DETERMINATION OF THE FERRIC IRON CONTENT OF DIAMOND INCLUSIONS FROM GEORGE CREEK USING MÖSSBAUER SPECTROSCOPY WITH IMPLICATIONS FOR MANTLE OXYGEN FUGACITY DURING DIAMOND GENESIS

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Inclusions in diamond can provide chemical and mineralogical information about the source region and the genesis of diamond. Many tools are available to obtain detailed information on major and trace element chemical compositions of inclusions, but none are able to distinguish between different oxidation states, for example between Fe²⁺ and Fe³⁺, which is crucial to determination of redox conditions during mineral formation. An understanding of the relations between redox conditions and the thermal, tectonic, magmatic and metasomatic evolution of the mantle is needed to explain such processes as diamond formation and kimberlite magmatism. Mössbauer spectroscopy is an ideal method to distinguish between Fe²⁺ and Fe³⁺, 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 as small as 100 µm.

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/cm²) is replaced by a point source (specific activity \geq 2000 mCi/cm²), 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/cm²) 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



Fig. 1. Mössbauer spectrum of garnet GC020B. The sample diameter is ca. 200 μ m., and the subspectrum corresponding to Fe³⁺ is shaded black.

recorded on samples with diameters as small as $100 \ \mu m$ (see McCammon, 1994).

The George Creek diamonds were taken from the K1 (section 28) kimberlite located in the State Line District of the Colorado Wyoming Province. Previous studies of mantle xenoliths and diamond inclusions from the State Line region have indicated considerable heterogeneity of the lithospheric mantle sampled by the kimberlite eruptions (see Eggler et al., 1988). The inclusions from George Creek are dominantly of the eclogitic paragenesis. Black rosettes of graphite are common, followed in abundance by clinopyroxene, garnet, rutile and ilmenite, and rare moissanite and quartz/coesite (one inclusion each). Many of the garnets recovered contain tiny ilmenite inclusions within the garnet, which has never been reported before. Estimates using the garnet-cpx thermometer of Ellis and Green (1979) yield

temperatures of 1071-1178 °C at 50 kb for non-touching pairs, while touching pairs of garnet-cpx and opx-cpx yield lower temperatures of 912-977°C using the Ellis and Green (1979) and Bertrand and Mercier (1985) methods. The most striking feature of George Creek diamonds is the presence of two diamond growth generations which formed under different conditions. Anomalous cathodoluminescence colours and infrared absorption spectra reveal a generation containing sub-microscopic inclusions of high pressure CO2, and complex intergrowth relations between the CO₂-bearing and CO₂-free generations.

After detailed description of the host diamond, mineral inclusions were liberated and mounted in epoxy for electron microprobe analysis, which was performed at the University of Cape Town. For Mössbauer measurements, inclusions were removed from the epoxy and mounted using

specimen grain size (diameter) assemblage	GC007F 200 μm gt-cnx-br	GC020B 250 µm	GC055C 100 µm gt-(gt-il)-cpx	
	gt-cpx-oi	groph	gt-(gt-II)-opx	
weight percent of oxid	des:			
SiO2	39.5	39.5	39.2	
TiO	0.89	0.79	0.63	
AlpOp	21.6	21.5	21.5	
Cr_2O_2	n d	n d	n d	
FeO	18.6	17.51	17.65	
FeoOo*	0.0	0.77	1 27	
MnO	0.31	0.41	0.37	
MaO	8 91	9.89	8 23	
CaO	0.70	9.25	11 1	
NaoO	0.31	0.21	0.14	
K _a O	0.51 n d	0.21 n d	0.14 n d	
R20	n.u.	n.u.	n.a.	
Σ	99.22	99.83	99.11	
-				
cation proportions bas	sed on 12 oxygen	atoms:		
Si	2.996	2.983	2.987	
Ti	0.051	0.045	0.036	
Al	1.933	1.914	1.931	
Cr	n.d.	n.d.	n.d.	
Fe ²⁺	1.180	1.106	1.116	
Fe ³⁺	0.000	0.044	0.044	
Mn	0.020	0.026	0.024	
Mg	1.008	1.113	0.935	
Ca	0.789	0.748	0.906	
Na	0.045	0.029	0.020	
K	n.d.	n.d.	n.d.	
4				
Σ	8.022	8.008	7.999	
Matt	46.07	50.16	45 50	
$Fe^{3+}/\Sigma Fe^{(\%)}$	0.07	3 8+0 7	6 1+2 2	

Table 1. Electron microprobe analyses for garnet inclusions measured using Mössbauer spectroscopy

gt: garnet; cpx: clinopyroxene; br: black rosette of graphite; il: ilmenite; n.d.: not detected *recalculated based on Fe³⁺/ Σ Fe determined from Mössbauer analysis

cellophane tape within a 200 μ m diameter hole drilled in 250 μ m thick Ta foil. The foil acts as a collimator, absorbing more than 99% of the 14.4 keV gamma rays. Absorber densities based on the thickness of the samples and chemical compositions are ca. 5 mg Fe/cm² for the garnet and 1.5 mg Fe/cm² for the clinopyroxene inclusions. These absorber densities are comparable to those used in conventional experiments. Mössbauer spectra were collected at room temperature over periods ranging from 2-4 weeks, where the relatively long count times were required due to the old age of the radioactive source (> 1 year). The remainder of inclusions in the George Creek suite will be measured after delivery of a new radioactive source. The quality of spectra was sufficiently high that robust determinations of Fe³⁺/ Σ Fe could be made. The Mössbauer spectrum of sample GC020B garnet is shown in Fig. 1, and Fe³⁺/ Σ Fe values measured from the garnet inclusions are listed in Table 1, accompanied by the chemical composition data.

While Fe³⁺/ Σ Fe values of the garnet may reflect fO2 conditions, they are also a function of pressure, temperature and composition of the coexisting phases. The bimineralic eclogite system lacks sufficient constraints to allow direct determination of f02, but systematic studies in related systems as well as experimental investigations will assist in constraining knowledge of the redox conditions during diamond formation. Compositions of other minerals (e.g. ilmenite) would provide complementary information. A comprehensive model to explain the genesis and subsequent mantle residence history of George Creek diamonds would combine information from inclusion compositions, temperature estimates from inclusions and nitrogen aggregation state, cathodoluminescence and physical characteristics. The presence of at least two diamond growth generations, both of which have experienced considerable etching, resorption and deformation, indicates that conditions in the mantle fluctuated between conditions conducive to, and detrimental to diamond formation/preservation. Changing redox conditions have played a significant role in the evolution of the mantle, and may also have distinguished distinct mantle domains of different composition and history. Processes such as melt extraction, metasomatism, and recycling of oceanic material by subduction would have a profound effect on the redox conditions of the mantle, and need to be constrained if the products of mantle magmatism are to be understood.

References

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