American Mineralogist, Volume 71, pages 1343–1353, 1986

Stable-isotope geochemistry of high-grade metapelites from the Central zone of the Limpopo belt

MARK HUEBNER, T. KURTIS KYSER, EUAN G. NISBET
Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan S7N 0W0, Canada

ABSTRACT

The Central zone of the Limpopo belt, near Beitbridge, Zimbabwe, contains high-grade metamorphic rocks of Archean age. $\delta^{18}O$ values of coexisting quartz and garnet in metapelites yield apparent equilibration temperatures of 621–846°C, whereas quartz-biotite and quartz-feldspar pairs give nearly concordant, although lower, equilibration temperatures of 383–643°C. The quartz-garnet isotope temperatures agree with temperatures calculated from thermometers based on cation partitioning. The apparent temperature disequilibrium among the mineral phases can be attributed to variable diffusion rates and closure temperatures wherein the quartz and garnet have retained their compositions since the closure temperature of garnet and the feldspar and biotite reflect prograde events.

Whole-rock $\delta^{18}O$ values of metapelites, metabasites, and calc-silicates, when compared to their probable precursors, suggest a relatively closed-system redistribution of isotopes among the various lithologic units. The isotopic compositions of waters that are calculated to be in equilibrium with the hydrous minerals present in these samples are similar to those of most metamorphic fluids from other regionally metamorphosed terranes but may contain a substantial meteoric water component.

INTRODUCTION

The widespread exposure of Archean high-grade metamorphic terranes provides an opportunity to examine the Earth's early continental crust. Mineral assemblages in various rock types of these regions often retain a record of the pressure and temperature prevalent at the time of their formation. Furthermore, patterns of chemical modifications can provide information about the processes operative in the early history of the Earth. The Central zone of the Limpopo belt, which straddles the Zimbabwe–South Africa boundary, is an Archean metamorphic terrane in which a variety of high-grade metamorphic rocks is preserved. Various aspects of the regional geology and petrology of this region have been studied by several researchers (Chinner and Sweatman, 1968; Light et al., 1977; Light and Watkeys, 1978; Watkeys, 1979; Broderick, 1979; Horrocks, 1980; Light, 1982; Harris and Holland, 1984; Windley et al., 1984). These studies, together with radiometric age results (Manton, 1968; van Breemen and Dodson, 1972; Barton and Ryan, 1977; Barton et al., 1977) suggest a long and varied metamorphic evolution. Estimates of the equilibration pressures and temperatures of samples from the Limpopo belt have been based on the partitioning of cations among various mineral phases. Knowledge of the apparent equilibration temperatures of various phases is critical to understanding the metamorphic evolution of this area. In conjunction with a recent study of the cation thermobarometry of a series of metapelites from the Beitbridge region of the Central zone (Harris and Holland, 1984), a companion stable-isotope study was undertaken in order to compare cation and anion geothermometry and possibly reveal information about the processes involved in the evolution of portions of the continental crust.

REGIONAL GEOLOGY

The Limpopo belt lies between the Zimbabwe (Rhodesian) and Kaapvaal cratons in southern Africa and contains a variety of metamorphic rocks ranging from early to late Archean in age (van Breemen and Dodson, 1972; Barton and Ryan, 1977; Barton et al., 1977). The marginal zones (Fig. 1a) are bounded by the orthopyroxene isograd (Robertson, 1973) and contain a variety of granitoid intrusions and supracrustal rocks, all of which have been metamorphosed in the granulite facies. The mineral assemblage of orthopyroxene + quartz is characteristic of large areas of the marginal zones. In contrast, the Central zone (Figs. 1a, 1b) is a patchwork of granulite facies and upper-amphibolite facies rocks with assemblages of biotite + quartz and amphibole + quartz. Supracrustal rocks comprise a significant proportion of the Central zone terrane relative to the marginal zones. The rocks of the Central zone have undergone at least two major metamorphic events, the first in the granulite facies and the second, a retrograde event, in the upper-amphibolite facies. In addition, the Central zone records several periods of deformation and several lesser retrograde metamorphic events. The oldest rocks in the Beitbridge area, the Macuville Group, are a series of migmatites and banded gneisses. They have been correlated by Watkeys (1979) with the

0003–004X/86/1112–1343$02.00

Sand River gneisses, which have been dated at 3.78 Ga (Barton et al., 1977). The Macuville Group basement gneisses are unconformably overlain by the Beitbridge Sequence, comprising the lower Diti Metamorphic Suite and the overlying Nulli Metamorphic Suite. These two suites contain a lithologically diverse supracrustal assemblage of metasedimentary and metavolcanic rocks.

A minimum age for the granulite-facies metamorphic event in the Central zone is provided by the Messina layered intrusion, which was emplaced into the Beitbridge Sequence around 3.27 Ga (Barton et al., 1977). Field relations and petrographic studies suggest that the upper-amphibolite-facies metamorphic event occurred contemporaneously with the intrusion of the Bulai Gneiss around 2.7 Ga (van Breemen and Dodson, 1972; Mason, 1973; Light and Watkeys, 1978). Two later, less intense metamorphic events occurred in the middle-amphibolite and the greenschist facies, but their ages are obscure (Tankard et al., 1982). After uplift and erosion of the metamorphic complex, the Soutpansberg Group, a sequence of sediments and volcanics, was unconformably deposited during the middle Proterozoic (Barton and Ryan, 1977). Later, the overlying Mesozoic Karoo sediments and Karoo volcanics were deposited while Karoo age intrusives were emplaced.

GEOTHERMOMETRY AND GEOBAROMETRY OF THE CENTRAL ZONE

The results of several studies have been published on the thermobarometry of rocks from the Central zone. Chinner and Sweatman (1968) deduced from the mineral assemblage of enstatite + cordierite + sillimanite + quartz (originally enstatite + kyanite + quartz), in a sample near Beitbridge, that the granulite-facies metamorphic event in the Central zone occurred at $T > 860°C$ and at $P > 11$ kbar. The upper-amphibolite-facies mineral assemblages, which are best recorded in the metabasites, suggest equilibrium conditions of $T = 600–700°C$ and $P = 5–7$ kbar (Horrocks, 1980).

Most recently, Harris and Holland (1984) used the cation distributions of Mg among phases in the MgO-Al_2O_3-SiO_2 system (garnet, spinel, cordierite, hypersthene) to argue that the equilibrium temperature of the mineral assemblages present in metapelites from the Beitbridge area of the Central zone was in excess of 670°C and that the pressure was between 4 and 5 kbar. They further concluded that these are minimum estimates of the equilibration temperatures and pressures because the mineral assemblages display textural disequilibrium. Their applications of other thermobarometers to the same rocks and to some intercalated metabasites yielded estimates of apparent equilibrium conditions of $T = 750 \pm 50°C$ and $P = 3.5–5.0$ kbar (Table 1). The assemblages in these samples, therefore, are largely representative of the upper-amphibolite-facies event.

PETROGRAPHY AND CHEMISTRY

The samples examined in this study are from the sample collection studied by Harris and Holland (1984), which were collected from localities within 15 km of the town of Beitbridge, Zimbabwe. They include metapelites and semipelites containing the assemblage biotite + garnet + feldspar ± cordierite ± quartz ± orthopyroxene ± spinel ± sillimanite. Modal compositions of the samples are given in Table 2. Retrograde reactions of garnet, orthopyroxene, and sillimanite to form cordierite are apparent from reaction rims in several samples [i.e., Bb11d(2), Bb13b, Bb20, Bb25c]. Excluding retrograde reactions, most of the minerals appear to be unaltered by secondary alteration, although in a few samples [i.e., Bb11d(2), Bb13b,

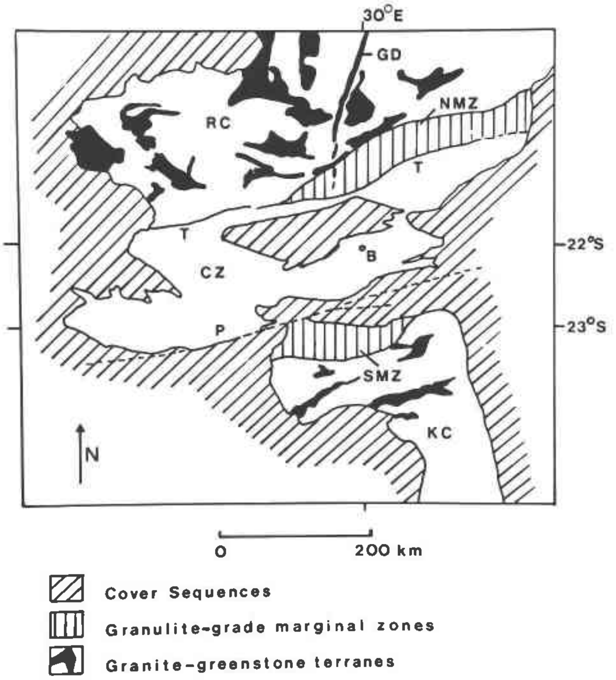

Fig. 1a. Map showing relationships of the Limpopo belt with the Zimbabwe (Rhodesian) and Kaapvaal cratons (after Du Toit et al., 1983); RC—Zimbabwe (Rhodesian) craton, KC—Kaapvaal craton, SMZ—Southern marginal zone, NMZ—Northern marginal zone, CZ—Central zone, P—Palala shear zone, T—Tuli-Sabi shear zone, B—Beitbridge, GD—Great Dyke.

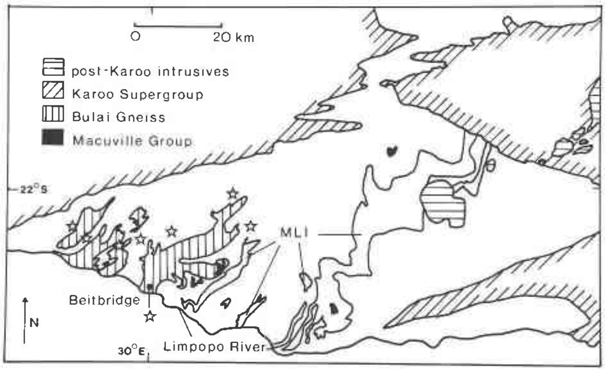

Fig. 1b. Simplified geology of the Beitbridge region (after Watkeys et al., 1983); MLI—Messina layered intrusion; stars represent sample localities.

Table 1. Results of geothermometry for Beitbridge samples

Geothermometer	T (°C)
Metapelites	
Fe-Mg exchange, biotite-garnet	600–950
Fe-Mg exchange, cordierite-garnet	<650
Al distribution, garnet-orthopyroxene	740–820
Garnet + plagioclase + Al_2SiO_5 + quartz assemblage	740–820
Metabasites	
Fe-Mg exchange, garnet-clinopyroxene	740–840
Al distribution, garnet-orthopyroxene	700
Two pyroxene	800–975

Note: From Harris and Holland (1984).

Bb16c, Bb17a] there is variable sericitization of the feldspars and pinitization of the cordierite. The almandine-rich garnets often have thin reaction rims and can contain 5–15% inclusions consisting mainly of quartz, biotite, feldspar, and sillimanite. Biotites, showing the red-brown color normally associated with high-grade conditions, are also unaltered with little or no chlorite present except in sample Bb17a. Some of the samples (i.e., Bb11d, Bb25c) show myrmekitic intergrowths of quartz with feldspar and symplectic intergrowths of quartz with cordierite indicative of retrograde reactions of earlier minerals with fluids. Also noted in one sample [Bb11d(2)] are inclusions of spinel and sillimanite in feldspar. The inclusions make up less than 5% of the feldspar volume and are not considered to affect the $\delta^{18}O$ value of the feldspar separate.

ANALYTICAL PROCEDURE

Mineral separates were prepared by use of heavy liquids, magnetic separation, etching with hydrofluoric acid, and hand picking. The purity of the individual mineral separates was typically greater than 95%. Oxygen was extracted from silicate minerals and rock powders using the BrF_5 method of Clayton and Mayeda (1963). Yields for the oxygen extracted from garnets showed a range from 36 to 96%, although extractions of the same samples giving various yields suggest that there is no correlation between yield and $\delta^{18}O$ value of garnets. Many of the garnet samples were also treated with HF to remove the outer portion of the grains and were then ground and analyzed. These stripping experiments suggest that the garnets are not zoned in ^{18}O even though they are chemically zoned (Harris and Holland, 1984). All values are reported in the familiar δ notation in units of per mil relative to V-SMOW. The isotopic values of most minerals are reproducible to ±0.1‰ except for biotite and the whole-rock powders, where the values are accurate to ±0.2‰. The value of NBS-28 quartz obtained by this procedure is +9.6‰. H was extracted from hydrous minerals using the procedures outlined by Kyser and O'Neil (1984). The isotopic values for H, also reported in the δ notation relative to V-SMOW, are accurate to ±3.0‰. The value of NBS-30 biotite obtained by this procedure is −65‰.

The temperature dependence of the partitioning of oxygen isotopes among coexisting minerals in the temperature range of metamorphic rocks has been estimated from both laboratory experiments and empirical methods. Equations of the form $\Delta^{18}O_{a-b} = A + (B \times 10^6)/T^2$ are normally used to describe the relation between temperature and the fractionation of oxygen isotopes between two minerals. $\Delta^{18}O_{a-b}$ is defined as 1000 ln α_{a-b} and, for relatively small fractionations, can be approximated by $\delta^{18}O_a - \delta^{18}O_b$ (e.g., Friedman and O'Neil, 1977; Deines, 1977), where a and b are two minerals whose isotopic compositions have been measured, α is the fractionation factor between two minerals, and A and B are coefficients derived from either experimental data or empirically from natural samples.

The use of experimentally derived fractionation factors is usually preferable to the use of empirically derived curves to calculate equilibration temperatures of mineral phases because one must assume that equilibrium was obtained in the samples used to generate the empirical curve. For minerals that are of interest in this study, however, published experimental results exist only for quartz (Matsuhisa et al., 1979), pyroxene and feldspar (Matthews et al., 1983), and muscovite, which can be used as an approximation for biotite (Garlick and Epstein, 1967; Graham, 1981). The empirical isotope geothermometers of Bottinga and Javoy (1973, 1975) have been chosen for this study because they include a complete and internally consistent set of fractionation factors for all the minerals of interest.

Recent experimentally determined fractionation curves indicate that Bottinga and Javoy may have underestimated the amount of retrograde exchange that occurred in certain minerals used in their empirical formulation which leads to excessively high equilibration temperatures. For example, apparent equilibration temperatures for both quartz + biotite and quartz + feldspar pairs in the Beitbridge samples calculated using experimentally derived fractionation factors are consistently lower than those calculated from the factors of Bottinga and Javoy (1975) by about 140 deg (Table 4). Similarly, the quartz-garnet temperatures calculated using preliminary results from experiments by Matthews and Graham (pers. comm.) are 70 deg lower than those calculated using the empirical thermometers. Isotope equilibration temperatures of polymetamorphic rocks may not represent real temperatures but do indicate possible equilibrium among various

Table 2. Modal compositions of metapelites from the Beitbridge area

Sample	Qtz	Bio	Grt	Sil	Crd	Plg	Ksp	Opx	Spn	Opa	Pin	An
Bb11b	55	15	5	—	—	25	—	—	—	<1	—	25
Bb11d(1)	45	15	10	—	—	30	<1	—	—	<1	—	25
Bb11d(2)	40	20	10	<1	—	20	<1	—	<1	—	5	25
Bb12a	30	15	35	—	—	20	—	—	—	—	—	50
Bb13b	20	15	40	1	—	15	—	—	<1	<1	10	50
Bb13e	<1	1	15	5	75	10	—	—	—	<1	—	25
Bb16c	20	5	40	<1	—	30	—	—	—	<1	5	15
Bb17a	40	10	20	—	—	25	—	—	—	<1	15	50
Bb20	30	20	20	5	15	10	—	—	—	<1	—	50
Bb25c	40	15	10	5	25	—	—	5	—	<1	—	—

Note: Compositions estimated from thin-section examination. Qtz = quartz, Bio = biotite, Grt = garnet, Sil = sillimanite, Crd = cordierite, Plg = plagioclase, Ksp = potassium feldspar, Opx = orthopyroxene, Spn = spinel, Opa = opaques, Pin = pinite, An = anorthite content of feldspars determined by optical methods.

Table 3. δ^{18}O and δD values of Beitbridge metapelites

Sample	WR	Qtz	Fsp	Bio	δD	Gnt	Crd	Opx	Sil
Bb11b	8.8	9.9	8.0	4.8	−58	6.6	—	—	—
Bb11d(1)	9.2	11.3	9.2	6.2	−49	8.3	—	—	—
Bb11d(2)	9.2	11.4	9.3	6.0	—	8.2	—	—	—
Bb12a	9.5	11.2	9.2	6.2	−61	8.5	—	—	—
Bb13b	9.9	11.6	9.2	6.1	−64	8.6	—	—	—
Bb13e	—	11.5	9.1	—	—	7.9	8.9	—	—
Bb16c	9.6	10.6	8.7	5.9	−54	8.3	—	—	—
Bb17a	—	11.4	8.9	6.1	−57	8.8	—	—	—
Bb20	9.6	11.1	9.2	6.2	−58	8.8	—	—	—
Bb25c	8.9	10.2	—	6.4	−65	7.0	—	7.9	8.1

Note: WR = whole rock. δD values are those for biotite.

Table 4. Apparent equilibration temperatures (°C) of quartz-mineral pairs

Sample	Qtz-Fsp (1)	Qtz-Fsp (2)	Qtz-Grt (1)	Qtz-Bio (1)	Qtz-Bio (3)
Bb11b	562	398	683	532	392
Bb11d(1)	463	329	707	539	392
Bb11d(2)	463	329	661	511	368
Bb12a	460	325	750	539	400
Bb13b	464	334	707	505	360
Bb13e	384	271	621	—	—
Bb16c	538	381	846	561	427
Bb17a	437	315	779	518	375
Bb20	541	384	846	528	408
Bb25c	—	—	707	643	534

Note: Calculated using empirically and experimentally determined fractionation factors. (1) Bottinga and Javoy (1975); (2) Matsuhisa et al. (1979); (3) From approximation of muscovite for biotite (Garlick and Epstein, 1967) and experimental quartz-muscovite curve of O'Neil and Taylor (1969).

phases. As such, only the relative equilibration temperatures for various mineral pairs are critical, and these are similar for both the empirical set of thermometers and those derived from experimentally determined fractionation factors despite marked differences in their absolute temperatures.

The effect of pressure on the fractionation of oxygen isotopes has to be considered for high-pressure metamorphic rocks. Experimentally determined fractionation factors in the system $CaCO_3$-H_2O indicate that oxygen-isotope partitioning is not affected to any significant extent by pressures up to at least 20 kbar (Clayton et al., 1975). This has been confirmed for silicate-bearing systems by the experimental work of Matsuhisa et al. (1979) and Matthews et al. (1983). Therefore, high pressures should not affect the oxygen-isotope fractionation between coexisting mineral phases in metamorphic rocks of upper amphibolite or granulite facies.

RESULTS AND DISCUSSION

Whole-rock values

The range of whole-rock δ^{18}O values for the Beitbridge metapelites is +8.8 to +9.9 (Table 3). These compositions are similar to those of other Archean metasedimentary rocks (Longstaffe and Schwarcz, 1977; Fourcade and Javoy, 1973). The protoliths for metapelites are clastic sediments composed of detrital quartz, feldspars, clays, and rock fragments derived from a variety of igneous, metamorphic, and sedimentary terranes. Mixed in with these components are authigenic and diagenetic minerals. The isotopic compositions of the protoliths are a function of the isotopic compositions of the endmembers, with δ^{18}O being +15 to +30 for clay minerals (Savin and Epstein, 1970) and +5 to +10 for primary igneous rocks (Taylor, 1968). Based on the chemical and mineralogic compositions, the original protolith for the metapelites probably had a δ^{18}O value of +10 to +15.

Interlayered with the metapelites are calc-silicates (δ^{18}O = +6.7 to +8.9) and metabasites (δ^{18}O = +7.5 to +8.7). Carbonates from the Archean of southern Africa include those of the Fig Tree Group (>2.9 Ga), which have δ^{18}O isotopic compositions of +12.1 to +16.6, and those of the Shamavian Group (>2.5 Ga), which have values of +20.6 to +28.0 as reported by Perry and Tan (1972). The δ^{18}O compositions of modern limestones are on the whole more positive with a range of +20 to +28 (Keith and Weber, 1964; Veizer and Hoefs, 1976). The Fig Tree Group carbonates have been metamorphosed to lower-greenschist facies and together with the Shamvian Group carbonates have undergone oxygen-isotope exchange with either infiltrating metamorphic or meteoric waters thereby lowering their δ^{18}O values. Modern basalts have a rather restricted range of δ^{18}O values from +5.5 to +7.2 (Kyser et al., 1982). Comparison of the Beitbridge whole-rock values with the assumed values for the protoliths (Fig. 2) implies that a redistribution of oxygen isotopes has occurred among the various lithologic units. Oxygen-isotope redistribution of this type suggests exchange with either pervasive metamorphic water in a nearly open system or a closed-system redistribution of oxygen via fluid communication among the various lithologic units.

Dewatering of fluids from a sedimentary pile during burial results in a decrease in porosity and permeability. Below a certain depth, the strength of the rock is no longer able to hold fractures open, and the fluid pressure can exceed the lithostatic pressure (Walther and Wood, 1984). Hydrofracturing is a proposed mechanism for dewatering that occurs when the fluid pressure exceeds that of the lithostatic pressure and leads to the development of fractures in the rock. These fractures tend to cut across lithologic boundaries and provide pathways for unidirectional fluid escape (Norris and Henley, 1976; Fyfe et al., 1978). Rumble and Spear (1983) argued that it is via these channelways that isotopic exchange can occur between lithologic units and suggested that the degree to which the lithologic units have reached equilibrium may be indicated by the isotopic composition of a common mineral such as quartz. δ^{18}O values of quartz from the metapelites range from 9.9 to 11.6, although the majority are near 11.2, and are indicative of a reasonable approach to isotopic equilibrium among the metapelite units (Table 3). In contrast, the δ^{18}O values of quartz from all lithologic units vary substantially from 8.5 to 11.6 (Huebner, unpub.), which suggests that isotopic equilibrium was not obtained among all the lithologic units in the metamorphic pile.

Walther and Orville (1982) discussed two endmember cases for fluid flow that have a bearing on the limits of

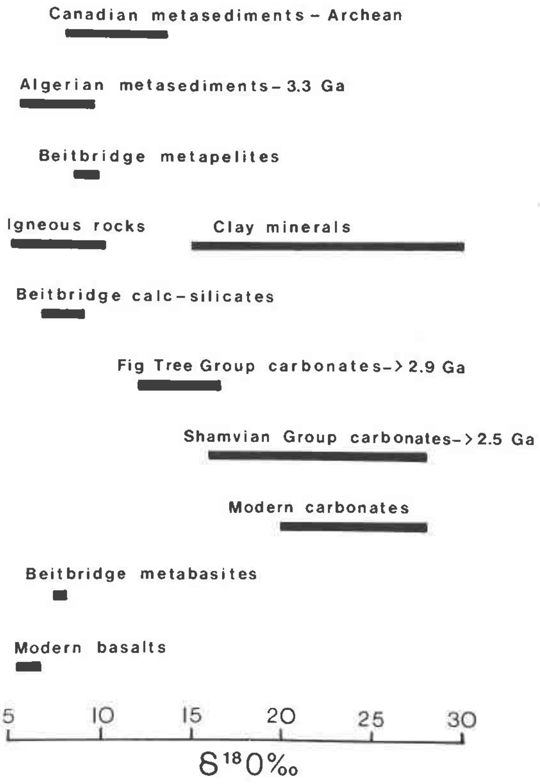

Fig. 2. Range in whole-rock $\delta^{18}O$ values of Beitbridge metamorphic rocks, Canadian metasediments (Longstaffe and Schwarcz, 1977), Algerian metasediments (Fourcade and Javoy, 1973), igneous rocks (Taylor, 1968), clay minerals (Savin and Epstein, 1970), Fig Tree Group and Shamvian Group carbonates (Perry and Tan, 1972), recent carbonates (Keith and Weber, 1964; Veizer and Hoefs, 1976), and recent basalts (Kyser et al., 1982).

fluid-rock interaction. In the first case, the fracture spacing is on the order of grain size; therefore, all rocks above where the fluids originate will come in contact with the escaping volatiles and have a chance to react. The second case has the bulk of the fluids escaping in widely spaced fractures so that the bulk of the rocks overlying will not be in contact with the escaping fluids. The episodic nature of fluid loss, the duration allowed for equilibration to occur, the mechanism utilized for fluid escape and the fluid/rock ratio may preclude isotopic equilibration between the lithologic units, as is recorded in the Beitbridge rocks. The progressive decrease in porosity and permeability with increasing depth of burial eventually may have restricted the intercommunication of fluids between the lithologic units, leading to the development of localized mineral equilibrium and distinct $\delta^{18}O$ values within each unit.

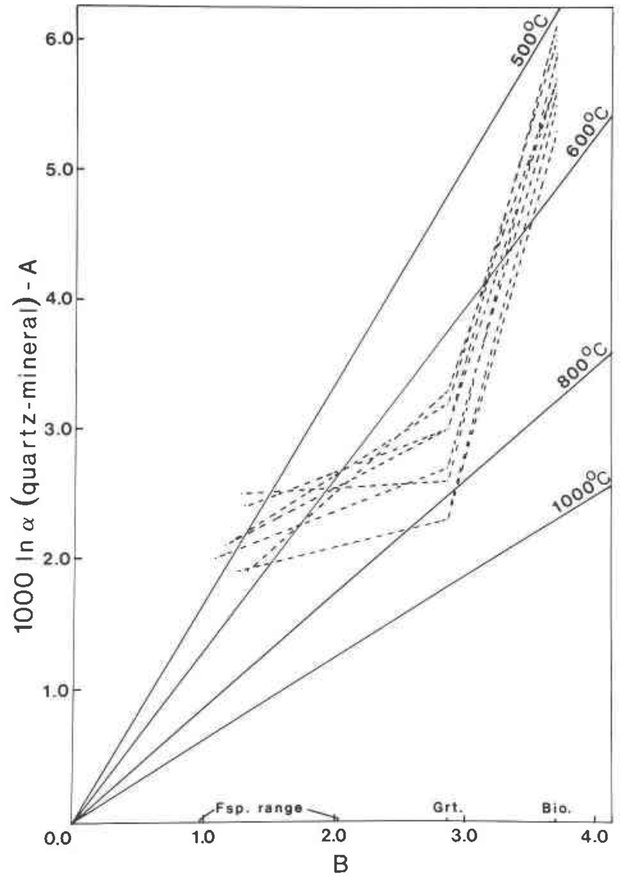

Fig. 3. Isotherm plot for quartz-mineral pairs from the Beitbridge metapelites. The slope of the line represents the ideal equilibration temperature of the mineral assemblage using the empirically derived fractionation factors of Bottinga and Javoy (1975). Temperatures for the same quartz-mineral pairs using experimentally derived fractionation factors would be lower by 100–200°C.

Oxygen-isotope geothermometry

Isotopic data from Table 3 are plotted on an "isotherm" plot (Javoy et al., 1970) in Figure 3 to assess the degree of relative isotopic equilibrium among the minerals in each sample. The solid lines represent the theoretical equilibrium fractionation between quartz and other minerals at the temperatures of 500, 600, 800, and 1000°C using the empirical thermometers of Bottinga and Javoy (1975). As discussed previously, temperatures calculated using experimentally determined fractionation factors would be somewhat lower although the differences among the temperatures of each pair are nearly the same. The dashed lines represent data for individual samples of the Beitbridge metapelites and connect several quartz-mineral pairs for which apparent temperatures have been calculated. Equilibrium partitioning of oxygen isotopes between all mineral phases would result in a linear relation similar to those represented by the reference isotherms. Apparent equilibration temperatures calculated from either empirical or experimental curves for quartz-biotite and quartz-feldspar are reasonably concordant for individual samples (Table 4), although the intersample variation in temperatures is 220 deg. This is in contrast to the quartz-garnet pairs, which yield consistently higher apparent equilibration temperatures.

The majority of apparent temperatures calculated from

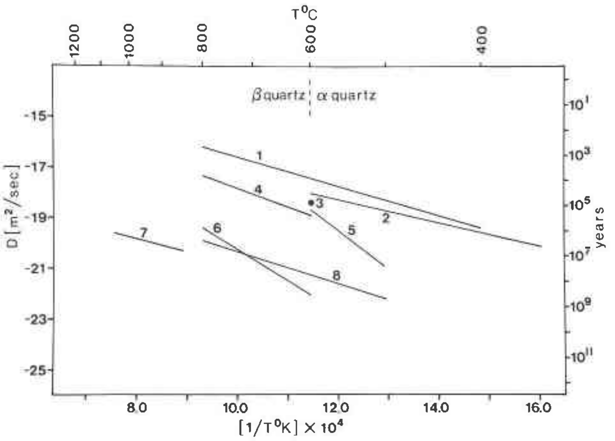

Fig. 4. Diffusion rate of ^{18}O in various minerals plotted as a function of temperature. 1 = feldspar (An_{96}; Giletti et al., 1978), 2 = feldspar (An_3; Giletti et al., 1978), 3 = feldspar (An_0; Freer and Dennis, 1982), 4 = β-quartz normal to **c** axis (Giletti and Yund, 1984), 5 = α-quartz parallel to **c** axis (Giletti and Yund, 1984), 6 = β-quartz parallel to **c** axis (Giletti and Yund, 1984), 7 = garnet (Freer and Dennis, 1982), 8 = phlogopite (Giletti and Anderson, 1977). All rates measured using secondary ion mass spectrometry except for phlogopite which was determined using the bulk-isotope method. On the right margin of the diagram are the times required for the oxygen isotopes in a 1-mm-radius spherical crystal to equilibrate with a fluid.

the quartz-garnet pair agree well with those calculated from the cation geothermometers used by Harris and Holland (1984) and with other cation thermobarometers (Table 1), whereas apparent isotope equilibration temperatures calculated from quartz-biotite and quartz-feldspar pairs are significantly lower. This lack of agreement between some of the temperatures calculated from anion-based thermometers and those from cation geothermometers has been noted in previous studies of granulite-facies rocks (McNaughton and Wilson, 1980, 1983; Wilson and Baksi, 1984).

Crystal growth and diffusion effects on isotopic compositions

Isotopic disequilibrium may result from (1) noncontemporaneous nucleation and growth of minerals during different metamorphic conditions or (2) contemporaneous nucleation and growth of minerals having different closure temperatures of isotope exchange so that some phases may continue to change their $^{18}O/^{16}O$ ratios during cooling and exhumation.

The timing associated with the crystallization of mineral phases during metamorphism is potentially important in the development of the $\delta^{18}O$ value of any mineral. The parameters pressure, temperature, and fluid composition vary continually during the metamorphic cycle, and therefore minerals that nucleate and grow at different times may reflect those differences. Several stable-isotope studies of polymetamorphic Alpine terranes (e.g., Frey et al., 1976; Hoernes and Friedrichsen, 1978) suggest that, through a judicious choice of samples, it is possible to characterize the conditions and isotope compositions prevalent at the time of the growth of new minerals during different metamorphic events. From studies on samples containing minerals that obviously formed during different events, it is apparent that overprinting by later events can obscure earlier compositions either by recrystallization or by interaction with infiltrating fluids. In the Beitbridge samples, the only obvious evidence for recrystallization or new mineral growth during later metamorphic events is the presence of thin cordierite rims or the insignificant quantities of symplectic intergrowths present in some samples.

Contemporaneous crystallization of mineral phases may result in isotopic disequilibrium if the exchange rates between various minerals and fluids are substantially different. When a mineral passes through a temperature where it ceases to exchange anions or cations, its composition becomes fixed. Parameters pertinent to oxygen-isotope exchange that are available for the phases of interest in this study are shown in Figure 4 and in Table 4 along with calculated diffusion rates at 650°C. Most of the diffusion data have been obtained under hydrothermal conditions and may not reflect conditions prevalent during high-grade metamorphism. Touret (1971), in a study of fluid inclusions in metamorphic rocks, has suggested that the fluids present during high-grade metamorphism are CO_2 rich. Muehlenbachs and Kushiro (1974) provided limited data for oxygen-isotope diffusion in rocks and minerals in the

Table 5. Diffusion rates of ^{18}O in various minerals

Mineral	T (K)	D_0 (m²/s)	Q (kJ/mol)	D (650°C)	Ref*
Quartz	1073–873	1.0×10^{-4}	234	5.71×10^{-18}	1
Quartz	1073–873	4.0×10^{-7}	142	3.68×10^{-15}	1
Quartz	873–773	1.9×10^{2}	284	1.61×10^{-14}	1
Feldspar (Ab_{97})	623–873	2.31×10^{-13}	89	2.12×10^{-18}	2
Feldspar (An_{96})	673–1073	1.39×10^{-11}	109	8.83×10^{-18}	2
Feldspar (An_0)	873			3.97×10^{-19}**	3
Phlogopite	773–1073	1.03×10^{-14}	122	1.32×10^{-21}	4
Grossular	1123–1323	2.67×10^{-16}	102	4.5×10^{-22}	3
Enstatite	1553	6.0×10^{-16}	377	2.77×10^{-37}	5
Diopside	1553	2.4×10^{-16}	377	1.34×10^{-37}	5

* References: (1) Giletti and Yund (1984), (2) Giletti et al. (1978), (3) Freer and Dennis (1982), (4) Giletti and Anderson (1977), (5) Muehlenbachs and Kushiro (1974).

** Diffusion measured at 873 K.

Table 6. Calculated $\delta^{18}O$ and δD values of waters in equilibrium with hydrous minerals from the Beitbridge samples

Sample	T (°C)	$\delta^{18}O$	δD
Bb11b	532	7.3	−22
Bb11d(1)	539	8.7	−13
Bb12a	539	8.7	−26
Bb13b	505	8.5	−32
Bb16c	561	8.4	−21
Bb17a	518	8.5	−20
Bb20	528	8.7	−22
Bb25c	643	9.0	−37
Bb4d*	649	8.0	−45
Bb1b*	482	7.7	−30

Note: $\delta^{18}O$ calculated from Bottinga and Javoy (1973) using temperatures obtained from quartz-biotite and quartz-amphibole empirical curves; all δD calculated from fractionation factors given by Suzuoki and Epstein (1976). * Hornblende; rest are biotite.

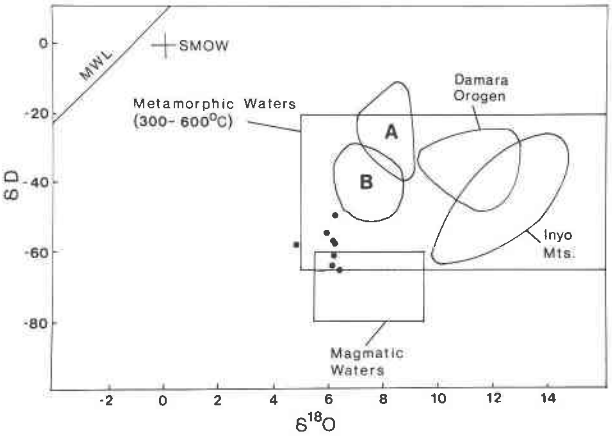

Fig. 5. δD versus $\delta^{18}O$ diagram showing the values for biotites from the Beitbridge metapelites (●) and the field of values for waters calculated to be in equilibrium with biotite (A) and hornblende (B) from the Beitbridge samples. Also plotted are values of fluids calculated from the metamorphic terranes of the Inyo Mountains (Shieh and Taylor, 1969) and Damara orogen (Hoernes and Hoffer, 1979).

presence of CO_2 (Table 5), which when calculated to 650°C yield very low diffusion rates. In addition, the experimental determination of diffusion coefficients for quartz, garnet, and feldspar were done by examining diffusion profiles using secondary ion mass spectrometry (SIMS), whereas diffusion rates for phlogopite were measured using the bulk isotope method, which often yields slower rates of diffusion than the SIMS method. An estimation for bulk diffusion in quartz is probably a value between the rates for diffusion parallel to the **c** axis and that perpendicular to the **c** axis. From these results, the order of oxygen-isotope closure among minerals from earliest to latest is garnet, quartz, and feldspar, with the closure for phlogopite perhaps being intermediate between that of garnet and quartz.

The diffusion data suggest that quartz and feldspar continue to exchange to lower temperatures than does garnet or, perhaps, biotite, which has important implications for the significance of the calculated isotope equilibration temperatures. Because the calculated temperatures are based on the partitioning of oxygen between two phases, if one phase ceases oxygen-isotope exchange with the fluid while the other phase continues the exchange, the temperatures determined from the pair of phases do not reflect equilibrium values. If the phase that continues to exchange oxygen with a fluid to lower temperatures does so with a fluid whose isotope composition is buffered by low water/rock ratios, the isotopic composition of the mineral will remain constant because it is buffering the fluid.

The isotopic disequilibrium seen in the minerals from the Beitbridge samples may be the result of differential exchange rates of the minerals with fluids. Freer and Dennis (1982) suggested that isotopic geothermometry using the quartz-garnet pair may record near-peak metamorphic temperatures because of slow diffusion rates, whereas the quartz-biotite and quartz-feldspar pairs would not. The limited diffusion data on garnet, which suggest that it has the highest closure temperatures, in conjunction with the similarity between the quartz-garnet equilibration temperatures calculated from both anion and cation thermobarometry, are evidence that the isotope ratio of quartz did not change significantly as the temperature fell below the closure temperature of garnet. The isotopic composition of the fluid present must have been buffered by the rock under conditions of a low fluid/rock ratio. That garnet and quartz effectively buffered the isotopic composition of the fluid is substantiated by the modal compositions which indicate that these two minerals comprise the bulk of the oxygen in most samples.

Quartz-biotite and quartz-feldspar pairs provide apparent temperatures that differ substantially from those of the quartz-garnet pairs and, in most cases, that differ slightly from each other. The diffusion data suggest that biotite should reach its closure at a temperature much higher than that of either quartz or feldspar. Such large differences in the closure temperatures between biotite and feldspar may be an artifact of the two different methods that were used to calculate the diffusion coefficients, although most certainly the relative sense of the diffusion data is correct. Quartz-biotite pairs provide slightly higher apparent equilibration temperatures than do the quartz-feldspar pairs. If the isotopic composition of quartz has not changed significantly with time as has been suggested, the equilibration temperatures calculated using the experimentally determined quartz-feldspar curves of Matsuhisa et al. (1979) and the approximation for biotite from the curves of muscovite (Garlick and Epstein, 1967; Graham, 1981) may have some relevance. These temperatures (Table 4) are much lower than those that have been suggested for upper-amphibolite facies and are probably representative of one of the lower-grade events that occurred in the Central zone. It is difficult to assess whether isotope diffusion or recrystallization was predominant in the re-equilibration process. Because most mineral ages for the Central zone have been reset to 2.1 Ga (Watkeys, 1983) regardless of which isotopic system is used, recrystallization was probably ongoing at the same time as diffusion.

The isotopic compositions of waters from various metamorphosed terranes and those calculated to be in equilibrium with the biotites from the metapelites and hornblendes from associated metabasites from the Beitbridge area at temperatures equivalent to those provided by the empirical quartz-biotite or quartz-hornblende fractionation curves of Bottinga and Javoy (1975) are listed in Table 6 and shown in Figure 5. If the experimentally derived fractionation factors and resulting temperatures are used, the δD values for the calculated waters are more positive by 12‰ and $\delta^{18}O$ values are lower by about 2‰. Exchange rates for D/H between water and hydrous minerals are much faster than those for oxygen-isotope exchange (O'Neil and Kharaka, 1976; Graham, 1981) so that hydrogen may continue to exchange well below the closure temperature of oxygen. The $^{18}O/^{16}O$ partitioning between quartz and biotite may represent too high an apparent temperature for H-isotope exchange so that the δD values of the fluids calculated to be in equilibrium with the hydrous minerals represent the minimum values. The fluids at Beitbridge lie near the metamorphic water box (Taylor, 1974) but because the δD represented in this diagram are minimum values and the $\delta^{18}O$ are probably maximum values, the fluids had a distinct component of meteoric water.

Fluid dynamic controls on isotopic compositions

The nearly concordant temperatures from the quartz-biotite and quartz-feldspar pairs may have implications for the geologic history of the Beitbridge region. Graham (1981) reviewed two different processes and their implications for diffusion rates and stable-isotope exchange in high-grade metamorphic rocks: (1) prograde metamorphism and (2) catastrophic loss of fluid from a system.

During prograde metamorphism the fluid/rock ratio decreases as fluid is expelled. The fluid/rock ratio can become so small as to no longer be able to change the bulk isotopic composition of the rock and may only serve to catalyze exchange by acting as an exchange medium. Thompson (1983) argued that fluid-absent metamorphism may be the norm for all metamorphism except where reactions take place such as at isograds. By "fluid-absent" he suggested that the mineral grain boundaries may be coated with a water layer that is only one or two molecules thick, which would correlate well with the concept of very low fluid/rock ratios. In rocks with low fluid/rock ratios, the isotopic composition of the fastest-diffusing mineral is somewhat controlled by the closure of the second-fastest-diffusing mineral. When the second-fastest-diffusing mineral reaches its closure temperature, the fastest-diffusing mineral effectively stops exchanging as the fluid cannot affect the isotopic composition of the mineral. Later examination of the isotopic compositions reveals a pattern of "equilibrium" at least among the two fastest-diffusing minerals. If a third mineral, such as garnet or quartz, had reached the closure temperature prior to the second-fastest mineral, the pattern would be one of apparent isotopic disequilibrium such as that observed in the Beitbridge samples. Infiltration of late fluids would also produce this pattern because the minerals with the fastest diffusion or reaction rates would be most affected.

Catastrophic loss of fluid essentially depletes the system of the buffering agent or catalyst for isotopic exchange and should therefore allow effective preservation of the isotopic compositions at the time of the loss. Later examination of the phases may reveal equilibrium or disequilibrium depending on the closure temperatures of the individual minerals and and the temperature at which the loss of fluid occurred. Loss of fluid can occur in the following ways: (1) the fluid may be consumed by retrograde reactions during the cooling, (2) the opening of cracks and fractures during the exhumation of a metamorphic orogen may allow fluid escape, and (3) extraction of fluids by the development of a melt phase. Because the temperature of fluid loss is likely to be different for each of these processes, different patterns of mineral isotopic compositions should result.

The partial adjustment of a mineral assemblage to a new set of conditions has been noted in several of the Beitbridge samples as reaction rims of cordierite around garnet, sillimanite, and orthopyroxene. Quartz and feldspar symplectites also suggest a change in the chemical compositions of the feldspars toward more albite-rich compositions. Although no hydrous minerals per se were produced, cordierite can contain water in its structure lattice (Martignole and Sisi, 1981). The reactions therefore could be the result of a fluid phase being consumed during retrograde cooling. However, the isotopic systematics of the Beitbridge samples with or without these reaction products are the same, which suggests that the consumption of fluids by retrograde reactions was not a major process affecting the isotopic composition of garnet, feldspar, and biotite.

There is field evidence that large amounts of fluids have passed through the shear zones that form the boundaries of the Central zone (Tankard et al., 1982). It is not known if the fluids were meteoric or metamorphic, so that the estimation of the contribution of this mechanism to the isotopic systematics is very difficult. In the Beitbridge area, fluid loss could have occurred as a result of massive overthrusting (Coward, 1984).

A melt phase produced under high-grade metamorphic conditions would be undersaturated with respect to water. The partitioning of water into the melt phase would effectively dehydrate the surrounding rock and thereby preserve the isotopic compositions of the minerals at the time of the melt production. The apparent equilibration temperatures provided by the quartz-biotite, quartz-feldspar, and biotite-feldspar pairs using the experimental calibration curves suggest that exchange between biotite and feldspar took place to low temperatures and therefore that a fluid must have been present.

Anion and cation geothermometry in metamorphic terranes

The experimental diffusion data, if applicable to the metamorphic process, indicate that exchange rates for cations, on which most of the thermobarometers are based, are often faster than those for anion-exchange rates especially if the vehicle for anion exchange involves a CO_2-rich fluid. The high-temperature assemblage of Fe-Mg minerals of the Beitbridge samples are garnet + biotite ± hypersthene ± spinel, and the cation-diffusion rates for garnets are very slow (Freer, 1979; Cygan and Lasaga, 1985). Therefore, when garnet ceased exchanging Fe and Mg with the fluid, it left biotite as the major Fe-Mg mineral along with minor hypersthene and spinel. If the only remaining Fe-Mg mineral were biotite, exchange would be effectively stopped, and the cation compositions of both the garnet and biotite would reflect the time (and temperature) of closure of garnet. The later event that produced cordierite would provide the next opportunity for Fe-Mg exchange, but it is probable that the cordierite would derive Fe and Mg ions from the consumption of the garnet with only subsidiary exchange with biotite. This suggests that the thermobarometers dependent on cation partitioning between a limited number of minerals are less likely to distinguish polymetamorphic events because the exchange of ions is only between a few specific minerals. In contrast, oxygen-isotope compositions will record most polymetamorphic events, as the majority of minerals in any metamorphic rock are oxygen bearing and closure temperatures for exchange with fluids are variable among silicates. The development of isotopic equilibrium temperatures is probably contingent on the rapid cooling or fluid loss from peak metamorphic conditions.

CONCLUSIONS

1. Stable-isotope systematics of the upper-amphibolite-facies metamorphic rocks from the Central zone of the Limpopo belt yield different apparent equilibration temperatures among various minerals.
2. Of the mineral pairs examined, the mineral pair quartz-garnet yields isotope equilibration temperatures that are closest to those given by the mineralogical and cation geothermometers. Because garnet and quartz comprise most of the oxygen in the Beitbridge samples, the $\delta^{18}O$ value of these minerals probably did not change after the closure temperature of garnet. The other two pairs, quartz-biotite and quartz-feldspar, give lower isotope equilibration temperatures than does quartz-garnet and are slightly different from each other. They appear to represent conditions of later, lower-grade metamorphic events.
3. A combination of diffusion of oxygen isotopes and recrystallization of mineral phases is responsible for the isotope systematics of these assemblages.
4. The waters calculated to be in equilibrium with hydrous minerals from Beitbridge samples are similar to other regional high-grade metamorphic terranes but may contain a component of meteoric water.
5. Small but significant differences among the whole-rock $\delta^{18}O$ values of different lithologic units at Beitbridge suggest a partially closed system of metamorphism and generally low water/rock ratios.

ACKNOWLEDGMENTS

This work was much improved by detailed criticism from C. M. Graham, A. Matthews, and an anonymous referee. Collection of the samples was possible through a grant from the Royal Society, London, to E.G.N., in association with G. T. R. Droop, N. B. W. Harris; and T. J. B. Holland, who participated in field work. We thank Tim Broderick, Tony Martin, the Geological Survey of Zimbabwe and the Zimbabwe Republic Police (Inspectors Magama and and Samkange) for their great help, and Constables Maquta and Khanye for their escort in a region of high element activity.

In Canada the work was funded by NSERC grants to Nisbet and Kyser, and by a University of Saskatchewan scholarship to Huebner.

REFERENCES

Barton, J.M., Jr., and Ryan, B. (1977) A review of the geochronologic framework of the Limpopo mobile belt. Geological Survey of Botswana Bulletin, 12, 183–200.

Barton, J.M., Jr., Fripp, R.E.P., and Ryan, B. (1977) Rb-Sr ages and geological setting of ancient dykes in the Sand River area, Limpopo mobile belt, South Africa. Nature, 267, 487–490.

Bottinga, Y., and Javoy, M. (1973) Comments on oxygen isotopic geothermometry. Earth and Planetary Science Letters, 20, 250–265.

——— (1975) Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. Reviews of Geophysics and Space Geophysics, 13, 401–408.

Broderick, T.J. (1979) Explanation of the geological map of the country south of Nuanetsi, Nuanetsi and Beitbridge Districts. Rhodesian Geological Survey Short Report, 46.

Chinner, G.A., and Sweatman, T.R. (1968) A former association of enstatite-kyanite. Mineralogical Magazine, 36, 1052–1060.

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. Geochimica et Cosmochimica Acta, 27, 43–52.

Clayton, R.N., Goldsmith, J.R., Karel, K.J., Mayeda, T.K., and Newton, R.C. (1975) Limits on the effects of pressure on isotopic fractionation. Geochimica et Cosmochimica Acta, 39, 1197–1201.

Coward, M.P. (1984) Major shear zones in the Precambrian crust; examples from N.W. Scotland and southern Africa and their significance. In A. Kröner and R. Greiling, Eds. Precambrian tectonics illustrated, 207–236. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Cygan, R.T., and Lasaga, A.C. (1985) Self-diffusion of Mg in garnet at 750–900°C. American Journal of Science, 285, 328–350.

Deines, P. (1977) On the oxygen isotope distribution among mineral triplets in igneous and metamorphic rocks. Geochimica et Cosmochimica Acta, 41, 1709–1730.

Du Toit, M.C., van Reenen, D.D., and Roering, C. (1983) Some aspects of the geology, structure and metamorphism of the southern marginal zone of the Limpopo metamorphic complex. In W.J. van Biljon and J.H. Legg, Eds. The Limpopo belt, 121–142. Geological Society of South Africa Special Publication 8, Johannesburg.

Fourcade, S., and Javoy, M. (1973) Rapports $^{18}O/^{16}O$ dans les roches vieux sade catazonal d'In Ouzzal (Sahara, Algerien). Contributions to Mineralogy and Petrology, 42, 235–244.

Freer, R. (1979) An experimental measurement of cation diffusion in almandine garnet. Nature, 280, 220–222.

——— (1981) Diffusion in silicate minerals and glasses; a data digest and guide to the literature. Contributions to Mineralogy and Petrology, 76, 440–454.

Freer, R., and Dennis, P.F. (1982) Oxygen diffusion studies I. A preliminary ion microprobe investigation of oxygen diffusion in some rock-forming minerals. Mineralogical Magazine, 45, 179–192.

Frey, M., Hunziker, J.C., O'Neil, J.R., and Schwander, H.W. (1976) Equilibrium-disequilibrium relations in the Monte Rosa granite, western Alps: Petrology, Rb-Sr, and stable isotope data. Contributions to Mineralogy and Petrology, 55, 147–179.

Friedman, I., and O'Neil, J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. United States Geological Survey Professional Paper 440-KK.

Fyfe, W.S., Price, N.J., and Thompson, A.B. (1978) Fluids in the Earth's crust, Elsevier, Amsterdam.

Garlick, G.D., and Epstein, S. (1967) Oxygen isotope ratios in coexisting minerals from regionally metamorphosed rocks. Geochimica et Cosmochimica Acta, 31, 181–214.

Giletti, B. J., and Anderson, T.F. (1977) Studies in diffusion: II. Oxygen in phlogopite mica. Earth and Planetary Science Letters, 28, 225–233.

Giletti, B.J., and Yund, R.A. (1984) Oxygen diffusion in quartz. Journal of Geophysical Research, 89, 4039–4046.

Giletti, B.J., Semet, M.P., and Yund, R.A. (1978) Studies in diffusion: III. Oxygen in feldspars: An ion microprobe determination. Geochimica et Cosmochimica Acta, 42, 45–57.

Graham, C.M. (1981) Experimental hydrogen isotope studies: III. Diffusion of hydrogen in hydrous minerals and stable isotope exchange in metamorphic rocks. Contributions to Mineralogy and Petrology, 76, 216–228.

Harris, N.B.W., and Holland, T.J.B. (1984) The significance of cordierite-hypersthene assemblages from the Beitbridge region of the central Limpopo belt; evidence for rapid decompression in the Archaean. American Mineralogist, 69, 1036–1049.

Hoernes, S., and Friedrichsen, H. (1978) Oxygen and hydrogen isotope study of the polymetamorphic area of the northern Otztal-Stubai Alps (Tyrol). Contributions to Mineralogy and Petrology, 67, 305–315.

Hoernes, S., and Hoffer, E. (1979) Equilibrium relations of prograde metamorphic mineral assemblages: A stable isotope study of rocks of the Damara orogen, from Namibia. Contributions to Mineralogy and Petrology, 68, 377–389.

Horrocks, P.C. (1980) Ancient Archaean supracrustal rocks from the Limpopo mobile belt. Nature, 286, 596–599.

Javoy, M., Fourcade, S., and Allègre, C.J. (1970) Graphical method for examination of $^{18}O/^{16}O$ fractionations in silicate rocks. Earth and Planetary Science Letters, 10, 12–16.

Keith, M.L., and Weber, J.N. (1964) Isotopic composition and environmental classification of selected limestones and fossils. Geochimica et Cosmochimica Acta, 38, 1787–1816.

Kyser, T.K., and O'Neil, J.R. (1984) Hydrogen isotope systematics of submarine basalts. Geochimica et Cosmochimica Acta, 48, 2123–2133.

Kyser, T.K., O'Neil, J.R., and Carmichael, I.S.E. (1982) Genetic relations among basic lavas and ultramafic nodules: Evidence from oxygen isotope compositions. Contributions to Mineralogy and Petrology, 81, 88–102.

Light, M.P.R. (1982) The Limpopo belt: A result of continental collision. Tectonics, 1, 325–342.

Light, M.P.R., and Watkeys, M.K. (1978) An outline of the Archaean and early Proterozoic geological history of the region around Beitbridge. Rhodesia Geological Survey Annals, 3, 35–40.

Light, M.P.R., Broderick, T.J., and Watkeys, M.K. (1977) A preliminary report on the Central zone of the Limpopo mobile belt, Rhodesia. Geological Survey of Botswana Bulletin, 12, 61–73.

Longstaffe, F.J., and Schwarcz, H.P. (1977) $^{18}O/^{16}O$ of Archean clastic metasediments; a petrogenetic indicator for Archean gneisses. Geochimica et Cosmochimica Acta, 41, 1303–1312.

Manton, W.I. (1968) The origin of associated basic and acid rocks in the Lebombo-Nuanetsi igneous province, southern Africa, as implied by Sr isotopes. Journal of Petrology, 9, 23–39.

Martignole, Jacques, and Sisi, J.C. (1981) Cordierite-garnet-H_2O equilibrium: A geological thermometer, barometer and water fugacity indicator. Contributions to Mineralogy and Petrology, 77, 38–46.

Mason, R. (1973) The Limpopo mobile belt—southern Africa. Royal Society of London Philosophical Transactions, series A, 273, 463–485.

Matsuhisa, Y., Goldsmith, J.R., and Clayton, R.N. (1979) Oxygen isotope fractionation in the system quartz-albite-anorthite-water. Geochimica et Cosmochimica Acta, 43, 1131–1140.

Matthews, A., Goldsmith, J.R., and Clayton, R.N. (1983) Oxygen isotope fractionations involving pyroxenes: The calibration of mineral-pair geothermometers. Geochimica et Cosmochimica Acta, 43, 631–644.

McNaughton, N.J., and Wilson, A.F. (1980) Problems in oxygen isotope geothermometry in mafic granulite-facies rocks from near Einasleigh, northern Queensland. Precambrian Research, 13, 77–86.

——— (1983) The geochemical and oxygen isotope affinities of Proterozoic mafic granulites from the Einasleigh metamorphics, northern Queensland. Precambrian Research, 21, 21–37.

Muehlenbachs, K., and Kushiro, I. (1974) Oxygen isotope exchange and equilibration of silicates with CO_2 or O_2. Carnegie Institution of Washington Year Book 73, 232–236.

Norris, R.J., and Henley, R.W. (1976) Dewatering of a metamorphic pile. Geology, 4, 333–336.

O'Neil, J.R., and Kharaka, Y.K. (1976) Hydrogen and oxygen isotope exchange reactions between clay minerals and water. Geochimica et Cosmochimica Acta, 40, 241–246.

O'Neil, J.R., and Taylor, H.P., Jr. (1969) Oxygen isotope equilibrium between muscovite and water. Journal of Geochemical Research, 74, 6012–6022.

Perry, E.C., Jr., and Tan, F.C. (1972) Significance of oxygen and carbon isotope variations in early Precambrian cherts and carbonate rocks of southern Africa. Geological Society of America Bulletin, 83, 647–664.

Robertson, I.D.M. (1973) The geology of the country around Mt. Towla, Gwanda District. Geological Survey of Rhodesia Bulletin, 68.

Rumble, D., III, and Spear, F.S. (1983) Oxygen-isotope equilibration and permeability enhancement during regional metamorphism. Geological Society of London Journal, 140, 619–628.

Savin, S.M., and Epstein, S. (1970) The oxygen and hydrogen isotope geochemistry of clay minerals. Geochimica et Cosmochimica Acta, 34, 25–42.

Shieh, Y.N., and Taylor, H.P., Jr. (1969) Oxygen and carbon isotope studies of contact metamorphism of carbonate rocks. Journal of Petrology, 10, 307–331.

Suzuoki, T., and Epstein, S. (1976) Hydrogen isotope fractionation between OH-bearing minerals and water. Geochimica et Cosmochimica Acta, 40, 1229–1240.

Tankard, A.J., Jackson, M.P.A., Eriksson, K.A., Hobday, D.K., Hunter, D.R., and Minter, W.E.L. (1982) Crustal evolution of southern Africa: 3.8 billion years of earth history, Springer-Verlag, New York.

Taylor, H.P., Jr. (1968) The oxygen isotope geochemistry of igneous rocks. Contributions to Mineralogy and Petrology, 19, 1–71.

——— (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Economic Geology, 69, 843–888.

Thompson, A.B. (1983) Fluid absent metamorphism. Geological Society of London Journal, 140, 533–547.

Touret, J. (1971) Le facies granulite de norvege meridoniale. II. Les inclusions fluides. Lithos, 4, 423–436.

van Breemen, O., and Dodson, M.H. (1972) Metamorphic chronology of the Limpopo belt, southern Africa. Geological Society of America Bulletin, 83, 2005–2018.

Veizer, J., and Hoefs, J. (1976) The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimentary carbonate rocks. Geochimica et Cosmochimica Acta, 40, 1387–1397.

Walther, J.V., and Orville, P.M. (1982) Volatile production and transport in regional metamorphism. Contributions to Mineralogy and Petrology, 79, 252–257.

Walther, J.V., and Wood, B.J. (1984) Rate and mechanism in prograde metamorphism. Contributions to Mineralogy and Petrology, 88, 246–259.

Watkeys, M.K. (1979) Explanation of the geological map of the country west of Beitbridge. Rhodesia Geological Survey Short Report, 45.

——— (1983) Brief explanatory notes on the provisional geological map of the Limpopo belt and environs. In W.J. van Biljon and J.H. Legg, Eds. The Limpopo belt, 5–8. Geological Society of South Africa Special Publication 8, Johannesburg.

Watkeys, M.K., Light, M.P.R., and Broderick, T.J. (1983) A retrospective view of the Central zone of the Limpopo belt, Zimbabwe. In W.J. van Biljon and J.H. Legg, Eds. The Limpopo belt, 65–80. Geological Society of South Africa Special Publication 8, Johannesburg.

Wilson, A.F., and Baksi, A.K. (1984) Oxygen isotope fractionation and disequilibrium displayed by some granulite facies rocks from the Fraser Range, western Australia. Geochimica et Cosmochimica Acta, 48, 423–432.

Windley, B.F., Ackermand, D., and Herd, R.K. (1984) Sapphirine/kornerupine bearing rocks and crustal uplift history of the Limpopo belt, southern Africa. Contributions to Mineralogy and Petrology, 86, 342–358.

Manuscript received August 22, 1985
Manuscript accepted July 8, 1986