

# <sup>57</sup>Fe Mössbauer spectroscopy used to develop understanding of a diamond preservation index model

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**Abstract** <sup>57</sup>Fe Mössbauer spectroscopy has provided precise and accurate iron redox ratios  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in ilmenite,  $\text{FeTiO}_3$ , found within kimberlite samples from the Catoca and Camatxia kimberlite pipes from N.E. Angola. Ilmenite is one of the key indicator minerals for diamond survival and it is also one of the iron-bearing minerals with iron naturally occurring in one or both of the oxidation states  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . For this reason it is a good indicator for studying oxygen fugacities ( $f\text{O}_2$ ) in mineral samples, which can then be related to iron redox ratios,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . In this paper we demonstrate that the oxidation state of the ilmenite mineral inclusion from sampled kimberlite rock is a key indicator of the oxidation state of the host kimberlite assemblage, which in turn determines the genesis of diamond, grade variation and diamond quality. Ilmenite samples from the two different diamondiferous kimberlite localities (Catoca and Camatxia) in the Lucapa graben, N.E. Angola, were studied using Mössbauer spectroscopy and X-Ray Diffractometry, in order to infer the oxidation state of their source regions in the mantle, oxygen partial pressure and diamond preservation conditions. The iron redox ratios, obtained using Mössbauer spectroscopy, show that the Catoca diamond kimberlite is more oxidised than kimberlite found in the Camatxia pipe, which is associated within the same geological tectonic structure. Here we demonstrate that <sup>57</sup>Fe Mössbauer spectroscopy can assist geologists and mining engineers to effectively evaluate and determine whether kimberlite deposits are economically feasible for diamond mining.

**Keywords** Ilmenite · Mössbauer · Diamond · Kimberlite

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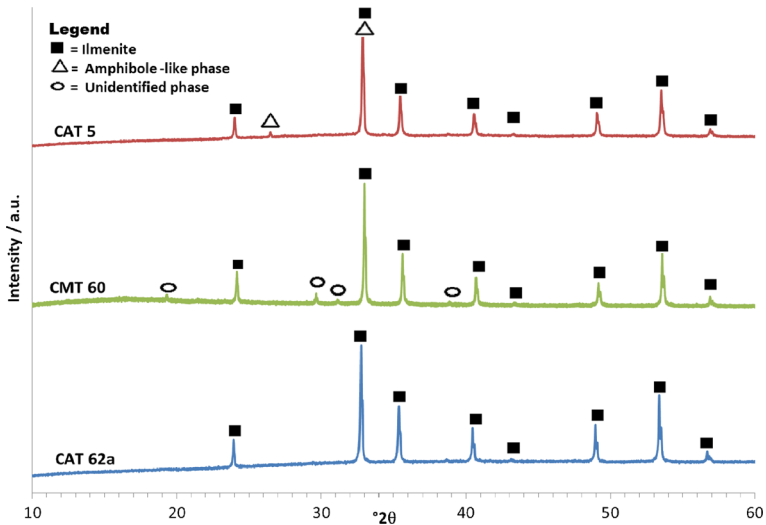
## 1 Introduction

In terms of the determination of the diamond preservation index within sampled kimberlite mantles, it is crucial to consider the use of a precise method to determine the oxidation state and thereby estimate the oxygen fugacity or partial pressure present during the formation and transportation of key diamond indicator minerals. Ilmenites with high  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios are associated with higher diamond contents than those with lower  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios. In kimberlite pipes, ilmenites with high  $\text{Fe}^{3+}$  are also associated with low MgO contents [1, 2]. For this study we have considered ilmenite samples from two different diamondiferous kimberlite localities (Catoca and Camatxia) in the Lucapa graben, NE Angola, using  $^{57}\text{Fe}$  Mössbauer spectroscopy and X-Ray Diffractometry, in order to infer the oxidation state of their source regions in the mantle, oxygen fugacity and diamond preservation conditions.

## 2 Samples and experimental procedures

For this research, a mineral assemblage of ilmenite in diamondiferous kimberlite rocks was studied using Mössbauer spectroscopy and X-Ray Diffractometry. Three samples, obtained from two different kimberlite pipes (CAT62a and CAT5 from the Catoca pipe and CMG60 from the Camatxia pipe) from the Lunda Province in NE Angola were studied. Ilmenite samples were separated from the host kimberlite rock, which was obtained from different depths from the two kimberlite pipes. In each case this separation was carried out by first crushing representative kimberlite rock samples and sieving to  $\leq 1$  mm using a hand-picked method to achieve very high visual purity, using an optical microscope and tweezers to visually separate the samples from the crushed surrounding rock. This separation proved highly successful and very little contaminant mineral phases were found to be attached to these separated particles. Once separation was completed, the ilmenite samples were crushed and approximately 100 mg of powdered ilmenite (with particle size  $<75 \mu\text{m}$ ) was mixed with 40–50 mg of graphite powder in order to fill a Mössbauer absorber disc to obtain a Mössbauer sample. The quantities used are a similar amount of sample as those described by Sobolev et al. [3] who stated that Mössbauer spectroscopy requires relatively large amounts of sample ( $\geq 50$  mg containing 10 wt% FeO). At the present time Mössbauer spectroscopy is the only reliable method for determining accurate  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios in samples prepared in such a way [3–6]. This ratio is important for determination of oxidation state/s of iron in ilmenite, and consequently for estimating oxygen fugacity or partial pressure during ilmenite formation and transport [4, 7, 8], and thereby for determination of a diamond preservation index within sampled kimberlites.

Mössbauer spectra of the samples of powdered homogeneous ilmenite from diamondiferous kimberlite were measured over a velocity range of  $\pm 12 \text{ mm s}^{-1}$  in order to detect any possible presence of hyperfine splitting, which, if present, would be associated with potential contaminant iron oxides minerals such as magnetite or haematite. A calibration was performed using a natural  $\alpha\text{Fe}$  foil over the same velocity range. All centre shift and quadrupole splitting values are reported relative to this standard.  $^{57}\text{Fe}$  Mössbauer spectroscopy was performed at room temperature of 293 K. The room-temperature Mössbauer spectroscopic measurements were made using a 25 mCi  $^{57}\text{Co}$  source in a Rh matrix, which was driven at constant acceleration. X-Ray Diffractometry was performed on the ilmenite samples prior to preparation for Mössbauer spectroscopy using a Panalytical Empyrian



**Fig. 1** X-Ray Diffraction patterns of selected ilmenite samples obtained from crushed kimberlite rock

X-Ray diffractometer equipped with a sample spinner, diffracted-beam and using Cu  $K\alpha$  radiation. Powder specimens were measured between 10 and 60° $\theta$  (Fig. 1). Data analysis was carried out using the Panalytical High Score Plus program

### 3 Results and discussion

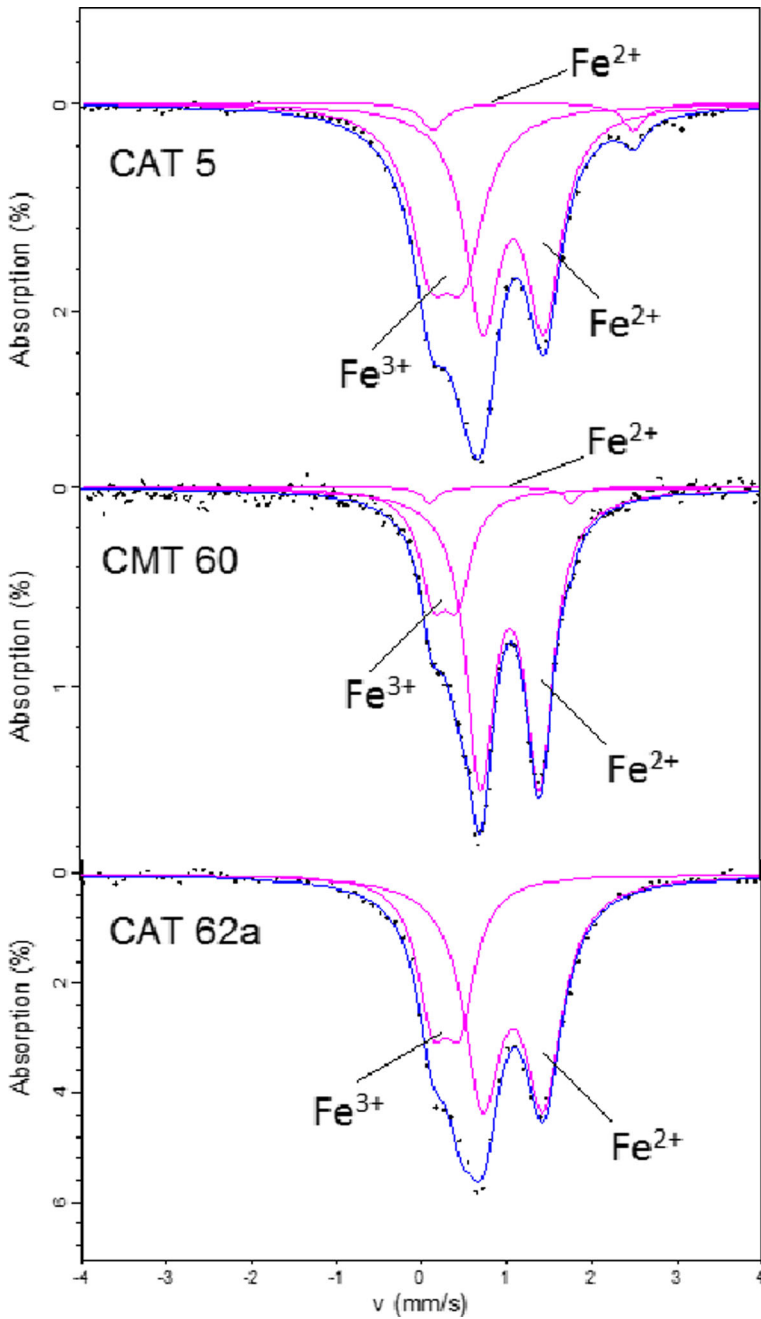
In order to confirm the phase assemblages present in the studied diamondiferous ilmenite samples, and prior to Mössbauer spectroscopy analysis being carried out, the samples were evaluated by powder X-Ray Diffractometry (XRD) (Fig. 1). As illustrated in Fig. 1, the majority of our XRD analysis confirms ilmenite as the only major phase present in the studied samples. Ilmenite is a crucial indicator mineral for diamond preservation conditions within the context of economically-viable diamondiferous kimberlite exploration. Each crystalline solid has its own characteristic X-ray diffraction pattern which can be used as a fingerprint for its identification [9]. Results (Fig. 1) show that ilmenite is by far the most abundant phase in all three of the samples studied. Sample CAT62a is essentially phase-pure, and the other samples contain only very low levels of an amphibole-like phase (CAT5) and an unidentified phase (CMT60).

The analysed  $^{57}\text{Fe}$  Mössbauer results are tabulated in Table 1 and spectra are shown in Fig. 2. The two sampled and studied kimberlite pipes, Catoca and Camatxia, are associated within the same geological tectonic structure (Lucapa graben) but the studied ilmenite samples from these primary diamond pipes show significant differences upon analysis. Differences in the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios for the different samples obtained from Mössbauer spectroscopy show that, in general, the ilmenite in samples CAT5 and CAT62a is more oxidised than the ilmenite in sample CMT60. This indicates that a more oxidising environment occurred during formation and eruption in the Catoca pipe than in the Camatxia pipe and this is associated with higher oxygen fugacities [2, 4, 10] which can have a nega-

**Table 1** Room temperature hyperfine parameters of mineral inclusions determined from Mössbauer spectroscopy, (CS =centre shift; QS = quadrupole splitting, W = half width half maximum line width)

Sample	Fe <sup>2+</sup>				Fe <sup>3+</sup>				Redox ratio
	CS mm/s	QS mm/s	W mm/s	Area %	CS mm/s	QS mm/s	W mm/s	Area %	
Analysed samples	±0.02	±0.02	±0.02	±1	±0.02	±0.02	±0.02	±1	Fe <sup>2+</sup> /Fe <sup>3+</sup>
CAT 62a (Ilmenite phase)	1.07	0.71	0.26	67.4	0.28	0.32	0.22	32.6	2.06
CMT 60 (Ilmenite phase)	1.05	0.69	0.19	73.6	0.30	0.28	0.19	24.1	3.05
CMT 60 (Amphibole phase)	0.93	1.66	0.19	2.3	–	–	–	–	–
CAT 5 (Ilmenite phase)	1.08	0.71	0.24	53.7	0.31	0.39	0.29	41.9	1.28
CAT5 (Amphibole phase)	1.32	2.36	0.15	4.4	–	–	–	–	–

tive impact on diamond survival criteria. In contrast the Camatxia kimberlite pipe exhibits a higher value of Fe<sup>2+</sup>/Fe<sup>3+</sup>, showing a more reduced environment which is indicative of better diamond preservation conditions. Whilst the analysed redox ratios of the two Catoca samples differed, both are indicative of considerably more oxidising conditions than from the Catoca pipe. These results are consistent with the first authors' personal experience of diamond exploration results from these pipes, which show that diamond preservation in the Camatxia pipe is superior to that in the Catoca pipe. Ilmenite was selected for this research because of the variable oxidation state of iron in natural ilmenite mineral inclusions [11]. Therefore ilmenite is a good indicator of the oxidation state of iron in the host kimberlite assemblage, which in turn indicates the  $fO_2$  during ascent and hence the origin and diamond preservation conditions [1, 12, 13]. By using homogenous crystals of ilmenite from different diamond pipes, our Mössbauer spectroscopy results indicate a lower  $fO_2$  environment for sample CMT60 from the Camatxia pipe, which is dominated by Fe<sup>2+</sup> and which occurs in a moderate to good diamond preservation zone. In contrast a more oxidising environment is found in the Catoca diamondiferous kimberlite (CAT 5 and CAT 62a) with increased Fe<sup>3+</sup>, and is consistent with the poor diamond preservation conditions which have been observed for this pipe. Based on these facts, we have concluded that under these conditions, diamond resorption is normally high in the Catoca CAT5 and CAT62a samples due to the elevated oxygen fugacity within this kimberlite pipe [4, 14, 15]. This conclusion is qualitatively in agreement with the work of Nowicki et al. [2, 10] who used perovskite as an oxygen barometer, and illustrates that ilmenites with high Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios are associated with higher diamond contents than those with a lower fraction of ferric iron (Fe<sup>3+</sup>). This demonstrates that resorption of diamonds is high when the mantle or kimberlite magma contains ilmenites with high Fe<sup>3+</sup> contents, which are themselves indicative of higher oxygen fugacities. It also provides further evidence which demonstrates the feasibility of applying <sup>57</sup>Fe Mössbauer spectroscopy to economically-feasible diamond exploration.



**Fig. 2** Fitted room temperature Mössbauer spectra of ilmenite inclusion samples from diamondiferous pipes Catoca (CAT-5, CAT 62a) and Camatxia (CMT 60). Data were fitted with  $Fe^{2+}$  and  $Fe^{3+}$  doublets as shown

## 4 Conclusions

Our results demonstrate that the observed diamond grade variation and abundance within Lucapa graben (NE Angola) is associated with factors that include oxygen fugacity, and that this can be successfully measured by studying ilmenite inclusions in the host kimberlite rock using  $^{57}\text{Fe}$  Mössbauer spectroscopy. By using hand-picked crystals of ilmenite from different diamond pipes, our Mössbauer spectroscopy results indicate a lower  $f\text{O}_2$  environment for sample CMT60 from the Camatxia pipe, which is dominated by  $\text{Fe}^{2+}$  and which occurs in a moderate-to-good diamond preservation zone. In contrast, a more oxidising environment is found in the Catoca diamondiferous kimberlite samples (CAT5 and CAT 62a) which exhibit increased levels of  $\text{Fe}^{3+}$ . This is consistent with the poor diamond preservation conditions which have been observed for the Catoca pipe. This evidence is central to the conclusion that diamond resorption is higher in Catoca kimberlite than in the Camatxia kimberlite. Our findings give further support for ilmenite being used as an indicator mineral for diamond preservation conditions.

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