

## Intra- and Inter-Mineral Oxygen Isotope Variations in Kimberlitic Zircons

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Studies on the formation of diamonds have emphasized their complex and extended growth history. Evidence has come from the  $\delta^{13}\text{C}$  and trace element record of diamonds, the minerals and fluids that they include, and the state of nitrogen aggregation in them.

Fluids present during the formation of diamonds also have left their signature in kimberlitic zircons. In kimberlites zircons are found as separate discrete minerals, occurring at about the same concentration level as diamonds, as accessories in metasomatized veined harzburgite xenoliths, and as inclusions in diamonds. Age determinations on all three zircon types have been reported in the literature and have led to the conclusion that in some kimberlite environments zircon formation occurred over more than 3 Ga, terminating shortly before kimberlite eruption.

The time span recorded in zircons is consistent with the degree of nitrogen aggregation observed in diamonds. Therefore, it can be suggested that diamonds and zircons in kimberlites were formed in several distinct growth environments and over a long time span. The last phase in the formation of both minerals could occur shortly prior to kimberlite eruption, and the fluids responsible for their growth might well also be responsible for the formation of the kimberlite magma. The picture which hence emerges is one in which fluids moving through the mantle caused metasomatism, diamond and zircon formation over an extended period and culminated in the formation and eruption of the kimberlite magma.

We are investigating currently whether this hypothesis can be supported and documented, in greater detail, by examining jointly the radiogenic and oxygen isotope record of kimberlitic zircons from several kimberlites. Our sampling and analytical strategies are governed by the following observations: 1. In one kimberlite several generations of zircons can occur. 2. Within individual zircon grains variations in chemistry can be expected. 3. Individual zircon grains can contain radiogenic lead of different provenances.

Currently we are investigating a suite of zircons (64) from Orapa, Botswana. The minerals were recovered as part of the diamond separation from the host kimberlite. The kimberlite was crushed, and underwent a heavy mineral separation employing an Fe-rich slurry. Subsequently the heavy mineral separate was treated with HF, and the zircons were recovered by X-ray-fluorescence along with diamonds.

The zircons show a multitude of shapes and coloring. Fluorescence colors vary from white grey through light blue grey to yellow orange and brownish orange. The internal fracturing of the grains varies from intense to barely detectable. The appearance of the grains suggests the presence of several populations. The differences in fluorescence reflect different trace element concentrations. The size and shape of the zircon grains are determined by the process of crystallization, subsequent abrasion and fragmentation during transport in the kimberlite eruption as well as possible crushing in the milling process. The first two of these factors can potentially differ for separate zircon generations. Some grains are well rounded and have very regular surfaces, in some cases these are slightly pitted, and have the appearance of pebbles. Some surfaces appear glassy while others show

a white overgrowth (baddeleyite). Sharp edges suggesting breakage are very common. Earlier studies have demonstrated that different diamond generations can be recognized in a kimberlite. However, the documentation of the zircon morphological characteristics was probably not detailed enough to permit the detection of links between the shape of zircons and their geochemical properties. We have used different measures to characterize the grain morphology in order to be able to test for the existence such links. If connections between the zircon appearance and geochemistry can be discovered, these would aid in the elucidation of the history of the mineral and could guide future sampling strategies for kimberlitic zircon studies.

The weight of the samples ranges from 5.64 mg to 576.1 mg; its sampling frequency distribution has a mode around 125 mg and is skewed toward high values. From the weight of the sample and the density of the mineral, one may compute the radius of an equivalent sphere which has the same mass as the mineral grain. The radii vary from 0.31 to 0.07 cm; their sampling frequency distribution may be bimodal.

The sphericity of each grain was calculated from the ratio of the radius of the equivalent sphere to the measured radius of the circumscribing sphere, (Krumbein and Pettijohn, 1938). The sphericity of the zircons is normally distributed with a mean of 0.71 and a standard deviation (std.) of 0.1. The zircons can be classified by sphericity into: high (more than 1 std. above the mean), average (one std. around the mean), and low (below one std. of the mean). The radius of the equivalent sphere and the sphericity are correlated. Larger grains have higher sphericity. This could be explainable if the smaller grains represented mainly fragments of larger grains. In this case the roundness of the smaller grains would be expected to be lower. Roundness was classified according to the classes of Folk (1955) (Dietrich R.V. et al., 1982 ). No particular relationship between roundness and weight of the samples or the estimated preserved volume of the samples was found. This is taken as an indication that the smaller grains are not simply the result of the break up of larger grains.

Zingg (1935) classified grain shapes on the basis of the ratios of the major axes (A, B, and C). The major axes were measured for each grain. About half of the grains fall into Zingg's class I (spherical) 25% into class IV (rod-like), 14% into class I (disc-shaped) and 11% into class III (bladed).

The maximum radius of curvature of each grain was also estimated; its frequency distribution shows a peak at 0.8 cm with skewness toward smaller radii. From the largest estimated diameter the original volume of the zircon grain can be computed and compared to the volume of the equivalent sphere, evaluated from the mass of the grain. This yields an estimate of the fraction of original zircon volume which remains. The maximum of the preserved volume is about 80% and the minimum is close to zero. The frequency distribution of the estimated remaining volume may be bimodal with a major mode at about 20% and a minor one between 50 and 70%. This suggests that most of the zircon samples represent only a small fraction of the original grain.

The length of the major axes, A, B and C, may be used to compute the volume of a corresponding ellipsoid which can be compared with the actual volume of the grain. This ratio has been called ellipsoidicity. The ellipsoidicity values, determined for the grains, range from about 0.7 to 1.7. Values larger than one indicate that the computed volume is in excess of an ellipsoid of dimensions  $A/2$   $B/2$   $C/2$  (half major axes), which is the case if the grains were box-shaped rather than ellipsoidal. About 22% of the grains are well represented by an ellipsoid, 66% show an excess computed volume and 12% of the zircons have volumes that are not well represented by an

ellipsoid. Half of the last group show a high degree of sphericity.

In view of the reported concentration variations of U and Th in zircons, the suggested presence of two generations of radiogenic lead in some zircons, and our plan to determine the Pb and Hf isotopic composition of zircons to collect age information, it was thought prudent to examine the oxygen isotopic composition of individual zircons in some detail. Zircons retain the oxygen isotope record well, even at elevated temperatures (Valley et al, 1994, Gilliam and Valley, 1997).

Detailed oxygen isotope studies (127 analyses on six grains) have been carried out using a laser fluorination line. Analysis of variance of the collected data demonstrates that significant differences in oxygen isotopic composition within and among zircon grains exist. The internal variability is characterized by an average standard deviation of 0.38 o/oo. The oxygen isotope variations across the grains are not random, segments of distinct  $\delta^{18}\text{O}$  values can be discerned.

The mean weighted isotopic compositions of the grains lie between 5.42 and 5.84 o/oo vs. SMOW and fall in the range reported by Schulze et al. ( 1996 ). Two of the samples have isotopic compositions of 5.42 and 5.35 respectively while the isotopic composition of the remaining four lies between 5.64 and 5.84. The two samples with lower  $\delta^{18}\text{O}$  values have the highest sphericities of the zircons analyzed.

The data collected to date on the Orapa zircons indicate that on the basis of their shape and oxygen isotope data separate populations can be recognized. The internal oxygen isotope variability is larger than expected and indicates that individual zircon grains have experienced more than one stage of growth.

## References

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