

## OXYGEN ISOTOPE MEASUREMENTS OF ALBITE-QUARTZ-ZEOLITE MINERAL ASSEMBLAGES, HOKONUI HILLS, SOUTHLAND, NEW ZEALAND

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**Abstract**—The oxygen isotopes of albite, quartz, and zeolites from the Hokonui Hills, New Zealand, constrain crystallization temperatures and the type of pore fluids present during diagenesis. A section of altered vitric tuffs in this region contains an extremely sharp reaction boundary between a heulandite-chlorite assemblage containing fresh detrital plagioclase and a laumontite-albite-quartz assemblage. A laumontite vein follows the local joint pattern and forms the reaction boundary, suggesting that laumontitization occurred as a result of fracturing and increased fluid flow during uplift. The albite ( $\delta^{18}\text{O} = +15.0$ )-quartz ( $\delta^{18}\text{O} = +19.9$  to  $+20.5$ ) geothermometer constrains the temperature of alteration between 145° and 170°C with a pore water  $\delta^{18}\text{O}$  of  $+1.8$  to  $+3.5$ . The tuff was buried to an estimated maximum temperature of about 225°C, indicating that alteration occurred after maximum burial.

Framework oxygen was extracted from zeolites by reaction with  $\text{ClF}_3$  after the zeolites were thermally dehydrated in a vacuum. Laumontite was dehydrated at 300°C, and stilbite at 150°C. The precision of the method is typically about  $\pm 0.45\text{‰}$ . Fractionation curves for dehydrated zeolites are based on a general expression from the literature for feldspars, which depends only on the Si/Al ratio of the mineral. Measured  $\delta^{18}\text{O}$  values for laumontite in the groundmass of the altered tuff were  $+14.4\text{‰}$ . The laumontite-quartz pair constrains the temperature to between 139° and 162°C, in excellent agreement with the albite-quartz pair, and supporting the petrographic observation of co-crystallizing albite-laumontite.

Oxygen isotope values for fracture-filling laumontite in the vitric tuff, as well as those for groundmass and vein laumontite from other parts of the stratigraphic section, cluster around  $+14.5$ , suggesting that laumontite probably crystallized under similar conditions throughout much of the section. Oxygen isotope values for stilbite veins from various parts of the section indicate that this mineral crystallized at lower temperatures than the laumontite, for a given fluid isotopic composition, in agreement with the observed cross-cutting of laumontite by stilbite.

**Key Words**—Albite, Diagenesis, Formation temperature, Heulandite, Laumontite, Oxygen isotopes, Quartz, Stilbite, Zeolites.

### INTRODUCTION

Traditionally, diagenesis is viewed as a process occurring during burial, yet the importance of diagenetic events during uplift is becoming increasingly apparent. For example, Coombs (1954) documented a distinct burial sequence of diagenetic minerals in the Southland syncline of New Zealand, which later became the reference section where the zeolite facies was defined. Coombs found that in the Taringatura Hills area heulandite- and analcime-altered rock containing fresh plagioclase at shallow depths was replaced by laumontite-altered rock containing albitized feldspars at deeper levels. Alteration was attributed chiefly to increasing temperature due to progressive burial. Later studies in the Hokonui Hills, where the upper section is better

exposed, showed that laumontite is common at shallow levels (Jurassic) and that heulandite occurs throughout the sequence (Boles, 1971, 1974; Boles and Coombs, 1975, 1977). Thus, factors other than burial were apparently important.

The role of fluid mobility and composition became apparent because of (1) sharp contacts at high angles to bedding between heulandite- and laumontite-altered tuff and between analcime- and albite-altered tuff, apparently related to the local joint pattern; (2) abundant stilbite and laumontite veins in brittlely fractured rock; (3) coarse-grained rocks that are more extensively albitized than fine-grained rocks; and (4) mineral reactions that involved replacement of Ca-rich phases by Na-rich phases on a scale of at least a few meters. These results indicated that some of the diagenetic reactions were triggered by rock fracturing, presumably during the Cretaceous folding and uplift of the Southland syncline.

To obtain greater constraints on the timing of mineral reactions and the conditions under which they took place during burial and uplift, oxygen isotope ratios were determined for mineral pairs. From these data

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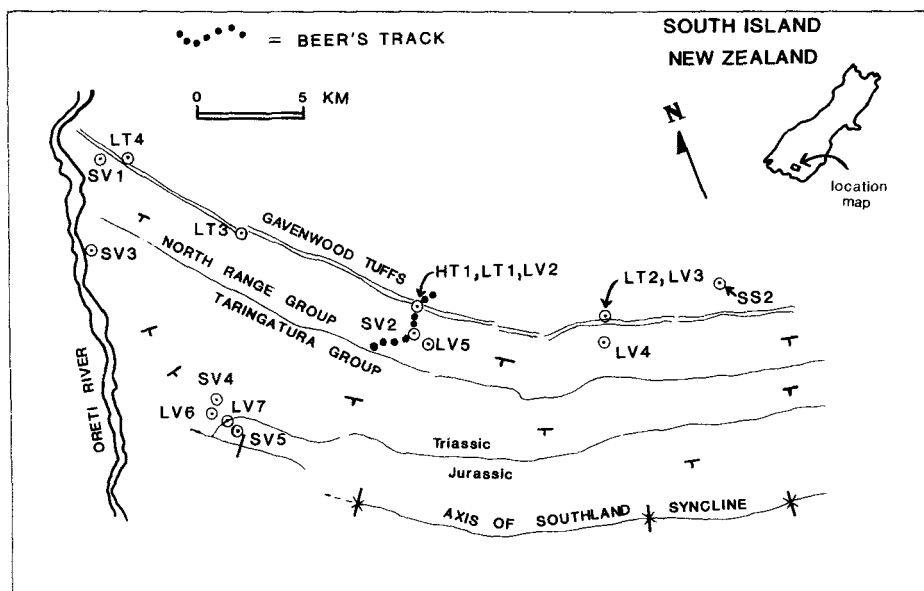


Figure 1. Map of the Hokonui Hills region, Southland, New Zealand, showing sample locations. Axis of Southland syncline and major stratigraphic boundaries are shown.

for co-crystallizing minerals, precipitation temperatures and isotopic composition of the pore fluids at the time of crystallization may be calculated (see, e.g., Land and Milliken, 1981; Yeh and Savin, 1977). Pore-fluid isotopic compositions can indicate the extent of water-rock interaction and meteoric vs. connate fluid types.

In this paper we present new data on the isotopic composition of framework oxygen in zeolites as part of an effort to understand zeolite crystallization temperatures. Two major problems exist in this type of work. First, zeolitic water, which probably does not reflect the conditions of crystallization, must be removed from the system before framework oxygen, which probably *does* represent the original crystallization conditions, can be measured. Ideally, such water should be removed from the zeolite structure at low temperatures so as not to alter the isotopic composition of the framework oxygen. Second, experimental curves relating the fractionation of oxygen between the zeolite framework and the coexisting solution are not available. Consequently, an empirical equation from O'Neil and Taylor (1967), based on quartz-water and feldspar-water experimental systems, was used to estimate fractionation curves for individual zeolite-water reactions. The results are consistent with petrographic observations regarding the relative timing of zeolite crystallization.

#### BACKGROUND GEOLOGY AND MINERALOGY

A unique opportunity to study the reaction of heulandite to laumontite and associated albitization is in

the Gavenwood Tuffs of the Hokonui Hills, Southland, New Zealand (Boles and Coombs, 1975, 1977). An outcrop along the Beer's Track (see Figure 1 for location of samples HT1, LT1, and LV2) reveals an extremely sharp (<3 mm) reaction boundary between green-gray heulandite-altered tuff (sample HT1) containing fresh feldspars and buff-yellow laumontite-altered tuff (sample LT1) containing completely albitized feldspars. The contact cuts across the vertical beds at a steep angle and appears to follow the local joint pattern (Boles, 1971). These joints are commonly filled with laumontite (sample LV2).

The heulandite-altered tuff is dark green-gray and consists of 70–75% heulandite-altered shards, about 15% chloritic phyllosilicate, 6–8% plagioclase, 2–4% quartz, and traces of magnetite, green-brown hornblende, clinopyroxene, and biotite (Boles and Coombs, 1975; Stallard, 1986). Fe-rich chlorite generally rims the heulandite shard pseudomorphs, and these two phases represent alteration products of fresh volcanic glass (Boles and Coombs, 1975).

The laumontite-altered tuff is yellow-gray and consists of about 70% laumontite crystals, each of which replaces several heulandite-altered shards plus the matrix, and locally replaces plagioclase. The remainder consists of 16–18% quartz, most of which is authigenic and appears as discrete clear patches or intergrowths with laumontite crystals; ~6% albitized feldspar containing varying amounts of small sericite flakes and minute dusty brown inclusions; 1–2% clear, authigenic K-feldspar; 1–2% hematite, generally lining small cracks; and traces of chlorite.

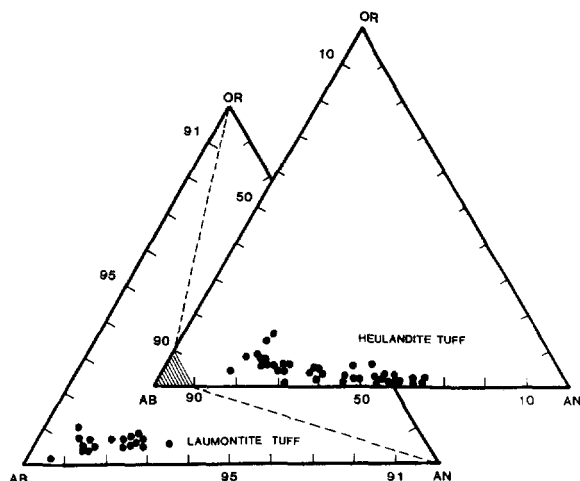


Figure 2. Feldspar compositions, heulandite-altered tuff (46 points) and laumontite-altered tuff (20 points), Gavenwood Tuffs, Beer's Track, Hokonui Hills, from electron microprobe analyses.

Plagioclase ( $Ab_{30}$ – $Ab_{80}$ ) from the heulandite-altered tuff is clear, euhedral to anhedral, angular, and ranges in size from 30 to 150  $\mu\text{m}$  (Figure 2). The compositional range is similar to plagioclase compositions of other vitric and vitric crystal tuffs from the Southland syncline (Boles and Coombs, 1975). These compositions apparently reflect a detrital mixture of mostly pyroclastic plagioclase plus a component of plutonic or metamorphic plagioclase (based on provenance fields of Trevena and Nash, 1981). No evidence has been found for post-depositional alteration of feldspars in the heulandite-altered tuff (Stallard, 1986).

All plagioclase from the laumontite-altered tuff has been albitized and has an albite component between  $Ab_{96.5}$  and  $Ab_{99.2}$  (Figure 2). This albitized plagioclase contains abundant minute inclusions (vacuoles?) in contrast with the inclusion-free fresh plagioclase. The albitized plagioclase has a dark brown luminescence, compared with the more brightly luminescent fresh plagioclase. About 15–20% of the feldspar is authigenic K-feldspar ( $Or_{96.3}$  to  $Or_{99.1}$ ). The crystals are small (20–75  $\mu\text{m}$ ) and clear, but commonly appear to be fractured.

Whole rock analyses of the heulandite and laumontite tuffs reveal remarkably similar compositions considering the striking difference in their appearance and mineralogy (see analyses 2 and 3 from Table 1 of Boles and Coombs, 1975). Silica apparently was released from the heulandite-to-laumontite reaction and crystallized as authigenic quartz or was consumed by albitization of plagioclase on the laumontite side. Released Na also appears to have contributed to albitization, whereas the Ca lost during albitization went to laumontite. Released K from the heulandite-to-laumontite reaction and from albitization reappeared as authigenic K-feld-

spar. The only significant losses associated with these reactions are Mg and total Fe, due to the nearly complete absence of chlorite in the laumontite rock; and  $\text{H}_2\text{O}$ , due to the heulandite-to-laumontite + quartz dehydration reaction, as well as to the loss of chlorite. Increase in  $\text{Fe}^{3+}/\text{Fe}^{2+}$  on the laumontite side reflects the increased presence of iron-oxide lining cracks and in veinlets.

## MATERIALS AND METHODS

### *Quartz-feldspar mineral separations, isotope measurements, and fractionation curves*

Both the extremely fine-grained nature of the tuff and the similar physical and chemical properties of feldspar, quartz, and zeolites complicated the separation process. The following procedure was used to separate plagioclase from fine-grained zeolitic tuffs:

(1) The tuff was gently crushed and sieved to the plagioclase size range (30–150  $\mu\text{m}$ ). The zeolites tended to crush relatively easily, and the authigenic potassium feldspar was finer-grained, so plagioclase and quartz were concentrated within this size range.

(2) The size fraction was cleaned ultrasonically in distilled water to remove ultrafine particles adhering to the grains.

(3) Dibromomethane (density = 2.497  $\text{g}/\text{cm}^3$ ) was used in a separatory funnel to separate the zeolite (density = 2.1–2.3  $\text{g}/\text{cm}^3$ ) further from the quartz and feldspar (density = 2.6–2.7  $\text{g}/\text{cm}^3$ ). This procedure was only partly successful in concentrating the quartz and feldspar, because of flocculation of grains and because chlorite adhering to the heulandite grains significantly increased the density of those grains.

(4) The zeolite concentrate was separated magnetically, first with a hand magnet, then with a Franz magnetic separator. The heulandite-altered tuff from the Gavenwood Tuff contained about 1% magnetite, which had to be removed with a hand magnet before using the Franz. The chlorite rimming the heulandite-altered glass shards was so intimately associated with them that a clean separation of heulandite + chlorite from quartz (about 10% of the separate) and plagioclase (90%) was possible with the Franz. It was also possible to produce a fraction containing mostly plagioclase (about 65%) + quartz (25%) + laumontite (10%) from the laumontite-altered tuff because of minor amounts of iron in the laumontite.

(5) The quartz (and laumontite) was handpicked, leaving a pure plagioclase fraction. This was accomplished under a binocular microscope using a single stiff hair from a powder brush mounted to a small stick.

The quickest and most thorough way to get a good quartz separate from the Gavenwood Tuffs was to take a powdered whole-rock fraction and dissolve everything except the quartz using  $\sim 5$  M HF. The quartz separate was then thoroughly rinsed with distilled  $\text{H}_2\text{O}$ ,

cleaned ultrasonically, rinsed with acetone, and dried. The origin of the quartz fraction (high-temperature volcanic or low-temperature authigenic) was determined using cathodoluminescence.

To obtain oxygen isotope measurements on the quartz and feldspar separates, 6–17 mg of each sample was reacted with  $\text{ClF}_3$  at 550–600°C for at least 5 hr. The oxygen released was converted to  $\text{CO}_2$  (as described by Clayton and Mayeda, 1963), and the yield was measured in terms of  $\mu\text{mole CO}_2/\text{mg sample}$ .  $^{18}\text{O}/^{16}\text{O}$  ratios of the generated  $\text{CO}_2$  were measured on a modified Nier 6-inch, double-collecting, isotope-ratio mass spectrometer.  $^{18}\text{O}/^{16}\text{O}$  values were calculated as per mil (‰) deviations from SMOW (Standard Mean Ocean Water).

Temperatures of crystallization and pore water isotopic compositions were derived from the feldspar and quartz oxygen isotope data using fractionation curves based on experimental data from 350° to 800°C for feldspars (O'Neil and Taylor, 1967) and from 200° to 750°C for quartz (Clayton *et al.*, 1972).

#### *Zeolite mineral separations, isotope measurements, and fractionation curves*

Obtaining pure zeolite fractions was generally not a problem. Most zeolite samples were handpicked from well-defined veins containing crystals several millimeters long. This included all stilbite samples, SV1 through SV5, which consisted of euhedral, wedge-shaped crystals 3–5 mm long, laumontite sample LV3 containing euhedral prismatic crystals 3 mm long, and laumontite samples LV5 and LV6 containing subhedral crystals about 1 mm long. Finer-grained ground-mass zeolites (samples LT1, LT2, LT3, LT4, and SS2) and those in more disseminated veins (samples LV2, LV4, and LV7) were separated from quartz and feldspar using dibromomethane. Crystals in these samples were anhedral and very small (30–500  $\mu\text{m}$ ).

The dehydration and extraction line used for the oxygen isotope analyses of zeolites consisted of 10 nickel reaction tubes, each encased in an independently controlled oven. The 10 tubes were connected to a mercury diffusion pump and a mechanical backing pump which maintained a vacuum of <0.1 mTorr throughout the system. With this system, the dehydration of a zeolite mineral could be examined *in vacuo* over a range of temperatures during a single experiment.

Stilbite samples SV4 and SV1 and laumontite samples LV7 and LV3 were chosen for the experiments (see Figure 1 for sample locations). These samples were collected from vein fillings from which pure zeolite was handpicked as described above. All samples were cream to buff in color.

For each experiment, a 100–200-mg aliquot of sample was handpicked from the vein fillings, ground and sieved to 100–150  $\mu\text{m}$ , and stored in a desiccator. Each

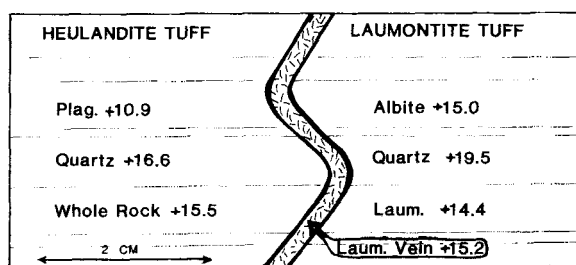


Figure 3. Oxygen isotopic data (in ‰ relative to SMOW) for a heulandite-tered (sample HT1) and laumontite-tered (sample LT1) vitric tuff, Gavenwood Tufts, Beer's Track, Hokonui Hills, New Zealand. See Table 1 for complete list of the data.

nickel reaction tube was loaded with 13–17 mg of sample. The tubes were then evacuated and heated to the temperature of interest over a period of 4 hr, with the preset temperature being attained within about 30 min. On the basis of air-dehydration data reported by Breck (1974), stilbite was heated to fixed temperatures from 25° to 400°C, and laumontite was heated from 25° to 500°C. After heating, the reaction tubes were maintained in a vacuum and sealed. The samples were then prepared for isotopic analysis as described above for quartz and feldspar.

Based on the results of these experiments, which are described below, all other stilbite samples were dehydrated *in vacuo* at 150°C for 4 hr prior to fluorination. The heulandite sample was also dehydrated at 150°C, because thermal dehydration curves for heulandite are very similar to those for stilbite (see, e.g., Breck, 1974; Gottardi and Galli, 1985). All other laumontite samples were dehydrated *in vacuo* at 300°C.

In the absence of experimental fractionation curves for oxygen in dehydrated zeolite-water pairs, the general expression for oxygen fractionation between tectosilicates and water developed by O'Neil and Taylor (1967) was used. This expression, derived from experimental data for alkali and plagioclase feldspars between 350° and 800°C and for quartz from 200° to 750°C, is:

$$1000 \ln \alpha = (2.64 \gamma + 0.93) (10^6 T^{-2}) + 2.80 \gamma - 5.51,$$

where  $\gamma = \text{Si}/(\text{Si} + \text{Al})$  and  $T$  is the absolute temperature. This expression reflects the conclusion of O'Neil and Taylor (1967) that the framework Si/Al ratio controls the isotopic properties of framework aluminosilicates and that other cations have very little effect. Because of the structural similarities of feldspars and zeolites, approximate fractionation curves for completely dehydrated zeolites were calculated from the above equation. Accurate Si/(Si + Al) values for the zeolites in question were obtained from microprobe analyses (Stallard, 1986). The following fractionation curves were then calculated:

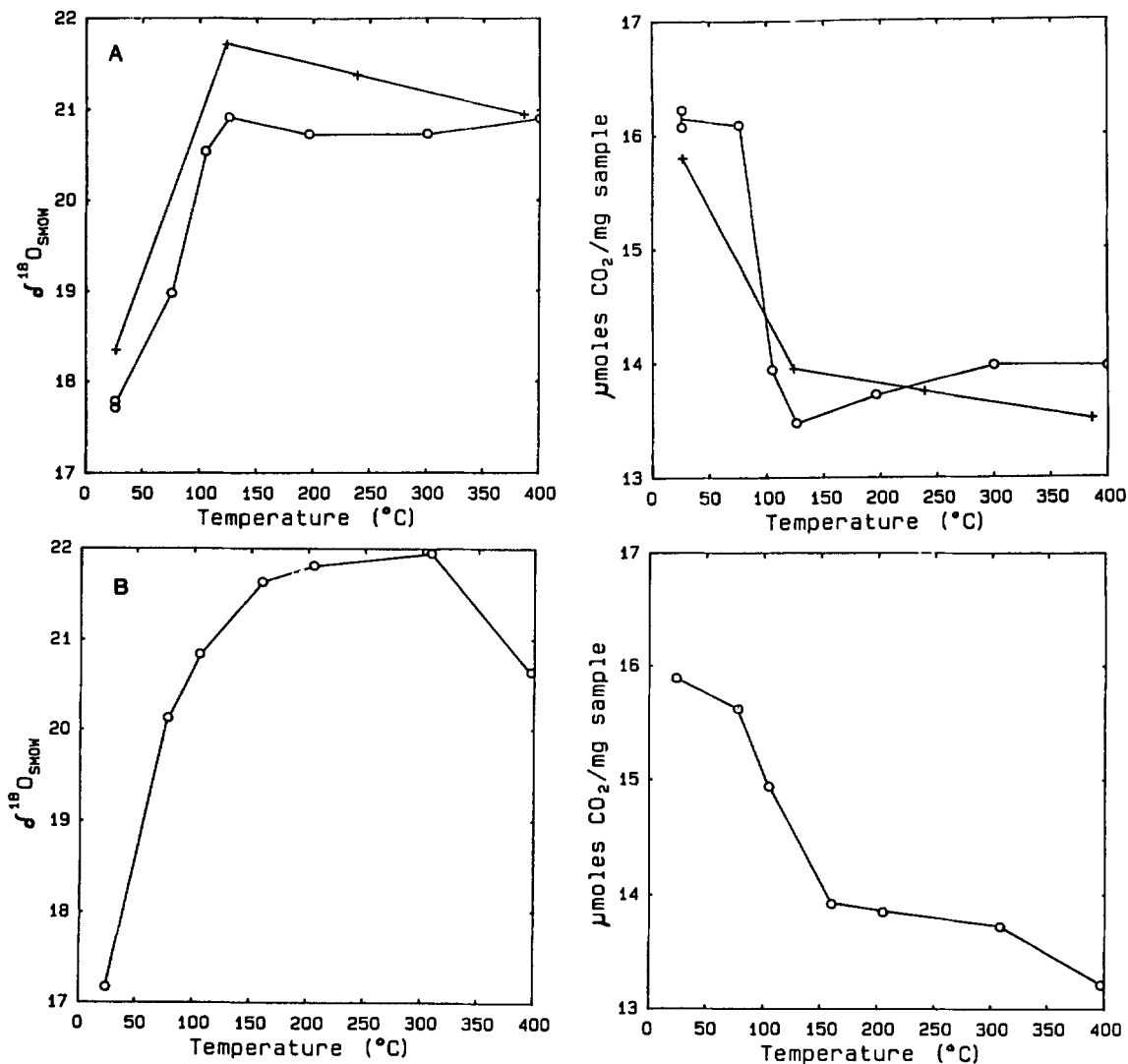


Figure 4. Dehydration results for stilbite veins SV4 (A) and SV1 (B) *in vacuo*, heating time 4 hr. Left:  $\delta^{18}\text{O}_{\text{SMOW}}$  of stilbite versus temperature in  $^{\circ}\text{C}$ . Right: yield in  $\mu\text{mole CO}_2/\text{mg}$  of stilbite versus temperature.  $\circ$  = run 1,  $+$  = Run 2.

#### Stilbite veins:

$$1000 \ln \alpha = 2.934(10^6)(T^{-2}) - 3.385$$

(Si/(Si + Al) = 0.759) mean of 25 analyses

#### Laumontite veins:

$$1000 \ln \alpha = 2.73(10^6)(T^{-2}) - 3.60$$

(Si/(Si + Al) = 0.682) mean of 47 analyses

#### Laumontite groundmass:

$$1000 \ln \alpha = 2.744(10^6)(T^{-2}) - 3.586$$

(Si/(Si + Al) = 0.687) mean of 25 analyses

## RESULTS

### Quartz-feldspar isotopes

Oxygen isotope values for quartz and feldspar from the Gavenwood Tuff are given in Figure 3 and Table

1. Ideally, several more replicate analyses would have been performed on each sample, but the extreme difficulty of obtaining pure separates of these minerals limited the number of analyses to two or three. With the exception of the quartz analyses for the heulandite-altered tuff, however, standard deviations fall within the acceptable range for stable oxygen isotope analyses.

### Zeolite isotopes

The results of the experiments on stilbite and laumontite are shown in Figures 4 and 5, respectively. The left half of each figure shows the measured  $\delta^{18}\text{O}$  value of the mineral at different temperatures. In each experiment, the mineral's  $\delta^{18}\text{O}$  is greater at higher temperatures. The right half of each figure shows the oxy-

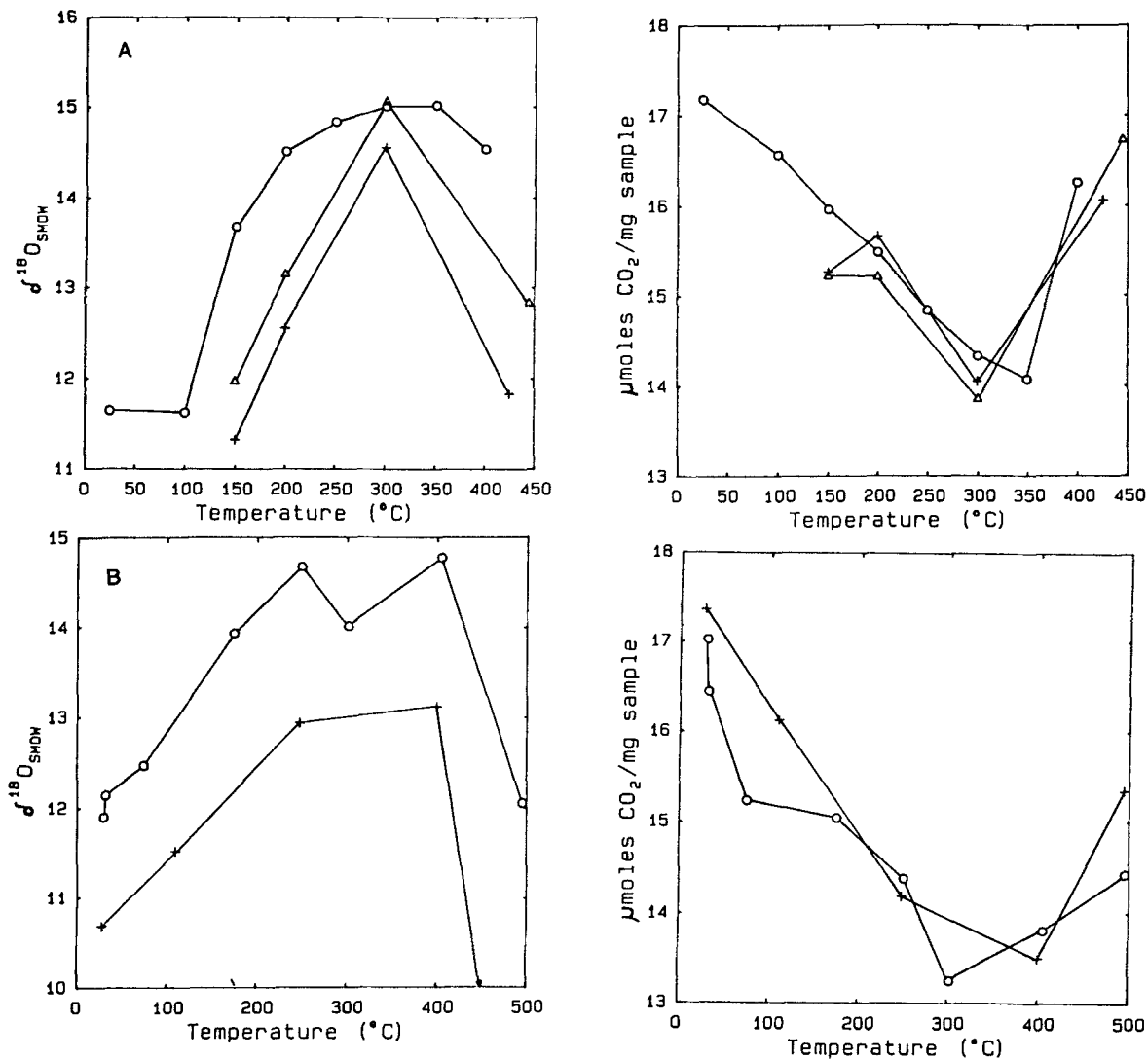


Figure 5. Dehydration results for laumontite vein LV3 (A) and LV7 (B) *in vacuo*, heating time 4 hr. Left:  $\delta^{18}\text{O}_{\text{SMOW}}$  of laumontite versus temperature in  $^{\circ}\text{C}$ . Right: yield in  $\mu\text{moles CO}_2/\text{mg sample}$  vs. temperature.  $\circ$  = Run 1,  $+$  = Run 2,  $\triangle$  = Run 3.

gen yield, expressed in terms of  $\text{CO}_2$ , plotted against reaction temperature. The left-hand figure is interpreted to indicate the progressive loss of isotopically light structural water with increasing heating temperatures. The drop in yield shown in the right-hand figure is also interpreted to represent loss of structural water. The yield in  $\mu\text{mole CO}_2/\text{mg sample}$  can be translated into the remaining number of structural water molecules.

Figure 4a summarizes results for two different runs using stilbite sample SV4. The plots show continuous dehydration up to  $125^{\circ}\text{C}$  and then a fairly stable plateau from  $125^{\circ}$  to  $400^{\circ}\text{C}$ . The ideal stilbite formula  $((\text{Ca}, \text{Na}_2, \text{K}_2)\text{Al}_2\text{Si}_7\text{O}_{18} \cdot 7\text{H}_2\text{O})$  has seven structural  $\text{H}_2\text{O}$

molecules. Microprobe analyses (Stallard, 1986) suggest a maximum of only 4.5  $\text{H}_2\text{O}$  molecules, if calculated from the difference between the analysis total and 100%, perhaps because the sample is under vacuum when probed and loses some of its water. Because the samples were stored in an evacuated dessicator for several days before being weighed for the isotope experiments, they also contained about 4.5  $\text{H}_2\text{O}$  molecules when weighed. Based on this assumption, the yield for samples evacuated for 4 hr at room temperature (about  $25^{\circ}\text{C}$ ) was about  $16 \mu\text{mole CO}_2/\text{mg sample}$  and corresponds to about 3.25  $\text{H}_2\text{O}$  molecules in the formula. This result was obtained from the following calculation:

(1) Using an average stilbite formula of  $\text{Ca}_{1.03}\text{Na}_{1.11}\text{K}_{0.03}\text{Al}_{2.2}\text{Si}_{6.8}\text{O}_{18} \cdot 4.5\text{H}_2\text{O}$  (calculated from 25 microprobe analyses), the gram formula weight of stilbite sample SV4 = 664 g.

(2) A yield of 16  $\mu\text{mole}$  of  $\text{CO}_2/\text{mg}$  average stilbite gives:

$$\begin{aligned} & (16 \mu\text{mole CO}_2/\text{mg SV4})(664 \text{ g/mole SV4}) \\ & = 10.62 \text{ mole CO}_2/\text{mole SV4} \\ & = 21.25 \text{ mole oxygen/mole SV4} \end{aligned}$$

(3) 21.25 oxygen atoms – 18 framework oxygen  
= 3.25 structural  $\text{H}_2\text{O}$  molecules

Using a similar calculation, the yield of about 13.75  $\mu\text{mole CO}_2/\text{mg}$  sample for stilbite heated *in vacuo* for 4 hr at 125°C or higher corresponds to essentially complete dehydration (a yield of 13.55  $\mu\text{mole}/\text{mg}$  corresponds to no remaining water in the zeolite). Inasmuch as the yield and the isotopic composition remained constant from 125° to 400°C, complete dehydration probably was attained. Similar results were obtained for stilbite vein sample SV1 (Figure 4b).

Runs 1 and 2 for sample SV4 (Figure 4a) gave approximately parallel patterns of dehydration, but the run 2 results were shifted to the isotopically lighter side of the run 1 results. This shift of about 0.5‰ exceeded that which could be explained by the usual error margin inherent in fluorination procedures ( $\pm 0.2\%$ ). The cause of this shift between runs could have been minor host rock contamination, inhomogeneity of the vein's oxygen isotope content, differences in vacuum efficiency, minor differences in humidity of the environment, or a combination of these. Experiments on laumontite (described below) suggest that host rock contamination and/or vein inhomogeneity were the main causes of these shifts.

The  $\delta^{18}\text{O}$  values and  $\text{CO}_2$  yields for experiments on laumontite samples LV3 (Figure 5a) and LV7 (Figure 5b) suggest continuous loss of zeolitic water between room temperature and 250°C and then only slight change between 250° and 400°C. Samples dehydrated at temperatures >400°C yielded lower  $\delta^{18}\text{O}$  values and higher  $\text{CO}_2$  yields, similar to those results obtained at much lower temperatures (see Figure 5). These unusual results may be due to the reaction at high temperatures of the water released from the zeolite with the walls of the nickel reaction tubes to form nickel oxide or hydroxide. Such products would have adhered to the vessel walls and been fluorinated along with the dehydrated zeolite. If this was the cause for these unusual results, similar results for high-temperature dehydration of other zeolites would be expected. Although the stilbite experiments were run only up to 400°C, which appears to be near the minimum temperature required for this effect, results at 400°C for sample SV1 (Figure 4b) show a drop in  $\delta^{18}\text{O}$  but no corresponding increase in yield. More experiments at temperatures >400°C

need to be performed to verify that reaction with the nickel tube is responsible for the anomalous high-temperature results. In any case, the minimum in yield and maximum in  $^{18}\text{O}$  content recorded for laumontite samples heated to about 300° to 350°C suggest that the samples were completely dehydrated at these temperatures.

Replicate runs on laumontite sample LV3 (Figure 5a) yielded differences similar in magnitude to those discussed above for stilbite, but experiments using laumontite sample LV7 yielded significantly larger differences in isotopic compositions (see Figure 5b). The fine-grained and disseminated nature of the laumontite in the vein from which sample LV7 was collected compared with the euhedral crystals and well-defined boundaries of the veins from which samples LV3, SV1, and SV4 were collected suggests that minor host rock contamination was responsible for these differences of about 1‰.

Isotope data for the zeolites used in these experiments, as well as for all other zeolite samples, are summarized in Tables 1 and 2. Based on the experimental results, all stilbite samples were dehydrated *in vacuo* at 150°C for 4 hr prior to reaction with  $\text{ClF}_3$ . The heulandite sample was also dehydrated at 150°C, whereas all laumontite samples were dehydrated at 300°C.

## DISCUSSION

### *Quartz-feldspar isotope data*

From the quartz and feldspar data alone, the following can be concluded regarding albitization in the Gavenwood Tuff:

1. Most significant are the data for the feldspar fractions, which give an average  $\delta^{18}\text{O}$  of +10.9‰ for the unaltered plagioclase and +15.0‰ for the albitized plagioclase. These values indicate that albitization in the laumontite-altered tuff was a result of reequilibration of the framework oxygen, implying the dissolution and reprecipitation of the feldspar grains (as suggested by Boles, 1982).

2. The oxygen isotope value of +10.9‰ for the plagioclase in the heulandite-altered tuff suggests that these feldspars consist of mostly volcanic plagioclase, along with minor plutonic or metamorphic plagioclase, as mentioned above (see Kastner and Siever, 1979).

3. The  $\delta^{18}\text{O}$  of +16.6‰ for quartz in the heulandite-altered tuff probably reflects a mixture of high-temperature detrital quartz (volcanic, plutonic, and/or metamorphic) and some lower-temperature (authigenic) quartz. The value of +19.5‰ for quartz in the laumontite-altered tuff is probably due to the quartz crystallized during the heulandite-to-laumontite reaction, plus the quartz inherited from the heulandite-altered tuff. Using estimates of 2–4% inherited quartz and 16–18% total quartz in the laumontite-altered tuff, the  $\delta^{18}\text{O}$

Table 1. Oxygen isotope data for the Gavenwood Tuffs, Beer's Track, Hokonui Hills, New Zealand.

Sample	$\delta^{18}\text{O}_{\text{SMOW}} (\text{‰})$		
	Measured	$\bar{X}$	SD
Heulandite tuff (sample HT1)			
Whole rock	15.53	15.53	—
Quartz	16.99, 16.30	16.65	0.49
Plagioclase	10.67, 10.93, 11.01	10.87	0.18
Laumontite tuff (sample LT1)			
Laumontite	14.26, 14.98, 13.97	14.40	0.52
Albite	15.07, 14.81, 14.98	14.95	0.13
Quartz	19.44, 19.55	19.50	0.08
Laumontite vein (sample LV2)			
	15.30, 15.18	15.24	0.08

of the authigenic quartz in the laumontite tuff can be calculated:

$$\text{minimum: } \frac{2}{18} (+16.6\text{‰}) + \frac{16}{18} (+19.5\text{‰})$$

$$\delta^{18}\text{O} = +19.9\text{‰}$$

$$\text{maximum: } \frac{4}{16} (+16.6\text{‰}) + \frac{12}{16} (+19.5\text{‰})$$

$$\delta^{18}\text{O} = +20.5\text{‰}$$

This range of +19.9 to +20.5‰ can be used in conjunction with the albite  $\delta^{18}\text{O}$  of +15‰ to constrain the temperature of albitization, as well as the isotopic composition of the water present. Using the curves from Friedman and O'Neil (1977), the albitization occurred at temperatures between 145° and 170°C in the presence of water having a  $\delta^{18}\text{O}$  between +1.8 and +3.5‰. Presumably, the marine water trapped in these sediments initially had a  $\delta^{18}\text{O}$  near zero. A positive value is consistent with water-rock interactions which generally tend to enrich the water in  $^{18}\text{O}$  (Clayton *et al.*, 1966; Savin, 1980).

#### Zeolite isotope data

Using this range of +1.8 to +3.5‰ for the water present at the time of albitization in the laumontite tuff at Beer's Track, the temperature of laumontitization was calculated from the measured laumontite  $\delta^{18}\text{O}$  of +14.4‰ and the laumontite groundmass-water fractionation curve proposed above. The result is a temperature range of 139°–162°C. Field and petrographic relations show that laumontite, quartz, and albite probably formed contemporaneously. The close agreement between the calculated laumontite crystallization temperature and the temperature range derived from the quartz-albite pair (145°–170°C) indicates that the proposed laumontite curve is reasonable.

The closeness in  $\delta^{18}\text{O}$  values for laumontite (+14.4‰) and albite (+15.0‰) reflects the similarity of their oxy-

Table 2. Oxygen isotope data for laumontite and stilbite from the Hokonui Hills, New Zealand.

Sample <sup>1</sup>	Maximum burial depth (km) <sup>2</sup>	$\delta^{18}\text{O}_{\text{SMOW}} (\text{‰})$		Number of analyses
		$\bar{X}$	SD	
Groundmass				
SS2	8.8	14.3	0.20	2
laumontite				
LT2	8.8	15.0	0.12	2
LT3	10.2	12.5	0.20	2
LT4	10.3	14.1	0.21	2
Vein laumontite				
LV7	3.5	14.5	0.41	3
LV6	5.0	11.9	0.36	2
LV5	7.5	15.1	0.24	2
LV4	7.9	14.9	0.09	2
LV3	8.8	14.8	0.25	2
Vein stilbite				
SV5	3.0	18.4	0.45	5
SV4	5.0	21.1	0.34	7
SV2	7.5	21.1	0.13	2
SV3	8.0	19.9	0.01	2
SV1	10.0	20.7	0.37	6

<sup>1</sup> See Figure 1 for sample locations and Stallard (1986) for sample descriptions.

<sup>2</sup> Maximum burial depths determined as described by Boles (1974).

gen isotope fractionation with water. In other words, the oxygen isotope fractionation between albite and laumontite is very small, making them an unsuitable pair for oxygen isotope geothermometry.

The  $\delta^{18}\text{O}$  values of most other laumontite samples, both groundmass and vein material, fall within a narrow range (+14.1 to +15.2), suggesting that laumontitization of much of the rock occurred under similar conditions and was related to fracturing. Stilbite veins, which commonly cross-cut the laumontite veins (Coombs *et al.*, 1959; Boles, 1971), have heavier  $\delta^{18}\text{O}$  values (mostly 20.7–21.1), which suggest that the stilbite crystallized at lower temperatures than the laumontite. Given the cross-cutting relationship, the veins may have crystallized during uplift rather than during progressive burial.

Two vein samples (laumontite sample LV6 and stilbite sample SV5) have  $\delta^{18}\text{O}$  values about 2.5‰ lighter than the values listed above. This result could be due to one of two factors (or a combination of the two): (1) higher temperatures of crystallization, or (2) crystallization from isotopically lighter water. Both samples are stratigraphically high in the section (see Table 2), making higher crystallization temperatures unlikely. Because all these laumontite and stilbite veins fill fractures that were presumably formed during uplift in the Rangitata orogeny, an influx of isotopically light meteoric water, especially into the upper parts of the stratigraphic section, seems a probable explanation for these isotopic results. Additional zeolite samples, both of vein material and groundmass, must be analyzed before the alteration history is determined fully.



## SUMMARY AND CONCLUSIONS

The experimental results for laumontite and stilbite indicate that these zeolites can be completely dehydrated *in vacuo* and that nearly consistent isotopic data (having standard errors of about  $\pm 0.45\%$ ) can be obtained for the framework oxygen of the dehydrated zeolite. The trial fractionation curves gave geologically reasonable temperatures and water compositions when applied to isotope results for samples from the Hokonui Hills.

The possibility of post-crystallization oxygen exchange between the zeolite framework and the zeolitic water seems unlikely at temperatures less than 200°C because the exchange would require breaking the Si-O bonds. Several recent studies (Gensse *et al.*, 1980; von Ballmoos and Meier, 1982), however, have shown that oxygen exchange can occur in some synthetic zeolites even at room temperature. Unpublished results on natural stilbite suggest that significant oxygen exchange may occur at temperatures as low as 50°C (Samuel Savin, Department of Earth Sciences, Case Western Reserve University, Cleveland, Ohio, personal communication, 1987). This issue should be settled in the laboratory for each zeolite before that mineral is widely applied as an isotope geothermometer in natural geologic settings.

Still, the results for zeolites from the Hokonui Hills are consistent with other geologic evidence, suggesting that post-crystallization exchange is not a problem at these temperatures. Especially encouraging are the similar temperatures obtained from the albite-quartz pair and from the laumontite-quartz pair in a vitric tuff; petrologic evidence clearly indicates that these phases co-crystallized.

The zeolite oxygen isotope data also lend credence to the idea that at least some of the laumontite alteration in the Hokonui Hills occurred as a result of Cretaceous uplift and that rock fracturing can trigger dehydration reactions (Fyfe *et al.*, 1958; Coombs *et al.*, 1959; Boles and Coombs, 1977). The sharp reaction boundary between heulandite alteration and laumontite alteration exposed in the Gavenwood Tuffs, the overall distribution of laumontite, and the abundance of laumontite fracture-fillings are field evidence supporting this idea. The similarity in  $\delta^{18}\text{O}$  values of groundmass laumontite and vein laumontite and the presence of isotopically lighter veins in the upper part of the stratigraphic section are two pieces of isotopic evidence suggesting laumontitization during uplift and an influx of meteoric water into the upper part of the section.

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