_3PO_4 at 25°C (McCrea, 1950). Calcite is the only carbonate reported from BR7 by Browne and Ellis (1970), and several of the present carbonate samples showed no significant amounts of Mg or Fe on chemical analysis.

All carbon dioxide samples were analyzed on an NAA 6-60 RMS, 15 cm radius, 60° sector mass spectrometer,¹ and isotopic compositions are given in terms of a SMOW scale (Craig, 1961), on which NBS-28 (Friedman and Gleason, 1973) "reads" 9.8 permil, Te Kuiti Limestone (Craig, 1957) 26.06 permil, and PDB1 (Craig, 1957) 30.36 permil. These data define the scale of reporting, and the values actually used for $\alpha_{\text{CO}_2\text{-H}_2\text{O}}^{25^\circ\text{C}}$ and the CO_2 -calcite kinetic fractionation factor (1.01025, modified after Sharma and Clayton, 1965) are no longer required for that purpose.

Because of the likelihood of analytical bias between the δO^{18} scales for carbonates and silicates, any comparison involving both scales (for example, for a quartz-calcite thermometer) is critically dependent on reference values for each scale. For example, in the case of silicates it is known that different laboratories obtain $\delta\text{O}^{18}_{\text{SMOW}}$ values differing by up to 0.5 permil (see Onuma, Clayton, and Mayeda, 1972). If at the same time the calcite scale remains unchanged, quartz-calcite "temperatures" may differ by 100°C on account of this. To check for proportional errors in our δO^{18} scale, we use two calcite samples differing in composition by about 23 permil (Blattner and Hulston, 1975).

For the isotopic fractionation between two phases, (A) and (B), the definition

$$\Delta_{\text{AB}} = 10^3 \ln \alpha_{\text{AB}}$$

is adopted, where

$$\alpha_{\text{AB}} = \frac{(\text{O}^{18}/\text{O}^{16})_{\text{A}}}{(\text{O}^{18}/\text{O}^{16})_{\text{B}}} = \frac{1 + 10^{-3} \delta\text{O}^{18}_{\text{A}}}{1 + 10^{-3} \delta\text{O}^{18}_{\text{B}}}$$

For data from the lower part of BR7 and using the SMOW scale, the approximation $\Delta_{\text{AB}} \approx \delta_{\text{A}} - \delta_{\text{B}}$ is always better than 0.05 permil.

Results are given in table 1. Waters from Broadlands drillhole discharges have been analyzed by Giggenbach (1971). Their reported $\delta\text{O}^{18}_{\text{SMOW}}$ varies between -4.4 and -5.3 permil and is similar to that of surface water of the area. Water of that composition would be in isotopic equilibrium with the volcanogenic bedrock at $\leq 200^\circ\text{C}$. Apart from the fact that a discharge sample provides only one datum for a potentially complex hydrological profile, analysis of liquids may not be related with confidence to analyses of solid phases, unless special precautions are taken (Blattner and Bird, 1974). The results of Giggenbach and the mineral data of table 1 do show, however, rough agreement with previously estimated mineral- H_2O fractionations (for example, Epstein and Taylor, 1967).

GEOHERMAL RECORD AND CONDITIONS OF CRYSTAL GROWTH

Figures 1 and 2 show geological, thermal, and δO^{18} profiles for drillhole BR7, which has been the best combined source so far of geothermal quartz, K-feldspar, and calcite.

$${}^{\circ}\text{‰} \delta\text{O}^{18} = \left[\frac{(\text{O}^{18}/\text{O}^{16})_{\text{sample}}}{(\text{O}^{18}/\text{O}^{16})_{\text{standard}}} - 1 \right] 10^3$$

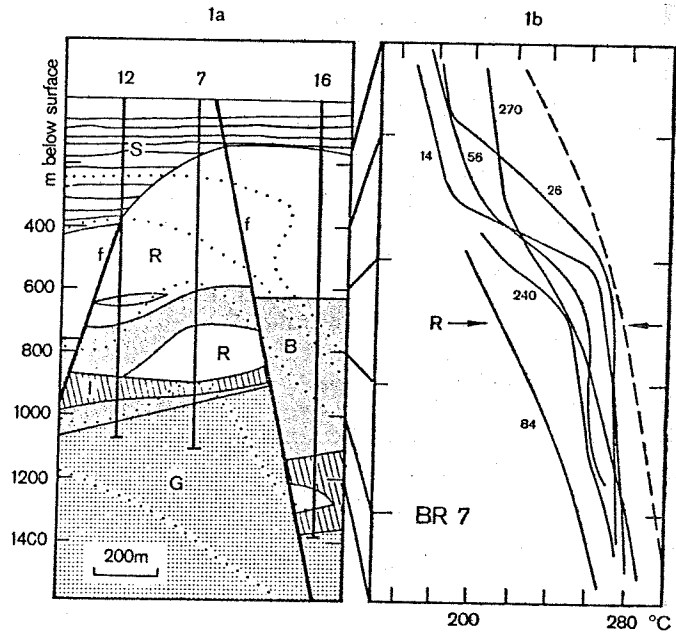


Fig. 1A (left). Geological profile from Grindley (1970). Abbreviations: S = siltstones, sandstones, and tuffs (Huka Falls Formation), R = Broadlands rhyolite and dacite, B = poorly sorted breccia (Rautawiri B.), I = Rangitaiki ignimbrite, G = graywacke and argillite, f = fault. Dotted lines are post-drilling isotherms showing approximate temperature distribution (25°C intervals). The ground surface is 300 m a.s.l. Drillhole numbers at top; for 12 read 10.

B (right). Note expanded depth scale. Post-drilling geothermograph profiles, hole BR 7 (Ministry of Works data). Numbers are days of blockage before profile was measured. R = top of lower rhyolite dome. Dashed line is ideal boiling point curve.

Drillhole data.—Substantial surface gas leakage was observed before drilling (Grindley, 1970), and ground temperatures around the site of BR7 constitute a local "high"; the discharge of hole BR7 has the highest steam/water ratio (~3.0) of the Broadlands field (Smith, 1970). In the lower part of the hole, pressures and temperatures are significantly higher than at equivalent depths in neighboring drillholes. Thus, we are dealing with a P-T culmination, and the source of the BR7 discharge is considered by Grindley and Browne (1968) and Grindley (1970) to be the lower dome of Broadlands rhyolite (fig. 1A) and an underlying deep fissure zone. Temperature-depth profiles are sensitive to subsurface hydrology and will be disturbed by discharge from a drilled hole. Downhole measurements for the purpose of estimating pre-drilling temperature should therefore be made as drilling proceeds (White, 1968), or after a period of blocked discharge. White (1968) finds differences of less than about 10°C between "bottom-hole" temperatures and post-drilling geothermograph data in the Steamboat Springs area; original temperature reversals with depth are smoothed out in the post-drilling profiles. The BR7 geothermograph profiles of figure 1B show a sharp change between

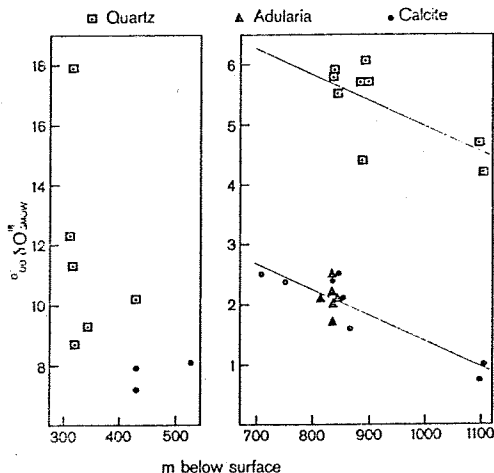


Fig. 2. $\delta^{18}O$ values for geothermal minerals, BR 7. Note that scale of right hand diagram is shifted upward and expanded. A step of about 4 permil or greater occurs between 550 and 700 m depth.

400 and 700 m, about the depth where a large change in the oxygen isotopic composition of minerals also occurs (500-700 m, fig. 2). The effect of increased duration of blockage, from 14 to 270 days, on the geothermograph profiles consists of a gradual de-emphasis of this step. For BR7 the geothermograph measurements with the longest preceding closure time are also, coincidentally, the latest after drilling, and the smoothing of temperature profiles may either be the effect of blockage (longer standing times restoring pre-drilling conditions) or may show the gradual establishment of changes induced by drilling the field. The isotope data are strong evidence for the existence of a significant step before drilling.

Isotopic equilibration of existing minerals.—In contrast to geothermal fluids, minerals may contain a long-term record of geothermal conditions, complicated by the fact that different minerals may have grown at different times and may exchange oxygen isotopes with solution at different rates. A summary of existing experimental and geothermal data will allow some speculation on relative exchange rates.

Isotopically zoned geothermal quartz crystals occur at Broadlands (see table 1: 886 m depth, hole 7; 1235 m depth, hole 1). Once grown, such crystals obviously did not have time to equilibrate internally. In experiments at 600°C, Blattner and Bird (1974) were unable to equilibrate isotopically quartz grains of more than 4 micron diameter. Probable equilibrium compositions were obtained by Clayton, O'Neil, and Mayeda (1972) and by Blattner and Bird (1974) with quartz of less than 2 micron grain size and were due to growth of new crystals following the dissolution of most of the original material, rather than to isotope exchange of existing crystals. Data on groundmass quartz from different

geothermal systems have been interpreted in different ways, one difficulty being that of recognizing and analyzing separately, primary and secondary (that is, geothermally grown) crystals. Groundmass quartz, presumably of detrital origin, from the Salton Sea system was analyzed by Clayton, Muffler, and White (1968) and may, at best, have partially equilibrated with solutions. Eslinger and Savin's (1973) data on groundmass quartz from Broadlands no. 16 drillhole suggest equilibrium with the geothermal solution, and the authors conclude that all this quartz is of authigenic geothermal origin.² Clayton and Steiner (1975) find that groundmass quartz from highly altered rocks of the Wairakei geothermal system is probably of detrital origin and has hardly exchanged oxygen isotopes with the geothermal solution at all; secondary, geothermal quartz seems to have grown in equilibrium with the solution. Full oxygen isotope exchange between *feldspar* and solution has been obtained under laboratory conditions at temperatures down to 350°C, when accompanied by cation exchange (O'Neil and Taylor, 1967). Complete isotope exchange between *calcite* and solution in the laboratory was reported by O'Neil, Clayton, and Mayeda (1969) at temperatures as low as 200°C and was accompanied by gross recrystallization. According to B. H. T. Chai (personal commun.; unpub. experimental data) all this exchange may be explained by a solution/redeposition mechanism. Clayton, Muffler, and White (1968) conclude that *country rock calcite* of the Salton Sea system has come to isotopic equilibrium with the geothermal solution. Baertschi (1957) has studied a calcite crystal of 5 cm length, which has probably grown below 100°C (Jura Mts), and found differences up to 2 permil $\delta^{18}\text{O}$ between adjacent analyzed volumes of ~ 100 mm³. A surface layer may have reequilibrated after first growth of the crystal and could have escaped attention. This seems more likely to happen with calcite than with quartz, and in the case of the small calcite crystals from Broadlands such a surface layer could form a significant fraction of the whole.

For lack of other evidence it will be assumed that geothermal crystals *grow* in isotopic equilibrium with solution. In view of the present summary it will also be assumed that fissure quartz, once grown, does not *exchange* oxygen isotopes with solution, whereas *adularia* and *calcite* may do so to some extent.

Hydrology based on mineral isotopic compositions.—The range of quartz compositions from above 400 m depth in hole BR7 suggests substantial changes of temperature and/or solution isotopic composition with time in this zone. By extrapolation of higher temperature data in

² Below 600 m depth there is close agreement between the depth- $\delta^{18}\text{O}$ correlation for groundmass quartz, hole BR16, of Eslinger and Savin (1973) and the same correlation for secondary quartz, hole BR7, as in figure 2 here. This may be a coincidence, because of the likelihood (P.R.L. Browne, personal commun.) that groundmass quartz does contain a primary quartz component. Otherwise this agreement would suggest that the post-drilling temperature distribution, given in figure 9, does not represent pre-drilling conditions.

the $1/T^2$ plot,³ a temperature change from about 200° to 100°C would be required to explain the compositional range of 9.2 permil δO^{18} by temperature alone. The change in the δO^{18} of calcite between 400 and 700 m could likewise be ascribed (O'Neil, Clayton, and Mayeda, 1969) to a temperature drop from 280° to 170°C. This is 30°C more than the drop indicated by the most accentuated geothermograph profiles.

Contrary to the data from above 400 m, quartz analyses from below 700 m depth in BR7 (fig. 2) reflect comparatively steady conditions. Quartz and calcite compositions from this part of the profile indicate a gradual decrease of solution δO^{18} and/or increase of temperature with depth. The quartz-calcite fractionation (Δ_{QC}) could show how much of the change is due to temperature but in view of the scattering of points is too insensitive. The calcite regression line of figure 2 corresponds to a temperature drop at constant solution composition of 10° to 20°C/100 m (between 250°-300°C, O'Neil, Clayton, and Mayeda, 1969). This gradient is steeper than the boiling point curve of figure 1B and is only just matched by the steepest of the geothermograph curves. An obvious conclusion for depths > 700 m is that part of the δO^{18} versus depth gradient for minerals is due to a temperature change, corresponding approximately to that of the boiling point curve, and the remainder, of about 0.2 permil δO^{18} /100 m, to change of the isotopic composition of the solution caused by loss of steam. Boiling in this area has also been postulated by Browne and Ellis (1970; see below). Based on the isotopic composition of minerals a quantitative statement is possible. The O^{18}/O^{16} equilibrium fractionation for steam and water ($\Delta_{\text{steam-water}}$) at 250° to 300°C is of the order of 1 permil according to Bottinga and Craig (1968). For a Rayleigh process, a change in solution composition of 0.8 permil (between 700 and 1100 m depth) would then require single-stage separation of 55 percent or two-stage separation of 33 percent of the solution. The high proportion of steam in the BR7 discharge and the existing temperature and δO^{18} steps at 400 to 700 m depth suggest that substantial additional boiling occurs near the top of the rhyolite dome.

Crystal growth and temperatures.—The crystallization of adularia and calcite is ascribed by Browne and Ellis (1970) to boiling and the consequent rise in solution pH. Isotopic evidence for boiling was discussed in the last section. Since solutions are saturated with respect to quartz and since the increase in pH caused by boiling will raise quartz solubility only marginally (Mahon, 1966, 1969; Fournier, 1973) a good case exists for simultaneous growth of quartz as well; no corrosion of geothermal quartz has been observed.

There are two ways of estimating the temperature at which minerals have grown: (1) BR7 downhole temperature profiles bear a close relation to the situation before drilling; note particularly how the "step" at

³ $\Delta_{Q-H_2O} = -2.59 + 3.65 \cdot 10^{-6} K^{-2}$. This equation is consistent with those in the appendix and with Δ_{K-H_2O} and Δ_{M-H_2O} of O'Neil and Taylor (1967, 1969).

400 to 700 m is borne out by mineral isotopic compositions. Between 800 and 900 m depth downhole temperatures (excepting the 84 day one) vary between 260° and 275°C. (2) Fluid inclusions of Broadlands geothermal quartzes were studied by Browne, Roedder, and Wodzicki (1974). Homogenization temperatures for numerous primary inclusions from 845 and 893 m depth in BR7 are 292° ± 5° and 294° ± 5°C. Some of the fluid inclusions at the 845 m level have trapped steam in the first place, which suggests that these values may be somewhat high estimates of actual crystallization temperatures. Isotopic analysis of one of the quartz samples examined by Browne, Roedder, and Wodzicki (1974) (892.5 m, table 1) indicates that the homogenization temperatures relate to the main cluster of quartz δO^{18} values in figure 2. The quartz overgrowth with $\delta O^{18} = 4.4$ permil has been examined for fluid inclusions but contained none suitable for temperature determination (A. Wodzicki, personal commun.). Numerous fluid inclusions considered secondary by Browne, Roedder, and Wodzicki (1974) gave homogenization temperatures of 270° ± 15°C. For the quartz-feldspar and quartz-calcite geothermometer calibration below, a temperature estimate for 850 m depth will be required. This can reasonably be 275° ± 20°C, corresponding to a boiling point curve somewhat depressed by dissolved gases.

CONSTRAINTS FOR QUARTZ-K-FELDSPAR-CALCITE
OXYGEN ISOTOPE FRACTIONATIONS

A major limitation of active geothermal systems with regard to geothermometer calibration lies in the tendency of minerals to retain compositions that are out of equilibrium for changing P-T-X conditions. It follows that the geothermal situation most useful for calibration purposes is a perfectly stable one, or, in practice, one where even an exhaustive search fails to turn up evidence of disequilibrium. Few situations, have been scrutinized in this respect (compare Clayton, Muffler, and White, 1968; Eslinger and Savin, 1973; Clayton and Steiner, 1975), and in no case have there been nearly as many analyses of secondary

TABLE 2
 δO^{18} of minerals from between 800 and 900 m depth, BR7
(in order of table 1), normalized to 850 m, on basis of change
with depth of δO^{18} of calcite. Numbers in brackets
are means of the unchanged data from table 1.

Quartz	Adularia	Calcite
5.73	1.93	
5.85	2.43	2.33
5.46	1.63	2.46
5.88	1.93	2.10
6.24	2.13	1.67
5.90	2.09	
Mean	5.65 (5.58)	2.02 (2.10)
		2.14 (2.15)

quartz and feldspar as for the BR7 profile. The lower part of this profile shows relatively little evidence of changing conditions and may be used for geothermometer calibration until better data become available.

Because of the presence of feldspar and the number of samples, the most interesting depth range is 800 to 900 m. Inside this interval quartzes occur at somewhat greater depth than the other minerals. Based on the evidence of calcite and supporting evidence of quartz compositions for a gradual change of temperature and/or solution- δO^{18} with depth (fig. 2), mineral compositions from the 800 to 900 m interval were therefore normalized to 850 m (table 2). Considering the scatter of data, the calcite slope is a sufficiently good measure of the correction required. Without correction the estimates of Δ_{QK} below would turn out too small by about 0.2.

The temperature of initial growth and possible later isotopic exchange of minerals at 850 m has been estimated as $275^\circ \pm 20^\circ C$. The K-feldspar-calcite fractionation Δ_{KC} at this temperature is taken as 0.0 ± 0.2 from the present measurements. Again the fact must be stressed that the use of different silicate reporting scales could lead to apparent changes of up to 0.5 in Δ_{KC} (see p. 000). A decision on the best corresponding range of quartz-K-feldspar oxygen isotope fractionations Δ_{QK} will depend primarily on the interpretation of the low- δO^{18} quartz overgrowth from 886 m. The most reasonable extreme cases may be considered as follows:

Model I.—Quartz and adularia have grown simultaneously (under somewhat fluctuating conditions), and subsequently no isotope exchange has taken place. The range of quartz isotopic compositions (1.6 permil) is larger than that for feldspar or calcite (0.8 permil) because an overgrowth was analyzed separately in the case of quartz, whereas adularia analyses represent mixtures of different generations. For model I, equilibrium compositions are estimated best by arithmetic means from table 2, $\Delta_{QK} = 5.65 - 2.02 = 3.6$.

Model II.—The reason for the range of feldspar and calcite isotopic compositions being smaller than that for quartz is that all but the latest generations of feldspar and calcite adjusted at least partly to P-T-X conditions after growth. Then, IIA, the quartz overgrowth may pertain to the most recent set of conditions. Assuming that in the case of adularia, too, the low end of the compositional range represents the most recent set of conditions,⁴ the best Δ_{QK} estimate is $4.55 - 1.63 = 2.9$. Or, IIB, the quartz overgrowth may reflect not the latest but any of a number of consecutive sets of conditions. Averages and Δ_{QK} are as for model I.

Model I seems acceptable enough, but the possibility that case IIA applies is real. The choice thus introduced by the quartz overgrowth leads to an anomaly (actually, bi-modality) of the "probability distri-

⁴The opposite is very unlikely to apply, since it would require an increase of temperature as well as of the δO^{18} of solution. The BR7 profile appears to show a negative correlation of these two variables.

but ion" from which the best estimate of Δ_{QK} has to be made. Considering the whole situation as discussed, a value of $\Delta_{QK} = 3.3 \pm 0.4$ for $275^\circ \pm 20^\circ\text{C}$ seems to express adequately the constraints to be gained from BR7.

CONCLUSION

Minerals from active geothermal systems, unless actually growing under observation, cannot replace experimentally grown ones, in that uncertainties of their interpretation cannot ultimately be resolved (see Goethe). Nevertheless, the appendix and figure 3 will show that the Δ_{QK} versus temperature error field from BR7 significantly reduces current uncertainty in oxygen isotope geothermometers involving quartz. Isotopic analyses of minerals could be useful to geothermal exploration in at least two ways: (1) As basis for the quantitative study of subsurface zones of boiling, using experimental calibrations of the calcite-water and water-steam systems by O'Neil, Clayton, and Mayeda (1969) and Bottinga and Craig (1968). (2) To determine the past, and therefore possibly future, hydrological stability of a system from the record of mineral isotopic compositions.

APPENDIX

QUARTZ-K-FELDSPAR, QUARTZ-MUSCOVITE, AND QUARTZ-CALCITE OXYGEN ISOTOPE GEOTHERMOMETERS

It has been assumed in the past that oxygen isotope fractionations Δ between minerals and H_2O , and therefore also between minerals, are a linear function of $T(^{\circ}\text{K})^{-2}$ (for example, Epstein and Taylor, 1967). O'Neil, Clayton, and Mayeda (1969) have shown experimentally that a very close to linear relationship exists between $\Delta_{\text{calcite-H}_2\text{O}}$ and T^{-2} for temperatures between 500° and 200°C , and possibly 0°C . Bottinga and Javoy (1973) are confident that corresponding linear relations exist for quartz, feldspar, muscovite, and magnetite between 800° and 500°C . In view of the current and still remaining uncertainty of calibration data, the provisional assumption that Δ versus T^{-2} functions are linear between 800° and 200°C is reasonable. Thus a mineral pair oxygen isotope geothermometer covering a large temperature interval may be obtained on the basis of only two calibration points, if these are sufficiently resolved on the T^{-2} scale. For the pair quartz-K-feldspar, two such points are available. They are (A) the 600°C experimental quartz-K-feldspar fractionation of Blattner and Bird (1974), and (B) the 275°C constraints imposed by the Broadlands no. 7 data. A calibration based on these points has the essential advantage that it does not involve analysis of solutions and will not be affected by errors arising from the comparison of δO^{18} of liquids and of solids (Blattner and Bird, 1974) or from possible effects of solution chemistry on mineral-solution equilibria (Truesdell, 1974). The calibration also relies entirely on the measurement of fractionations of less than 4 permil δO^{18} and is therefore insensitive to mass spectrometer errors of the type reported by Clayton, O'Neil, and Mayeda (1972).

Feldspar-solution and muscovite-solution calibrations have been reported by O'Neil and Taylor (1967, 1969). Since solutions had similar chemical compositions and solution δO^{18} values were obtained in the same manner in both studies, the K-feldspar-muscovite calibration resulting from their combination may be directly used to derive a quartz-muscovite curve from the present quartz-K-feldspar curve. Both curves and a quartz-calcite line tied to one quartz/silicate and one carbonate reference sample are given in figure 3. Broadlands no. 7 data were used for Δ_{KC} at 275°C , and the relative gradients of the quartz-K-feldspar and the quartz-calcite curves correspond to the relative gradients for the K-feldspar- H_2O data of O'Neil and Taylor (1967) and the calcite- H_2O data of O'Neil, Clayton, and Mayeda (1969). The divergence of K-feldspar and calcite compositions toward high temperatures is borne out also by recent analysis of feldspar-calcite pairs from medium to coarse grained calcite syenite from the Paleozoic of Antarctica (report in preparation).

The calibration curves adopted here, with their equations, are given in figure 3. It happens that these curves, obtained independently of applications, give reasonable temperature values when applied to mineral pairs from metamorphic and igneous rocks. Examples are:

1. $\Delta_{QK} = 1.6$ and $\Delta_{QM} = 2.5$ in migmatites (Blattner, 1971, 1972, and new results) — 750°C.
2. $\Delta_{QK} = 2.2$ and $\Delta_{QM} \approx 4$ in chlorite zone Otago Schist (Paterson, ms) — 430°C.
3. $\Delta_{QM} = 2.8$ for transition kyanite-sillimanite in New England (Garlick and Epstein, 1967) — 630°C.
4. $\Delta_{QM} = 3.9$ for upper stability limit of lawsonite in blueschists of New Caledonia (Black, 1974) — 430°C.

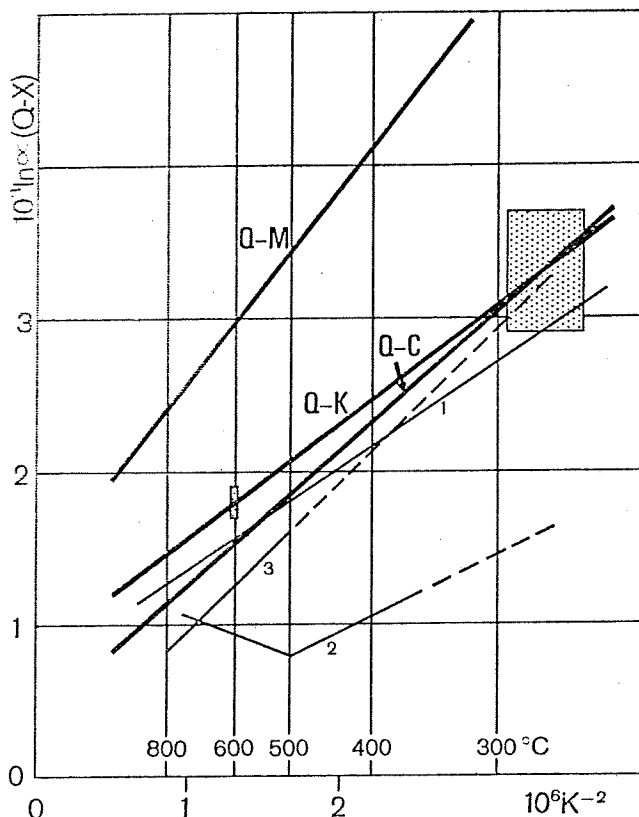


Fig. 3. Tentative quartz-K-feldspar (Q-K), quartz-muscovite (Q-M), and quartz-calcite (Q-C) oxygen isotope geothermometers. Equations are:

$$10^3 \ln \alpha (Q-K) = 0.82 + 0.74 \cdot 10^6 K^{-2}$$

$$10^3 \ln \alpha (Q-M) = 1.30 + 1.27 \cdot 10^6 K^{-2}$$

$$10^3 \ln \alpha (Q-C) = 0.37 + 0.88 \cdot 10^6 K^{-2} \text{ [NBS28} = 9.8/\text{PDB1} = 30.36]$$

The indicated fields of uncertainty relate to quartz-K-feldspar data of Blattner and Bird (1974) and of this paper. Previously available Q-K curves are shown for comparison: (1) is from Epstein and Taylor (1967), (2) is a combination from Clayton, O'Neil, and Mayeda (1972) and O'Neil and Taylor (1967), (3) is from Bottinga and Javoy (1973). See text for discussion.

If compared to other petrological temperature estimates the figures for cases (2) and (4) may seem somewhat high. On the other hand, the data of Garlick and Epstein (1967), based on the present $\Delta_{Q_{M}}$ curve, require the kyanite-sillimanite-andalusite triple point to lie below 630°C, in agreement with Richardson, Gilbert, and Bell (1969; see also Thompson, 1974), and if the triple point is in fact at 625°C, the $\Delta_{Q_{M}}$ curve provides a temperature that is either accurate or too low.

Earlier oxygen isotope calibrations involving quartz have also led to geologically reasonable temperatures. However, (A) insofar as they involve experimental data that have been rejected on technical grounds by Clayton, O'Neil, and Mayeda (1972) (curve 1 of fig. 3), this must be regarded as coincidental; and (B) insofar as they are not based on experiments and have been designed to yield acceptable temperatures (Bottinga and Javoy, 1973, p. 257, 262) (curve 3 of fig. 3), they are not independent calibrations. The quartz-H₂O calibration of Clayton, O'Neil, and Mayeda (1972) itself (leading to curve 2, fig. 3) requires a positive correction of unknown magnitude (0.77) in relation to $\alpha_{CO_2-H_2O}^{25^\circ C}$, before it can be combined with other mineral-H₂O calibrations, and at temperatures below 500°C may be out of equilibrium (Blattner and Bird, 1974).

Obviously, and although they are free of certain specific types of error, the present calibration curves themselves are not final ones. However, in view of the near-universal applicability of mineral pair oxygen isotope geothermometers one may hope for considerable improvements of laboratory, geothermal, and theoretical data.

ACKNOWLEDGMENTS

I am indebted to A. J. Ellis for pointing out the scientific value of the geothermal areas and to T. A. Rafter and J. R. Hulston for providing laboratory facilities and for encouragement when this work was begun in 1969. A. Rohde has performed many of the oxygen extractions, and Shirley Stuart has patiently typed this and other manuscripts. An initial tip on Broadlands minerals came from Pat Browne, and I am grateful to him, to E. Roedder, and to A. Wodzicki for much helpful information. I also thank E. V. Eslinger for a useful critical review.

REFERENCES

- Baertschi, P., 1957, Messung und Deutung relativer Häufigkeitsvariationen von O¹⁸ und C¹³ in Karbonatgesteinen und Mineralien: Schweizer. min. pet. Mitt., v. 37, p. 73-158.
- Black, P. M., 1974, Oxygen isotope study of metamorphic rocks from the Ouégoa District, New Caledonia: Contr. Mineralogy Petrology, v. 47, p. 197-206.
- Blattner, Peter, 1971, Migmatite by partial fusion and short range hydrothermal transfer, British Columbia: Schweizer. min. pet. Mitt., v. 51, p. 155-177.
- 1972, Oxygen isotopic composition of minerals from Lepontine gneisses, Valle Bodengo (Prov. di Sondrio, Italia): Schweizer. min. pet. Mitt., v. 52, p. 33-37.
- Blattner, Peter, and Bird, G. W., 1974, Oxygen isotope fractionation between quartz and K-feldspar at 600°C: Earth Planetary Sci. Letters, v. 23, p. 21-27.
- Blattner, Peter, and Hulston, J. R., 1975, Calcite reference samples for tracing proportional mass spectrometer errors: New Zealand Dept. Sci. Indus. Research, Inst. Nuclear Sci.: Open file report.
- Bottinga, Yan, and Craig, H., 1968, High temperature liquid-vapor fractionation factors for H₂O-HDO-H₂O¹⁸: Am. Geophys. Union Trans., v. 49, p. 356.
- Bottinga, Yan, and Javoy, M., 1973, Comments on oxygen isotope geothermometry: Earth Planetary Sci. Letters, v. 20, p. 250-265.
- Browne, P. R. L., and Ellis, A. J., 1970, The Ohaki-Broadlands hydrothermal area, New Zealand: mineralogy and related geochemistry: Am. Jour. Sci., v. 269, p. 97-131.
- Browne, P. R. L., Roedder, E., and Wodzicki, A., 1974, Past and present day geothermal waters from fluid inclusion studies, Broadlands field, New Zealand: Internat. Symposium on water-rock interaction, Prague.

- Clayton, R. N., and Mayeda, T. K., 1963, The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis: *Geochim. et Cosmochim. Acta*, v. 27, p. 43-52.
- Clayton, R. N., Muffler, L. J. P., and White, D. E., 1968, Oxygen isotope study of calcite and silicates of the River Ranch No. 1 well, Salton Sea geothermal field, California: *Am. Jour. Sci.*, v. 266, p. 968-979.
- Clayton, R. N., O'Neil, J. R., and Mayeda, T. K., 1972, Oxygen isotope exchange between quartz and water: *Jour. Geophys. Research*, v. 77, p. 3057-3067.
- Clayton, R. N., and Steiner, A., 1975, Oxygen isotope studies of the geothermal system at Wairakei, New Zealand: *Geochim. et Cosmochim. Acta*, in press.
- Craig, Harmon, 1957, Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide: *Geochim. et Cosmochim. Acta*, v. 12, p. 133-149.
- 1961, Standard for reporting concentrations of deuterium and oxygen-18 in natural waters: *Science*, v. 133, p. 1833-1834.
- Epstein, S., and Taylor, H. P., Jr., 1967, Variation of O^{18}/O^{16} in minerals and rocks, in Abelson, P. H., ed., *Researches in Geochemistry*, v. 2: New York, John Wiley & Sons, p. 29-62.
- Eslinger, E. V., and Savin, S. M., 1973, Mineralogy and oxygen isotope geochemistry of the hydrothermally altered rocks of the Ohaki-Broadlands, New Zealand, geothermal area: *Am. Jour. Sci.*, v. 273, p. 240-267.
- Friedman, I., and Gleason, J. D., 1973, A new silicate intercomparison standard for O^{18} analyses: *Earth Planetary Sci. Letters*, v. 18, p. 124.
- Fournier, R. O., 1973, Silica in thermal waters: Laboratory and field investigations, in *Proceedings of the International Symposium on Hydrogeochemistry and Biogeochemistry*, Japan, 1970, v. 1, Hydrogeochemistry: Washington, D.C., The Clarke Co., p. 122-139.
- Garlick, G. D., and Epstein, Samuel, 1967, Oxygen isotope ratios in coexisting minerals of regionally metamorphosed rocks: *Geochim. et Cosmochim. Acta*, v. 31, p. 181-214.
- Giggenbach, W. F., 1971, Isotopic composition of waters of the Broadlands geothermal field: *New Zealand Jour. Sci.*, v. 14, p. 959-970.
- Grindley, G. W., 1970, Subsurface structure and relation to steam production in the Broadlands geothermal field, New Zealand: *Geothermics*, Spec. Issue 2, p. 248-261.
- Grindley, G. W., and Browne, P. R. L., 1968, Geology of the Broadlands geothermal field: *New Zealand Dept. Sci. Indus. Research Geothermal Rept. 5*, p. 5-43.
- Helgeson, H. C., 1967, Solution chemistry and metamorphism, in Abelson, P. H., ed., *Researches in Geochemistry*, v. 2: New York, John Wiley & Sons, p. 362-404.
- Mahon, W. A. J., 1966, Silica in hot water discharged from drillholes at Wairakei, New Zealand: *New Zealand Jour. Sci.*, v. 9, p. 135-144.
- 1969, Recent chemical results from Broadlands drillholes: *New Zealand Dept. Indus. Research Geothermal Rept. C.D. 118/12-WAJM/55*.
- McCrea, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: *Jour. Chem. Physics*, v. 18, p. 849-857.
- Muffler, L. J. P., and White, D. E., 1969, Active metamorphism of upper Cenozoic sediments in the Salton Sea geothermal field and the Salton Trough, southeastern California: *Geol. Soc. America Bull.*, v. 80, p. 157-181.
- O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969, Oxygen isotope fractionation in divalent metal carbonates: *Jour. Chem. Physics*, v. 51, p. 5547-5558.
- O'Neil, J. R., and Taylor, H. P., Jr., 1967, The oxygen isotope and cation exchange chemistry of feldspars: *Am. Mineralogist*, v. 52, p. 1414-1437.
- 1969, Oxygen isotope equilibrium between muscovite and water: *Jour. Geophys. Research*, v. 74, p. 6012-6022.
- Onuma, N., Clayton, R. N., and Mayeda, T. K., 1972, Oxygen isotope temperatures of "equilibrated" ordinary chondrites: *Geochim. et Cosmochim. Acta*, v. 36, p. 157-168.
- Paterson, C. J., ms, 1975, Origin of scheelite mineralization at Glenorchy, Otago: Ph.D. Thesis, Univ. Otago, Dunedin, New Zealand.
- Richardson, S. W., Gilbert, M. C., and Bell, P. M., 1969, Experimental determination of kyanite-andalusite, and andalusite-sillimanite equilibria; the aluminum silicate triple point: *Am. Jour. Sci.*, v. 267, p. 259-272.

- Sharma, T., and Clayton, R. N., 1965, Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates: *Geochim. et Cosmochim. Acta*, v. 29, p. 1347-1353.
- Smith, J. H., 1970, Geothermal development in New Zealand: *Geothermics, Spec. Issue 2*, p. 232-247.
- Thompson, A. B., 1974, Calculation of muscovite-paragonite-alkali feldspar phase relations: *Contr. Mineralogy Petrology*, v. 44, p. 173-194.
- Truesdell, A. H., 1974, Oxygen isotope activities and concentrations in aqueous salt solutions at elevated temperatures: Consequences for isotope geochemistry: *Earth Planetary Sci. Letters*, v. 23, p. 387-396.
- White, D. E., 1968, Hydrology, activity and heat flow of the Steamboat Springs thermal system, Washoe Co., Nevada: U.S. Geol. Survey Prof. Paper 458-C, p. C1-C105.