Zircon megacrysts from kimberlite: Oxygen isotope variability among mantle melts

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Abstract The oxygen isotope ratios of Phanerozoic zircons from kimberlite pipes in the Kaapvaal Craton of southern Africa and the Siberian Platform vary from 4.7 to 5.9‰ VSMOW. High precision, accurate analyses by laser reveal subtle pipe-to-pipe differences not previously suspected. These zircons have distinctive chemical and physical characteristics identifying them as mantle-derived megacrysts similar to zircons found associated with diamond, coesite, MARID xenoliths, Cr-diopside, K-richterite, or Mg-rich ilmenite. Several lines of evidence indicate that these $\delta^{18}O$ values are unaltered by kimberlite magmas during eruption and represent compositions preserved since crystallization in the mantle, including: U/Pb age, large crystal size, and the slow rate of oxygen exchange in non-metamict zircon. The average $\delta^{18}O$ of mantle zircons is 5.3‰, ~0.1‰ higher and in equilibrium with values for olivine in peridotite xenoliths and oceanic basalts. Zircon megacrysts from within 250 km of Kimberley, South Africa have average $\delta^{18}O = 5.32 \pm 0.17‰$ (n = 28). Small, but significant, differences among other kimberlite pipes or groups of pipes may indicate isotopically distinct reservoirs in the sub-continental lithosphere or asthenosphere, some of which are anomalous with respect to normal mantle values of $5.3 \pm 0.3‰$. Precambrian zircons (2.1–2.7 Ga) from Jwaneng, Botswana have the lowest values yet measured in a mantle zircon, $\delta^{18}O = 3.4$ to 4.7‰. These zircon megacrysts originally crystallized in mafic or ultramafic rocks either through melting and metasomatism associated with kimberlite magmatism or during metamorphism. The low $\delta^{18}O$ zircons are best explained by subduction of late Archean ocean crust that exchanged with heated seawater prior to underplating as eclogite and to associated metasomatism of the mantle wedge. Smaller differences among other pipes and districts may result from variable temperatures of equilibration, mafic versus ultramafic hosts, or variable underplating. The narrow range in zircon compositions found in most pipes suggests magmatic homogenization. If this is correct, these zircons document the existence of significant quantities of magma in the sub-continental mantle that was regionally variable in $\delta^{18}O$ and this information restricts theories about the nature of ancient subduction.

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Introduction

Zircon is a common trace mineral in a wide range of rock types including kimberlite and is extensively studied because it provides reliable U/Pb determinations of magmatic crystallization age (see, Speer 1982; Heaman and Parrish 1991). Inheritance of U/Pb isotopic ratios is well documented in zircons that have withstood partial melting (Williams 1992; Paterson et al. 1992) and exchange rates for oxygen and cations are also very slow in non-metamict zircons (Valley et al. 1994; Watson and Cherniak 1997; Cherniak et al. 1997).

This study reports analyses of oxygen isotope ratios in zircon megacrysts from kimberlites in southern Africa and Siberia (Figs. 1 and 2). All samples come from commercially evaluated kimberlite pipes, many of which have been mined. Most zircon samples from Siberia and Botswana have also been analyzed by other means including in situ U-Pb geochronology by ion microprobe (P.D. Kinny et al. 1989, unpublished). Trace element compositions have been measured in many of the S. African zircons of the Table (Eldridge et al. 1995; Schulze et al. 1996).

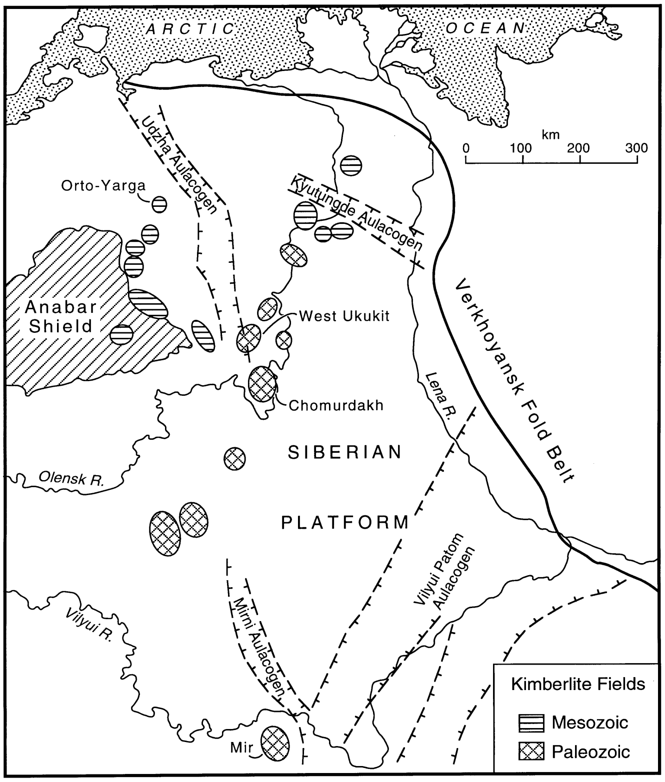


Fig. 1 Map of the Siberian Platform showing kimberlite fields of Mesozoic and Paleozoic eruption age. Values of $\delta^{18}O$ have a range of 0.87‰, from 4.73 to 5.60‰ for mantle-derived zircon megacrysts from 5 pipes. Each pipe is characterized by very homogenous values, better than ± 0.06‰, and subtle but significant regional variations in $\delta^{18}O$ are observed. One inherited zircon, dated at 674 Ma, has anomalously high $\delta^{18}O$ = 7.09‰

The goals of this study are: (1) to test the hypothesis that zircons preserve mantle oxygen isotope compositions; (2) to determine the variability within and among mantle regions sampled by kimberlite. While mantle $\delta^{18}O$ heterogeneity has been previously investigated using conventional techniques for olivine, pyroxene and whole rock analysis (see, Kyser 1986; Taylor and Sheppard 1986; Harmon and Hoefs 1995), the recently developed ability to obtain accurate analyses of refractory minerals such as zircon by laser heating provides higher precision and allows for discrimination of different reservoirs, and makes it possible to avoid the confounding effects of alteration. In spite of the broad regional oxygen isotope homogeneity that is demonstrated by high precision laser analysis of refractory minerals such as olivine in many suites of mantle-derived magmas and xenoliths (Mattey et al. 1994; Eiler et al. 1996), growing evidence suggests that deep-seated magmatic reservoirs exist which have isotopically anomalous values of $\delta^{18}O$ (Cartwright and Valley 1991; Eiler et al. 1997, King et al. in press). Igneous zircons can provide unique information for evaluating such magmatic sources because they may represent large domains in the mantle that have been homogenized by melting.

Zircon megacrysts in kimberlite

Whereas reported zircon contents range from 0.01 to 170 grams per ton in kimberlite (about the same concentration as diamond, Kresten et al. 1975), their large size (up to several cm), luminescence, and high density

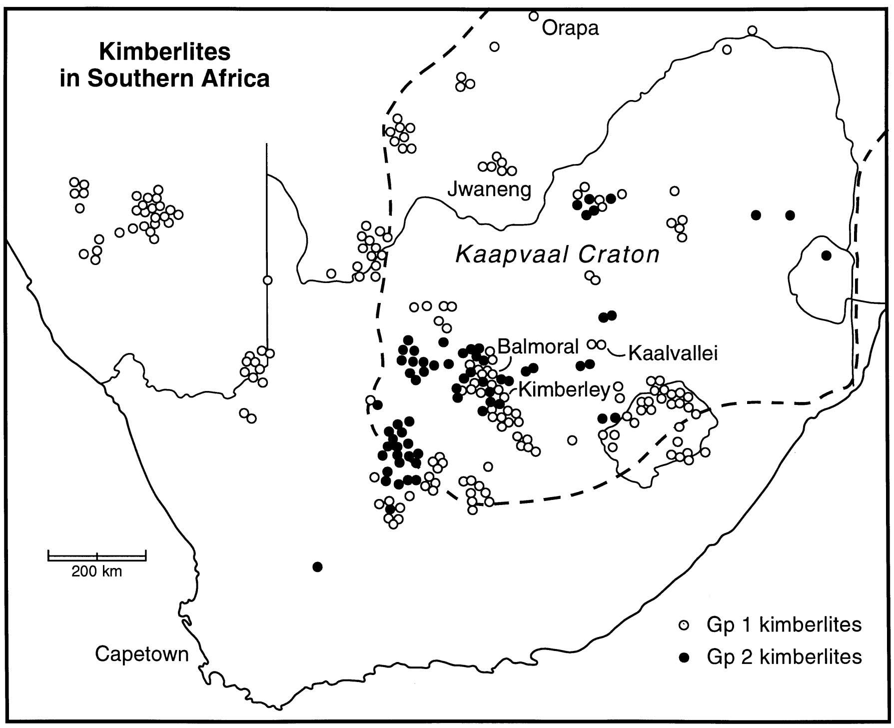


Fig. 2 Map of kimberlite pipes from southern Africa (after Skinner 1989). Zircons were analyzed for $\delta^{18}O$ from group 1 kimberlites of the Kaapvaal Craton in S. Africa and Botswana, revealing correlations of $\delta^{18}O$ with time and space. All 28 zircons from within 250 km of Kimberley average 5.32 ± 0.17‰ whereas 8 Permian zircons from Jwaneng, Botswana are significantly higher at 5.73 ± 0.13‰. Precambrian zircons from the same pipe at Jwaneng have anomalously low values of 3.37 to 4.69‰. Zircons from Orapa, north of Jwaneng, average 5.24 ± 0.22‰. Kamfersdam is in Kimberley. Leicester is adjacent to Balmoral

(4.5–4.7) allow them to be concentrated industrially during diamond mining. In addition to large size, zircon megacrysts from kimberlite have a number of distinctive characteristics and they have been discussed as a possible aid for diamond exploration (Kresten et al. 1975). These zircons are usually low in U (<60 ppm), Th, Y, P, and rare earth elements. Megacrysts show perfect cleavage or parting that is suggested to result from rapid pressure release. Crystals are non-metamict and frequently gemmy. Most zircon megacrysts are rounded and any original crystal faces are frosted and abraded. Many zircons are coated with whitish alteration to ZrO_2. In contrast, most zircon crystals separated for geochronology from plutonic crustal rocks are small (<0.5 mm), euhedral, poorly cleaved, and richer in uranium. These differences show that the kimberlite zircon megacrysts represent a distinct mantle suite rather than a random mixture of xenocrysts gathered from the crust by kimberlite magmas during ascent.

Most zircon megacrysts are found as isolated single crystals, selected from heavy mineral concentrates and the mineral association is unclear. Nevertheless, rare occurrences of zircon have been described intergrown with Mg-rich ilmenite, or in a few instances, with diamond or coesite, proving a high pressure history at depths in excess of 130 km for some zircons (Kresten et al. 1975; Moore et al. 1992; Sobolev et al. 1991, 1994), though others likely form at shallower depths in the mantle. Polymineralic zircon-bearing assemblages (presently under investigation, see below) provide clues to the paragenesis and origin of the single crystal zircons in the present study. Zircons have also been found in metasomatized peridotite, MARID (mica-amphibole-rutile-ilmenite-diopside), and other kimberlite-borne mantle xenoliths, indicating that formation can occur at more than one depth, temperature, or chemical environment.

Paragenesis, trace elements, and age

Mantle zircons can be divided based on paragenesis and trace element data. Differences are recognized between zircon populations from different pipes in southern Africa (Schulze et al. 1996). Many Balmoral and Leicester zircons are intergrown with Cr-diopside, Cr-rutile, and/or ilmenite, suggesting an origin related to a "Granny Smith-like" suite (see Boyd et al. 1984). Several Kamfersdam zircons are intergrown with various combinations of K-richterite, clinopyroxene, phlogopite, and ilmenite, consistent with an origin in the MARID suite (Dawson and Smith 1977). Such zircon-bearing MARID rocks, MARID-related veined peridotites, and PKP (phlogopite-K-richterite-peridotite) xenoliths are known from other Kimberley localities (Kinny and Dawson 1992; Konzett et al. 1995; Schulze et al. 1996). The Kimberley Pool zircons in this study may have the same origin, though uranium contents in MARID-related zircons are typically higher than the megacysts analyzed in the table (Davis 1977; Kinny 1996). Kaalvallei zircons may belong to the Cr-poor megacryst suite, based on zircon-ilmenite specimens at this locality and the absence of Granny Smith or MARID-type xenoliths at Kaalvallei. Granny Smith diopsides and Cr-rutile nodules are common at Orapa (Boyd et al. 1984; Tollo and Haggerty 1987) perhaps indicating an origin for Orapa zircons similar to the Balmoral and Leicester occurrences. Zircons from Jwaneng and Siberian pipes have no reported intergrown phases that would allow speculation as to their paragenesis.

In numerous studies where zircons have been dated by U/Pb, they give ages close to the time of kimberlite eruption (Davis et al. 1980; Kinny et al. 1995). A notable exception is Jwaneng where samples include zircons with the Permian age of the pipe as well as late Archean to early Proterozoic inherited zircons (Kinny et al. 1989). Inherited Proterozoic-age zircon megacrysts have also been found in Siberian kimberlite pipes (Kinny et al. 1995).

Genesis of zircon megacrysts

The genesis of zircon megacrysts is controversial, like the associated eclogites and peridotite xenoliths, and diamonds (see Smyth et al. 1989; Boyd 1989; Richardson et al. 1990; Jacob et al. 1994; Helmstaedt and Gurney 1995; Hart et al. 1997). One question involves the importance of subducted ocean crust. The sub-continental lithosphere beneath the Kaapvaal craton has been proposed to contain remnants of subducted ocean crust derived in the Archean from the Limpopo Mobile Belt (Light 1982; Helmstaedt and Schulze 1989). A similar model is proposed for eclogites from Siberia (Jacob et al. 1994). Xenoliths of Precambrian eclogite with $\delta^{18}O(WR) = 2.2$ to 8.4‰ are reported from the Roberts Victor and Bellsbank kimberlites, S. Africa (MacGregor and Manton 1986; Neal et al. 1990). These values extend well outside the normal range of mantle rocks and are further support for the presence of subducted ocean crust; low $\delta^{18}O$ is derived from high temperature exchange with sea water before subduction, and high $\delta^{18}O$ is caused by low temperature interaction (see, Muehlenbachs 1986). This conclusion is further strengthened by anomalous values of $\delta^{13}C$ in eclogitic diamonds and graphites, and $\delta^{34}S$ in sulfide inclusions within diamonds (Deines et al. 1987; Eldridge et al. 1991, 1995; Rudnick et al. 1993; Schulze et al. 1997). Whole rock $\delta^{18}O$ compositions for diamond-bearing eclogite nodules from the Udachnaya kimberlite in Siberia also show large variability, 4.8 to 9.1‰, though most are 5.2 to 7.0‰ and anomalously low $\delta^{18}O$ has not been reported to compare with those from S. Africa (Jacob et al. 1994; Snyder et al. 1995).

Zircons have been reported in eclogites and diamond-bearing gneisses exposed at the surface (Gebauer et al. 1985; Paquette et al. 1985; Claoué-Long et al. 1991) and presumably mantle eclogite also contains zircons with anomalous and variable $\delta^{18}O$ reflecting the whole rock value.

It should be kept in mind that anomalous $\delta^{18}O$ values outside of the mantle field support subduction, but that normal mantle values [$\delta^{18}O$ (Zrc) = 5.3 ± 0.3‰] are ambiguous in this regard. It is possible that such "normal" mantle eclogite nodules and any xenocrysts derived from them form by multiple processes including subducted ocean crust and primary mantle magmas. If zircon megacrysts are igneous and represent late stage differentiates of mantle melts (Kinny et al. 1989), no matter whether kimberlitic or not, their $\delta^{18}O$ will represent an averaged composition for the mantle source region that is less variable than that of metamorphic zircons in unmelted eclogite xenoliths. Thus variability provides a second diagnostic that is independent of average $\delta^{18}O$. Igneous zircons are expected to be highly homogeneous within a pipe or district due to large scale mixing within the magma. In contrast, zircons that form by metamorphic (i.e. subsolidus) growth in eclogites may preserve local heterogeneities of $\delta^{18}O$ that were present in hydrothermally altered ocean crust and thus be variable within a single pipe.

Techniques

Oxygen isotope analyses have been made by laser heating in a BrF_5 atmosphere, and using a dual-inlet gas-source mass-spectrometer. Isotope ratios are reported in the standard per mil (‰) notation relative to standard mean ocean water (VSMOW) with precision of ± 0.050 to 0.1‰ verified daily by multiple analyses of a garnet standard (UWG-2, Valley et al. 1995). Individual chips of zircon weighing 1–2 mg (<1 mm diameter) were obtained by crushing larger crystals or sawing 600 μm thick sections with a thin diamond saw blade to obtain pieces of core and rim from a single crystal.

In order to compare analyses of zircons from one locality to those of another, three statistical parameters are calculated: standard deviation (SD), uncertainty of the mean (σ), and "t-test" (Davis 1973). Values of standard deviation are reported as ±1 SD. The standard deviation is useful to predict the reproducibility of additional analyses to a sample population while the uncertainty of the mean describes how well the average value of that population is known. The t-test determines if the average values of two different populations are statistically different with a given confidence level. The use of these statistics implicitly assumes that: samples were collected randomly, sample populations are distributed normally, and variances of the populations are equal (Davis 1973). These parameters provide a useful basis for comparison even for small populations where these assumptions are difficult to evaluate.

Results

Values of $\delta^{18}O$ range from 4.73 to 5.93 for 59 Phanerozoic zircons from 13 kimberlite pipes or districts (Table). Figures 1 and 2 show the sample locations and Fig. 3C, D, and 4 plot data by location. Four zircons from the Kimberley group were tested for intracrystalline homogeneity and found to have the same $\delta^{18}O$ value for core and rim. For 25 of the 26 zircons that were analyzed twice, one chip per analysis, the average reproducibility is ±0.07‰, further evidence of isotopic homogeneity at the mm-scale. Only one zircon was found to reproduce poorly, Anomaly 134 pipe from the Ukukit West field (±0.42‰), however the available sample was used up and the one anomalous analysis was not repeated. Ion microprobe analysis of $\delta^{18}O$ in Kimberley zircon (KIM-2) and Jwaneng zircon (J1-1) indicates that homogeneity extends to the 20 μm-scale (±0.8‰, 1 SD) even across distinct magmatic zoning seen by cathodoluminescence (Valley et al. in press).

Taken together, the southern African Phanerozoic zircons are similar in average $\delta^{18}O$ to those from Siberia, 5.3 versus 5.2‰ (Fig. 4); however, small but statistically significant regional differences exist. Zircons from within 250 km of Kimberley, South Africa (Fig. 2) show remarkable regional homogeneity, $\delta^{18}O = 5.32 \pm 0.17$‰ (1 SD), considering the petrologic differences described above. Even within this tightly clustered grouping, subtle differences may exist between Balmoral ($\delta^{18}O = 5.45 \pm 0.11$, $\sigma = 0.05$) and Kamfersdam ($\delta^{18}O = 5.18 \pm 0.16$, $\sigma = 0.07$) which are statistically different at 99% confidence. Samples of Permian age zircons from Jwaneng, Botswana are also tightly clustered, but with a distinctly higher value of $\delta^{18}O = 5.73 \pm 0.13$‰. Eleven zircons from Orapa, Botswana yielded an average $\delta^{18}O = 5.24 \pm 0.22$‰. The Permian Jwaneng zircons are clearly higher in $\delta^{18}O$ than those from Orapa or S. Africa.

More distinct differences are seen among the lower $\delta^{18}O$ zircons from Siberian kimberlite pipes (Fig. 4) although the sample set, which is restricted to previously ion probed zircons, is small. In the Chomurdakh field, duplicated analyses of two zircon megacrysts from one pipe are identical and yield anomalously low $\delta^{18}O = 4.73 \pm 0.01$‰ while two samples from another pipe are also identical, but higher in $\delta^{18}O$, 5.07 ± 0.05‰. In contrast, four zircons from Mir are 5.53 ± 0.06‰. One duplicated analysis from the Leningrad pipe (Ukukit West field) is 7.09, however this zircon has 69 ppm of uranium and an anomalous age of 674 Ma that is older than the eruption age of the pipe, suggesting that the megacryst is either crustal or derived from older mantle melts.

Preservation of $\delta^{18}O$ from the mantle

Comparison of the values for $\delta^{18}O$(zircon) to values for carbonates and groundmass silicates from kimberlite show little relation. A review of 141 analyses of calcite from S. African and Lesothan kimberlites ranges from 6 to 24‰ (average = 12.9 ± 3.2‰, Kobelski et al. 1979). Average values are higher for fragmental kimberlite (13.4‰) than for massive (12.0‰) or tabular (11.7‰) suggesting late stage modification during or after eruption, processes that are also indicated by heterogeneity seen in $\delta^{18}O$(calcite) at the hand sample scale and low values of δD and $\delta^{18}O$ of groundmass serpentine and phlogopite (Sheppard and Dawson 1975). Clearly, such extreme late stage alteration has not affected the zircons of this study.

Although not modified by processes in the crust, the kimberlite zircons are more variable in $\delta^{18}O$ than major mantle reservoirs (Fig. 3A, B vs 3C, D). Olivine grains in spinel-, garnet- and diamond-facies mantle peridotite xenoliths from S. Africa, Siberia, Europe, N. America and Hawaii average $5.17 \pm 0.13‰$ (SD = 0.13, $\sigma = 0.02$, $n = 70$), and six olivine inclusions in diamonds are $5.24 \pm 0.24‰$ (Mattey et al. 1994). In most of these samples, olivine coexists with pyroxenes that have appropriate values for equilibration at mantle temperatures: δ^{18}O(clinopyroxene) = $5.57 \pm 0.16‰$, Δ(Cpx-Ol) = 0.38‰; δ^{18}O(orthopyroxene) = $5.69 \pm 0.14‰$, Δ(Opx-Ol) = 0.51‰. These mineral data are in general agreement with whole rock analyses of 92 peridotite xenoliths summarized from 3 continents by Ionov et al. (1994). Olivine phenocysts in many ocean island basalts, such as Mauna Loa and Loihi (Fig. 3B, $\delta^{18}O = 5.18 \pm 0.10‰$) are identical to those in the mantle xenoliths (Eiler et al. 1996).

It is evident that the mantle zircon megacryst suite that we have analyzed records a tighter and more self-consistent range of values than the matrix minerals of the kimberlite itself. The average for zircons from within 250 km of Kimberley is 0.15‰ higher than the average δ^{18}O value for mantle olivine from xenoliths. This fractionation is virtually identical to the best estimate for equilibrium, Δ^{18}O(Zrc-Ol) = 0.2‰ at 1200 °C and 0.3‰ at 1000 °C (Chiba et al. 1989; Valley et al. 1994; Rosenbaum and Mattey 1995). A basaltic whole rock or glass in equilibrium with these minerals would have a value near 5.7‰, identical to MORB and an ultramafic whole rock would be ~5.4‰. While limited variability is recognized among some OIBs, these zircon compositions are also in equilibrium with the dominant OIB reservoir (Eiler et al. 1997). Thus, the majority of the zircons that we have analyzed are within a tight window of mantle values, $5.3 \pm 0.3‰$.

Analyses of δ^{18}O by laser are routinely four to six times more precise than the $\pm$ 0.3‰ range of mantle values (Valley et al. 1995) and values from each kimberlite pipe or group of pipes cluster more tightly than from a larger region. In many cases these pipe-to-pipe differences are statistically distinct. Small differences can arise from variable whole rock chemistry (mafic vs ultramafic) or temperatures of crystallization, but larger differences, if magmatic, indicate anomalous mantle. The question remains, are the zircon megacrysts slightly modified by late-state processes within the kimberlite magma or do they faithfully record subtle regional differences within the mantle at the time of crystallization?

Oxygen exchange in zircon

Two processes could alter the δ^{18}O of a zircon: recrystallization/new crystal growth or solid state diffusion of oxygen. These processes have been studied in detail for a suite of igneous and metamorphic zircons from crustal plutonic rocks of Proterozoic age (Valley et al. 1994). It was found that some small uranium-rich (to 3000 ppm) zircons were altered in δ^{18}O after the time of crystallization, but that these zircons were further distinctive in being relatively magnetic and discordant in U/Pb isotopes, and these zircons were crazed by fine cracks due to radiation damage. In no instance were low magnetism, low uranium, isotopically concordant zircons demonstrated to have been altered in δ^{18}O after the time of crystallization in spite of subsequent granulite facies regional metamorphism and slow cooling. All of the kimberlitic zircons in this study have lower uranium contents than these Proterozoic zircons and, considering their younger ages and the general absence of crazing by micro-cracks, thus have not suffered significant radiation damage. Furthermore, the samples from Botswana and Siberia have been imaged by cathodoluminescence (CL) and analyzed for U/Pb isotope ratios by ion microprobe (Kinny et al. 1989; J. Fournelle, J.W. Valley and P.D. Kinny unpublished data). All of these samples plot within analytical error of concordia (though uncertainties by ion probe are relatively large for this age), and no overgrowths are seen by CL. The general homogeneity of δ^{18}O within single crystals, and among crystals from a single pipe, further disproves the existence of volumetrically important overgrowths of contrasting δ^{18}O. Furthermore, for the Permian Jwaneng zircons, the $^{206}Pb/^{238}U$ age of 243 $\pm$ 6 Ma is in good agreement with the Rb-Sr mica isochron age of 250 $\pm$ 17 Ma. None of the evidence is consistent with appreciable recrystallization or new crystal growth of the zircons in this study.

Exchange of oxygen isotopes by diffusion is governed by temperature, time and water activity. The diffusion coefficients of oxygen in zircon have been measured experimentally under both hydrous and anhydrous conditions (Watson and Cherniak 1997), and dry diffusion rates are among the slowest measured for silicate minerals. Thus, oxygen in coexisting minerals diffuses more rapidly than in zircon, effectively comprising an infinite reservoir for oxygen exchange (see, Eiler et al. 1993). If kimberlite magmas erupt explosively from depths of a few kilometers, temperatures may still be near to 1100 °C, but cooling is nearly instantaneous and no diffusion can occur. Prolonged high temperature residence in the mantle would be required to change the composition of zircon by diffusion. Thus, all evidence indicates that diffusion and recrystallization do not alter the δ^{18}O of zircons during eruption, that long periods of very high temperature annealing are necessary for diffusive exchange, and that the differences that we have found among Phanerozoic zircons from the mantle record deep-seated regional heterogeneity.

Precambrian mantle zircons

The Jwaneng DK2 kimberlite pipe in Botswana is unique in yielding both Permian and Precambrian zircons. Kinny et al. (1989) measured precise U-Pb ages and less precise Lu-Hf model ages by ion microprobe and we report laser analyses of δ^{18}O in the same zircon grains

Table Oxygen isotope compositions of zircon megacrysts from kimberlites in southern Africa and Siberia

Sample	Size mm	U ppm	Age Ma	Th/U	$\delta^{18}O$‰ raw	$\delta^{18}O$‰[1] VSMOW	reference[2]
Siberian Platform							
UWG-2 garnet standard[1] (n = 3)					5.80 ± 0.09[4]	5.80	
Orto-Yarga, Anomaly 12/853	3	23	158	0.52	4.92, 5.12	5.02	(3)
Orto-Yarga, Anomaly 12/853	3	23	158	0.52	5.03, 4.85	4,94	(3)
						4.98 ± 0.06	
Chomurdakh field, Khaiyrgastakh	3	56	421	0.71	4.73, 4.75	4.74	(3)
Chomurdakh field, Khaiyrgastakh	3	56	421	0.71	4.71, 4.76	4.73	(3)
						4.73 ± 0.01	
Chomurdakh field, Anomaly 180/78	3	30	436	0.40	5.14, 5.08	5.11	(3)
Chomurdakh field, Anomaly 180/78	3	30	436	0.40	5.07, 5.01	5.04	(3)
						5.07 ± 0.05	
Ukukit West field, Leningrad	3	69	674	0.40	7.05, 7.13	7.09	(3)
Ukukit West field, Anomaly 134	3	19	408	0.32	4.87, 5.66	5.26	(3)
Ukukit West field, Anomaly 152	3	26	419	0.29	5.02, 5.03	5.02	(3)
Mir-5	3				5.39, 5.55	5.47	(3)
Mir-61	4				5.48, 5.52	5.50	(3)
Mir-85	5				5.60, 5.48	5.54	(3)
Mir-115	5				5.61, 5.59	5.60	(3)
						5.53 ± 0.06, σ = 0.03	
Average-Siberia (n = 12, excluding Leningrad)						5.16 ± 0.30	
Kaapvaal Craton, Botswana							
UWG-2 garnet standard (J1 Samples, n = 5)					5.80 ± 0.12	5.80	
UWG-2 garnet standard (J2 samples, n = 9)					5.88 ± 0.11	5.80	
Jwaneng DK2, Permian, Hf model ages = −0.2 to 0.0 Ga, εHf = 6 to 11							
J1-4	3	33	237[5]	0.19	5.93	5.93	(1)
J2-1	1	31	231	0.19	5.75, 6.05	5.82	(1)
J2-2	1	18	241	0.17	5.61, 5.66	5.55	(1)
J2-3	1	38	248	0.20	5.78, 5.98	5.80	(1)
J2-4	1	33	240	0.19	5.74, 5.89	5.73	(1)
J2-5	1	61	242	0.21	5.60, 5.89	5.66	(1)
J2-11	1	44	246	0.21	5.89	5.81	(1)
J2-12	1	19	252	0.18	5.67	5.59	(1)
Average-Permian (n = 8)						5.74 ± 0.13, σ = 0.05	
Jwaneng DK2, Precambrian, Hf model ages = 3.2 to 3.6 Ga, εHf = −14 to −21							
J1-1	3	14	2643	0.52	4.85, 4.53	4.69	(1)
J1-2	2	10	2145	0.44	3.72, 3.98	3.85	(1)
J1-3	2	9	2589	0.51	4.56, 4.89	4.72	(1)
J2-7	1	7	2700	0.39	4.53, 4.57	4.47	(1)
J2-9	1	1	2579	0.37	3.45	3.37	(1)
Average-Precambrian (n = 5)						4.22 ± 0.59	
UWG-2 garnet standard (n = 4)					5.85 ± 0.06	5.80	
Orapa							
13-80-1					5.65, 5.53	5.54	
13-80-2					5.51, 5.69	5.55	
13-80-3					5.28	5.23	
13-80-4					5.10	5.05	
13-80-5					5.42	5.37	
13-80-6					5.52	5.47	
13-80-7					5.23	5.18	

13-80-8			5.10	5.05	
13-80-9			4.98	4.93	
13-80-10			5.36	5.31	
13-80-11			5.03	4.98	
Average-Orapa (n = 11)				$\overline{5.24}$ ± 0.22, σ = 0.07	
Kaapvaal Craton, South Africa					
UWG-2 garnet standard (n = 5)			5.66 ± 0.08[4]	5.80	
Kaalvallei Mine 13-54-84	~ 13		4.93	5.07	(2)
Kaalvallei Mine KLV-1	~ 10		5.32	5.46	(2)
Kaalvallei Mine KLV-2	~ 10		5.26	5.40	(2)
Kaalvallei Mine KLV-3	~ 10		5.24	5.38	(2)
Kaalvallei Mine KLV-4	~ 10		5.24	5.38	(2)
Kaalvallei Mine KLV-5	~ 10		5.09	5.23	(2)
				$\overline{5.32}$ ± 0.14, σ = 0.06	
Kamfersdam Mine KMF-1	~ 5	32[6]	4.98	5.12	(2)
Kamfersdam Mine KMF-2	~ 5	54	4.98	5.12	(2)
Kamfersdam Mine KMF-3	~ 5	36	4.90	5.04	(2)
Kamfersdam Mine KMF-4	~ 5	11	5.31	5.45	(2)
Kamfersdam Mine KMF-5	~ 5	31	5.01	5.15	(2)
				$\overline{5.18}$ ±0.16, σ = 0.07	
Leicester Mine LEI-1	~ 4		5.34	5.48	(2)
Leicester Mine LEI-2	~ 4		5.24	5.38	(2)
Leicester Mine LEI-3	~ 4		4.93	5.07	(2)
Leicester Mine LEI-4	~ 4		5.17	5.31	(2)
Leicester Mine LEI-5	~ 4		5.03	5.17	(2)
Leicester Mine LEI-6	~ 4		5.38	5.55	(2)
Leicester Mine LEI-7	~ 4		4.98	5.12	(2)
				$\overline{5.30}$ ± 0.18, σ = 0.07	
Balmoral Mine BLM-1	~ 6		5.24	5.38	(2)
Balmoral Mine BLM-2	~ 6		5.46	5.60	(2)
Balmoral Mine BLM-3	~ 6		5.41	5.55	(2)
Balmoral Mine BLM-4	~ 6		5.21	5.35	(2)
Balmoral Mine BLM-5	~ 6		5.19	5.33	(2)
Balmoral Mine BLM-6	~ 6		5.36	5.50	(2)
				$\overline{5.45}$ ± 0.11, σ = 0.05	
UWG-2 garnet standard (n = 5)			5.74 ± 0.04	5.80	
Kimberley Pool, KIM-1c[3]	~ 10		5.12	5.20	
Kimberley Pool, KIM-1r[3]	~ 10		5.15		
Kimberley Pool, KIM-2c	~ 10		5.65	5.62	
Kimberley Pool, KIM-2r	~ 10		5.48		
Kimberley Pool, KIM-3c	~ 10		5.15	5.26	
Kimberley Pool, KIM-3r	~ 10		5.25		
Kimberley Pool, KIM-4c	~ 10		5.20	5.33	
Kimberley Pool, KIM-4r	~ 10		5.35		
				$\overline{5.35}$ ± 0.19, σ = 0.09	
Average-Kaapvaal Craton, SA (n = 28)				5.32 ± 0.17, σ = 0.03	

[1] UWG-2 garnet standards analyzed with samples; raw data are corrected to $\delta^{18}O$(UWG-2) = 5.80‰ VSMOW (Valley et al. 1995)
[2] References: (*1*) Kinny et al. 1989, (*2*) (Schulze et al. 1996, (*3*) P.D. Kinny, unpublished
[3] Abbreviations (*r* rim of crystal, *c* core of crystal)
[4] Precision expressed as ± 1SD = standard deviation about the mean
[5] Ages revised by 8 Ma (Kinny, Personal communication 1997)
[6] M.P. Gorton and D.J. Schulze (unpublished)

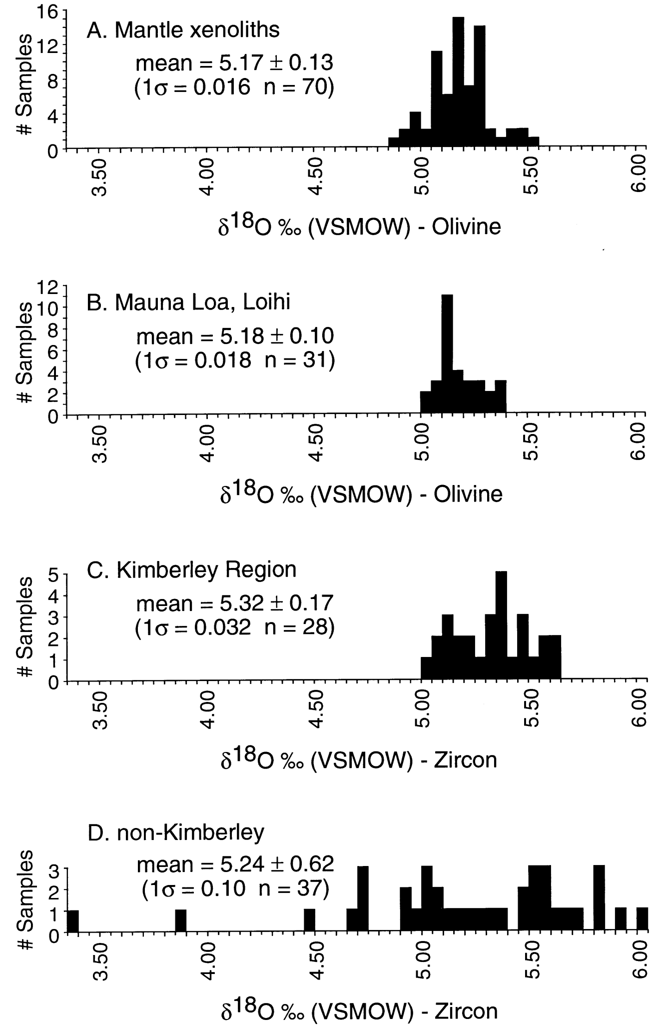


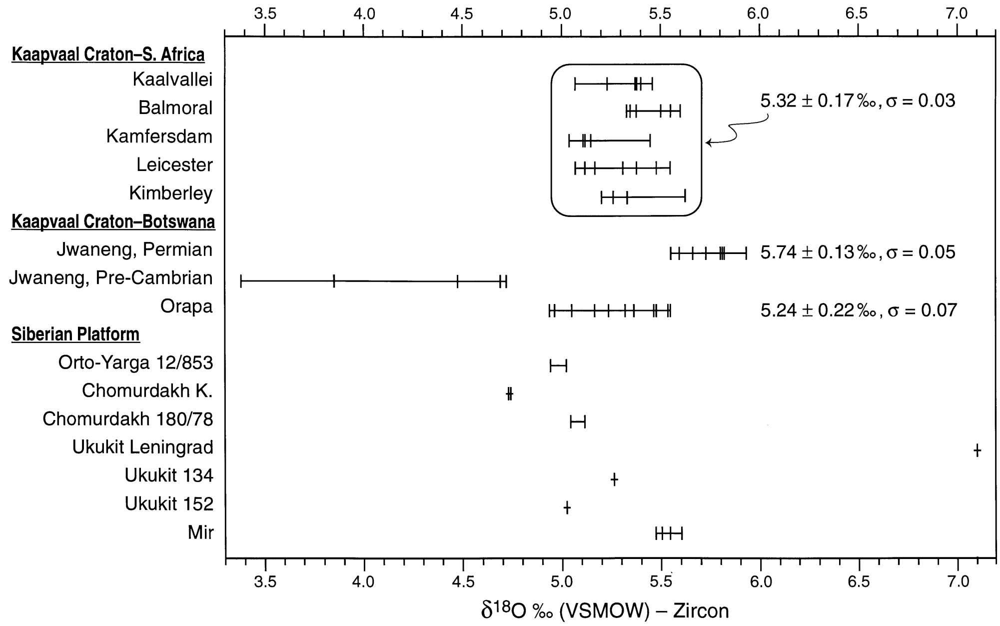
Fig. 3A–D Values of $\delta^{18}O$ for olivine and zircon from mafic and ultramafic rocks: **A** Olivine from mantle xenoliths worldwide (Mattey et al. 1994); **B** olivine phenocrysts from basalt, Mauna Loa and Loihi (Eiler et al. 1996); **C** zircon megacrysts from kimberlite pipes within 250 km of Kimberley, SA (this study); **D** zircon megacrysts from kimberlites in Botswana and Siberia (this study). Under equilibrium conditions in the mantle $\delta^{18}O$ for zircons is 0.2–0.3‰ higher than for olivines; thus the Kimberley zircons could be from the same homogeneous mantle as the olivines. Normal mantle values are $\delta^{18}O$(Zrc) = 5.3 ± 0.3‰. However, significant heterogeneity is demonstrated by non-Kimberley zircons

removed from the ion probe sample mounts (Table). The Permian zircons have blue CL under a 15 kV electron beam, 20–60 ppm U, Th/U ≈ 0.2, $^{206}Pb/^{238}U$ ages of 231–252 Ma, and Hf model ages of 0 ± 0.3 Ga. No overgrowths are observed optically or by CL for any of the Jwaneng zircons of this study. Eight individual Permian zircons have compositions ($\delta^{18}O = 5.73 \pm 0.13$‰) slightly but significantly higher than Phanerozoic zircons from S. Africa and Siberia (Fig. 4). In contrast, the Precambrian zircons have white CL, 1–20 ppm U, Th/U ≈ 0.4–0.5, $^{207}Pb/^{206}Pb$ ages of 2.1–2.7 Ga, and Hf model ages of 3.2–3.6 Ga. The young Hf model ages for the Permian zircons strongly support the conclusion that U-Pb dates are the time of zircon crystallization rather than the time that exchange and resetting stopped due to cooling upon eruption, and a likely genetic model involves metasomatic processes in the upper mantle that immediately precede kimberlite eruption (Kinny et al. 1989).

Several lines of evidence indicate that these Precambrian zircons crystallized in the mantle by processes similar to those forming the Permian zircons and are evidence for Precambrian kimberlites as proposed by Kinny et al. (1989). Eldridge et al. (1995, their Fig. 6) report in situ ion microprobe analyses of REE from both generations of zircon at Jwaneng. The Jwaneng zircons are distinct from typical crustal zircons in granitic to dioritic rocks with lower REE content and flatter HREE patterns. The Permian zircons are less fractionated and approximately two orders of magnitude lower in HREE. The Precambrian zircons that we measured were large, 1–3 mm in diameter; morphologically indistinguishable from the Permian zircons; and low in uranium and thorium content, 1–4 ppm and < 1–2 ppm. Zircons of both age groups have low hafnium contents of 0.51 to 0.81 wt% HfO_2. Some crystals, including J2-9, contained a network of fluid inclusions (Kinny et al. 1989, Fig. 15.3d) similar to that described as characteristic by Kresten et al. (1975, p. 50). The Th/U ratios are distinct for the two age groups, but both lie within the normal range for kimberlitic megacrysts. The Precambrian zircons with Th/U = 0.37–0.59 are indistinguishable from the Siberian zircons (0.29–0.71, Table). In contrast, Archean zircons of crustal origin have been analyzed for oxygen isotope ratio from the Superior Province, Canada: 59 plutonic rocks ($\delta^{18}O = 5.82 \pm 0.6$, 40–616 ppm U, King et al. 1998) and 39 volcanic rocks ($\delta^{18}O = 5.58 \pm 0.49$, 43–106 ppm U, 1 outlier, King et al. 1997). There is no overlap of crustal zircons with Precambrian zircons from Jwaneng (3.37–4.72‰). Zircons from 11 mostly plutonic rocks from crustal lithologies in Barberton Mountain Land in the Kaapvaal craton have $\delta^{18}O$ values (5.50 ± 0.67‰, E.M. King, D.W. Davis and J.W. Valley, unpublished) similar to other Archean crustal zircons, but also distinctly higher than those from Jwaneng. Ninety-four splits of Barberton zircons have Th/U = 0.0–22.6 (Kamo and Davis 1994). All of these crustal zircons measure less than 200 μm in diameter and have more than 40 ppm U. Thus, the Precambrian megacrysts share most characteristics with Phanerozoic mantle megacrysts, but contrast strongly to crustal zircons in size, morphology, $\delta^{18}O$, REE content, and ppm U or Th.

The Precambrian zircons have had a long pre-Permian history. Five Precambrian zircons (2145–2700 Ma) have the lowest values yet measured in any mantle zircon, $\delta^{18}O = 3.37$ to 4.72‰. These zircons also show the greatest variability of any pipe which suggests a metamorphic origin in subducted eclogite. The preservation of Precambrian U-Pb ages in these crystals and the lack of any detectable zoning in oxygen isotope ratio (by laser or by ion microprobe) suggest that these anoma-

Fig. 4 Values of $\delta^{18}O$ for mantle-derived zircon megacrysts from kimberlite pipes in southern Africa and Siberia. The Ukukit Leningrad sample at 7.1‰ is inherited (see text)



lous values were preserved for approximately two billion years. Where were these rocks for that time?

Exchange by diffusion sets limits on the conditions where zircons resided since the Archean. At 1100 °C and 2 Ga, diffusion distances for 50% exchange of oxygen isotope ratio in zircon are over 8 mm at low aH_2O and 55 mm at higher aH_2O (Watson and Cherniak 1997). Grain boundary diffusion is likely to be at least 10^6 faster than volume diffusion in zircon (Eiler et al. 1993), and grain boundary exchange and equilibration could occur at the kilometer-scale. Thus the 1–3 mm diameter, low $\delta^{18}O$ zircons were not preserved as individual xenocrysts or xenoliths surrounded by normal mantle compositions at such high temperatures. Either the zircons resided at shallower levels where temperatures were significantly lower (< 800 °C), or the zircons were encased in a low $\delta^{18}O$ rock matrix that represents large domains of low $\delta^{18}O$ sub-continental lithosphere that were broken up late in their history, probably by the formation of kimberlites in the Permian. Either way, low $\delta^{18}O$ compositions are consistent with subduction of ocean crust that interacted with sea water at high temperatures and which variably underplated the Kaapvaal Craton as slabs of eclogite in the Precambrian. The U-Pb ages of zircons from Jwaneng are consistent with Archean ocean crust subducted from the Limpopo Belt to the north.

Discussion

Variability of zircon $\delta^{18}O$ values has been observed on two scales. At Jwaneng, Precambrian zircons are lower in $\delta^{18}O$ than Permian zircons and these Precambrian zircons are the only suite analyzed thus far with significant variability from within a single kimberlite pipe. Such variability is similar to that seen in low $\delta^{18}O$ eclogite xenoliths and may indicate a metamorphic origin. If these crystals have undergone variable amounts of diffusive oxygen exchange, then compositions have been influenced by normal mantle and the analyzed values have been elevated from an original zircon $\delta^{18}O$ that was 3.4‰ or lower.

In contrast to Jwaneng, zircons from each of the other 12 pipes or groups of pipes are homogeneous and significant differences exist only on a regional scale. Some pipes, such as those near Kimberley, have zircon values that are homogeneous and within the mantle range of 5.3 ± 0.3‰ which appear to be normal mantle, but may or may not have a subducted component. In the case of Orapa, zircons have $\delta^{18}O = 5.24 \pm 0.22$ and are not in equilibrium with most associated eclogite xenoliths [$\delta^{18}O(\text{garnet}) = 6.2 \pm 1.0$, Deines et al. 1991] indicating that these zircons are not eclogitic. However, for other pipes the zircon compositions are anomalous (above 5.6 or below 5.0‰) and homogeneous suggesting that the zircons are derived from a single magmatic source at the scale of one pipe. Such consistency for metamorphic zircons would be highly coincidental and is not seen among eclogite xenoliths. If these zircons document compositions that are regionally averaged by magmatism then it is possible that anomalous values reflect the nature and proportion of subducted, hydrothermally altered ocean crust (± sediments) or the amount of associated metasomatism. It may thus be possible to use zircon $\delta^{18}O$ values to map tectonic terranes, to distinguish underplating of upper [$\delta^{18}O(\text{Zrc}) > 5.6$] versus lower ocean crust [$\delta^{18}O(\text{Zrc}) < 5.0$], or to determine the nature of ancient subduction.

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