U-Th-Pb Ages of Megacrystic Zircon from the Monastery Kimberlite, Free State, South Africa

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Precise emplacement ages of individual diatremes are needed to unravel the extended geochemical and tectonic history of many kimberlite provinces. Two decades ago Davis et al. (1976) and Davis (1977) established the usefulness of zircon in defining the eruptive ages of Cretaceous and Early Tertiary kimberlites on and peripheral to the southern African Kaapvaal Craton. Their ability to date zircon of presumed mantle origin, which was significantly lower in U and radiogenic Pb content than the crustal zircon previously analyzed, was attributable to improvements in the purification of chemical reagents and to the development of a hydrothermal method of sample digestion (Krogh, 1973). Nevertheless, at that time when even the improved chemistry Pb blank was still of the order of 100 pg, only the $^{206}Pb/^{238}U$ ages could be calculated with sufficient radiogenic Pb enrichment to be given a ±1.5% uncertainty. More recently, both conventional (Schärer et al., 1997) and ion microprobe (Kinny et al., 1989) mass spectrometry have been employed to investigate in some detail the U-Pb isotopic systematics of kimberlite zircon from specific localities, but in both cases zircon with either older ages or higher U contents than reported here were involved.

The present study evaluates the U-Th-Pb dating of zircon with especially low U content (3-14 ppm) and relatively young age (~90 Ma) from the Monastery kimberlite, Free State, South Africa. Previously, Davis et al. (1976) had reported a $^{206}Pb/^{238}U$ age of 90.4 Ma and a U content of 6.1 ppm--the lowest encountered from southern African localities--for a single Monastery zircon. Subsequently, several hundred rounded crystals of zircon were retrieved from this kimberlite in 1981-82 during a short period of renewed mining activity. The zircon, together with other large (>1 cm), single crystal minerals (olivine, orthopyroxene, clinopyroxene, garnet, ilmenite, and phlogopite), belongs to a distinctive suite of Cr-poor megacrysts, which has been interpreted by Moore (1986; see also Gurney et al., 1979; Moore et al., 1992) to have crystallized out of a highly evolved liquid that differentiated from the parental magma of the kimberlite.

Ten crystal fragments of several mm dimension and ranging in color from completely colorless to medium amber yellow were chosen to determine their U-Th-Pb ages and compositional variability within the suite. Each fragment was crushed in an alumina mortar and sieved to retain only the -100+40 μm fraction for analysis. In order to reduce surface contamination, the crushed samples were washed in warm 1N HNO_3 and 1N HCl, rinsed in distilled water, and dried before 1-2 mg splits were weighed into 1 mL teflon digestion vessels. Analytical procedure closely followed the hydrothermal bomb and anion resin exchange column method of Krogh (1973) for milligram size samples except as noted below. A mixed ^{205}Pb-^{235}U-^{230}Th spike was employed--making it possible to determine Th-Pb as well as U-Pb ages and to directly measure Th/U ratios.

The results of twelve analyses performed in the Radiogenic Isotope Laboratory of the University of Cape Town on the zircon megacrysts are presented in Table 1. At the time these data were obtained the laboratory Pb blank, which accounted for half or more of the common Pb in the analysis, fluctuated between 25 and 15 pg. Consequently, for many of the analyses the measured $^{206}Pb/^{204}Pb$ of 187-845 translates into rather large common Pb corrections and significant $^{207}Pb/^{206}Pb$ age uncertainties. For consistency the Pb isotopic composition of all

samples has been corrected for 20 pg of laboratory blank, and the remaining common Pb is assumed to have a Stacey and Kramers (1975) 90 Ma model isotopic composition. As with prior efforts to date such young and unradiogenic zircon, the U-Pb (and Th-Pb) ages are analytically most precise, and, assuming no postcrystallization loss of radiogenic Pb, provide the best constraint on the time of kimberlite emplacement. An independent measurement of initial Pb isotopic composition has not yet been made, but only the three samples with $^{206}Pb/^{204}Pb$ <300 would have their $^{206}Pb/^{238}U$ ages changed by more than 0.2 Ma if any reasonable isotopic composition for the mantle were substituted for the Stacey and Kramers model ratios.

Isotopic equilibration between sample and spike is essential to parent-daughter ages, and it is important to demonstrate the reproducibility of the analytical technique, especially in terms of complete sample digestion and sample/spike homogenization. Two approaches have been taken in this regard, (1) consistency of ages among a presumed cogenetic zircon population, and (2) replicate analyses of a 'standard' sample. All of the results reported in Table 1 were determined in three chemistry sessions (A, B, and C, sequentially), which, although using the same basic Krogh technique, differed from each other in several aspects. Sessions A and B involved a second HF digestion to insure complete dissolution of the sample, but after no evidence of an undissolved residue was found, a single digestion was used in session C. Also, total digestion time was progressively reduced from six weeks to four weeks to two weeks for sessions A, B, and C, respectively, with presumably no deleterious effects. The anion resin exchange columns were operated in the bromide rather than chloride mode in session B, but were returned to the chloride mode when poor Th recovery was experienced when the columns were used in the bromide mode.

The close grouping of $^{206}Pb/^{238}U$ ages between 89.2±0.4 and 92.8±0.5 Ma, although extending beyond the quoted uncertainties, suggests that no major difficulties were encountered with the chemical procedure. Interestingly, the 'standard' grain (grain 10), which was analyzed twice in session B and once in session C, gives ages spanning the entire range of the grouping. One discredited analysis in session B did yield an anomalous $^{206}Pb/^{238}U$ age of 105 Ma, but a repeat analysis of the same sample in session C failed to reproduce the discrepant result. Even so, this probable extreme case of incomplete mixing between sample and spike does raise the possibility that minor sample-spike disequilibrium might be the cause of some spread within the grouping itself. Without a priori criteria for excluding any of the analyses, however, a weighted average $^{206}Pb/^{238}U$ age of 90.1±0.5 Ma [MSWD = 3.9, sample 10-2 rejected; Ludwig, 1996] is currently considered the best value for the time of zircon passage below its blocking temperature for diffusive Pb loss, presumably in response to diatreme emplacement. This result is indistinguishable from the weighted average $^{207}Pb/^{235}U$ and $^{208}Pb/^{232}Th$ ages of 90.0±0.5 [MSWD = 1.7, sample 10-2 rejected] and 89.5±1.0 Ma [MSWD = 2.1], respectively. Although the $^{207}Pb/^{206}Pb$ ages have significantly greater uncertainties, they do scatter around the U-Pb and Th-Pb ages, and, thus, show no evidence of older radiogenic Pb inheritance, such as found by Schärer et al. (1997) for the Zairian Mbuji-Mayi kimberlite. Moreover, if any of the spread observed in the parent-daughter ages is to be attributed to pre-eruption mantle residence, that earlier 'memory' is restricted to only 2-3 Ma.

A positive correlation seems to exist between the measured Th/U ratios and increasing Th and U contents of the zircon. The geochemical significance of this relationship, or its correlation with any other trace elements, however, is not known but deserves further investigation. Except to set a general upper limit of ~10 ppb on the common Pb content of the zircon, this study can provide little insight into its distribution among samples until there is additional reduction in the laboratory Pb blank.

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Table 1. U-Th-Pb zircon ages for the Monastery kimberlite.

Grain	Weight	Measured[1]	Concentration, ppm				Age, in millions of years ($\pm 2\sigma$)			
Description	(mg)	$^{206}Pb/^{204}Pb$	U	Th	Pb_{rad}[2]	Th/U	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{232}Th$
1B, colorless	2.08	203	3.06	.72	.0417	.235	90.1±1.1	90.2±2.6	109±29	92.5±2.9
2A, colorless	1.96	235	3.63	.76	.0486	.208	89.3±1.0	89.4±2.3	77±27	88.1±3.5
3C, colorless	1.24	187	4.27	.86	.0569	.202	89.2±1.4	88.8±3.2	79±32	88.3±3.8
4A, lt. yellow	2.55	345	6.53	1.49	.0880	.229	89.7±0.9	89.2±1.8	75±20	85.3±4.0
5C, lt. yellow	1.21	424	6.97	2.00	.0978	.287	91.7±0.8	91.6±1.5	89±15	90.1±2.1
6A, med. yellow	2.05	536	9.77	2.36	.1337	.242	90.6±0.7	90.0±1.0	76±12	88.2±1.6
7B, med. yellow	2.28	450	9.87	2.59	.1360	.262	90.7±0.8	90.2±1.3	78±14	88.0±2.5
8C, med. yellow	.98	324	10.55	2.67	.1445	.253	90.2±0.9	90.5±1.9	97±21	89.6±2.8
9A, med. yellow	2.43	628	11.35	3.69	.1590	.326	90.3±0.6	90.9±0.9	107±10	90.9±1.3
10-1B, med. yellow	1.10	513	14.69	4.97	.2056	.339	89.8±0.7	89.4±1.1	77±13	90.7±1.8
10-2B, med. yellow	1.67	693	14.76	5.06	.2124	.343	92.8±0.6	93.0±0.7	100±8	88.5±1.5
10-3C, med. yellow	2.11	845	14.86	5.14	.2069	.346	89.2±0.5	89.3±0.6	94±5	90.1±1.2

Decay constants: $^{238}U = 1.55125 \times 10^{-10}$ yr^{-1}; $^{235}U = 9.8485 \times 10^{-10}$ yr^{-1}; $^{232}Th = 4.9475 \times 10^{-11}$ yr^{-1}; $^{238}U/^{2354}U = 137.88$. Letter following grain number (e.g., 4A) indicates chemistry session. 1 Corrected for fractionation and spike only. 2 Pb_{rad}, radiogenic Pb, corrected for 20 pg of laboratory blank and a Stacey and Kramers (1975) 90 Ma model isotopic composition.