

ZIRCON-OXIDE REACTIONS IN DIAMOND-BEARING KIMBERLITES

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Zircons (ZrSiO_4) and ilmenites (FeTiO_3) in kimberlites have widely contrasting distributions: the former are as rare or rarer than diamonds, whereas the latter are characteristic constituents. Our working hypothesis is that zircons and diamonds may be genetically related, and that ilmenites which are commonly associated with zircons provide the best estimate of ilmenite compositions which are likely to form during diamond nucleation. Although ilmenites are widely used as a placer prospecting guide to kimberlites, because they are finger-printed by having high MgO contents, low to intermediate Fe_2O_3 contents and the presence of Cr_2O_3 , no data to our knowledge are available on distinguishing barren kimberlites, from diamondiferous kimberlites based on associated mineralogy. Zircons are important from another aspect inasmuch as they provide among the most reliable age dates for kimberlites.

The objectives of this study are four fold: (1) to determine the compositions of ilmenites associated with zircons; (2) to determine the differences between rutile-zircon and ilmenite-zircon assemblages; (3) to characterize the reactions at rutile-zircon and ilmenite-zircon interfaces; and (4) to compare the inclusions in zircons with those present in diamonds.

In a petrographic and electron microprobe study of discrete zircons, and of zircons associated with ilmenite and rutile from the kimberley pipes, the Monastery mine, and the Mothae pipe, Lesotho we have established:

- (1) The compositions of ilmenites associated with zircons have a narrow range in MgO (8-10 wt %) and in Cr_2O_3 contents (0.02 - 0.85 wt %).
- (2) Subsolidus reactions, along the zircon-ilmenite interfaces, yield an exotic mineral assemblage consisting of zirconolite ($\text{CaZrTi}_2\text{O}_7$), Ti-rich baddeleyite ($[\text{TiZr}]_2\text{O}_2$), and diopside ($\text{CaMgSi}_2\text{O}_6$) in association with minor calcite (CaCO_3).
- (3) Rutile-zircon interface assemblages consist of zirconium-bearing armalcolite (FeMg) Ti_2O_5 , zirconolite, baddeleyite, sphene (CaSiTiO_5), calcite and diopside.
- (4) The most abundant inclusion in zircon is pyrrhotite, followed by pentlandite. Native Cu, diopside, rutile and ilmenite have also been identified. The overwhelming abundance of sulfides correlates with those of diamond inclusion studies.

Kimberlitic ilmenites exhibit an unexplained parabolic relationship for Mg vs Cr which reaches a minima at values of MgO between 6 and 10 wt % (Haggerty 1975). This minima is characterized by a relatively small number of data points, with the exception of Monastery, which we now propose reflects those ilmenites which formed in association with zircons. These ilmenite compositions may be indicative of a characteristic P-T regime which is not only suitable for zircon formation, but the probability exists also that it is within the diamond stability field.

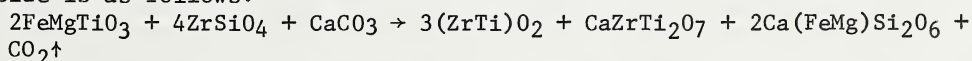
This is the first reported occurrence of zirconolite in a kimberlite and the Mothae locality is the second to contain armalcolite. Both minerals are rare in lunar, meteoritic, and terrestrial rocks and their common association has been identified in only one lunar highland anorthosite (Haggerty, 1973). The ZrO_2 contents of kimberlitic zirconolites vary between 41.9 and 71.3 wt %;

those from the Arbarastkh and the Afrikanda massifs vary between 33.0 and 33.5 wt%; and the lunar examples have ZrO_2 contents between 29.8 - 41.3 wt%. For TiO_2 , the variations from these localities are 16.7 - 40.5 wt%, 30.4 - 31.6 wt% and 26.6 - 35.8 wt% respectively. The kimberlitic examples have ZrO_2 contents which are substantially higher than those from other sources, whereas TiO_2 is both higher and lower. Although we have yet to undertake a detailed REE study of the kimberlitic zirconolites, preliminary data do suggest that these are in low abundances in contrast to the USSR and to the lunar examples which are in the range 3.5 - 21.7 wt%. The divalent cations are relatively constant for all zirconolites, and these are in the range 14 - 18 wt%. The Ti/Zr ratios are of particular interest because of the data by Wark et al., (1973) who show that this ratio may be temperature sensitive. These authors estimate $T=1400 - 1450^\circ C$ for lunar zirconolites, which have Ti/Zr ratios between 1.07 - 1.52, based on experimental data which yields Ti/Zr at $1500^\circ C = 1.31$ and at $1300^\circ C = 2.75$. The kimberlitic zirconolites have average Ti:Zr ratios of 1.49, 0.94 and 0.41 which yields $T = 1450^\circ, 1550^\circ$ and $1625^\circ C$ respectively; these temperatures seem extraordinarily high but the Ti:Zr ratio may also be pressure sensitive.

Of the occurrences of armalcolite, which was first recognized in the lunar samples, those from the Apollo 16 site and one of the rutile-zircon assemblages from Mothae are the only known varieties which are Zr-bearing. Our analytical totals for the latter yield 95-97 wt% and we have tentatively ascribed the deficiency to REE. For all major and minor elements the Mothae example differs in one way or another from lunar Zr-armalcolites and one major distinction is that for values of $ZrO_2 \approx 6$ wt% all lunar armalcolites are both Ca and Cr enriched ($CaO = 3.0 - 3.5$ wt%; $Cr_2O_3 = 4.3 - 11.5$ wt%); the Mothae sample has $CaO = 1.5$ wt% and $Cr_2O_3 < 1\%$. High pressure experimental data (Lindsley et al., 1974; Friel et al., 1977) show that armalcolite is stable as a single phase at $1200^\circ C$ and 10kb, but decomposes to a more magnesian armalcolite plus $Geik-Ilm_{ss}$ plus rutile ($dT/dP = 20^\circ C/kb$); at 14 kb and $1200^\circ C$ this three phase assemblage is replaced by rutile plus $Geik-Ilm_{ss}$ ($dT/dP = 30^\circ C/kb$). With the addition of Zr, decomposition is 1-2 kb less than that of Zr-free armalcolite; but with the addition of Mg the end member $MgTi_2O_5$ is stable to at least 20 kb. It is significant that all three of the rutile-zircon assemblages we have examined contain abundant sigmoidal lenses of ilmenite (7-9 wt% MgO) and this is most likely the result of primary armalcolite decomposition (Haggerty 1975). The interface Zr-armalcolite must clearly have formed at $P < 12$ kb.

A comparison of kimberlitic reaction baddeleyites with baddeleyites that are present in association with lunar zirconolite show that there are both minor differences and similarities in oxide concentrations. The outstanding feature is that both types are titaniferous (3.68 - 7.93 wt% TiO_2), a property which is not displayed by primary baddeleyite in gabbros which have TiO_2 concentrations ~ 0.5 wt% (Keil and Fricker, 1974).

Other minerals which are present in the interface reaction zone are diopside, calcite and sphene. Because these minerals and zirconolite are all Ca-bearing we consider that the mechanism which triggered the reaction was most likely that of a carbonatitic liquid, because all other components necessary for the formation of these minerals are already present in ilmenite and in zircon. One possible reaction to yield zirconolite + baddeleyite + diopside is as follows:



Analytical data on zircons show, on average, that these are close to

stoichiometric ZrSiO_4 with minor concentrations of other elements. Although the associated interface baddeleyites are titanian-rich, an evaluation of the P-T conditions of zircon and baddeleyite can be made from available thermodynamic data on coexisting zircon and baddeleyite at high pressures (Nicholls et al., 1971), from the experimental system $\text{ZrO}_2\text{-SiO}_2$ at latm. (Butterman and Foster, 1967), the system $\text{CaO - ZrO}_2 - \text{TiO}_2$ at latm and $T = 1450 - 1550^\circ\text{C}$ (Coughanour et al., 1955), and from the occurrences of zircon decomposition to baddeleyite and SiO_2 in impact glasses (El Goresy, 1965; Kleinmann, 1969). From these data we note: (1) Zircon + baddeleyite can coexist in the diamond stability field at $T = 1327^\circ\text{C}$, $P = 55.7$ kb; (2) Zircon is stable at $T < 1676^\circ\text{C}$ in association with tetragonal ZrO_2 , and at $T < 1170^\circ\text{C}$ in association with monoclinic ZrO_2 (baddeleyite), (3) Two of the three zirconolite-bearing assemblages plot within the correct two phase region zirconolite + baddeleyite, whereas the third plots in the one phase titanian-baddeleyite_{ss} field in the system $\text{CaO - ZrO}_2 - \text{TiO}_2$. If the Ti/Zr ratios of the zirconolites are considered as being $T^\circ\text{C}$ -dependent, then those assemblages in the two phase region are compatible with $T = 1450 - 1550^\circ\text{C}$. For the third assemblage, Ti/Zr yields 1625°C and this too may be compatible but is beyond the limit of available experimental data; and (4) Impactite studies suggest that temperatures $> 1676^\circ\text{C}$ and $P \approx 7$ kb are required for the reaction zircon \rightarrow baddeleyite + cristobalite.

From the available pressure and temperature estimates on zirconolite, armalcolite, and baddeleyite we conclude that the formation of these minerals at rutile-zircon and ilmenite-zircon interfaces took place at $P < 12$ kb (based on armalcolite) and $T < 1200^\circ\text{C}$ (based on, but unconfirmed, monoclinic baddeleyite, Kresten and Fels, 1975); higher temperatures are also likely $1450 - 1650^\circ\text{C}$ (based on zirconolite) in which case tetragonal ZrO_2 should be present. Because CaO is a major component of the interface assemblages we consider the availability of a carbonatitic liquid an essential constituent to promote intercrystalline reaction between zircon and either ilmenite or rutile. A broader conclusion from this study is that the compositions of ilmenites associated with zircons are in a critical range of Mg and Cr; this range may well be constrained by a P-T relationship which is compatible with that of diamond stability.

References: Butterman and Foster (1967). *Amer. Min.* 52, 880; Coughanour et al., (1955). *J. Res. Nat. Bur. Stds.* 54, 191; El Goresy (1965). *J. Geophys. Res.* 70, 3453; Friel et al., (1977). *Geochim. Cosmochim. Acta* 41, 403; Haggerty (1973) *ibid.* Suppl 4, 777; Haggerty (1975). *Phys. Chem. Earth*, 9, 295; Keil and Fricker (1974). *Amer. Min.* 59, 249; Kleinmann (1969). *EPSL* 5, 497; Kresten and Fels (1975). *Mineral. Deposita*. 10, 47; Nicholls et al., (1971). *Contrib. Min. Pet.* 33, 1; Wark et al., (1973). *Proc. L. S. C. IV.* Houston 764.