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Precise Mössbauer milliprobe determination of ferric iron in rock-forming minerals and limitations of electron microprobe analysis

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ABSTRACT

For estimations of *P-T* conditions of igneous and metamorphic rocks, Fe^{3+} in coexisting minerals is either assumed to be zero or is calculated from electron microprobe analyses (EMPA) based upon stoichiometry and charge balance. Geothermobarometers that involve Fe^{2+}-Mg^{2+} exchange can be significantly affected by either neglecting Fe^{3+} or using incorrect values. Ratios of $Fe^{3+}/\Sigma Fe$ in garnet and clinopyroxene measured by a Mössbauer milliprobe were compared to those calculated from EMPA of garnet and clinopyroxene from eclogite xenoliths from the Udachnaya kimberlite in Yakutia. The effects of Fe^{3+} contents in garnet and clinopyroxene on temperature estimations were evaluated.

The following $Fe^{3+}/\Sigma Fe$ (in at%) values were obtained (EMPA/Mössbauer): Gt = 9.4/6.0; 11.5/7.0; 19.4/16.0; and 24.7/15.0; Cpx = 22.0/22.9; 34.2/22.0. The effects of Fe^{3+} in clinopyroxenes on calculated temperatures are illustrated by taking eclogitic clinopyroxene compositions and changing contents of certain elements within the range of standard deviations for EMPA of those particular elements. Increasing Na_2O contents from 5.67 to 5.74 wt% (<2.0% relative error) would lead to increasing $Fe^{3+}/\Sigma Fe$ from 31.6 to 47.1%, thereby decreasing the calculated temperature from 1026 to 941 °C. Various $Fe^{3+}/\Sigma Fe$ values for garnet and clinopyroxene were also tested for their effects on calculated temperatures: for clinopyroxene, *T* decreases with increasing $Fe^{3+}/\Sigma Fe$ whereas for garnet, *T* increases with increasing $Fe^{3+}/\Sigma Fe$. This compensation effect between garnet and clinopyroxene moderates the variation in temperature estimations of eclogites based on Fe^{3+} corrected vs. uncorrected microprobe analyses.

Little correlation exists between EMPA-calculated and Mössbauer-measured $Fe^{3+}/\Sigma Fe$ values for these mantle-derived garnets and clinopyroxenes. Even a small relative error in Fe^{3+} may significantly change calculated temperatures of equilibration, seriously affecting petrologic interpretations. In particular, uncertainty in Fe^{3+} calculated from EMPA of silicate minerals leads to serious questions with regard to K_D values obtained from natural assemblages.

INTRODUCTION

Several chemical elements can occur in multiple oxidation states in both terrestrial and extraterrestrial minerals. Iron is one example of a multivalent element that is a common constituent of silicate minerals in igneous and metamorphic rocks. The significance of variation of $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ is difficult to overestimate. Many petrogenetic and thermodynamic parameters of Fe-bearing minerals involve Fe^{2+}, such as $X_{mg} = (Mg/[Mg + Fe^{2+}])$ and K_D, the Fe^{2+}-Mg distribution coefficient. These values are a direct function of Fe^{2+} and Fe^{3+} contents. However, in most cases, modern analytical techniques are incapable of measuring oxidation state, resulting in various assumptions (e.g., that all Fe present in a sample has the same valence).

Previously, there were only two analytical methods commonly used to determine $Fe^{3+}/\Sigma Fe$ and Fe_2O_3 content directly, Mössbauer spectroscopy, and wet chemistry. These methods permit distinction between Fe^{2+} and Fe^{3+}, which is crucial to any estimation of redox and *P-T* conditions during mineral formation. However, both techniques require relatively large amounts of sample (≥50 mg for Mössbauer spectroscopy for a sample containing 10 wt% FeO, and ≥0.5 g for wet chemistry). These mass requirements have made it impossible to analyze single mineral grains or minerals in thin section (i.e., in situ). Recently, another technique for $Fe^{3+}/\Sigma Fe$ measurement has become available, X-ray absorption near-edge struc-

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ture (XANES) spectroscopy (Delaney et al. 1996), which permits the measurement of $Fe^{3+}/\Sigma Fe$ in-situ in 50 × 30 μm areas.

It has been common practice to use the crystal chemistry of silicate phases analyzed by the electron microprobe (EMP) to calculate the Fe^{3+} content of a mineral. However, this can result in gross imprecision of $Fe^{3+}/\Sigma Fe$ determinations and, thus, large uncertainties in subsequent *P-T* estimations. Attempts have been made to compare and correlate measured and calculated Fe^{3+} contents in silicates from upper mantle xenoliths. Dyar et al. (1984) showed that Fe^{3+} contents measured using conventional Mössbauer spectroscopy are different from those calculated from EMP analyses of spinels, clino-, and orthopyroxenes. Wood and Virgo (1989) used Mössbauer-analyzed spinels as secondary EMP standards and stated that this technique improves the precision dramatically, approaching $\pm 0.002\ X_{Fe3O4}$ in analyzed spinels. These authors concluded that for routine EMP analysis of spinel, the largest systematic uncertainties are associated with the concentration of Al_2O_3. Luth et al. (1990) stated that for a peridotite mineral assemblage (i.e., garnet, olivine, clino-, and orthopyroxene), the values of $Fe^{3+}/\Sigma Fe$ measured by the Mössbauer technique and those calculated from EMP analyses were significantly different. They also determined a positive correlation between $Fe^{3+}/\Sigma Fe$ contents in garnet and temperature estimates.

Several studies have attempted to assess the precision of Fe^{2+}/Fe^{3+} determination by EMP analyses. The uncertainty in determination of formula proportions of cations (and Fe^{3+} in particular) from EMP analyses was addressed by Finger (1972) who showed that Fe^{3+} in chromite can be determined with a precision of ±12% (0.534 ± 0.065 Fe^{3+}). Canil and O'Neill (1996) used the method of Dollase and Newman (1984) to show that the level of imprecision in Fe^{3+} determined from EMP analyses is related to the total Fe content, and increases in the order spinel<garnet<clinopyroxene. The level of imprecision for clinopyroxenes may be too large to be useful petrologically (Canil and O'Neill 1996). Moreover, even minimal errors in determination of high-valence and high-abundance elements such as Si in clinopyroxene can significantly affect formula proportions of cations calculated from EMP analyses.

Recent advances in the Mössbauer technique, in particular the development of the Mössbauer milliprobe, have made it possible to perform in situ measurements of $Fe^{3+}/\Sigma Fe$ in single mineral grains on a routine basis (McCammon 1994). For example, McCammon et al. (1997) determined Fe^{3+} in garnets and clinopyroxenes inclusions (~200 μm in size) within diamond from the George Creek kimberlite. Their results showed that there is little correlation between $Fe^{3+}/\Sigma Fe$ determined by the EMP analyses and Mössbauer techniques for these inclusions.

We have used the Mössbauer milliprobe to determine $Fe^{3+}/\Sigma Fe$ in silicates from eclogites from the Udachnaya kimberlite, Yakutia. Eclogites are basically bimineralic rocks consisting of the primary minerals pyropic garnet and omphacitic clinopyroxene. Therefore, only geothermometers utilizing the garnet-clinopyroxene Fe-Mg exchange are applicable to this type of rock (e.g., Råheim and Green 1974; Ellis and Green 1979; Powell 1985; Krogh 1988). Due to the fact that only Fe^{2+} takes part in this cation exchange between garnet and clinopyroxene, determining accurate Fe^{3+} values is extremely important. In this paper, we compare the $Fe^{3+}/\Sigma Fe$ ratios of these minerals measured by the Mössbauer milliprobe to those ratios calculated from EMP analyses. In addition, we evaluate errors in other elements associated with routine EMP analyses with regard to calculated Fe^{3+} values. Last, we address the effects of Fe^{3+} contents in garnet and clinopyroxene on estimates of equilibration temperatures for minerals in eclogite xenoliths.

ANALYTICAL TECHNIQUES

Mössbauer analyses

Fe^{3+} was determined using a Mössbauer milliprobe at the Bayerisches Geoinstitut, Universität Bayreuth, Germany. The Mössbauer milliprobe is a conventional Mössbauer spectrometer linked to some additional equipment (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) was replaced by a point source (specific activity ≥2000 mCi/cm^2). The gamma rays were collimated to the selected sample diameter using a lead shield, and the source-to-sample distance was reduced to <5 mm. This reduction results in a solid angle similar to conventional experiments and, hence, a similar count rate. Because the signal quality depends on absorber density (measured in mg Fe/cm^2) and not on the total amount of Fe in the sample, the reduction in sample size has no effect on the effective thickness of the absorber.

The sample mount consisted of an epoxy disk embedded with sample grains approximately 850 μm thick and 750 μm in diameter. A 500 μm diameter hole was drilled in a piece of 25 μm thick Ta foil (absorbs 99% of 14.4 keV gamma rays) and placed over the grain to be studied. Samples were run at room temperature, and each set of spectra took 1–4 days to collect.

Electron microprobe analyses

Major-element compositions were determined by EMPA using the four-spectrometer CAMECA SX-50 in the Department of Geological Sciences at the University of Tennessee. The accelerating voltage was 15 kV, with a beam current of 20 nA for clinopyroxenes and 30 nA for garnets. The beam size was 10 μm, and counting times of 20 s were used for all elements and backgrounds, except for Na in garnet and K in clinopyroxene (60 s). All data were corrected using ZAF procedures adapted for the CAMECA probe.

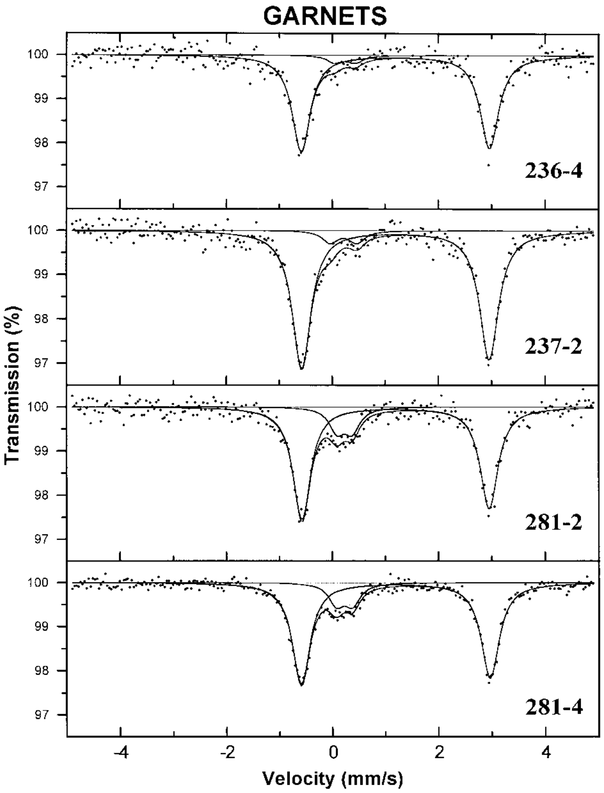

FIGURE 1. Mössbauer spectra of garnets from samples U-236, U-237, and U-281. Small doublet (shaded) in all spectra is Fe^{3+}.

SAMPLE CHARACTERIZATION

Eclogite xenoliths, from which garnet and clinopyroxene samples were extracted, represent part of an extensive suite of diamondiferous eclogites from the Udachnaya kimberlite pipe, Yakutia, Russia. They were described in detail in previous studies by our group (Jerde et al. 1993; Sobolev et al. 1994; Snyder et al. 1997).

The samples (U-236, U-237, and U-281) are coarse-grained and equigranular, and consist of a bimineralic assemblage of garnet and clinopyroxene. Modal proportions of garnet and clinopyroxene are 64:36 in U-236, 51:49 in U-237, and 60:40 in U-281 (Sobolev et el. 1994). Both garnet and clinopyroxene from these samples are chemically homogeneous, with the exception of U-281 where intra-grain Cr_2O_3 variation is present in garnet (0.50 to 1.50 wt% Cr_2O_3). All studied samples were classified as Group A eclogites (Sobolev et al. 1994) according to the criteria of Coleman et al. (1965), as modified by Taylor and Neal (1989). Garnets in all three xenoliths are relatively fresh, with <20–30% alteration, whereas clinopyroxenes are 60–70% altered (Sobolev et al. 1994). Fresh garnet and clinopyroxene pairs from each sample (only garnet for U-237) were selected for analyses. All selected grains lacked visible alteration products.

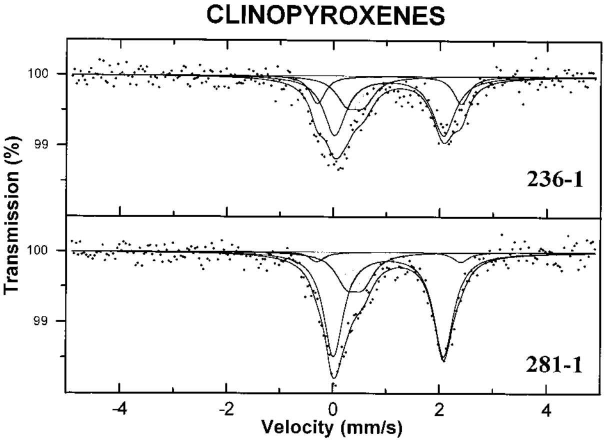

FIGURE 2. Mössbauer spectra of clinopyroxenes from samples U-236 and U-281. Small doublet (shaded) in both spectra is Fe^{3+}.

RESULTS

Mössbauer spectra of Udachnaya garnets and clinopyroxenes are shown in Figures 1 and 2. The garnet spectra were fit to one Fe^{2+} doublet and one Fe^{3+} doublet according to conventional models (e.g., Amthauer et al. 1976). The subspectra are well resolved, and $Fe^{3+}/\Sigma Fe$ can be determined with a high degree of confidence. Inasmuch as garnet is cubic, there should be no area asymmetry of component doublets due to texture effects. Nevertheless, the Fe^{2+} doublet appears to have a slight asymmetry, which is consistent with observations of Geiger et al. (1992); consequently, the area ratio of the Fe^{2+} doublet was allowed to vary. Otherwise, conventional constraints were applied (line widths and areas of components of each doublet were constrained to be 1:1).

The clinopyroxene spectra were fit to two Fe^{2+} doublets (corresponding to M1 and M2 sites) and one Fe^{3+} doublet according to conventional models (e.g., Luth and Canil 1993). Resolution of clinopyroxene spectra is significantly reduced compared to garnet spectra because of the similarity of hyperfine parameters for subspectra. Therefore, the following constraints were applied in addition to the conventional ones of equal line widths and areas of components: (1) the center shift, quadrupole splitting, and line width of the M1 doublet were constrained to average values observed by Luth and Canil (1993). Since the relative abundance of this doublet is small (<20%), errors in the hyperfine parameters of the doublet have little effect on the measured $Fe^{3+}/\Sigma Fe$ ratio; (2) for the U-236-1 clinopyroxene sample, where the signal:noise ratio was not as high, the center shift, quadrupole splitting, and line width of the Fe^{3+} doublet were constrained to the values determined for the U-281-1 clinopyroxene spectrum. This constraint contributes a higher error to the $Fe^{3+}/\Sigma Fe$ determination of this sample.

COMPARISON OF EMP AND MÖSSBAUER RESULTS

A comparison of EMP and Mössbauer analyses of four garnets and two clinopyroxenes are given in Table 1 and

TABLE 1. Garnet and clinopyroxene major-element compositions determined by electron microprobe

	Garnet								Clinopyroxene			
	236-4* E	236-4 M	237-2 E	237-2 M	281-2 E	281-2 M	281-4 E	281-4 M	236-1 E	236-1 M	281-1 E	281-1 M
SiO_2	40.8	40.8	40.8	40.8	40.8	40.8	40.5	40.5	54.5	54.5	54.7	54.7
TiO_2	0.31	0.31	0.33	0.33	0.47	0.47	0.55	0.55	0.45	0.45	0.20	0.20
Al_2O_3	22.8	22.8	22.9	22.9	21.7	21.7	20.8	20.8	5.72	5.72	1.81	1.81
Cr_2O_3	0.14	0.14	0.10	0.10	0.50	0.50	1.49	1.49	0.10	0.10	0.31	0.31
Fe_2O_3	1.17	0.75	1.50	0.91	2.61	2.16	3.34	2.03	0.62	0.63	1.58	1.02
FeO	10.2	10.6	10.4	10.9	9.78	10.2	9.18	10.4	1.92	1.91	2.74	3.25
MnO	0.24	0.24	0.30	0.30	0.48	0.48	0.49	0.49	0.02	0.02	0.11	0.11
MgO	14.8	14.8	15.9	15.9	17.6	17.6	17.4	17.4	13.6	13.6	16.3	16.3
CaO	9.35	9.35	7.56	7.56	5.77	5.77	6.20	6.20	19.7	19.7	20.6	20.6
Na_2O	0.08	0.08	0.08	0.08	0.06	0.06	0.07	0.07	3.03	3.03	1.57	1.57
K_2O	ND†	ND	ND	ND	ND	ND	ND	ND	<0.02	<0.02	<0.02	<0.02
FeO_T‡	11.3	11.3	11.7	11.7	12.1	12.1	12.2	12.2	2.48	2.48	4.17	4.17
Total	99.70	99.71	99.69	99.69	99.54	99.54	99.69	99.69	99.59	99.59	99.74	99.74
Si	2.974	2.976	2.964	2.967	2.964	2.967	2.948	2.957	1.963	1.963	1.986	1.988
Ti	0.017	0.017	0.018	0.018	0.026	0.026	0.030	0.030	0.012	0.012	0.005	0.005
^{IV}Al									0.037	0.037	0.014	0.012
^{VI}Al	1.957	1.959	1.960	1.963	1.858	1.860	1.784	1.789	0.206	0.206	0.063	0.066
Cr	0.008	0.008	0.006	0.006	0.029	0.029	0.086	0.086	0.003	0.003	0.009	0.009
Fe^{3+}	0.064	0.041	0.082	0.050	0.143	0.118	0.183	0.112	0.017	0.017	0.043	0.028
Fe^{2+}	0.621	0.647	0.629	0.663	0.594	0.619	0.559	0.632	0.058	0.058	0.083	0.099
Mn	0.015	0.015	0.018	0.019	0.030	0.030	0.030	0.030	0.001	0.001	0.003	0.004
Mg	1.603	1.604	1.723	1.725	1.901	1.903	1.888	1.891	0.732	0.732	0.881	0.882
Ca	0.730	0.731	0.588	0.589	0.449	0.449	0.483	0.485	0.760	0.760	0.800	0.801
Na	0.011	0.011	0.012	0.012	0.008	0.008	0.009	0.009	0.212	0.212	0.111	0.111
K									0.001	0.001	0.001	0.001
Total	8.000	8.008	8.000	8.011	8.000	8.008	8.000	8.024	4.000	4.000	4.000	4.005
X_{Mg}	0.72	0.71	0.73	0.72	0.76	0.75	0.77	0.75	0.93	0.93	0.91	0.90
$Fe^{3+}/\Sigma Fe$	9.4	6.0	11.5	7.0	19.4	16.0	24.7	15.0	22.6	22.9	34.2	22.0
T_E§ (°C)	953				1030							
T_M (°C)	930				1068							

Note: $Fe^{3+}/\Sigma Fe$ ratio is calculated from EMPA ("E" columns) and measured by Mössbauer spectroscopy ("M" columns).
* Each EMP analysis (E) is the average of 20 points on four grains.
† ND = not determined.
‡ All iron determined as FeO by EMPA.
§ Temperature estimates (Ellis and Green 1979) for samples U-236 and U-281 (4.5 GPa pressure is used).

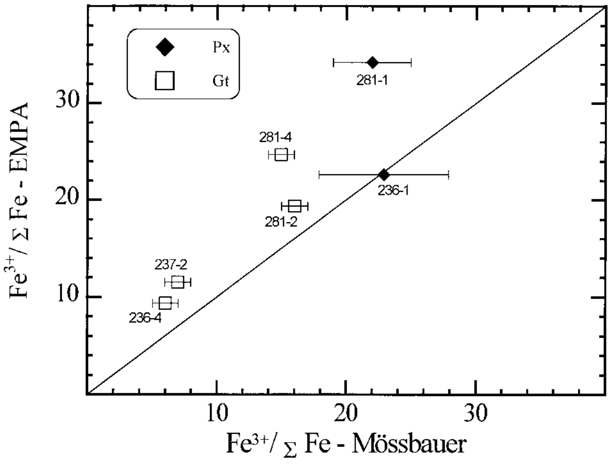

FIGURE 3. Comparison of analyzed (Mössbauer) and calculated (EMP) $Fe^{3+}/\Sigma Fe$ ratios of garnets and clinopyroxenes from Udachnaya eclogites. Error bars are shown for both garnet and clinopyroxene analyses.

shown in Figure 3. It is evident that, although measured $Fe^{3+}/\Sigma Fe$ ratios approach the calculated ones (e.g., Gt 281-2, Cpx 236-1), there is no direct (1:1) correlation between the two sets of data. Note that calculated Fe^{3+} values are always greater than measured ones, except clinopyroxene 236-1, where they are roughly equal. Two different garnets from one sample (U-281) produced no measurable differences in $Fe^{3+}/\Sigma Fe$ (Table 1, Fig. 3).

Some Fe^{3+} should be present in almost all igneous and metamorphic Fe-bearing silicate minerals, depending on the f_{O_2} of the system during their formation and equilibration. However, due to the differences in crystal structure and the amounts of total FeO, the $Fe^{3+}/\Sigma Fe$ ratio is different in coexisting minerals. The difference in $Fe^{3+}/\Sigma Fe$ between garnet and clinopyroxene in two different samples is illustrated by the results in Table 1, where two different $Fe^{3+}/\Sigma Fe$ ratios of garnets (6.0 and 15.0) correspond to similar (22.9 and 22.0) $Fe^{3+}/\Sigma Fe$ in clinopyroxenes (Table 1, samples 236 and 281).

Values of Fe^{3+} obtained from Mössbauer analyses of clinopyroxenes possess much larger errors than those of garnets (Fig. 3). This error is a result of relatively low FeO contents in clinopyroxene (2.48 wt% in U-236 and 4.17 wt% in U-281). Since the quality of a Mössbauer analysis depends on sample density (measured in mg Fe/

cm^2; McCammon et al. 1995), samples with the same thickness but different concentrations of FeO would have different precisions in the determination of $Fe^{3+}/\Sigma Fe$.

Although similar for some minerals (garnet 281-2, clinopyroxene 236-1, Table 1), $Fe^{3+}/\Sigma Fe$ obtained from the EMP and Mössbauer techniques are significantly different in most cases. However, temperatures calculated for eclogites using EMP-determined Fe^{3+} values are not greatly different from those calculated using Mössbauer values, and all are within ±40 °C range (Table 1). The reason for this is discussed below.

INFLUENCE OF Fe^{3+} ON FE-MG DISTRIBUTION IN ECLOGITIC MINERALS AND CALCULATED TEMPERATURES OF EQUILIBRATION

When calculating *P-T* parameters using Fe-bearing minerals, Fe^{3+} is either assumed to be zero, or it is calculated from EMP analyses based upon stoichiometry and charge balance. As discussed below, the EMP technique does not always provide an accurate Fe^{3+} value, particularly for silicates, which can seriously affect the petrologic interpretation of the results. The importance of separating different oxidation states of iron can be illustrated by looking at certain key petrologic parameters, such as X_{Mg} and the Fe^{2+}-Mg distribution coefficient (K_D). The distribution coefficient (K_D) forms the basis of several geothermometers (e.g., Råheim and Green 1974; Ellis and Green 1979; Powell 1985; Krogh 1988), therefore, the calculated temperature of equilibration strongly depends on it. Unfortunately, there are no experimental data on the effects of Fe^{3+} for existing geothermometers and geobarometers. Luth et al. (1990) showed that using a combination of the O'Neill and Wood (1979) geothermometer and the MacGregor (1974) geobarometer, the two values of $Fe^{3+}/\Sigma Fe$ of 0 and 0.12 would change calculated pressure from 59 to 74 kbar and calculated temperature from 1269 to 1505 °C, respectively. Note that neither of these geothermometers or geobarometers involves clinopyroxene, which may contain significant amounts of Fe^{3+}. It is obvious that those geothermometers and geobarometers that involve Fe^{2+}-Mg exchange would be most significantly affected by either neglecting Fe^{3+} or using incorrect values.

Electron microprobe calculated Fe^{3+}

The effect of Fe^{3+} in clinopyroxene on calculated temperatures can be illustrated by taking typical eclogitic clinopyroxene compositions (sample U-107/2, data from Sobolev et al. 1994) and clinopyroxene compositions from a Gt-Cpx intergrowth (sample A-143, data from Sobolev et al. 1997) and changing slightly the abundances of Si and Na within the range given by the analytical error, i.e., standard deviation (Table 2). Note that the error in $Fe^{3+}/\Sigma Fe$ is controlled largely by Si contents in garnet and clinopyroxene, due to its major abundance and +4 charge. In addition, eclogitic clinopyroxenes contain relatively high Na contents (up to 10.7 wt%, Sobolev 1974). Because of its low atomic number, sodium requires additional precision when analyzing clinopyroxene. The +1 charge of Na makes the error in Na analysis very sensitive when calculating formula proportions of cations.

We used ''auoestimated errors in EMP analyses''calculated by Canil and O'Neill (1996), which is based on the method proposed by Dollase and Newman (1984). As explained by Dollase and Newman (1984), the statistical validity of the method depends on a knowledge of the standard deviations of the measured concentrations of each oxide component. These errors were calculated with an assumption that the EMP analyses contain no systematic errors, so that these standard deviations result from counting statistics alone. With this in mind, we changed the SiO_2 and Na_2O contents of the clinopyroxenes as shown in Table 2. Although the errors proposed by Canil and O'Neill (1996) are optimistic, even these very conservative relative errors in Na (1.2%) and in Si (0.7%) analyses would drastically change the $Fe^{3+}/\Sigma Fe$ ratio and the estimated temperature of equilibration (Table 2). These changed values for SiO_2 and Na_2O are well within the range of precision for clinopyroxene compositions and reflect a real EMP analysis. Note that the temperature for sample A-143, estimated by assuming that $Fe^{3+}/\Sigma Fe = 0$, is 1544 °C (Table 2). This is 540 °C higher than the temperature estimated by using the Fe^{3+} calculated from the EMP analysis.

The lack of precision of EMP analyses also can lead to large errors in calculating formula proportions of cations. A method of estimating uncertainties associated with the coefficients of the mineral formula was proposed by Finger (1972). This was shown by assuming an error in EMP analyses of chromite of 2%, and the uncertainties for major elements were within 0.5–2% range. At the same time, the uncertainty in the Fe^{3+} contents was 12%. This method, however, may not be useful with eclogitic minerals where $Fe^{3+}/\Sigma Fe$ ratios seldom exceed values of 30.0 [compared to 62.0 in chromite (Finger 1972)]. The reproducibility (precision) in EMP analyses combined with inter- and intragranular compositional variations can also result in large errors in temperature estimates, on the order of ±100 °C or more. Thus, it is difficult to estimate an accurate temperature of equilibration since it may lie within a 200 °C range. The error may be even larger if an energy dispersive spectrometer (EDS) is used for quantitative analyses (e.g., Jacob et al. 1994), particularly since even small changes in Na_2O can have a significant affect on calculated Fe^{3+}.

Effect of K_D on Gt-Cpx thermometers

Although included as part of the Fe^{2+}-Mg exchange geothermometers, K_D itself is not significantly affected by the imprecision in Fe^{3+} estimation when values from EMP and Mössbauer analyses are compared. We used the data from Tables 1 and 2 and plotted Gt-Cpx pairs on a f_{Gt}-f_{Cpx} graph, where f is $Fe^{2+}/(Fe^{2+} + Mg)$ of the mineral (in mol%). There is almost no difference in f (Gt and Cpx) and K_D values in the sample 236 between EMP-calculated and Mössbauer-measured Fe^{2+}/Fe^{3+} ratios (Fig.

TABLE 2. Garnet and clinopyroxene major-element compositions of diamondiferous eclogite U-107/2 (Udachnaya kimberlite, Soboley et al. 1994) and garnet peridotite A-143 (Mir kimberlite, Soboley et al. 1997)

	U-107/2					A-143			
	Gt	Cpx	Cpx-1	Cpx-2	Cpx-3	Gt	Cpx	Cpx-4	Cpx-5
SiO_2	40.3	55.1	54.8	55.1	54.8	41.8	55.1	55.1	55.1
TiO_2	0.33	0.16	0.16	0.16	0.16	0.07	0.14	0.14	0.14
Al_2O_3	22.3	10.3	10.3	10.3	10.3	19.8	5.92	5.92	5.92
Cr_2O_3	0.05	0.04	0.04	0.04	0.04	4.98	6.09	6.09	6.09
Fe_2O_3	0.94	0.81	1.21	1.28	1.57	1.19	2.46	2.87	1.99
FeO	9.75	1.58	1.22	1.16	0.90	7.31	1.26	0.89	1.68
MnO	0.19	0.03	0.03	0.03	0.03	0.53	0.13	0.13	0.13
MgO	11.2	10.4	10.4	10.4	10.4	21.7	10.7	10.7	10.7
CaO	14.1	15.1	15.1	15.1	15.1	2.49	11.4	11.4	11.4
Na_2O	0.11	5.67	5.67	5.74	5.74	0.08	6.71	6.79	6.63
K_2O	ND	0.08	0.08	0.08	0.08	ND	<0.02	<0.02	<0.02
FeO_{tot}	10.6	2.31	2.31	2.31	2.31	8.38	3.47	3.47	3.47
Total	99.18	99.19	98.89	99.28	98.96	99.83	99.59	99.67	99.50
Si	2.988	1.966	1.960	1.963	1.958	2.995	1.985	1.982	1.988
Ti	0.018	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
^{IV}Al		0.034	0.040	0.037	0.042		0.015	0.018	0.012
^{VI}Al	1.948	0.399	0.394	0.396	0.391	1.667	0.236	0.233	0.240
Cr	0.003	0.001	0.001	0.001	0.001	0.282	0.173	0.173	0.174
Fe^{3+}	0.053	0.022	0.033	0.031	0.042	0.064	0.067	0.078	0.054
Fe^{2+}	0.605	0.047	0.037	0.037	0.027	0.438	0.038	0.027	0.051
Mn	0.012	0.001	0.001	0.001	0.001	0.032	0.004	0.004	0.004
Mg	1.238	0.553	0.555	0.552	0.554	2.316	0.572	0.571	0.573
Ca	1.120	0.577	0.579	0.576	0.578	0.191	0.438	0.437	0.439
Na	0.016	0.392	0.393	0.397	0.398	0.011	0.469	0.473	0.463
K		0.004	0.004	0.004	0.004		0.000	0.000	0.000
Total	8.000	4.000	4.000	4.000	4.000	8.000	4.000	4.000	4.000
Total*	8.018	4.007	4.011	4.011	4.011	8.021	4.022	4.026	4.018
X_{Mg}		0.92	0.94	0.94	0.94		0.94	0.96	0.92
$Fe^{3+}/\Sigma Fe$†	8.0	31.6	47.1	45.7	61.1	12.7	63.7	74.4	51.6
T °C		1026	941	949	851	1004		870	1143

Note: Temperatures were estimated with the geothermometer of Ellis and Green (1979); 4.5 GPa pressure was used. An error of 0.7% of the amount present (i.e., 0.3 wt% SiO_2) was subtracted from the real analysis (Cpx-1); an error of 1.2% of the amount present (i.e., 0.07 wt% Na_2O) was added (Cpx-2) for the sample U-107/2; both of the errors were applied (Cpx-3). An error of 0.08 wt% Na_2O is added (Cpx-4) and subtracted (Cpx-5) for the sample A-143. Relative precisions of 0.75% for SiO_2 and 1.5% for Na_2O are optimistic but are values used by Canil and O'Neil (1996).

* Before calculating Fe^{3+}.

† Calculated from EMPA.

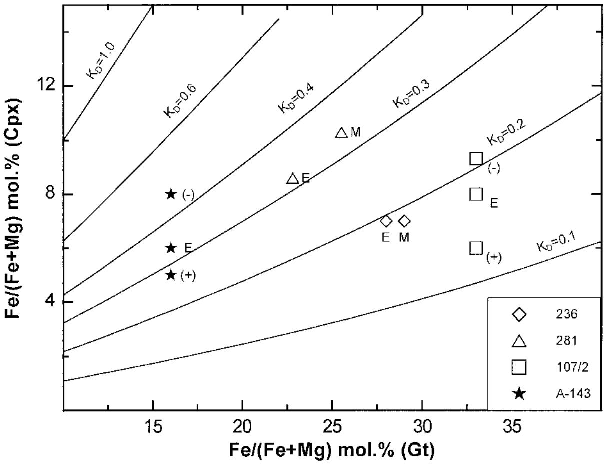

FIGURE 4. $Fe^{2+}/(Fe^{2+} + Mg)_{Gt}$ (f_{Gt}) vs. $Fe^{2+}/(Fe^{2+} + Mg)_{Cpx}$ (f_{Cpx}) for Udachnaya eclogites 236, 281, 107/2, and Mir peridotite A-143 ($f = Fe^{2+}/[Fe^{2+} + Mg]$ in mol%). E = EMP calculated; M = Mössbauer analyzed; (−) for star = subtracted 0.08 wt% of Na_2O; (−) for square = subtracted 0.07 wt% of Na_2O; (+) for star = added 0.08 wt% of Na_2O; (+) for square = added 0.07 wt% of Na_2O (see detailed explanation in Table 2 and text).

4). Although f values for garnet and clinopyroxene in sample 281 are different, the distribution coefficients are the same (Fig. 4).

The situation changes when clinopyroxene compositions with high Na_2O (>4–5 wt%) are considered. The distribution coefficient varies from 0.14 (+0.07 wt% of Na_2O) to 0.21 (−0.07 wt% of Na_2O) in sample 107/2 (Fig. 4), and from 0.25 (+0.08 wt% of Na_2O) to 0.47 (−0.08 wt% of Na_2O) in sample A-143 (Fig. 4). Therefore, a potential error in EMP analyses of high-Na clinopyroxenes may lead to a wide variation of Fe-Mg distribution coefficient as well as to significant differences in calculated temperatures.

It is clear that K_D is not only a function of temperature. It has been shown that pressure as well as garnet composition may affect Fe-Mg distribution coefficient in eclogites (e.g., Sobolev 1964; Banno 1970; Ai 1994). In fact, along with a strong positive correlation between K_D and calculated temperatures in Udachnaya, it can be seen that samples with similar distribution coefficients (0.20–0.30 range) may have 100–200 °C differences in temperature (Fig. 5). Another important geochemical parameter, X_{Mg}, does not vary significantly in either analyzed (by Möss-

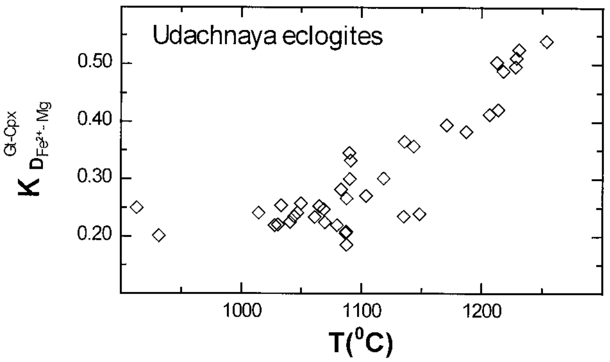

FIGURE 5. K_D Fe^{2+}-Mg distribution coefficient (K_D = $[Fe^{Cpx}Mg^{Gt}]/[Fe^{Gt}Mg^{Cpx}]$) vs. calculated temperature for Udachnaya eclogites (data from Sobolev et al. 1994).

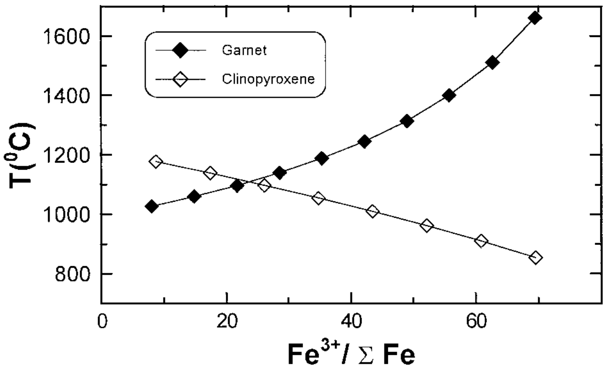

FIGURE 6. Temperature of equilibration vs. $Fe^{3+}/\Sigma Fe$ of garnet and clinopyroxene from eclogite U-107/2. $Fe^{3+}/\Sigma Fe$ vs. temperature for garnet was calculated assuming constant $Fe^{3+}/\Sigma Fe$ in clinopyroxene and vice versa.

bauer technique, Table 1) or tested (Table 2) samples with variation of Fe^{3+} contents. It can be seen in both Tables 1 and 2 that its variation does not exceed 2.5 relative percent.

Because a strong positive correlation exists between K_D and calculated temperatures, one can expect a similar correlation between the latter and Fe^{3+} contents. Luth et al. (1990) stated that the amount of Fe^{3+} in garnets correlates with the pressure and temperature of the host xenolith. In general, $Fe^{3+}/\Sigma Fe$ in garnet increases with increasing pressure and temperature. A positive correlation exists if different geothermometers (Wells 1977; Bertrand and Mercier 1985; Finnerty and Boyd 1987) and geobarometers (MacGregor 1974; Nickel and Green 1985) are applied. According to Luth et al. (1990), the amount of Fe^{3+} in garnets also correlates with differences in the textures of peridotites. Canil and O'Neill (1996) also showed that a positive correlation exists between $Fe^{3+}/\Sigma Fe$ in garnet and temperature of equilibration. However, only a slight correlation was found between Fe^{3+} in clinopyroxene and temperature (Canil and O'Neill 1996).

We used the compositions of garnet and clinopyroxene from diamondiferous eclogite xenolith U-107/2 (data from Sobolev et al. 1994) to check the dependence of Fe^{3+} on temperature, using the geothermometer of Ellis and Green (1979). The $Fe^{3+}/\Sigma Fe$ ratio in garnet was tested in the range from 8.0 to 70.0 at about seven different increments; each resulting composition was then used with coexisting clinopyroxene (same composition for each estimation). As shown in Figure 6, temperature increases with increasing $Fe^{3+}/\Sigma Fe$. The same calculation was performed with increasing $Fe^{3+}/\Sigma Fe$ of clinopyroxene, which resulted in a negative correlation (Fig. 6). It is apparent that some compensation actually occurs with increasing f_{O_2} of the system (as reflected in Fe^{3+} contents), thereby keeping temperatures from changing drastically. Note that this is true only when Fe^{2+}-Mg exchange geothermometers are applied to the Gt-Cpx (e.g., eclogitic) mineral assemblage.

It is clear that more experimental work is needed on the Fe^{2+}-Fe^{3+} substitution in eclogitic and peridotitic minerals. Although uncertainties in the pressure and temperature estimates for mantle xenoliths do not affect the calculated f_{O_2} significantly (Luth et al. 1990), the Fe^{3+} contents in mantle minerals provide information about the environment in which equilibration occurred. Due to the fact that all geothermometers for eclogites involve Fe^{2+}-Mg exchange, $Fe^{3+}/\Sigma Fe$ must be measured by a Mössbauer technique, and errors in temperature estimates for high-Na clinopyroxene eclogites using $Fe^{3+}/\Sigma Fe$ from EMP analyses can seriously affect petrologic interpretation. Moreover, because a constant value of Mg^{2+} dilutes the effect of possible error in determination of Fe^{3+} contents, the uncertainty in this determination may affect most Fe^{2+} K_D and Fe^{2+} diffusion coefficient values as well.

SUMMARY

(1) The results of this study demonstrate that there is no direct (1:1) correlation between Mössbauer-measured and EMP-calculated values for $Fe^{3+}/\Sigma Fe$ of eclogitic garnets and clinopyroxenes. Values of $Fe^{3+}/\Sigma Fe$ calculated from EMP analyses of silicate minerals are generally inaccurate, although they do not greatly affect temperature estimates in eclogites due to compensation effects between garnet and clinopyroxene.

(2) In silicates, the precision in determination of SiO_2 largely controls the $Fe^{3+}/\Sigma Fe$ values based on stoichiometry due to its abundance and +4 ionic charge contribution. In addition, high-Na clinopyroxenes (>4–5 wt% Na_2O) are even more sensitive to EMP error, and therefore can produce larger uncertainties in temperature estimates.

(3) The interpretation of the results of many previously published papers on Fe-Mg distribution between coexisting silicate minerals may be significantly changed due to possible error in Fe^{3+} estimation.

(4) Compensation effects between garnet and clinopyroxene exist, even with increasing f_{O_2}; this compensation moderates temperature from changing greatly with K_D in eclogites.

(5) The uncertainty in Fe^{3+} calculated from EMP analyses, due solely to inherent analytical precision, raises questions about most Fe^{2+} K_D and diffusion coefficient values determined with natural silicate minerals.

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