DETERMINATION OF FERRIC IRON VARIATION WITHIN ZONED GARNETS FROM THE WESSELTON KIMBERLITE USING A MÖSSBAUER MILLIPROBE

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The study of zoning profiles can provide extensive information regarding chemical processes that occurred during formation of the mineral assemblage. Tools such as the electron, proton and ion microprobes provide detailed information on major and trace element chemical compositions, but are unable to distinguish between different oxidation states, for example between ferrous and ferric iron. Such information is crucial to determination of redox conditions during mineral formation, which can have significant effects on many different processes (element partitioning, diffusivity, partial melting reactions, etc.). Mössbauer spectroscopy is an ideal method to distinguish between ferrous and ferric iron, and can provide an estimate of their relative abundances in individual phases. Normally experiments are performed on samples with ca. 1 cm diameter, but a recently developed technique enables routine Mössbauer measurements to be performed on samples with diameters of 500 μm or less.

The technique, also known as the Mössbauer milliprobe, is relatively simple and requires only a small amount of equipment in addition to a conventional Mössbauer spectrometer (full details of the method are given in McCammon et al., 1991). To obtain adequate count rates, the conventional Mössbauer source (typical specific activity 100 mCi/cm^2) is replaced by a point source (specific activity $\geq$ 2000 mCi/cm^2), which can be obtained commercially at a cost similar to conventional sources. The gamma rays are collimated to the selected sample diameter using a Pb shield, and the source-sample distance is reduced to < 5 mm. The latter results in a solid angle similar to conventional experiments, and hence a similar count rate. Since the signal quality depends on absorber density (measured in mg Fe/cm^2) and not the total amount of iron in the sample, the reduction in sample size has no effect on the effective thickness of the absorber. When electronic absorption due to heavier elements is low and the point source is relatively new (< 1 year old), high quality Mössbauer spectra (comparable to conventional measurements) can be recorded on samples with diameters as small as 100 μm (see McCammon, 1994).
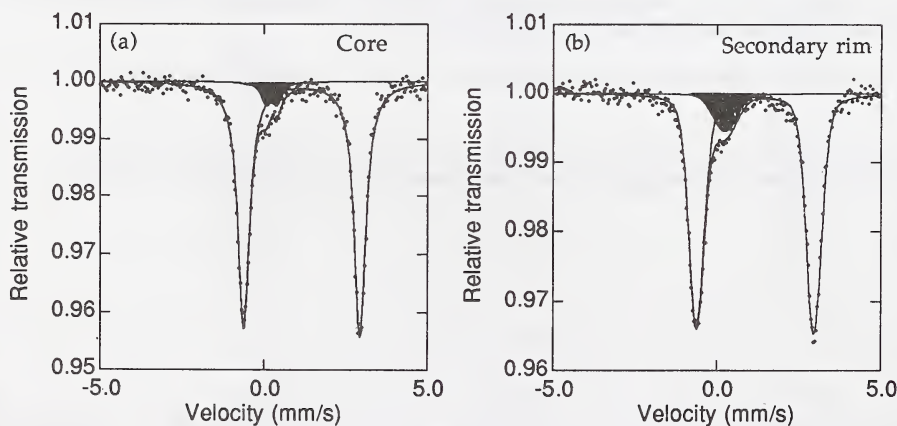

Fig. 1. Mössbauer spectra of garnet #940 showing the difference between core and rim for sample diameter of 400 μm. The subspectrum corresponding to Fe^{3+} is shaded black.

Garnets from the Wesselton kimberlite were mounted in epoxy disks and polished for preliminary analysis using the electron and proton microprobes. Zoning patterns were studied using the electron microprobe at CSIRO and Macquarie University (Australia) and using the proton microprobe at CSIRO (Australia). X-ray maps were prepared and used to locate interesting areas for Mössbauer analysis. Samples were prepared for Mössbauer spectroscopy by reducing the disk thickness to ca. 300 μm, which gives an iron density of ca. 5 mg Fe/cm^2 based on the chemical composition of the garnet. Note that since Mössbauer spectroscopy is a non-destructive technique, the polished surfaces of the disks are preserved for further analysis. To isolate different parts of the sample, a piece of 250 μm thick Ta foil drilled with a 400 μm diameter hole was positioned such that the hole was centred on the area to be analysed. X-ray maps showing differences in Ca and Ti composition were invaluable for route-finding. Mössbauer spectra were recorded at various parts on four samples (#933, #937, #940, #951) at room temperature over periods ranging from 1-5 days. The quality of the spectra was sufficiently high that robust determinations of Fe^{3+}/$\sum$Fe could be made. Typical spectra are shown in Fig. 1.

The phlogopite-harzburgite xenoliths from the Wesselton kimberlite contain garnets with zoning that ranges from low-Ca harzburgitic cores to rims with lherzolitic Ca-Cr relations. Increase in Ca and decrease in Cr and Mg is accompanied by increases in Zr, Y and Ti. There are secondary replacement rims on some of the garnets which consist of low Ca and Cr, but high Mg and Ti. For further details about the samples, see Griffin et al. Four garnets were studied:

#933   A single grain ca. 1.6 x 2.5 mm, surrounded by olivine and orthopyroxene. Composition varies somewhat irregularly from core to rim, and the grain is surrounded by a secondary garnet rim that varies from 100-150 μm in thickness.

#937   A single ovoid grain, of which an area ca. 1.7 mm across is available for analysis. It is surrounded by olivine. There is pronounced zoning from core to rim, and a secondary replacement rim of up to 500 μm in thickness.

#940   A single grain ca. 3.5 mm in the long diameter, surrounded by olivine and orthopyroxene. The primary garnet grain shows broad symmetrical zoning from core to rim, and on one side there is a 50-75 μm zone of secondary replacement garnet.

#951   An incomplete grain ca. 3 mm in diameter, surrounded by olivine and orthopyroxene. The relatively homogeneous core is surrounded by a rim of distinctly different composition.

The electron microprobe analysis from garnet #940 is given in Table 1.

Mössbauer results for Fe^{3+}/$\sum$Fe values are given in Table 2. In most cases the spectrum of only one phase was recorded, but in a few instances the spectra contained contributions from more than

Table 1. Electron microprobe analyses for garnet #940

	core	rim	secondary rim
SiO$_2$	41.17	40.83	41.71
TiO$_2$	0.03	0.18	0.16
Al$_2$O$_3$	17.51	17.72	18.21
Cr$_2$O$_3$	8.42	7.66	6.98
FeO	5.70	5.54	5.44
MnO	0.14	0.31	0.22
MgO	22.78	21.86	22.63
CaO	3.45	4.63	3.73
Na$_2$O	0.02	0.07	0.03
$\sum$	99.22	98.80	99.11

Table 2. $Fe^{3+}/\sum Fe$ values for zoned garnets and orthopyroxene from Wesselton kimberlite

garnet number	core	rim	secondary rim	opx
#951	5.9(8) 5.3(7)	6.1(6) *6.6(10)* *72%*		6.6(7)
#937	8.1(12)	*10.7(34)* *89%*	*10.5(26)* *63%*	
#933	6.2(6)	*11.8(24)* *64%*	11.9(5) 10.4(5)	4.0(13)
#940	6.0(5)	7.1(5)	*7.7(37)* *51%*	

Numbers in italics represent bulk $Fe^{3+}/\sum Fe$ values measured from mixed phase assemblages, with the relative proportion of garnet in the mixed phase indicated in %.
Standard deviations of the last digit are given in parentheses.

one phase. In this case only bulk $Fe^{3+}/\sum Fe$ values could be determined, and must be regarded as tentative at this point due to ambiguities in fitting. This problem will be addressed in further experiments, as well as to quantify the uncertainties due to preferred orientation (effectively a single crystal Mössbauer experiment).

The zoning pattern of the garnets is believed to be the result of a multistage metasomatic alteration that included diffusional modification of existing harzburgitic garnet, overgrowth of new lherzolitic garnet, and replacement of lherzolitic rims by a later harzburgitic garnet (Griffin et al.). We have been able to determine the change in $Fe^{3+}/\sum Fe$ for each of the zoning events. Results from garnets #940 and #951 indicate that there is little change in $Fe^{3+}/\sum Fe$ of the garnet during the first two events, while results from garnet #933 show that there is a large increase in $Fe^{3+}/\sum Fe$ during the latter event producing the secondary rim. The $Fe^{3+}/\sum Fe$ values can be used in conjunction with pressure, temperature, composition and activity data to calculate fO_2 (e.g. Luth et al., 1990). Data analysis is still underway. These results provide constraints on redox conditions existing during chemical evolution of the Wesselton kimberlite prior to eruption, with implications for related topics such as diamond preservation.

References

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