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STABLE ISOTOPIC SYSTEMATICS OF THE BUSHVELD COMPLEX: II. CONSTRAINTS ON HYDROTHERMAL PROCESSES IN LAYERED INTRUSIONS

CRAIG M. SCHIFFRIES* AND DANNY M. RYE**

ABSTRACT. Fluid-rock interactions play a significant role in modifying the mineralogy, chemical composition, isotopic ratios, and physical properties of the Earth's crust. Although epizonal hydrothermal systems are well understood, relatively little is known about the nature and significance of large-scale fluid flow at crustal depths greater than about 10 km and temperatures greater than 400°C. The Bushveld hydrothermal system provides a well constrained example of large-scale fluid flow that occurred at crustal depths ranging to at least 15 km and temperatures ranging to at least 700°C. This paper reports oxygen, hydrogen, and carbon isotopic data for hydrothermally altered samples from the Bushveld Complex and its contact aureole.

To a first approximation, the hydrology of the Bushveld Complex can be viewed as a rock-dominated recharge system that supplied fluids to a water-dominated system of structurally controlled fluid flow. The integrated water/rock mass ratio was probably less than 0.1 on a regional scale. Hydrothermal veins that crosscut the Bushveld Complex represent local regions that attained high water/rock ratios as a consequence of fracture-controlled fluid flow. Fluid-dominated conditions were also achieved on a local scale as a consequence of pervasive fluid flow channelized within certain lithologic units that functioned as aquifers.

Most of the hydrothermal fluids were derived from external fluid reservoirs. The dominant component of the hydrothermal fluids can be characterized as metamorphic water, reflecting the fact that the fluids exchanged with metamorphic rocks at elevated temperatures (>300°C) under rock-dominated conditions. The systematics of the isotopic data indicate that the δ¹⁸O, δ¹³C, and δD values of the fluids that interacted with the Bushveld Complex were largely controlled by different rock reservoirs. The δ¹⁸O values were set by isotopic exchange with the intrusive rocks, the δ¹³C values appear to reflect a large contribution of carbon from marine carbonates in the Transvaal Supergroup, and the δD values appear to have been strongly controlled by reactions involving hydrous minerals in the Transvaal

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Supergroup. The hydrothermal fluids were strongly enriched in $^{18}$O relative to meteoric waters and seawater.

The hydrological, chemical, and thermal features of the Bushveld hydrothermal system created favorable conditions for the formation of hydrothermal mineral deposits. Further consideration should be given to the possibility that hydrothermal processes played a more significant role in determining the distribution of sulfide minerals and precious metals than has been previously recognized.

INTRODUCTION

A wide variety of geological phenomena are governed by interactions between fluids and rocks. Fluids play a significant role in modifying the mineralogy, chemical composition, isotopic ratios, and physical properties of the continental and oceanic crust. Although fluid flow is well understood in epizonal hydrothermal systems, relatively little is known about the nature and significance of large-scale fluid flow at crustal depths greater than about 10 km and temperatures greater than 400°C. On the one hand, it is commonly assumed that rocks are nearly impermeable above 400°C (Cathles, 1983) and that fluid flow is negligible or has a passive effect on deep-seated crustal rocks. On the other hand, numerous studies have documented that high temperature fluid flow plays an important role in driving mineralogical reactions as well as in the transfer of heat and mass during metamorphism or hydrothermal alteration of deep-seated crustal rocks (Rye and others, 1976; Ferry 1983, 1984; Rumble and others 1982; Tracy and others, 1983; Nabelek and others, 1984; Wickham and Taylor, 1985, 1987). A reconciliation of these divergent views requires better documentation of the effects that fluids have on deep seated crustal rocks. The well documented hydrothermal system associated with the Bushveld Complex (Schiffries and Skinner, 1987) is an ideal system to study the interaction between fluids and rocks at crustal depths of a least 15 km.

There are several approaches that can be used to examine the history of fluids in rocks. These include studies of the phase relationships in veins and host rocks, fluid inclusion studies, and stable isotope studies. This paper reports oxygen, carbon, and hydrogen isotopic data for hydrothermal veins that crosscut the Bushveld Complex and for country rocks from the contact aureole that surrounds the intrusion.

The major aim of this paper is to characterize the fluid-rock interactions that occurred in the Bushveld Complex and surrounding rocks during fluid flow associated with the extensive hydrothermal system that operated as the Bushveld Complex cooled.

This is the third paper in a series of publications arising from an ongoing research project on the Bushveld Complex. The first paper (Schiffries and Skinner, 1987) documents the discovery of extensive networks of hydrothermal veins that crosscut the intrusion. Field data establish that a major paleo-hydrothermal system operated in the Bushveld Complex while the complex crystallized and cooled. Field and petrologic constraints require that the hydrothermal system operated at
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...crustal depths of a least 15 km and temperatures ranging from less than 300 ° to at least 700 °C. The second paper (Schiffries and Rye, 1989) reports oxygen isotopic data for a suite of petrographically fresh rocks from all major stratigraphic subdivisions of the intrusion. These data place constraints on the magmatic evolution of the Bushveld Complex, and they also provide a framework for interpreting the stable isotopic data for hydrothermally altered samples.

GEOLOGICAL SETTING

The Bushveld Complex is the world’s largest layered igneous intrusion and the greatest repository of magmatic mineral resources ever discovered (Wager and Brown, 1968; Willemse, 1969; von Gruenewaldt, 1979; von Gruenewaldt and others, 1985). It has a thickness ranging between 7 and 9 km and is exposed as three major lobes that enclose an area of 65,000 km² (fig. 1). The Bushveld Complex is 100 to 1000 times larger than the Skaergaard intrusion, the Stillwater Complex, and the Cuillin Complex (Willemse, 1969). Size alone draws attention to the Bushveld Complex, but it is also famous for the remarkable persistence and regularity of its igneous layering. Individual layers and cyclic units have been traced along strike for more than 100 km in both the eastern and western lobes of the Bushveld. Some of the layers contain vast mineral resources, and these deposits produce a major fraction of the world’s output of chromium, vanadium, and the platinum-group elements.

The Bushveld Complex contains a broad spectrum of plutonic rock types. The magmatic stratigraphy is divided into four major zones (fig. 1): the Lower Zone consists of ultramafic rocks, including dunite, orthopyroxenite, and hartzburgite; above the Lower Zone lies the Critical Zone, which contains abundant norite, anorthosite, and orthopyroxenite, as well as approx 20 chromite layers which individually are up to 2 m thick; the Main Zone is dominated by gabbro and contains subordinate amounts of anorthosite; and the Upper Zone is composed of magnetite gabbro, ferrodiorite, anorthosite, and approx 25 magnetite layers.

The age of the Bushveld Complex is 2050 ± 25 Ma (λRb = 0.0142 Ga⁻¹; Hamilton, 1977; Sharpe, 1985). The Complex is intruded into a 12 km thick pile of early Proterozoic sedimentary and volcanic rocks which belong to the Transvaal Supergroup. The Transvaal Supergroup unconformably overlies Archean basement rocks of the Kaapvaal craton. The emplacement of the Bushveld was preceded by an extensive period of volcanism as recorded in the Rooiberg Felsite and the mafic to intermediate Dullstroom Volcanics. Intrusion of the mafic rocks was followed by a period of granitic plutonism recorded in the Bushveld Granite.

Schiffries and Rye (1989) report oxygen isotopic data for petrographically fresh samples from the Bushveld Complex. They found that the Bushveld magmas have large δ¹⁸O values (6.8 ± 0.2 permil) relative
to "normal" mantle-derived mafic magmas (5.7 ± 0.2 permil, Taylor, 1968) and that the isotopic fractionation between the coexisting plagioclase and pyroxene (Δ^{18}O_{plag-opx} = 0.4 ± 0.1 permil; Δ^{18}O_{cpx-opx} ~ 0 permil) is indicative of equilibration at magmatic temperatures (fig. 2). As the magmatic clinopyroxene and orthopyroxene have indistinguishable δ^{18}O values, we do not distinguish between magmatic clinopyroxene and orthopyroxene in our isotopic arguments. Schiffries and Rye (1989) also report oxygen isotopic data for the principal rock types in the contact aureole surrounding the Bushveld Complex, and these data are summarized in figure 3. The isotopic composition of each rock type falls within
the normal range of values for Phanerozoic examples of the same rock type (Hoefs, 1987).

The Bushveld Hydrothermal System

Occurrence and classification of hydrothermal veins.—The most obvious manifestations of hydrothermal activity are mineralized veins formed by hydrothermal solutions and the zones of secondary alteration adjacent to the flow channels. Schiffries and Skinner (1987) describe extensive networks of hydrothermal veins that occur in each of the
Fig. 3. Oxygen isotope analyses of sedimentary and volcanic country rocks belonging to the Transvaal Supergroup (Schiffries and Rye, 1989). The $\delta^{18}O$ values for each rock type fall within the range of normal values for Phanerozoic examples of the same rock type (Hoesf, 1987).

major stratigraphic units that comprise the eastern Bushveld Complex. The veins occur across a stratigraphic thickness of 9 km and along a strike length of at least 100 km. The Bushveld hydrothermal system has affected tens of thousands of cubic kilometers of rock in and around the eastern lobe alone. The roof rocks had a stratigraphic thickness of approx 6 km at the time the Bushveld Complex was emplaced (Sharpe and Hulbert, 1985), and therefore fluid flow occurred at crustal depths ranging to at least 15 km.

Petrologic studies of veins indicate that fluid-rock interactions occurred over a wide range of physical and chemical conditions, producing a broad variety of hydrothermal veins. Schiffries and Skinner (1987) have grouped the post-magmatic hydrothermal veins into three temporal groups on the basis of their relative chronology as determined by crosscutting relations. The three groups are referred to as early, middle, and late veins. The mineral assemblages in the early, middle, and late veins are similar to those found in mafic igneous rocks formed and/or equilibrated under conditions corresponding to amphibolite, greenschist, and zeolite to prehnite-pumpellyite metamorphic facies, respectively (table 1). The mineral assemblages in the three families of veins exhibit a decreasing temperature sequence with decreasing relative age.
Table 1

Summary of vein characteristics

<table>
<thead>
<tr>
<th></th>
<th>Early Stage</th>
<th>Middle Stage</th>
<th>Late Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major vein minerals</td>
<td>Calcic amphibole</td>
<td>Actinolite</td>
<td>Prehnite</td>
</tr>
<tr>
<td></td>
<td>Calcic plagioclase</td>
<td>Clinopyroxene</td>
<td>Pumppellyte</td>
</tr>
<tr>
<td></td>
<td>Fe-Ti oxides</td>
<td>Quartz</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>Clinopyroxene</td>
<td>Sphene</td>
<td></td>
</tr>
<tr>
<td>Additional minor minerals</td>
<td>Biotite</td>
<td>Albite</td>
<td>Chlorite</td>
</tr>
<tr>
<td></td>
<td>Orthopyroxene</td>
<td>Pumpellyte</td>
<td>Carbonate</td>
</tr>
<tr>
<td></td>
<td>Sulfides</td>
<td>Epidote</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Microcline</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Biotite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Clinozoisite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfides</td>
<td></td>
</tr>
<tr>
<td>Facies equivalent</td>
<td>Upper amphibolite</td>
<td>Greenschist</td>
<td>Prehnite-pumppellyte</td>
</tr>
<tr>
<td>Temperature</td>
<td>&gt;600°C</td>
<td>300°–600°C</td>
<td>&lt;300°C</td>
</tr>
<tr>
<td>Frequency</td>
<td>0.2 to 2 m⁻¹</td>
<td>0.2 to 1 m⁻¹</td>
<td>&lt;10 to &gt;100 m⁻¹</td>
</tr>
<tr>
<td>Vein width</td>
<td>0.5 to 5 cm</td>
<td>0.5 to 5 cm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Type locality</td>
<td>Onverwacht 152 JS</td>
<td>Kwaggskop 359 JS</td>
<td>Dwars River 372 KT</td>
</tr>
<tr>
<td></td>
<td>Upper Zone</td>
<td>Main Zone</td>
<td>Critical Zone</td>
</tr>
<tr>
<td>Host rock at type locality</td>
<td>Magnetite Gabbro</td>
<td>Gabbro</td>
<td>Mottled anorthosite</td>
</tr>
</tbody>
</table>

Source: Schiffries and Skinner (1987)

The temperature sequence represents an alternative basis for classifying the veins: high, intermediate, and low temperature veins correspond to early-stage, middle-stage, and late-stage respectively. The following summary of the vein characteristics is based on the data reported by Schiffries and Skinner (1987). Similar types of hydrothermal veins are also present in the Skaergaard intrusion (Norton, Taylor, and Bird, 1984; Bird, Rogers, and Manning, 1986; Bird, Manning, and Rose, 1988).

High temperature veins.—The type examples of early-stage, high temperature veins occur in the magnetite gabbros of the Upper Zone on the farm Onverwacht 152 JS (fig. 1). Early-stage hydrothermal veins from the type locality have mineral assemblages characteristic of upper amphibolite facies metamorphism conditions. The veins are composed predominantly of calcic amphibole and calcic plagioclase, with subordinate amounts of clinopyroxene and Fe-Ti oxides ± biotite ± orthopyroxene ± sulfides. Calcic amphibole ranges in composition from actinolite to a ferroan pargasite, and no distinct miscibility gap was observed in the compositions. The absence of a distinct miscibility gap in the measured compositions of the amphiboles suggests they formed above 600°C under supersolvus conditions (for example, see Kimball, Spear, and Dick, 1985). Pargasitic hornblende is the most common amphibole
variety. Many veins contain plagioclase substantially more calcic than that in the surrounding rock: differences up to 25 mole percent anorthite occur across the margins of many veins. Early-stage veins are typically 0.5 to 5 cm wide.

Intermediate temperature veins.—A regionally extensive swarm of middle-stage, intermediate temperature veins has been traced for more than 15 km between Stoffberg and Belfast (fig. 1), and this area is the type locality selected for middle-stage veins. Middle-stage veins in this region are bright green in color and are surrounded by a whitish-colored inner zone of intense wall-rock alteration. Next to the inner zone is a more subtle dark colored outer zone of alteration. The strong color contrast between the inner white alteration halo and the dark gray gabbro host rocks makes the veins very conspicuous.

The middle-stage veins are generally between 0.5 and 5 cm in width, but some veins reach a thickness of 10 cm. The white alteration zone is commonly about one-third the width of the vein. The outer alteration zone is commonly about one-half the width of the white alteration zone.

The mineralogy of green, middle-stage veins is variable. Some veins are composed largely of hydrothermal clinopyroxene and quartz, with subordinate amounts of sphene, actinolite, and carbonate. However, in other veins the most abundant mineral is actinolite or actinolitic hornblende. Quartz contains abundant aqueous fluid inclusions and occurs as anhedral grains that are commonly interstitial to the clinopyroxene grains. Some veins have been affected by multiple episodes of fracturing and mineral growth, and early clinopyroxene can be seen to be replaced partially by later actinolite.

The mineralogy of the white wall-rock alteration (inner zone) is dominated by clinopyroxene, albite, and pumpellyite, with subordinate amounts of sphene, actinolite, quartz, microcline, carbonate, and epidote. Plagioclase in the white wall-rock alteration halo is completely replaced by an extremely fine-grained intergrowth of albite and pumpellyite, plus trace amounts of microcline and epidote.

The outer alteration zone is dominated by clinopyroxene, plagioclase, and orthopyroxene, and it is enriched in ferromagnesian minerals, particularly biotite, actinolite, and chlorite, relative to the unaltered gabbro.

The clinopyroxene that formed through hydrothermal processes in the middle-stage veins occurs as equigranular, euhedral to subhedral grains which are substantially coarser than the grains of igneous clinopyroxene in the adjacent host rock. Igneous clinopyroxenes exhibit a series of progressive textural and chemical changes through the alteration zones as the veins are approached. These changes include enrichment of Ca, depletion in non-quadrilateral components, coarsening of exsolution lamellae, development of granular exsolution, and, immediately adjacent to the vein, the formation of relatively homogeneous grains that display little twinning or exsolution.
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The mineral assemblages of the middle-stage veins do not always provide tight constraints on the conditions under which they formed. However, the alteration halos have mineral assemblages typical of metamorphosed mafic igneous rocks that have equilibrated between 300° and 600°C (Schiffries and Skinner, 1987).

Low temperature veins.—The type examples of late-stage low temperature veins occur in anorthosites of the Critical Zone on the farm Dwars River 372 KT (fig. 1). The veins are white to light green in color, they tend to be less than 1 mm wide, and they occur in great abundance. Most of the late-stage veins in the type area consist largely of prehnite and quartz, with subordinate amounts of pumpellyite. Fluid inclusions are commonly observed in the quartz. Other minerals, including chlorite, calcite, zeolites, and sulfides are locally abundant. Some late-stage veins are surrounded by a zone of wall-rock alteration that is several times as wide as the vein. Because the mineral assemblage present in these veins is representative of prehnite-pumpellyite facies conditions, Schiffries and Skinner (1987) suggest that they probably formed at temperatures below 300°C.

In general, the development of alteration minerals has progressed further adjacent to low and intermediate temperature veins than it has adjacent to high temperature veins.

Quartz veins.—Hydrothermal veins, pods, and plugs composed predominantly of quartz occur sporadically throughout the Bushveld Complex. Most of the hydrothermal quartz contains abundant aqueous fluid inclusions.

Pervasive alteration.—Some areas of the Bushveld Complex are pervasively altered. The mineralogy of pervasive alteration generally resembles that of intermediate or low temperature veins. Layers of anorthosite in the Upper Zone have a greater tendency to be pervasively altered than other rock types. In many cases the effect of pervasive alteration is produced by the overlapping alteration halos of closely spaced veins. The intensity of pervasive alteration is highly variable. The primary minerals in some highly altered samples are completely pseudomorphed by secondary minerals. The isotopic effects of pervasive alteration may have an important bearing on the interpretation of stable isotopic data for layered intrusions.

Mafic pegmatoids.—The Bushveld Complex contains numerous bodies of discordant and concordant mafic pegmatoid composed predominantly of clinopyroxene and plagioclase, with subordinate amounts of quartz ± biotite ± amphibole ± sulfides. Similar bodies occur in the Skaergaard intrusion (Taylor and Forester, 1979; Irvine, 1987). The origin of the mafic pegmatoids is uncertain. One possibility is that they crystallized from a water-rich magma. Another possibility is that they represent mafic cumulates that recrystallized in the presence of an aqueous fluid. In either case, the mafic pegmatoids may represent an important aspect of the aqueous fluid history of the Bushveld Complex. Some quartz occurs as open space fillings and contains abundant fluid
inclusions, suggesting that the quartz may have been deposited as a hydrothermal mineral.

SAMPLES AND ANALYTICAL PROCEDURES

Sample Selection

The samples selected for isotopic analysis were chosen to span the range of hydrothermal conditions attained during the subsolidus cooling history of the Bushveld Complex (table 1). Many of the samples are from the type localities (fig. 1) of high, intermediate, and low temperature veins described by Schiffries and Skinner (1987). The veins in each of the type localities are hosted by rocks composed predominantly of plagioclase and pyroxene. In addition to studying the various types of veins, we have analyzed samples from mafic pegmatoids as well as samples of country rocks from the contact aureole surrounding the intrusion.

The majority of the data consist of oxygen isotope analyses of silicates, but we also report carbon and oxygen isotopic data for carbonates and hydrogen isotopic data for waters extracted from fluid inclusions in quartz.

Analytical Methods

The mineral separates analyzed in this study were prepared by hand picking individual grains (approx 50 mesh) with tweezers under a binocular microscope. Every grain was individually examined for mineral inclusions, alteration, adhering particles, and other contaminants. Except for samples that are described as “altered,” the mineral separates are believed to be at least 99 percent pure.

The isotopic ratios reported in this study were measured in the stable isotope laboratory at the Department of Geology and Geophysics, Yale University. Oxygen was extracted from silicates by reaction with BrF$_5$ and then converted to CO$_2$ by reaction with a hot graphite rod in the presence of platinum (Clayton and Mayeda, 1963). Additional details of our silicate extraction procedure are provided by Schiffries and Rye (1988). Carbon dioxide was extracted from carbonates by reacting the samples with phosphoric acid (McCrea, 1950). The carbon and oxygen isotopic composition of CO$_2$ gas was measured on a Finnegan MAT 251 EM mass spectrometer equipped with an automatic gas handling system. Fluid inclusion water was extracted from its host mineral by crushing samples in an evacuated stainless steel tube. The water was separated from trace amounts of CO$_2$ and other gases using standard cryogenic techniques. Hydrogen was liberated from the water by reduction with hot uranium metal. The D/H ratio of hydrogen gas was measured on a 3-60 RMS Nuclide spectrometer.

Representation of the Isotopic Data

Oxygen isotopic data are presented in the standard delta notation:

$$\delta^{18}O = 10^3 \left[ \frac{^{18}O/^{16}O}_{\text{sample}} - 1 \right]$$
where the sample is either a mineral separate or a whole rock, and the standard is V-SMOW.

The isotopic fractionation between two coexisting phases (A and B) is expressed as

$$\Delta^{18}O_{A-B} = \delta^{18}O_A - \delta^{18}O_B$$

$$\approx 1000[\ln (\alpha_{A-B})]$$

where

$$\alpha_{A-B} = \frac{(^{18}O/^{16}O)_A}{(^{18}O/^{16}O)_B}$$

The expressions for $\delta^{13}C$, $\Delta^{13}C_{A-B}$, $\delta D$, and $\Delta D_{A-B}$ are analogous to the preceding equations. The standard is V-SMOW for hydrogen and PDB for carbon.

**Precision of the Isotopic Data**

During the course of the Bushveld study we extracted and analyzed the oxygen from 16 aliquots of standard NBS-28. The mean and standard deviation (1σ) of the 16 analyses is 9.70 ± 0.1 permil. The precision of $\delta D$ data for fluid inclusion waters is approx ±5 permil (1σ). The precision of $\delta^{18}O$ and $\delta^{13}C$ data for carbonates is approx ±0.1 permil (1σ).

**RESULTS**

**Igneous Rocks**

Schiffries and Rye (1989) demonstrated that most of the igneous rocks from the Critical and Main Zones are petrographically and mineralogically fresh. They also demonstrated that the mineralogically fresh samples from the Bushveld Complex have $\Delta^{18}O_{plag-opx}$ values of 0.4 ± 0.1 permil, typical of magmatic values (~0.5 permil). The systematics of the oxygen isotopic data for coexisting plagioclase and pyroxene do not exhibit any characteristics that are diagnostic of appreciable subsolidus exchange with hydrothermal fluids under either equilibrium or disequilibrium conditions (Schiffries and Rye, 1989). The simplest interpretation of the $\Delta^{18}O_{plag-opx}$ data is that the $\delta^{18}O_{plag}$ and $\delta^{18}O_{opx}$ values were set at magmatic temperatures (approx 1200°C) and were not appreciably modified by subsequent subsolidus processes.

**High Temperature Veins**

**Oxygen isotopic data.**—An isotopic profile across a type-locality high temperature vein, the adjacent alteration zone, and the surrounding wall rock (sample 85-54a-) is presented in figure 4 and table 2. The vein is composed almost entirely of calcic amphibole (>90 percent amphibole), and therefore the values of $\delta^{18}O_{rock}$ (5.9 permil) and $\delta^{18}O_{amph}$ (6.0 permil) are indistinguishable within the limits of analytical uncertainty. Calcic amphibole is present in both the vein and the alteration
zone, and the values of $\delta^{18}O_{amph}$ in the two zones are the same (6.0 permil). Plagioclase in the alteration zone (7.5 permil) is slightly depleted in $^{18}O$ relative to plagioclase in the host rock (7.7 permil). Variations in the $\delta^{18}O_{rock}$ value (5.9–6.5 permil) reflect variations in the mineralogy and modal composition of the samples: the vein consists largely of amphibole; the alteration halo contains subequal amounts of amphibole and plagioclase; and the gabbro contains subequal amounts of pyroxene and plagioclase with subordinate magnetite.

The $\delta^{18}O$ values of calcic amphibole from two high temperature veins (samples 86-245 and 86-244) from a higher stratigraphic level in the intrusion are 6.4 and 6.6 permil (table 2). The two samples are enriched in $^{18}O$ relative to those from the type locality. Variations in the $\delta^{18}O_{amph}$ value may reflect variations in the $\delta^{18}O_{water}$ value or variations in the $\Delta^{18}O_{amph-water}$ value that arise from differences in either temperature or amphibole composition, especially the proportions of $^{14}Al$ and $Fe^{3+}$.

Isotopic thermometry.—The partitioning of oxygen isotopes between coexisting plagioclase (7.5 permil: An$_{73}$) and amphibole (6.0 permil) from the alteration zone (fig. 4) indicates that the minimum tempera-
Table 2
Oxygen isotope analyses of hydrothermal veins

<table>
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<th>Sample Number</th>
<th>Mineral</th>
<th>$\delta^{18}O$</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>85-54a-1</td>
<td>whole rock</td>
<td>5.91</td>
<td>Center of amphibole vein</td>
</tr>
<tr>
<td>85-54a-1</td>
<td>amphibole</td>
<td>5.95</td>
<td></td>
</tr>
<tr>
<td>85-54a-2</td>
<td>whole rock</td>
<td>6.50</td>
<td>Altered gabbro adjacent to vein</td>
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<td>85-54a-2</td>
<td>amphibole</td>
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<td></td>
</tr>
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<td>85-54a-2</td>
<td>plagioclase</td>
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<td>85-54a-3</td>
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<td>6.45</td>
<td>Gabbro adjacent to alteration halo</td>
</tr>
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<td>amphibole</td>
<td>5.89</td>
<td>From pod in vein</td>
</tr>
<tr>
<td>85-78-1d</td>
<td>whole rock</td>
<td>5.68</td>
<td>Amphibole vein</td>
</tr>
<tr>
<td>85-78-1d</td>
<td>amphibole</td>
<td>5.49</td>
<td></td>
</tr>
<tr>
<td>85-78-1e</td>
<td>whole rock</td>
<td>7.93</td>
<td>Inner alteration zone</td>
</tr>
<tr>
<td>85-78-1c</td>
<td>whole rock</td>
<td>7.90</td>
<td>Inner alteration zone</td>
</tr>
<tr>
<td>85-78-1c</td>
<td>altered plag</td>
<td>8.56</td>
<td></td>
</tr>
<tr>
<td>85-78-1b</td>
<td>whole rock</td>
<td>6.64</td>
<td>Outer alteration zone</td>
</tr>
<tr>
<td>85-78-1a</td>
<td>whole rock</td>
<td>6.92</td>
<td>Gabbro adjacent to outer alteration zone</td>
</tr>
<tr>
<td>85-78-1a</td>
<td>plagioclase</td>
<td>6.97</td>
<td></td>
</tr>
<tr>
<td>85-78-1a</td>
<td>pyroxene</td>
<td>6.61</td>
<td></td>
</tr>
<tr>
<td>85-131</td>
<td>quartz</td>
<td>9.80</td>
<td>Quartz pod in intermediate temperature vein</td>
</tr>
<tr>
<td>85-132</td>
<td>quartz</td>
<td>9.41</td>
<td>Quartz vein associated with intermediate temperature vein</td>
</tr>
<tr>
<td>85-134</td>
<td>quartz</td>
<td>9.27</td>
<td>Quartz from intermediate temperature vein</td>
</tr>
<tr>
<td>85-198b-1</td>
<td>whole rock</td>
<td>5.07</td>
<td>Vein containing prehnite and quartz</td>
</tr>
<tr>
<td>85-198b-2</td>
<td>whole rock</td>
<td>7.02</td>
<td>Alteration zone adjacent to vein</td>
</tr>
</tbody>
</table>

Intermediate temperature veins

Low temperature veins

Pervasive alteration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>$\delta^{18}O$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>UZ-2a</td>
<td>plagioclase</td>
<td>7.91</td>
<td></td>
</tr>
<tr>
<td>BH10-1-1</td>
<td>plagioclase</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td>BH12-3-2</td>
<td>plagioclase</td>
<td>7.51</td>
<td></td>
</tr>
<tr>
<td>BH21-3a-2</td>
<td>plagioclase</td>
<td>7.44</td>
<td></td>
</tr>
<tr>
<td>BH23-36-2</td>
<td>plagioclase</td>
<td>7.53</td>
<td></td>
</tr>
<tr>
<td>BH33-11-2</td>
<td>plagioclase</td>
<td>8.16</td>
<td></td>
</tr>
<tr>
<td>BH40-1-1</td>
<td>plagioclase</td>
<td>7.36</td>
<td></td>
</tr>
</tbody>
</table>
ture of the fluid-rock interactions was 710°C, based on the empirical temperature calibration of the $\Delta^{18}O_{\text{plag-amph}}$ value for mafic rocks (Bottinga and Javoy, 1974). The results of the isotopic geothermometer are consistent with independent temperature estimates based on the occurrence of supersolvus calcic amphibole (Kimball, Spear, and Dick, 1985) and the stability limits of the upper amphibolite facies mineral assemblage ($T > 600°C$; Schiffries and Skinner, 1987).

**Oxygen isotopic composition of the fluid.**—The calculated values of $\delta^{18}O_{\text{water}}$ in equilibrium with the vein, the altered zone, and the wall rock are shown in figure 4. The results are based on the plagioclase-water and amphibole-water ($\Delta^{18}O_{\text{plag-water}} - \Delta^{18}O_{\text{plag-amph}}$) fractionation factors (Bottinga and Javoy, 1974; O’Neil and Taylor, 1967; Bottinga and Javoy, 1973), the plagioclase compositions ($An_{75}$ for vein and $An_{35}$ for host rock; Schiffries and Skinner, 1987), and the isotopic temperature ($710°C$) calculated in the preceding section. Although there are variations in $\delta^{18}O_{\text{rock}}$ between adjacent zones, the calculated value of $\delta^{18}O_{\text{water}}$ is constant at 8.7 permil across the entire profile.

**Intermediate Temperature Veins**

**Oxygen isotopic data.**—Isotopic profiles across two intermediate temperature veins are shown in figures 5 and 6, and the data are listed in table 2. The veins are depleted in $^{18}O$ relative to the local wall rocks, but

---

![Graph](image)

**Fig. 5.** Oxygen isotope profile across an intermediate temperature vein. The vein is depleted in $^{18}O$ relative to the host rock, but the inner alteration zone (IAZ) and outer alteration zone (OZ) have approximately the same $\delta^{18}O$ values as the host rock. The isotopically heavy “plagioclase” in the inner alteration zone is pseudomorphed by secondary minerals.
the alteration selvages are variably enriched or depleted in $^{18}$O relative to the local wall rocks. Large variations among the $\delta^{18}$O$_{\text{rock}}$ values of middle-stage veins (5.7–5.9 permil), the adjacent alteration zones (6.6–7.9 permil), and the local gabbro (6.9 permil) are due largely to major differences in the mineralogy and modal composition of the samples. The available data indicate that the $\delta^{18}$O values of the major vein minerals, such as quartz (9.3–9.8 permil) and amphibole (5.4–5.9 permil), are nearly constant despite large variations in both their relative abundance and the $\delta^{18}$O$_{\text{rock}}$ value.

The mineralogical controls on the $\delta^{18}$O values of the alteration selvages are extremely complex. For example, plagioclase in the inner alteration zone is pseudomorphed by secondary minerals that are intergrown on a length-scale of 10 microns. The extremely fine-grained secondary minerals cannot be distinguished by optical microscopy, but detailed electron microprobe analyses and backscattered secondary electron (BSE) imaging have established that plagioclase is partially replaced by a wide variety of secondary minerals, including pumpellyite, albite, microline, epidote, quartz, chlorite, calcicamphibole, and calcite.

There is a one permil difference between $\delta^{18}$O values of hydrothermal clinopyroxene (5.6 permil) and magmatic clinopyroxene from the adjacent fresh gabbro (6.6 permil). Hydrothermal clinopyroxene is
chemically and texturally distinct from its magmatic counterpart (Schiffries and Skinner, 1987; Manning and Bird, 1986) and has a much larger grain size than magmatic pyroxene. The extremely coarse-grained hydrothermal clinopyroxene may represent authigenic hydrothermal pyroxene that precipitated directly from the fluid, or it may represent recrystallized magmatic pyroxene that grew as a consequence of local dissolution and reprecipitation (Schiffries and Skinner, 1987). In either case, clinopyroxene in veins was precipitated from hydrothermal fluids and probably reached isotopic equilibrium with the fluid.

Fresh gabbroic rocks that are predominantly composed of pyroxene and plagioclase generally exhibit the relation:

$$\delta^{18}O_{\text{pyx}} < \delta^{18}O_{\text{rock}} < \delta^{18}O_{\text{plag}}$$

Two samples of gabbro collected a few centimeters from an intermediate temperature vein have $$\delta^{18}O_{\text{rock}}$$ values that are larger than the $$\delta^{18}O_{\text{plag}}$$ values (samples 85-127-12 and 85-127-15; table 2). These samples contain plagioclase that is clear and fresh, as well as plagioclase that is cloudy and partially replaced by secondary minerals. The analyzed mineral separates were composed entirely of the clearest and freshest plagioclase in the samples. The $$\delta^{18}O_{\text{plag}}$$ value is 6.9 permil for both samples. This value is indistinguishable from the average $$\delta^{18}O$$ value for fresh plagioclase from the Main Zone (7.0 ± 0.2 permil; Schiffries and Rye, 1989). Although the samples collected near a vein were mildly affected by hydrothermal alteration, the freshest fractions of the primary minerals appear to have retained their magmatic $$\delta^{18}O$$ values.

**Isotopic thermometry.**—Assuming isotopic equilibrium was achieved, the partitioning of oxygen isotopes between coexisting clinopyroxene ($$\delta^{18}O = 5.6$$) and quartz ($$\delta^{18}O = 9.8$$) from the vein shown in figure 5 indicates that the minimum temperature of the fluid-rock interactions was 530°C. The temperature dependence of the $$\Delta^{18}O_{\text{grz-pyx}}$$ value was calculated from the temperature calibration of the fractionation factors for quartz-water (Clayton, O’Neil, and Mayeda, 1972) and pyroxene-water (Bottinga and Javoy, 1974; O’Neil and Taylor, 1967). The results of the isotopic geothermometer are consistent with an independent temperature estimate (Schiffries and Skinner, 1987) that is based on the stability limits of the greenschist facies mineral assemblage (300°–600°C).

The isotopic fractionation between coexisting fresh plagioclase and pyroxene was measured for a sample of gabbro (sample locality 85-78) collected 4 cm from an intermediate temperature vein (fig. 6). The $$\Delta^{18}O_{\text{plag-px}}$$ value is 0.4 permil ($$T = 1220°C$$), which is identical to the average $$\Delta^{18}O_{\text{plag-opx}}$$ value for unaltered intrusive rocks from the Main Zone (Schiffries and Rye, 1989). This fact indicates that the magmatic $$\delta^{18}O$$ signature of the wall rock has not been appreciably affected by the fluid-rock interactions that formed the nearby vein.

**Oxygen isotopic composition of the fluid.**—The calculated value of $$\delta^{18}O_{\text{water}}$$ in equilibrium with an intermediate temperature vein (85-127-9) is 7.4 ± 0.2 permil. This result is based on the quartz-water
fractionation factors of Clayton, O’Neil, and Mayeda (1972) and the isotopic temperature (530°C) calculated in the preceding section. The uniformity of the $\delta^{18}O$ values of quartz and amphibole indicates that $\delta^{18}O_{\text{water}}$ value was likely uniform and that the $\delta^{18}O$ values of the minerals in the vein were controlled by the hydrothermal fluid. The calculated $\delta^{18}O_{\text{water}}$ value for the intermediate temperature vein is, within the limits of analytical uncertainty, in isotopic equilibrium with fresh igneous plagioclase ($\delta^{18}O_{\text{plag}} = 7.0 \pm 0.2$ permil) from the Main Zone at the temperature ($\Delta^{18}O_{\text{plag-water}} = 0.3$ permil at 530°C) of vein formation.

**Hydrogen isotopic composition of fluid inclusions.**—Quartz associated with intermediate temperature veins contains abundant aqueous fluid inclusions. The $\delta D$ values of water extracted from fluid inclusions in quartz associated with intermediate temperature veins range from $-71$ permil to $-38$ permil (table 3). The $\delta^{18}O$ values of quartz from intermediate temperature veins range from 9.3 to 9.8 permil (table 3). The small range of $\delta^{18}O$ values for the intermediate temperature veins suggests that all the veins analyzed precipitated under similar conditions (for example: minimum temperature $\sim 550^\circ C$; $\delta^{18}O_{\text{water}} = 7.4$ permil). The $\delta D_{\text{water}}$ values of the fluid inclusions are plotted against the calculated $\delta^{18}O$ values of water in equilibrium with the host quartz in figure 7.

**Isotopic composition of carbonates.**—Calcite is an accessory mineral in intermediate temperature veins and in the adjacent alteration selvages. Large calcite crystals, 1 to 6 cm in length, occur in quartz-rich pods commonly associated with intermediate temperature veins. The isotopic composition of calcite is $\delta^{18}O = 8.8$ to 12.7 and $\delta^{13}C = -2.7$ to +0.1 (table 4). The $\delta^{13}C$ values of vein calcite are similar to those of marine carbonate in the Transvaal Supergroup (table 4; Buchanan and others, 1981). The vein calcite is strongly enriched in $^{13}C$ relative to the bulk

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\delta^{18}O_{\text{quz}}$</th>
<th>$\delta D_{\text{water}}$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>85-131</td>
<td>9.80</td>
<td>-71</td>
<td>Quartz pod in intermediate temperature vein</td>
</tr>
<tr>
<td>85-132</td>
<td>9.41</td>
<td>-38</td>
<td>Quartz vein associated with intermediate temperature veins</td>
</tr>
<tr>
<td>85-134</td>
<td>9.27</td>
<td>-63</td>
<td>Quartz from intermediate temperature vein</td>
</tr>
<tr>
<td>D-28</td>
<td>9.72</td>
<td></td>
<td>Quartz from mafic pegmatoid below the UG-2 chromitite layer</td>
</tr>
<tr>
<td>D-51</td>
<td>9.01</td>
<td></td>
<td>Quartz from transgressive mafic pegmatoid in the hangingwall of the UG-2 chromitite layer</td>
</tr>
<tr>
<td>D-106</td>
<td>9.87</td>
<td>-47</td>
<td>Mafic pegmatoid near Driekop dunite pipe</td>
</tr>
<tr>
<td>85-12</td>
<td>11.09</td>
<td>-53</td>
<td>Quartz vein near Stoffberg</td>
</tr>
<tr>
<td>85-240</td>
<td>7.91</td>
<td>-48</td>
<td>Margin of quartz plug in Main Zone</td>
</tr>
<tr>
<td>85-234</td>
<td>8.66</td>
<td>-29</td>
<td>Center of quartz plug in Main Zone</td>
</tr>
<tr>
<td>85-336</td>
<td>10.10</td>
<td>-34</td>
<td>Quartzite from country rock (Transvaal series) beneath the Bushveld Complex</td>
</tr>
</tbody>
</table>
Fig. 7. The measured $\delta D$ values of fluid inclusion water are plotted against the calculated $\delta^{18}O$ values of water in equilibrium with the host quartz. The data (table 3) are for samples from intermediate temperature veins (circles), quartz veins (triangles), a transgressive mafic pegmatoid (diamond), and a quartzite layer from the contact aureole (square). For each sample, the $\delta^{18}O_{\text{water}}$ value is calculated at three temperatures: 500°C (left hand side of error bar), 600°C (symbol), and 700°C (right hand side of error bar). The waters have a narrow range of $\delta^{18}O$ values but a wide range of $\delta D$ values. The width of the rectangle delineates the range of $\delta^{18}O_{\text{water}}$ values in equilibrium with igneous plagioclase ($An_{50}$) at 500° to 700°C. The height of the rectangle corresponds to the range of measured $\delta D$ values for fluid inclusion waters. The fact that the data points plot in or near the rectangle is consistent with the proposition that the $\delta^{18}O_{\text{water}}$ values of the hydrothermal fluids were controlled by exchange with silicate minerals, particularly plagioclase, under rock-dominated conditions at elevated temperatures. The meteoric water line (MWL) and seawater (SW) are shown for reference.
Table 4
Isotopic analyses of carbonates

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Locality</th>
<th>δ¹³C (PDB)</th>
<th>δ¹⁸O (SMOW)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malmani Dolomite, Transvaal Supergroup*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VAA/13</td>
<td>Tweefontein 238 KR</td>
<td>-2.8</td>
<td>21.3</td>
<td>1.01 km from intrusion</td>
</tr>
<tr>
<td>VAA/11</td>
<td>Tweefontein 238 KR</td>
<td>-2.6</td>
<td>20.4</td>
<td>0.86 km from intrusion</td>
</tr>
<tr>
<td>VAA/10</td>
<td>Tweefontein 238 KR</td>
<td>-2.8</td>
<td>21.3</td>
<td>0.78 km from intrusion</td>
</tr>
<tr>
<td>VAA/5</td>
<td>Tweefontein 238 KR</td>
<td>-2.3</td>
<td>19.0</td>
<td>0.42 km from intrusion</td>
</tr>
<tr>
<td>VAA/4</td>
<td>Tweefontein 238 KR</td>
<td>-2.2</td>
<td>20.3</td>
<td>0.58 km from intrusion</td>
</tr>
<tr>
<td>247/56</td>
<td>Tweefontein 238 KR</td>
<td>-5.1</td>
<td>19.3</td>
<td>0.09 km from intrusion</td>
</tr>
</tbody>
</table>

Vein Calcite in the Bushveld Complex#

|          |                      |            |             |                                             |
| 86-96C-a | Colorado Quarry      | -2.57      | 9.31        | Pod in intermediate temp. vein              |
| 86-96A-2 | Colorado Quarry      | -2.54      | 12.67       | Pod in intermediate temp. vein              |
| 86-99-C  | Belfast United Quarry| -2.70      | 8.83        | Pod in intermediate temp. vein              |
| 85-96    | Marlin Quarry        | +0.06      | 9.27        | Pod in intermediate temp. vein              |

Pervasively altered rocks from the Bushveld Complex#

|       |                      |            |             |                                             |
| BDS-66 | Mapochsrongo 500 JS  | -3.57      | 9.93        | Anorthosite layer                           |
| BH10-1-1| Mapochsrongo 500 JS  | -4.38      | 10.89       | Anorthosite layer                           |
| BH23-36-2| Mapochsrongo 500 JS | +1.40      | 9.98        | Anorthosite layer                           |

*Data from Buchanan and others, 1981.
#Data from this work.

mantle (δ¹³C = -5 to -7 permil) and to biogenic graphite (< -15 permil).

The δ¹⁸O values of vein calcite are not in isotopic equilibrium with other secondary minerals, such as quartz and amphibole, at the temperature of vein formation. The oxygen isotopic composition of calcites require that they were precipitated at temperatures approx 25° to 50°C lower than quartz if they were precipitated from the same fluid. Vein calcite commonly occurs in vugs, pods, and texturally late veinlets. In most cases, the calcite was probably deposited late in the paragenetic sequence of a vein in response to declining temperatures during the waning stages of mineralization.

Low Temperature Veins

Oxygen isotopic data.—Low temperature veins tend to be very small, typically less than 1 mm wide, and the minerals are commonly very fine-grained. These factors make it difficult to prepare high quality mineral separates, and therefore we have not undertaken a comprehensive isotopic study of the low temperature veins. The oxygen isotopic composition of a low temperature vein and the pervasively altered wall rock are given in table 2. The low temperature vein has a smaller whole rock δ¹⁸O value (5.1 permil) than any of the high and intermediate temperature veins we have measured.
Pervasive Alteration

Oxygen isotopic data.—Seven samples of variably altered plagioclase from an anorthosite layer in the Upper Zone immediately below the Main Magnetite layer have δ^{18}O values ranging from 6.6 to 8.2 permil (table 2). With the exception of one sample, the δ^{18}O values of altered plagioclase are larger than or equal to the δ^{18}O values of fresh plagioclase (δ^{18}O = 7.1 ± 0.2 permil; Schiffries and Rye, 1989). The magnitude of the 18O-shift does not always correlate with the relative intensity of mineralogic alteration. For example, sample BH40-1-1 is highly altered, but its δ^{18}O value is indistinguishable from that of fresh plagioclase.

Fine-grained secondary minerals are intimately intergrown with the plagioclase in the pervasively altered samples. The secondary minerals include pumpellyite, albite, epidote, quartz, chlorite, amphibole, and calcite. These minerals have highly variable δ^{18}O values, and, therefore, the bulk fractionation factor between the fluid and the rock is strongly dependent on the modal composition of the secondary mineral assemblage. In some samples, the bulk δ^{18}O value of the secondary assemblage is apparently very close to the value of δ^{18}O_{plag}, and, therefore, a large amount of alteration does not produce an appreciable 18O-shift. In other samples, the bulk δ^{18}O value of the secondary assemblage is considerably larger or smaller than the δ^{18}O_{plag} value, and, therefore, a relatively small amount of alteration produces a large 18O-shift.

Carbon isotopic data.—Samples of pervasively altered anorthosite contain trace amounts of texturally late, disseminated carbonate. The isotopic composition of the carbonate is δ^{18}O = 9.9 to 10.9 and δ^{13}C = −4.4 to +1.4 (table 4).

Quartz Veins

Oxygen isotopic data.—Hydrothermal veins, pods, and plugs composed predominantly of quartz occur sporadically throughout the Bushveld Complex. The δ^{18}O values of quartz samples range from 7.9 to 11.1 permil (table 3). The quartz sample with a δ^{18}O value greater than 11 permil is associated with low temperature alteration, the rest of the samples are associated with intermediate temperature alteration.

Hydrogen isotopic data.—Most hydrothermal quartz contains abundant aqueous fluid inclusions. The δD values of water extracted from fluid inclusions range from −29 to −53 permil (table 3). The δD_{water} values of the fluid inclusions are plotted against the calculated δ^{18}O values of water in equilibrium with the host quartz in figure 7 (assuming a temperature of 600° ± 100°C for quartz associated with intermediate temperature veins and alteration, and a temperature of 300°C for the vein associated with low temperature alteration).

Mafic Pegmatoids

Oxygen isotopic data.—The δ^{18}O values of quartz from mafic pegmatoids range from 9.0 to 9.9 permil (table 3). The δ^{18}O_{qtz} values for the
of the Bushveld Complex: II. Hydrothermal processes  229

mafic pegmatoids are similar to those for intermediate temperature hydrothermal veins. Quartz from the mafic pegmatoids is not in isotopic equilibrium with igneous plagioclase and pyroxene at magmatic temperatures. The isotopic data are consistent with textural observations, including evidence for open space filling, which indicate the quartz was deposited late in the paragenetic sequence.

Hydrogen isotopic data.—Fluid inclusion water extracted from a quartz vug near the core of a zoned mafic pegmatoid has a δD value of −47 permil (table 3). This value falls within the range of δD values for fluid inclusions extracted from intermediate temperature veins. As both the δD and δ¹⁸O values obtained for quartz from mafic pegmatoids are similar to the values obtained on quartz from intermediate temperature veins, it is likely that the quartz in both occurrences formed under similar conditions. The δD_{water} value is plotted against the calculated δ¹⁸O_{water} value of water in equilibrium with the host quartz in figure 7, assuming that the quartz formed under conditions similar to the intermediate temperature veins.

Contact Aureole

Oxygen isotopic profile.—A δ¹⁸O_{qtz} profile of the Steenkampsberg quartzite within 10 km of the contact with the Bushveld Complex is shown in figure 8 (data from Schiffries and Rye, 1989). With the exception of one sample, there is a systematic decline in the δ¹⁸O_{qtz} value as the intrusion is approached. The sample that plots above the trend in figure 8 was collected near the base of the quartzite layer, and it may have been affected by fluids that interacted with the underlying shale. The ¹⁸O-shifted samples have been completely recrystallized to a very coarse grain size, and they contain abundant secondary fluid inclusions.

Hydrogen isotopic data.—Fluid inclusion water extracted from a quartzite layer in the contact aureole has a δD value of −34 permil (table 3). This value is heavier than primary magmatic water, but it falls within the range of δD values for fluid inclusions extracted from intermediate temperature veins. The δD_{water} value is plotted against the calculated value of water in equilibrium with the host quartz in figure 7.

DISCUSSION

Evidence for Rock-dominated Conditions on a Regional Scale

Isotopic systematics-general.—The stable isotopic systematics observed in wall rocks and veins yield different information about a hydrothermal system. If fluids are not in isotopic equilibrium with the wall rocks, the isotopic systematics of the wall rocks will record the amount of fluid that interacted with them at specific points along the flow path integrated over the time the minerals were being exchanged or precipitated. In contrast, the isotopic composition of the veins will reflect the isotopic composition of the fluid source, the isotopic fractionation factor, and the amount of wall rock the fluids have interacted with.
along the entire fluid flow path. As a consequence of these facts, wall rocks yield information about the time integrated local fluid to rock ratio, whereas veins yield information about the space and time integrated fluid to rock ratio in the whole hydrothermal system.

Isotopic systematics of fresh igneous rocks.—The coordinated use of $\delta^{18}O_{\text{plag}}$ and $\delta^{18}O_{\text{pyx}}$ data provides a sensitive tool for monitoring the effects of subsolidus isotopic exchange in gabbroic rocks (Taylor and Forester, 1979; Gregory and Taylor, 1981; Criss, Gregory, and Taylor, 1987; Gregory and Criss, 1986). An important constraint on the local time integrated fluid to rock ratio of the Bushveld Complex can be obtained from oxygen isotopic data for a suite of petrographically fresh samples from the Critical and Main Zones (fig. 2). As most samples appear to be mineralogically fresh and have retained their magmatic oxygen isotopic signature, we conclude that the time integrated fluid to rock mass ratio for the portion of the intrusion we observed must have been low (<0.1). The value of 0.1 is chosen because fluid to rock mass ratios of ~0.1 or less do not produce any appreciable $\delta^{18}O$ shift in rocks (see discussion below). Systems with fluid to rock ratios that are small enough that the $\delta^{18}O$ values of the rocks and minerals are not shifted by exchange with the fluid will be referred to as rock-dominated systems in the following discussion. Further evidence that the time integrated fluid
to rock ratio for the Bushveld magmatic-hydrothermal system was low is provided by the oxygen isotopic data from the country rocks.

*Isotopic heterogeneity of the country rocks.*—Oxygen isotopic data for the principal types of country rock in the Bushveld contact aureole are: 5.5 permil for volcanic rocks; 10 ± 1 permil for quartzites; 11 to 15 permil for pelites (hornfels); and 20 ± 1 permil for carbonates (fig. 3: Schiffries and Rye, 1989). The δ¹⁸O values of each rock type fall within the normal range for Phanerozoic examples of the same rock type (Hoefs, 1987). Fluid-dominated hydrothermal systems tend to homogenize the initial isotopic variations among different types of supracrustal rocks. The preservation of large isotopic contrasts among the various lithologic types in the contact aureole surrounding the Bushveld Complex suggests that the hydrothermal system was rock-dominated on a regional scale. Modest variations in the isotopic composition of metaquartzite immediately adjacent to the intrusion are discussed in a later section of this paper.

*Isotopic heterogeneity of the hydrothermal fluids.*—The δD<sub>water</sub> versus δ¹⁸O<sub>water</sub> systematics of a hydrothermal system can be used to distinguish between rock-dominated conditions and water-dominated conditions. Simple mass balance equations for oxygen and hydrogen isotopes can be manipulated to construct an isothermal exchange trajectory between a fluid reservoir and a rock reservoir (Taylor, 1977; Campbell, Rye, and Peterson, 1984). Assuming a closed-system equilibrium model, the mass balance expression for oxygen is:

\[
(δ¹⁸O_{water})^f = \left[ \frac{(C_w/C_r)(W/R)(δ¹⁸O_{water})^i + (δ¹⁸O_{rock})^i - (Δ¹⁸O_{rock-water})^f}{1 + (C_w/C_r)(W/R)} \right]
\]

where W/R is the water to rock mass ratio, (C_w/C_r) is the concentration ratio of oxygen in water to oxygen in the rock, and the superscripts i and f refer to the initial and final conditions, respectively. An expression analogous to the above equation can be constructed for hydrogen. Single-pass, open-system models produce exchange trajectories topologically similar to those produced by the simple closed-system model (Taylor, 1977). We are interested in the general shape of the trajectory, and, therefore, the following discussion is restricted to the relatively simple case of closed-system equilibrium.

A set of isothermal exchange trajectories between a fluid reservoir and a pelitic rock reservoir is shown in figure 9. An exchange trajectory can be divided into a rock-dominated portion and a water-dominated portion. The water-dominated portion is characterized by uniform δD values but highly variable δ¹⁸O values. The rock-dominated portion is characterized by highly variable δD values but uniform δ¹⁸O values. For a wide range of initial conditions, the distinction between rock-dominated conditions and water-dominated conditions occurs at an integrated water/rock mass ratio of approx 0.1 (fig. 9).

The Bushveld hydrothermal system is characterized by a large range of δD<sub>water</sub> values but a narrow range of δ¹⁸O<sub>water</sub> values (over a
Fig. 9. Isothermal exchange trajectories are shown for closed-system equilibrium between meteoric water and pelitic shale at 300°, 400°, and 600°C. The labeled points give the W/R mass ratio. Rock-dominated conditions are characterized by highly variable δD values but uniform δ¹⁸O values. Water-dominated conditions are characterized by uniform δD values but highly variably δ¹⁸O values. The initial conditions for the model are: (δD) = −100 permil, (δ¹⁸O) = 13.75 permil, and Cw/Cr = 1.8. The values of ΔDwater at 300°, 400°, and 600°C are 4.9, 2.6, and 0.2 for oxygen, and −65, −45, −24 for hydrogen, respectively.

restricted temperature interval). According to the preceding analysis (fig. 9), the data are consistent with a hydrothermal system that had low but highly variable water/rock mass ratios (for example, 0.01–0.1). It should be noted, however, that the large range in δDwater values probably reflects the effects of fluid-rock interactions that occurred in the
country rocks rather than in the intrusive rocks (see below). In either case, the large range in δD values coupled with the narrow range of δ18O values is consistent with a rock-dominated hydrothermal system in which the fluid to rock ratios were low but highly variable. Other processes that could be responsible for generating a large range of δD values are discussed in a later section.

Evidence for Local Fluid-dominated Conditions within and near Veins

Oxygen isotopic systematics of hydrothermal veins.—Oxygen isotopic profiles across hydrothermal veins demonstrate that there are moderately large variations in the value of δ18Orock for a hydrothermal vein, the adjacent alteration selvages, and the local wall rock (figs. 4, 5, and 6; table 2). The available data indicate that the δ18O values of secondary minerals, such as quartz and amphibole, from a given locality are nearly constant despite large variations in their modal abundance. Given that the δ18O values of the secondary minerals are nearly constant, it follows that the equilibrium value of δ18Owater is also constant. These observations lead us to the following conclusions: (1) open system conditions are indicated by variations in the value of δ18Orock across an isotopic profile; (2) the δ18O values in the secondary minerals were controlled by externally derived fluids; (3) the original values of the secondary minerals were not significantly modified by subsequent closed-system exchange among coexisting minerals; (4) the δ18Orock values were largely controlled by the δ18O value of the externally derived fluid and by the modal composition of the sample; and (5) the hydrothermal veins represent local regions that attained extremely high fluid to rock ratios as a consequence of fracture-controlled fluid flow.

Mass transfer and metasomatic zoning.—A detailed discussion of metasomatic zoning and chemical mass transfer by the hydrothermal fluids is beyond the scope of this paper. However, two simple observations support the proposition that the hydrothermal veins represent regions that locally attained extremely high fluid to rock ratios as a consequence of fracture-controlled fluid flow. First, the presence of large differences in bulk composition among a hydrothermal vein, its alteration zones, and its local wall rock indicates that some components were added and/or removed by the fluids. Because some of the mobile components have low solubilities in aqueous fluids, it follows that very large fluid to rock ratios are required to produce appreciable variations in bulk composition. Secondly, the presence of metasomatic zones with high variance mineral assemblages indicates that the chemical potentials of certain components were externally buffered, presumably by the fluids responsible for the formation of the veins.

Localized fluid-dominated conditions in the contact aureole.—An isotopic profile of the Steenkampsberg quartzite (fig. 8) shows a progressive decrease in the value of δ18Oquartz as the intrusion is approached. Three alternative interpretations of the 18O-shift are: (1) grain boundary diffusion between the intrusion and the country rocks; (2) pervasive
exchange with fluids that flowed away from the intrusion: and (3) pervasive exchange with fluids that flowed toward the intrusion. The first possibility can be discounted because the length scale of grain boundary diffusion adjacent to intrusive contacts is on the order of 1 m (Shieh and Taylor, 1969), whereas the quartz samples are depleted in $^{18}$O over a distance of 2 km.

Ubiquitous and abundant secondary fluid inclusions in samples of the Steenkampsberg quartzite provide direct evidence for pervasive fluid flow in this lithologic unit. Simple thermal considerations indicate that the fluids probably flowed toward the thermal anomaly. Regardless of the direction of fluid flow, the isotopic data confirm that the quartzite layer was pervasively infiltrated by externally derived fluids. A lower bound on the minimum integrated water/rock ratio of the $^{18}$O-depleted region can be estimated using the simple mass balance relations discussed above, where $(δ^{18}O_{rock})^f$ is the $δ^{18}O_{\text{Qtz}}$ value far from the contact (10.0 permil), and $(δ^{18}O_{rock})^i$ is the $δ^{18}O_{\text{Qtz}}$ value immediately adjacent to the intrusion (9.2 permil). Geothermometry of metamorphic mineral assemblages in the contact aureole record a temperature of approx 750 °C within 1 km of the intrusion (Nell, 1985). At this temperature the value of $Δ^{18}O_{\text{rock-water}}$ is approx 0.2 (Bottinga and Javoy, 1973). Estimation of the value of $(δ^{18}O_{water})^i$ introduces the greatest uncertainty in the calculation. If the fluid continuously approached isotopic equilibrium with quartzite at progressively higher temperatures as it flowed toward the intrusion, then the time integrated fluid/rock ratio was greater than 1.0. For example, if the initial fluid approached isotopic equilibrium with quartz at 600 °C, then $(δ^{18}O_{water}) = 8.3$ permil and W/R = 1.1. The fluid/rock ratio in the quartzite may have been much greater than 1.0 near the intrusion if the fluids had previously exchanged with quartz at temperatures greater than 600 °C. The quartzite layer appears to have behaved as an aquifer for fluids that exchanged with large volumes of rock at elevated temperatures. Fluid-dominated conditions may have been achieved on a local scale as a consequence of pervasive fluid flow that was channelized within these and other layers. Given the initial mineralogy and bulk composition of the quartzite, infiltration of large volumes of fluid did not result in the formation of appreciable quantities of secondary minerals. The only significant mineralogical effect of the fluid-rock interactions is intense recrystallization of the original clastic quartz grains.

Controls on the Isotopic Composition of the Vein Fluids

Local controls on the value of $δ^{18}O_{\text{water}}$.—The $δ^{18}$O values of water in equilibrium with high and intermediate temperature veins were determined on the basis of detailed isotopic data for profiles across individual veins (see above). The calculated $δ^{18}$O values of water in equilibrium with high and intermediate temperature veins are 8.7 and 7.4 permil, respectively. The estimated values of $δ^{18}O_{\text{water}}$ in equilibrium with hydrothermal quartz from a variety of environments (table 3) are shown on a δD versus $δ^{18}$O diagram (fig. 7).
To a good approximation, the $\delta^{18}O$ values of the fluids responsible for the formation of early- and middle-stage veins were in isotopic equilibrium with igneous plagioclase at the temperature of vein formation. This relation is illustrated in figure 7, which shows that the $\delta^{18}O_{water}$ values of the hydrothermal fluids plot within a box that delineates the range of $\delta^{18}O_{water}$ values in equilibrium with igneous plagioclase ($An_{95}$) at 500$^\circ$ to 700$^\circ$C. Schiffries and Rye (1988) demonstrated that the $\delta^{18}O_{plag}$ and $\delta^{18}O_{opx}$ values of the gabbroic host rocks were set at magmatic temperatures (approx 1200$^\circ$C), and the values were not appreciably modified by subsequent subsolidus processes. These results require that the space-time integrated fluid/rock ratio was low enough that the $\delta^{18}O$ value of $H_2O$ was controlled by essentially fresh plagioclase. This requirement is consistent with the observation that plagioclase in the intrusive rocks has retained its magmatic $\delta^{18}O$ value.

The conclusion that the $\delta^{18}O$ values of the fluids were controlled by exchange with plagioclase rather than pyroxene is consistent with the fact that the isotopic exchange rate between plagioclase and water is much greater than the isotopic exchange rate between pyroxene and water (Taylor and Forester, 1971, 1979; Forester and Taylor, 1977; Gregory and Taylor, 1981).

The high and intermediate temperature hydrothermal fluids were strongly enriched in $^{18}O$ relative to meteoric waters and seawater. The large $\delta^{18}O$ values of the hydrothermal fluids reflect the fact that the value of $\Delta^{18}O_{plag-water}$ is negative at temperatures greater than 550$^\circ$C ($An_{95}$), and that the values of $\delta^{18}O_{plag}$ are unusually large (Schiffries and Rye, 1989).

**External controls on the value of $\delta D_{water}$.**—Although the $\delta^{18}O_{water}$ values of the hydrothermal fluids were ultimately controlled by the intrusive rocks, it appears that the $\delta D_{water}$ values were not strongly affected by interactions with the intrusive rocks. Unaltered mafic cumulates are nearly anhydrous, and therefore they have a very limited capacity to buffer the $\delta D$ value of a coexisting aqueous fluid. Isotopic exchange reactions between fresh mafic cumulates and aqueous fluids cannot have an appreciable effect on the value of $\delta D_{water}$ unless the integrated fluid to rock ratio is extremely low ($< 0.01$). The large range of $\delta D_{water}$ values (42 permil) for fluid inclusions extracted from intermediate temperature veins indicates that the $\delta D$ values of the fluids were not controlled by isotopic exchange with the trace amounts of hydrous minerals that are present in the mafic cumulates.

Large amounts of secondary hydrous minerals are locally present in the hydrothermal veins and the adjacent alteration zones. Although hydration reactions produce changes in the $\delta D_{water}$ value of the vein-forming fluids, the isotopic shift is small unless the fluid to rock ratio is low. The oxygen isotopic data indicate that the veins formed under fluid-dominated conditions, and therefore the large range of $\delta D_{water}$ values were probably not produced by local hydration and exchange reactions. This conclusion is supported by the observation that the $\delta D$ value of fluids emanating from submarine hot springs at oceanic ridges
are only several permil heavier than seawater (Bowers and Taylor, 1985) despite the formation of large quantities of hydrous minerals.

Variations in the speciation of hydrogen in a fluid can have a large effect on the value of $\delta D_{\text{water}}$. For example, variations in the amount of CH$_4$ can produce large changes in the $\delta D$ value of coexisting water. Although CH$_4$-rich fluid inclusions have been identified in pervasively altered anorthosite (Schiffries, 1985), such inclusions are not common in the hydrothermal veins. If CH$_4$ had a major effect on the $\delta D_{\text{water}}$ values, then it would also have an effect on the $\delta^{13}C$ values. The nearly uniform $\delta^{13}C$ values of about -3 permil observed in vein calcite (see below) are not consistent with a significant role for CH$_4$. Although variations in the speciation of hydrogen in the fluids cannot be entirely eliminated as the primary mechanism for producing large variations in the $\delta D_{\text{water}}$ values, this possibility is not supported by independent evidence.

Given the lithological diversity of the country rocks and the existence of steep thermal gradients near the intrusion, it is likely that externally derived fluids would have a large range of $\delta D_{\text{water}}$ values at the time they initially interacted with the intrusive rocks. The large range of measured $\delta D_{\text{water}}$ values may therefore reflect the isotopic heterogeneity of the externally derived fluids. Three mechanisms capable of producing large variations in the $\delta D_{\text{water}}$ values of externally derived fluids are: (1) isothermal exchange with hydrous minerals in the country rocks at low but highly variable fluid to rock mass ratios (0.01-0.1: fig. 9); (2) polythermal exchange and dehydration reactions; and (3) variations in the bulk fractionation factor ($\delta D_{\text{water}}$) that result from differences in the mineralogy and modal composition of the country rocks. All three mechanisms probably played a significant role in producing large variations in the $\delta D_{\text{water}}$ values of externally derived fluids that interacted with the Bushveld Complex.

External controls on the value of $\delta^{31}C$ fluid.—Carbon is a minor constituent of both the mafic cumulates and the aqueous fluids that formed the hydrothermal veins. Marine carbonates of the Transvaal Supergroup probably constitute the dominate carbon reservoir of the hydrothermal system. The $\delta^{13}C$ values of calcite from intermediate temperature hydrothermal veins ($-2.5,-2.6,-2.7$, and $+0.1$ permil: table 4) are similar to those of typical marine carbonates in the country rocks ($-2.8$ to $-2.3$ permil). This fact is consistent with derivation of carbon in the veins from dissolution of the carbonates in the country rocks. If there is no change in the speciation of carbon in the fluid, then the $\delta^{13}C$ value of calcite that precipitates from a fluid will be similar to that of the original carbonate dissolved by the fluid (Ohmoto and Rye, 1979). The uniformity of the $\delta^{13}C_{\text{calcite}}$ values suggests that the speciation of carbon in the fluid was not highly variable.

Marine carbonates have the highest $^{13}C/^{12}C$ ratio of the major carbon reservoirs on Earth. Isotopic exchange with other carbon reservoirs, such as graphite or other carbon-rich phases in igneous and sedimentary rocks, would tend to decrease the $\delta^{13}C$ value of a fluid
containing isotopically heavy carbon derived from dissolution of marine carbonate. The large and uniform $\delta^{13}C$ values of vein calcite from the Bushveld Complex indicate that relatively little carbon was derived from other carbon reservoirs.

**Origin and Evolution of the Hydrothermal Fluids**

**Isotopic constraints.**—Stable isotopic data provide a powerful tool for placing constraints on the origin and evolution of hydrothermal fluids. Given the size and geological setting of the Bushveld Complex, it is likely that fluids were derived from several geologically distinct reservoirs and that there were significant spatial and temporal variations in the relative contribution from each reservoir. Identification of the fluid sources is further complicated by the fact that the initial $\delta^{18}O$ and $\delta^{D}$ values were modified as a consequence of fluid-rock interactions along the flow paths. For example, we have established that the $\delta^{18}O$ values of the fluids were controlled by exchange with the plagioclase in the intrusive rocks, and therefore the identity of the fluid source cannot be inferred from the $\delta^{18}O$ values.

**Magmatic water.**—There is no evidence that primary magmatic water was a major component of the hydrothermal fluids. If magmatic water were responsible for the formation of the early-, middle-, and late-stage veins, then the waters must have been convectively recycled over a temperature interval of at least 500°C. This is unlikely because single-pass fluid flow generally dominates over multi-pass flow at crustal depths greater than 5 km (Wood and Walther, 1986) and because the water content of mantle-derived mafic magmas is very low (<1 wt percent). Unless convective recycling of primary magmatic water was a significant factor, the Bushveld hydrothermal system must have been dominated by externally derived fluids.

The $\delta^{D}$ values of water extracted from fluid inclusions do not indicate the presence of a large component of primary magmatic water in the hydrothermal fluids. Primary water in mantle-derived mafic magmas has a very restricted range of $\delta^{D}$ values ($-80 \pm 5$ permil: Kyser and O'Neil, 1985), and the $\delta^{D}$ values of fluid inclusion waters ($-29$ to $-71$ permil) are all less negative than the normal values of mantle-derived mafic magmas. However, this evidence is equivocal because a significant amount of crustal material was assimilated by the Bushveld magmas (Schiffries and Rye, 1989), and it is likely that crustal contamination caused an appreciable increase in the $\delta^{D}$ value of the magma.

**Surface waters.**—There is no evidence that large amounts of unexchanged surface waters (seawater or meteoric water) interacted with the intrusive rocks. If the intrusion interacted with unexchanged seawater, then the fluids would have uniformly heavy hydrogen isotopic compositions. If the intrusion interacted with unexchanged meteoric water then the fluids would have uniform $\delta^{D}$ values, and the $\delta^{D}$ values would probably be small. Given the highly variable $\delta^{D}$ values of water
extracted from fluid inclusions, it is unlikely that unexchanged surface waters were a significant component of the Bushveld hydrothermal fluids. If the hydrothermal fluids were ultimately derived from surface waters, then their isotopic ratios were strongly modified by interactions with supracrustal rocks along the flow path. Typical expected exchange paths are illustrated in Figure 9. As discussed earlier, a wide range of $\delta D$ values can be achieved by isothermal exchange at low but variable fluid to rock ratios, by polythermal exchange at a constant fluid to rock ratio, or by variations in $\delta D_{f-r}$ that reflect variations in the modal composition of the rocks.

**Metamorphic waters.**—Metamorphic water is defined as water produced by metamorphic dehydration reactions or water that equilibrated with metamorphic rocks at temperatures above approx $300^\circ$C. Metamorphic waters were probably a major component of the hydrothermal fluids that interacted with the Bushveld Complex. A significant amount of metamorphic water was internally generated by dehydration reactions during contact metamorphism of the Transvaal Supergroup. For example, the transformation of pelitic shale to hornfels resulted in a 4 wt percent reduction in the water content of the rock (Nell, 1985). A large quantity of metamorphic water was probably derived from basinal pore fluids (for example, formation waters or basinal brines) that were heated by the intrusion. Basinal pore fluids consist of fluids trapped in the sediments at the time of deposition, fluids generated by devolatilization reactions during diagenesis ($T < 300^\circ$C), and fluids introduced from outside the basin that exchanged with the supracrustal rocks at temperatures less than $300^\circ$C. A preliminary fluid inclusion study of the Bushveld Complex indicates that the hydrothermal fluids had very high salinities (Schiffries, 1985), which is a common characteristic of basinal brines and metamorphic waters.

Metamorphic waters and basinal brines can have a wide range of isotopic compositions depending on the initial isotopic compositions of the rocks and fluids, the temperatures of the fluid-rock interactions, and the extent of reaction progress. The Bushveld hydrothermal fluids have a large range of $\delta D$ values (Table 3), and this range is characteristic of fluids derived from basinal brines and metamorphic waters under rock-dominated conditions.

Figure 10 shows the calculated $\delta^{18}$O values of metamorphic waters in equilibrium with the principal rock types at intermediate to high temperatures ($500^\circ$–$700^\circ$C). The $\delta^{18}$O values of waters in equilibrium with gabbro, quartzite, and volcanic rocks differ by only 0 to 4 permil. An implication of this fact is that fluid-rock interactions may not produce large $^{18}$O-shifts in the gabbros if the fluids had previously exchanged with large volumes of quartzite or volcanic rocks at elevated temperatures. Although the $^{18}$O-shifts that result from isotopic exchange reactions may be small under these circumstances, it is still generally possible to detect the effects of fluid-rock interactions by the occurrence of isotopic disequilibrium between coexisting minerals, or
Fig. 10. The rectangles represent the expected range of δD and δ\(^{18}\)O values for waters that have exchanged with large volumes of gabbro, quartzite, pelite, and volcanic rocks. The width of the rectangles represents the calculated δ\(^{18}\)O values of metamorphic waters in equilibrium with each lithology at intermediate to high temperatures (500° to 700°C). The height of the rectangles correspond to the range of measured δD values of water extracted from fluid inclusions. The δ\(^{18}\)O values of waters in equilibrium with gabbro, quartzite, and volcanic rocks differ by only 0 to 4 permil. An implication of this fact is that fluid-rock interactions may not produce large 18O-shifts in the gabbros if the fluids had previously exchanged with large volumes of quartzite or volcanic rocks at elevated temperatures.
perhaps by the presence of secondary alteration minerals that produce strong isotopic fractionations. Metamorphic waters that exchanged with large volumes of pelite at intermediate to high temperatures would be capable of producing relatively large $^{18}O$-shifts in the intrusive rocks. The magnitude of the effect can be evaluated by constructing an isotopic profile across a contact between the intrusion and a pelitic layer in the contact aureole.

**High Temperature Fluid Flow in Deep-seated Crustal Rocks**

Although it is commonly assumed that rocks are nearly impermeable above 400°C and at crustal depths greater than about 10 km, several recent studies have provided field, petrologic and isotopic evidence for both pervasive and channelized fluid flow under these conditions. Contemporary circulation of fluids has been documented at a depth of 12 km in a super-deep borehole in the Kola Peninsula (Kerr, 1984). Tracy and others (1983) present evidence for channelized fluid flow at a depth of approx 22 km during regional metamorphism of the Wepawaug formation in south-central Connecticut. Ferry (1983) concludes that fluid-rock interactions pervasively affected all rocks within beds of pelitic schist and impure carbonate above the biotite isograd during regional metamorphism in the Waterville-Vassalboro area of southeast Maine. Rumble and others (1982) show that reaction-enhanced permeability helps facilitate channelized fluid flow along sedimentary bedding. Nabelek and others (1984) demonstrate that pervasive flow was channelized within specific sedimentary beds during contact metamorphism adjacent to a granitic pluton. Wickham and Taylor (1985, 1987) provide evidence that surface waters circulated to a depth of 12 km during regional metamorphism in the Pyrenees, and they conclude that crustal anatexis was promoted by fluid infiltration. The significance of pervasive fluid flow during metamorphism has been questioned by Wood and Walthers (1986): they demonstrate that the available data cannot always distinguish between small amounts of internally generated fluids and relatively large amounts of externally derived fluids.

The Bushveld hydrothermal system provides a well constrained example of fluid flow to crustal depths of at least 15 km and temperatures that exceeded 700°C. To a first approximation, the hydrology of the Bushveld Complex can be viewed as a rock-dominated recharge system that supplied fluids to a water-dominated vein and aquifer system. The relative importance of pervasive and channelized fluid flow appears to have been highly variable in the Bushveld hydrothermal system. The extensive networks of hydrothermal veins in the intrusion and the contact aureole provide a detailed record of channelized fluid flow. However, it is much more difficult to recognize and assess the significance of pervasive fluid flow. Mineralogical and isotopic evidence indicate that pervasive fluid flow was locally important in the Bushveld
Complex at low and intermediate temperatures. The absence of pervasive mineralogical alteration does not preclude the possibility that pervasive fluid flow occurred in the intrusion at very high temperatures because the original minerals may remain stable under these conditions (Taylor and Forester, 1979; Norton and Taylor, 1979). Isotopic data indicate that quartzite layers were pervasively infiltrated by large quantities of fluid at high temperatures, but the fluid-rock interactions did not result in the formation of appreciable quantities of secondary minerals.

The systematics of the isotopic data indicate that the $\delta^{18}O$, $\delta^{13}C$, and $\delta^D$ values of the fluids that interacted with the Bushveld Complex were largely controlled by different rock reservoirs. The $\delta^{18}O$ values were set by isotopic exchange with the plagioclase in the intrusive rocks, the $\delta^{13}C$ values appear to reflect a large contribution of carbon from marine carbonates, and the $\delta^D$ values appear to have been strongly controlled by reactions involving hydrous minerals in the Transvaal Supergroup. These results indicate that the $\delta^{13}C$ and $\delta^D$ values of the fluids were nearly constant along fluid pathlines that traversed many kilometers of rocks containing very low concentrations of carbon and hydrogen, respectively. In contrast to the behavior of hydrogen and carbon, it appears that the $\delta^{18}O$ value of the fluids varied throughout the flow path in response to changes in temperature and the $\delta^{18}O$ value of the host rocks.

**Implications for the Formation of Hydrothermal Mineral Deposits**

The chemical, thermal, and hydrological characteristics of the Bushveld hydrothermal system created favorable conditions for the formation of hydrothermal mineral deposits. Many of the hydrothermal fluids that circulated through the Bushveld Complex were highly saline brines (Schiffries, 1985; Schiffries and Skinner, 1987), and fluids of this type are effective agents for chemical mass transfer due to the complexing capabilities of the chloride ligand. Fluid-rock interactions occurred over an extremely broad range of physiochemical conditions, and therefore the solubilities of ore minerals may have been highly variable along certain fluid pathlines. The evolution of fluid-flow conditions from a rock-dominated recharge region to a fluid-dominated vein system can result in the transfer of certain trace elements from a large volume of rock in the recharge region to a relatively small volume of rock in the vein system.

Chalcopyrite and other sulfide minerals are locally abundant in some hydrothermal veins (Schiffries and Skinner, 1987). This indicates that copper and other base metals were leached from a large volume of rock, transported by the hydrothermal fluids, and then deposited in a relatively small volume of rock. Given the presence of enormous quantities of platinum-group elements in the Bushveld Complex, an obvious extension of this research is to determine whether or not the veins and aquifers contain high concentrations of precious metals.
CONCLUSIONS

We report oxygen, hydrogen, and carbon isotopic data for veins and hydrothermally altered samples from the Bushveld Complex and its contact aureole. This study places new constraints on the nature of the Bushveld hydrothermal system, and it increases our general understanding of large-scale fluid flow at crustal depths in excess of 10 km and temperatures ranging to at least 700°C. The general conclusions are summarized below:

1. The Bushveld hydrothermal system can be characterized as a rock-dominated system on a regional scale. The integrated reactive water/rock mass ratio was probably less than 0.1 for the entire region.

2. Fluid-dominated conditions were achieved on a local scale as a result of structural controls on fluid flow. The hydrothermal veins represent local regions that achieved high water/rock ratios as a consequence of fracture-controlled fluid flow. Fluid-dominated conditions were also achieved on a local scale as a consequence of pervasive fluid flow channelized along certain lithologic units, such as metamorphosed quartzite layers in the contact aureole. These layers behaved as aquifers for fluids that had previously exchanged with large volumes of rock.

3. Most of the hydrothermal fluids were derived from reservoirs external to the Bushveld Complex. The externally derived fluids probably were isotopically heterogeneous at the time they initially interacted with the intrusive rocks.

4. The dominant component of the hydrothermal fluids can be characterized as metamorphic water, reflecting the fact that the fluids equilibrated with metamorphic rocks at elevated temperatures (>300°C) under rock-dominated conditions.

5. The δ18O, δD, and δ13C values of the fluids appear to have been largely controlled by different rock reservoirs.

6. The δ18O values of the hydrothermal fluids were controlled by exchange with igneous minerals, primarily plagioclase, under rock-dominated conditions at elevated temperatures. The hydrothermal waters were strongly enriched in 18O relative to meteoric waters and seawater.

7. The δD values of the hydrothermal fluids appear to have been controlled by fluid-rock interactions involving hydrous minerals in the country rocks. A large range in δD values were generated as a consequence of isotopic exchange at low but highly variable water/rock ratios and at variable temperatures.

8. The δ13C values of the hydrothermal fluids are consistent with derivation of the carbon from marine carbonates in the country rocks.

9. The fluids responsible for the formation of the hydrothermal veins were chloride-rich brines (Schiffries and Skinner, 1987) that had previously exchanged with large volumes of rock at elevated temperatures. These conditions are very favorable for large-scale chemical mass transfer. Further consideration should be given to the possibility that
hydrothermal processes played a significant role in redistributing sulfide minerals and precious metals.

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