Determination of Fe^{3+}/Fe_{Total} in Amphiboles using the Electron Microprobe

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1. Introduction

Mineral equilibria have commonly been applied to rocks from the crust and mantle in an effort to quantify important parameters such as P, T, fO_2, and fH_2. Fe is a common constituent in the earth's crust and upper mantle and application of mineral equilibria involving Fe requires chemical characterization of the relevant phases and, in some cases, this characterization must include Fe^{3+}/Fe_{Total} (where $Fe_{Total} = Fe^{3+} + Fe^{2+}$). Most useful would be an analytical technique that permits determination of values of Fe^{3+}/Fe_{Total} within a single mineral grain that is contained within a standard petrographic thin section. The excellent spatial resolution and relative accessibility of the electron microprobe (EMP) have resulted in various attempts to use this instrument to determine values of Fe^{3+}/Fe_{Total}. These efforts have typically involved quantifying characteristics of the Fe Lα and/or Fe Lβ peaks. We employ the method of Fialin et al. (2001), who have shown that the location of the Fe Lα peak changes as a function of Fe-content and values of Fe^{3+}/Fe_{Total}, to determine values of Fe^{3+}/Fe_{Total} in amphiboles.

Objectives

Our goal is to determine if, for any given Fe content, Fe Lα peak locations determined for amphiboles shift in a linear fashion as a function of Fe^{3+}/Fe_{Total}. If so, then it should be possible derive a calibration based on amphibole with known Fe^{3+}/Fe_{Total}, and assess the precision of the peak-shift technique when applied to these minerals.

2. Samples:

Hematite & Magnetite "Standards"

Four Amphiboles:

Three amphiboles have been experimentally treated hydrothermally, and in air, to produce samples of each that have constant Fe_{Total} but different values of Fe^{3+}/Fe_{Total}.
- **Titanian pargasite megacryst from Vulcan's Throne (VT)** Arizona (Popp et al., 1995)
- **Kaersutite from Greenland (GK)** (Popp et al., 2006a; 2006b)
- **Titanian ferroan pargasitic hornblende from the Tschicoma Formation, New Mexico (TH)** (Popp et al., 2006a; 2006b).

A fourth amphibole analyzed for this study is a natural **pargasitic hornblende from Ontario, Canada (OPH).**

Table 1. Amphibole Compositions (weight % oxide with all Fe reported as FeO)

	Tschicoma Hornblende This Study Average n = 269	Tschicoma Std Dev	Popp et al. (2006a) Average	Vulcan's Throne This Study Average n = 22?	Vulcan's Std Dev	Popp et al. (1995) Average	Greenland Kaersutite This Study Average	Greenland Std Dev	Popp et al. (2006a)	Ontario Pargasitic Hornblende This Study Average n = 20	Ontario Std Dev
SiO_2	43.35	0.79	43.54	40.57	0.28	40.32	0.20		38.70	42.72	0.20
TiO_2	7.28	0.37	2.82	3.74	0.20	3.84	0.17		6.89	0.90	0.07
Al_2O_3	11.04	0.59	10.89	15.67	0.15	15.35	0.14		13.25	11.90	0.27
Cr_2O_3	0.03	0.01		0.03	0.02	BDL			0.01	0.01	0.02
MgO	13.58	0.56	13.93	14.53	0.18	14.53	0.14		13.19	14.41	0.19
CaO	11.06	0.22	11.11	10.42	0.65	10.46	0.14		12.48	11.59	0.07
MnO	0.22	0.04	0.21	0.08	0.03	BDL			0.11	0.29	0.03
FeO	12.34	0.67	13.13	7.42	0.19	7.70	0.18		10.10	10.96	0.28
Na_2O	2.06	0.11	2.13	2.68	0.08	2.74	0.05		2.52	2.62	0.09
K_2O	0.60	0.04	0.63	1.62	0.07	1.60	0.06		1.00	2.02	0.12
F	0.13	0.09	BDL	0.09	0.06	0.08	0.03		0.34	2.18	0.11
Cl			BDL	NA		BDL				BDL	
H_2O*	1.96		0.73	2.01	0.03	1.27			1.05	NA	
Total	98.94		98.93	98.86		97.89			99.63	100.56	

BDL = Below detection limits; NA = Not analyzed
* Calculated - based on mineral stoichiometry

3. Analyses

Accelerating Voltage: 15 kV
Beam Currents: 20 & 100 nA
Scan Range (TAP crystal):
400 steps - 2000×10^{-5} sin θ
200 steps - 1000×10^{-5} sin θ
Counting Time: 200 ms/step
Add scans to increase total count times.
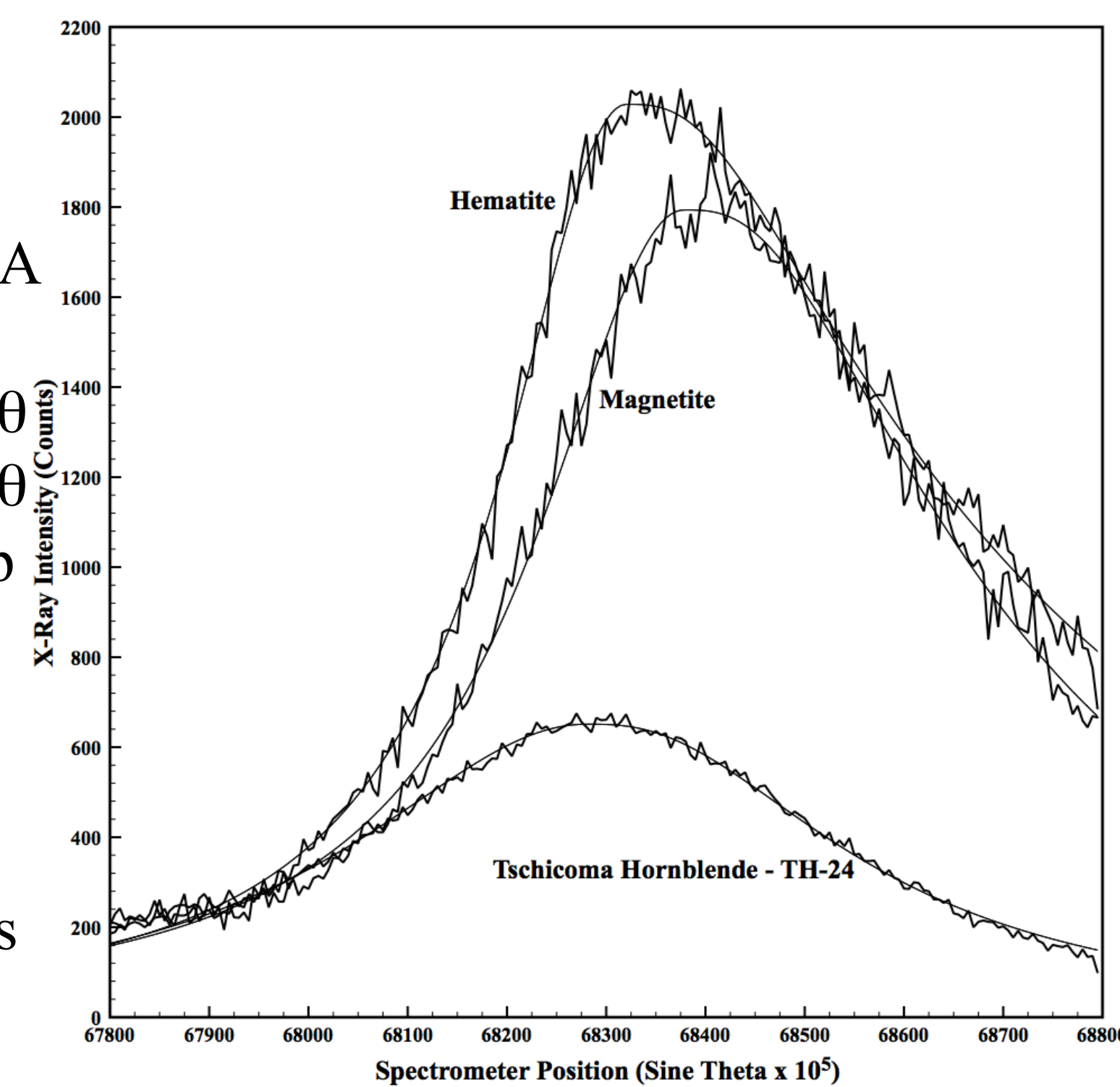Analytical times:
Hematite: ≈ 1 hour
Amphiboles: ≈ 1 to 9 hours often multiple grains

Example of measured peaks with "fits".

The resulting peaks were fit using an asymmetric function that employs five different variables: (1) the peak location, (2) peak height, (3) peak width at half height, (4) a factor to describe the distribution as either Gaussian and Lorenzian or some mixture of the two, and (5) an exponential "tail" factor ("ET" M. Wersemann – http://plot.micw.eu/).

The Fe Lα peak shape of hematite was characterized during each analytical session in part because Fe Lα peak characteristics for a given sample may vary from one analytical session to the next. Thus, all peak positions are reported relative to the hematite peak such that the **relative peak position (RPP) = hematite peak position - amphibole peak position.**

4. Reproducibility
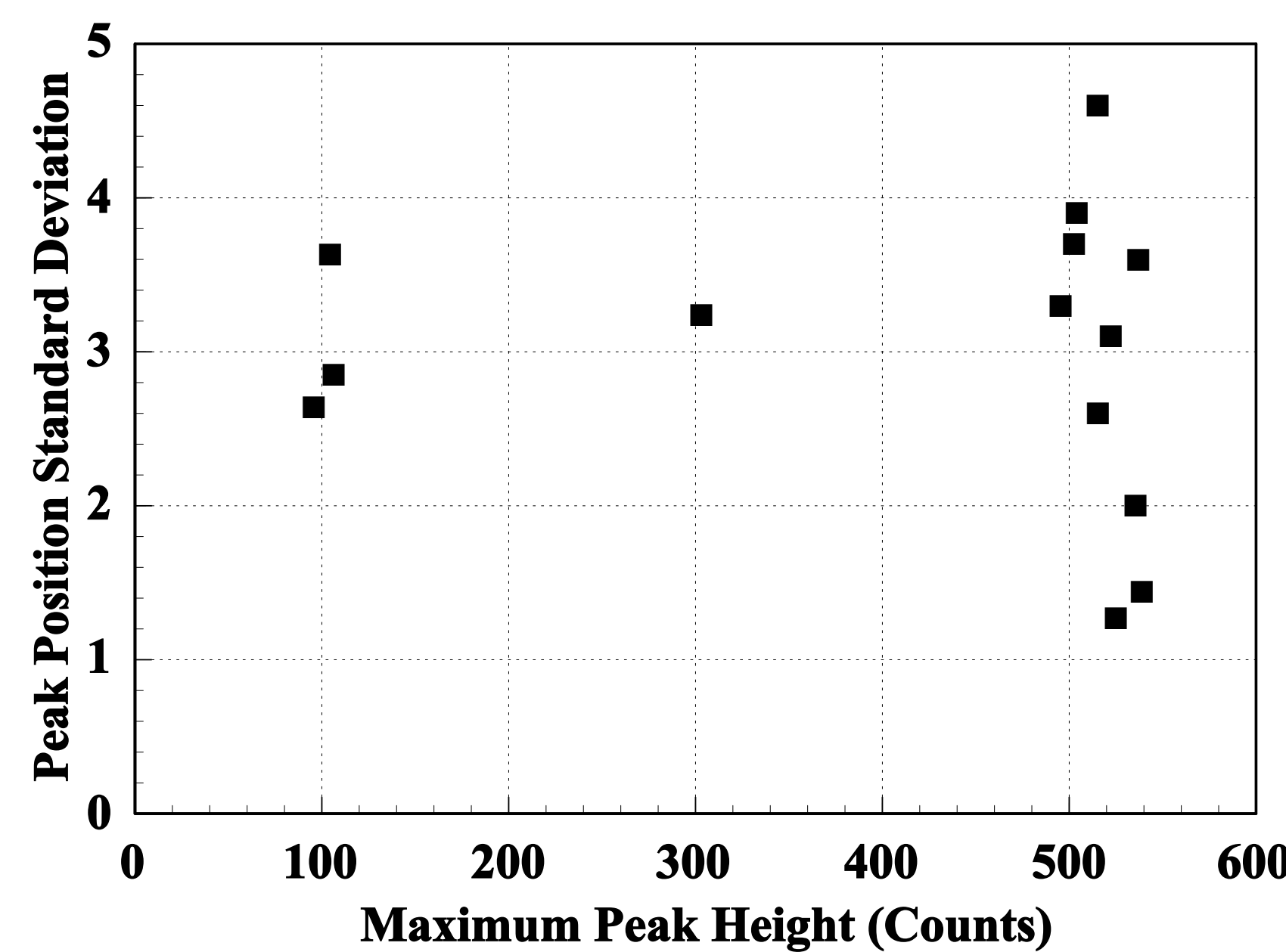
Replicate measurements on a hematite standard: this diagram plots the average maximum peak height versus the 1σ standard deviation (n = 4 to 40) about the mean peak position (units are sine theta x 10^5). The average 1σ standard deviation for all data points of 3.0 ± 0.9 is taken as representative of the precision of peak position determinations.

5. Results
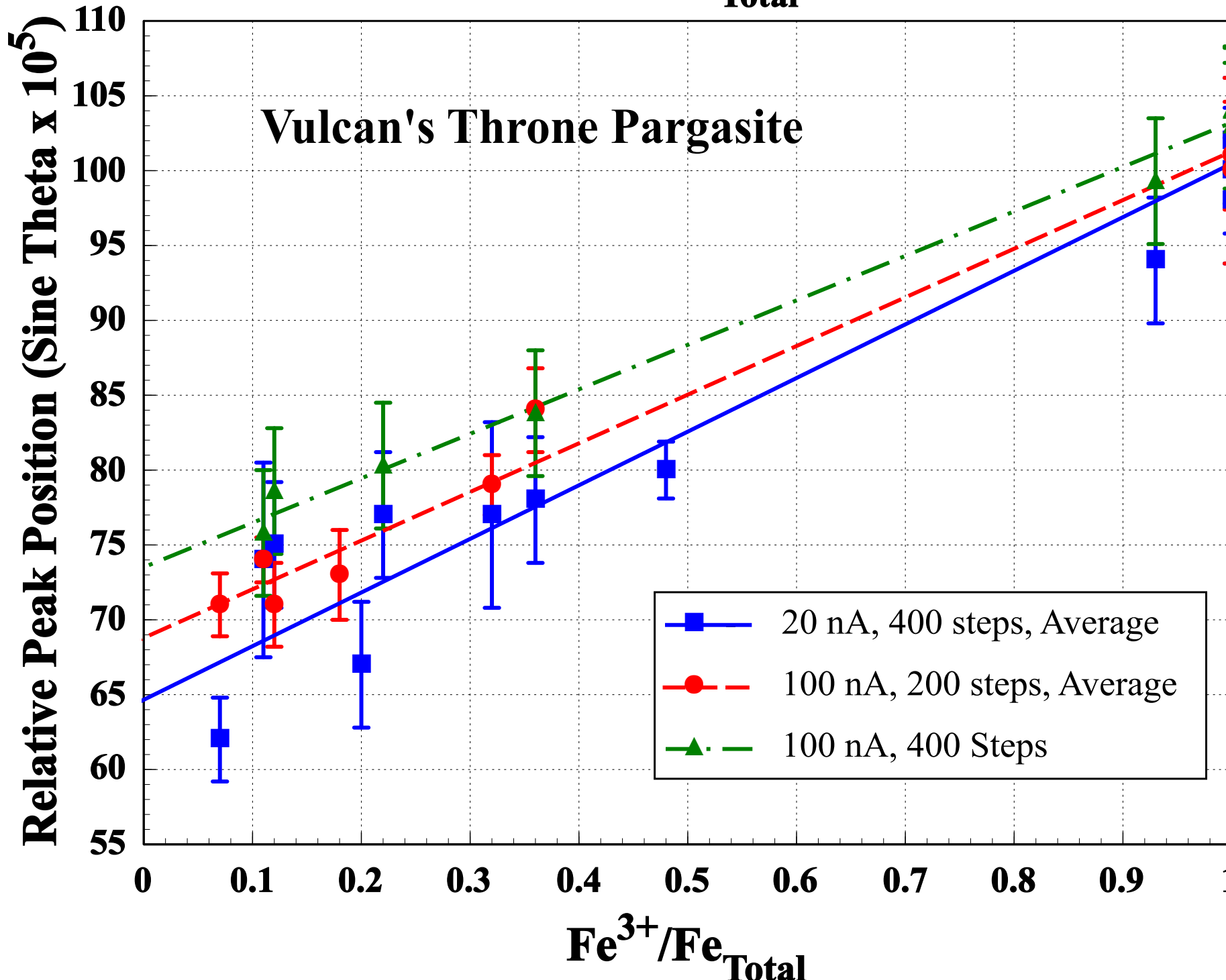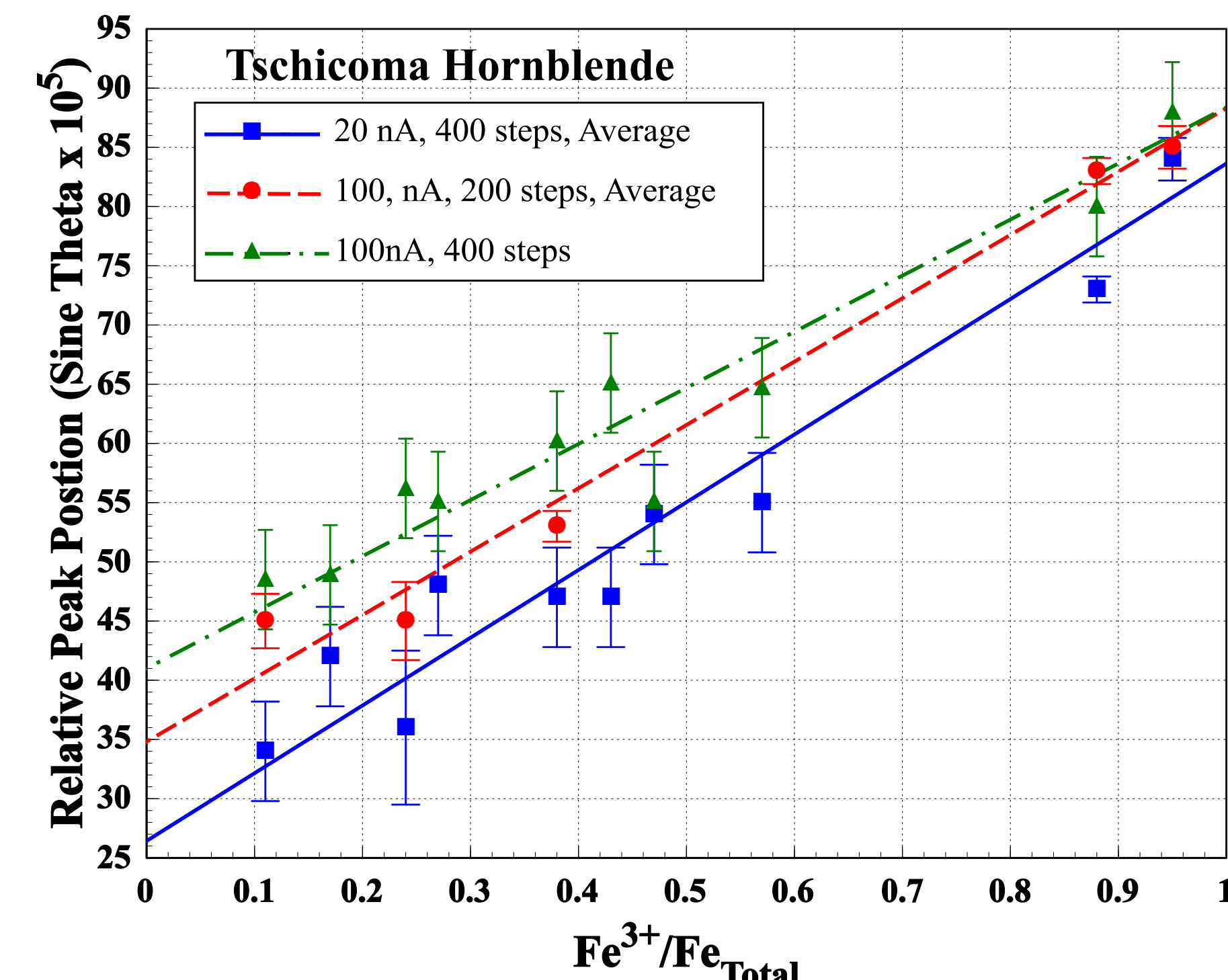
RPPs plotted against values of Fe^{3+}/Fe_{Total} as determined from ^{57}Fe Mössbauer spectroscopy. Error bars are either: (1) 1 σ standard deviations, or (2) ± 4.2 sine theta x 10^{-5} as estimated from reproducibility experiments on hematite. These data suggest that these amphiboles may have lost some H during the analyses conducted at 100nA for 400 steps.

6. Results II.
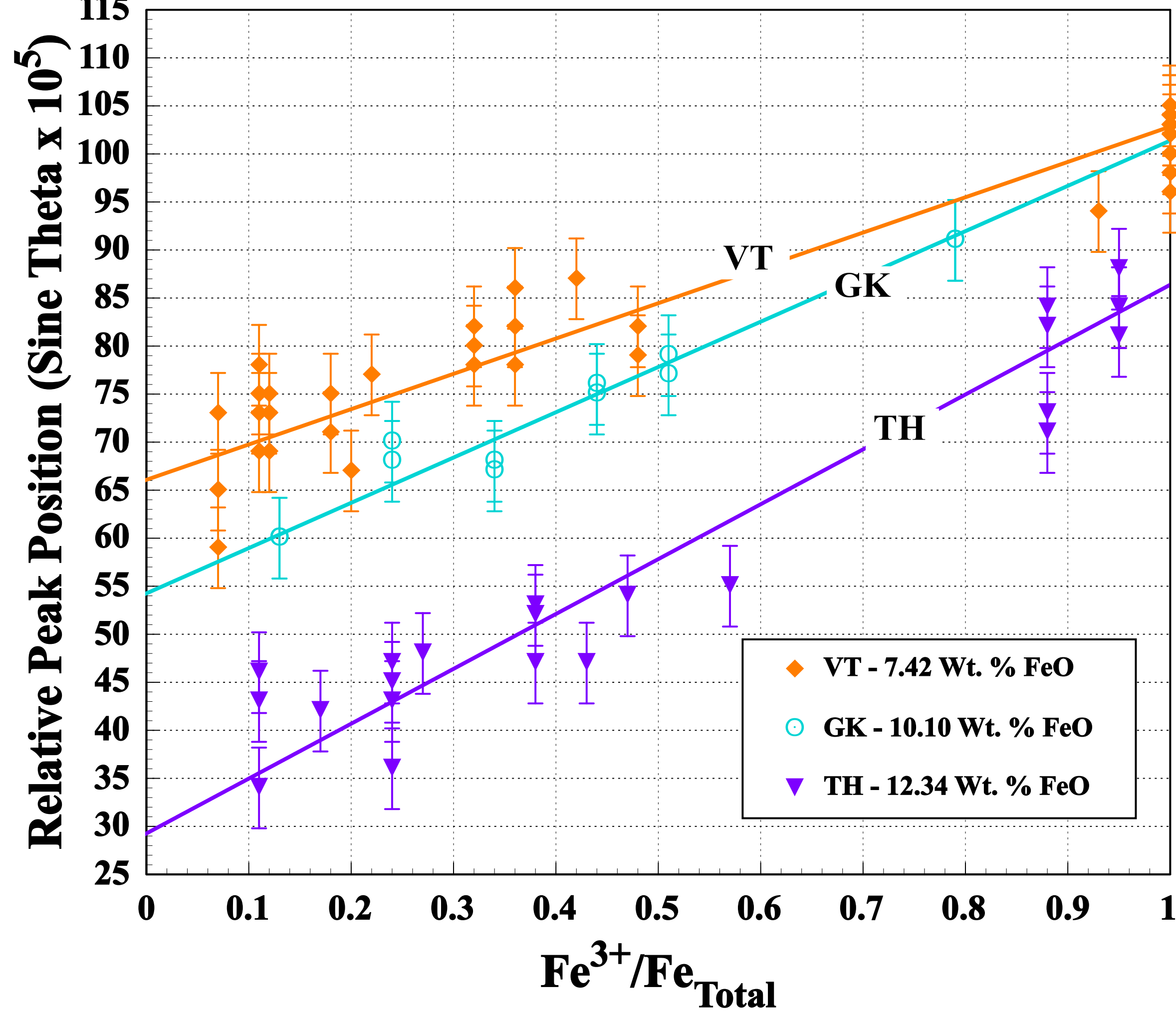
RPPs for samples of the three different amphiboles plotted against Fe^{3+}/Fe_{Total} as determined from ^{57}Fe Mössbauer spectroscopy. Error bars are ± 4.2 sine theta x 10^{-5}. Linear least squares fits to the TH ($R^2 = 0.93$), VT ($R^2 = 0.91$), and the GK ($R^2 = 0.96$) RPP data are shown.

The intercepts of the three lines at $Fe^{3+}/Fe_{Total} = 0$ yield values of the RPP of 66, 54, and 29 for FeO contents of 7.42, 10.1, and 12.34 wt. %, respectively. A 2nd order polynomial was fit to these three data points, yielding

$$RPP(0) = -1.37\ FeO^2 + 19.59\ FeO - 3.85\ (1)$$

Where FeO refers to the weight % FeO. Similarly, the intercepts of the three lines at $Fe^{3+}/Fe_{Total} = 1$ yield three values of the RPP of 103, 101, and 86 for FeO contents of 7.42, 10.1, and 12.34 wt. %, respectively. A 2nd order polynomial was fit to these three data points, yielding:
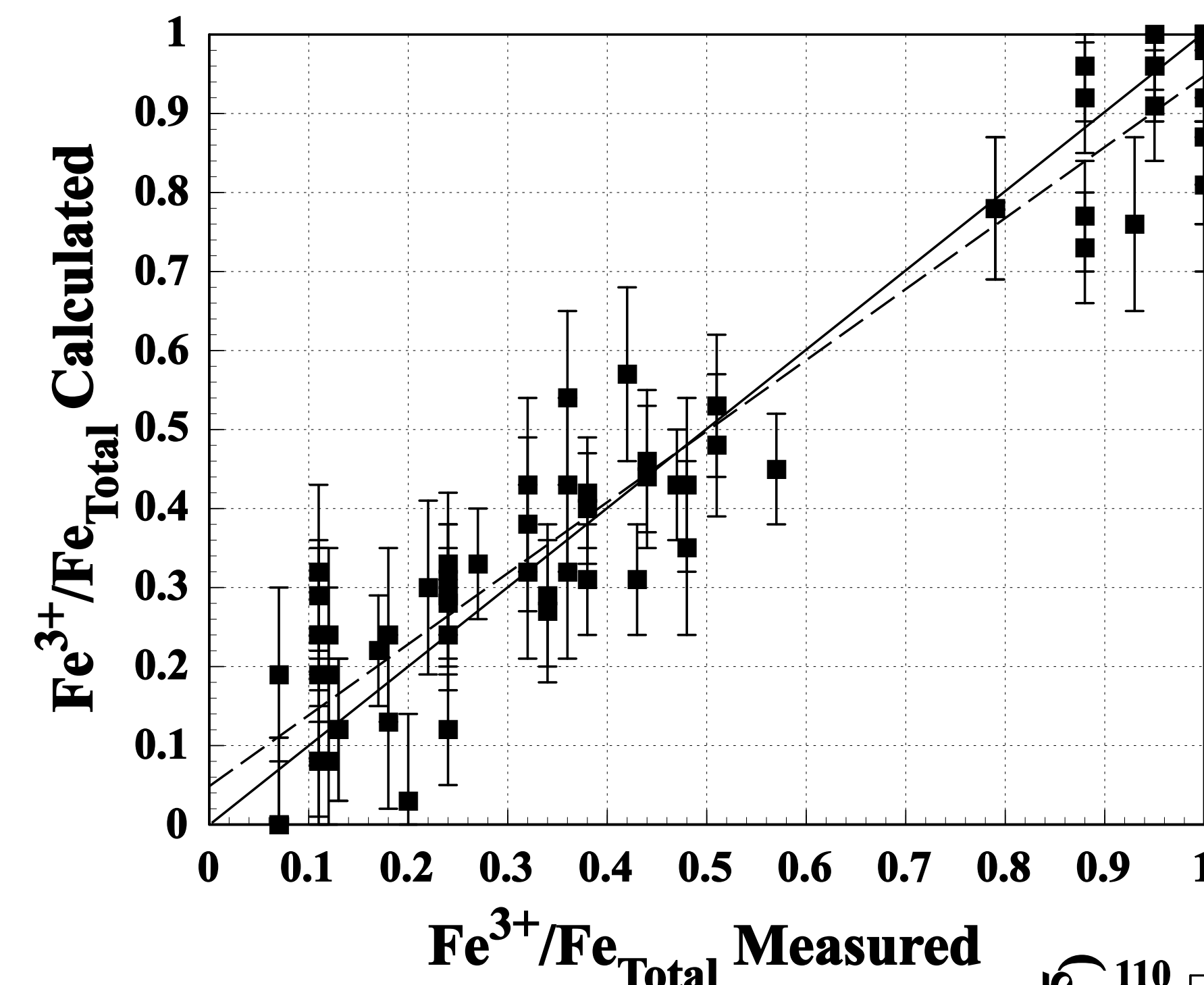
$$RPP(1) = -1.25\ FeO^2 + 21.39\ FeO + 13.05\ (2).$$

7. Accuracy & Precision

For any given Fe content, if values of Fe^{3+}/Fe_{Total} in amphiboles vary in a linear manner between the curves given by equation (1) and (2), then the relation between RPP, Fe Content, and Fe^{3+}/Fe_{Total} is:

$$Fe^{3+}/Fe_{Total} = RPP – RPP(0)\ /\ RPP(1) – RPP(0) \quad (3)$$

where RPP is the measured relative peak positions of the mineral in question and RPP(0) and RPP(1) are calculated using equations 1 and 2, respectively.

The calculated values of Fe^{3+}/Fe_{Total} (equation 3 using values of RPP for VT, GK, and TH) are plotted against values of Fe^{3+}/Fe_{Total} determined using ^{57}Fe Mössbauer spectroscopy (above). The average of the absolute values of the difference between the calculated and measured is 0.07.

Contours of constant Weight % FeO calculated using equation 3. Also plotted are the values for the OPH (Table 1) at RPP = 73 and 10.96 wt. % FeO. Based on Equation (3), a value for Fe^{3+}/Fe_{Total} of 0.54 is obtained which is comparable to the value of 0.44 that was independently determined for the OPH.
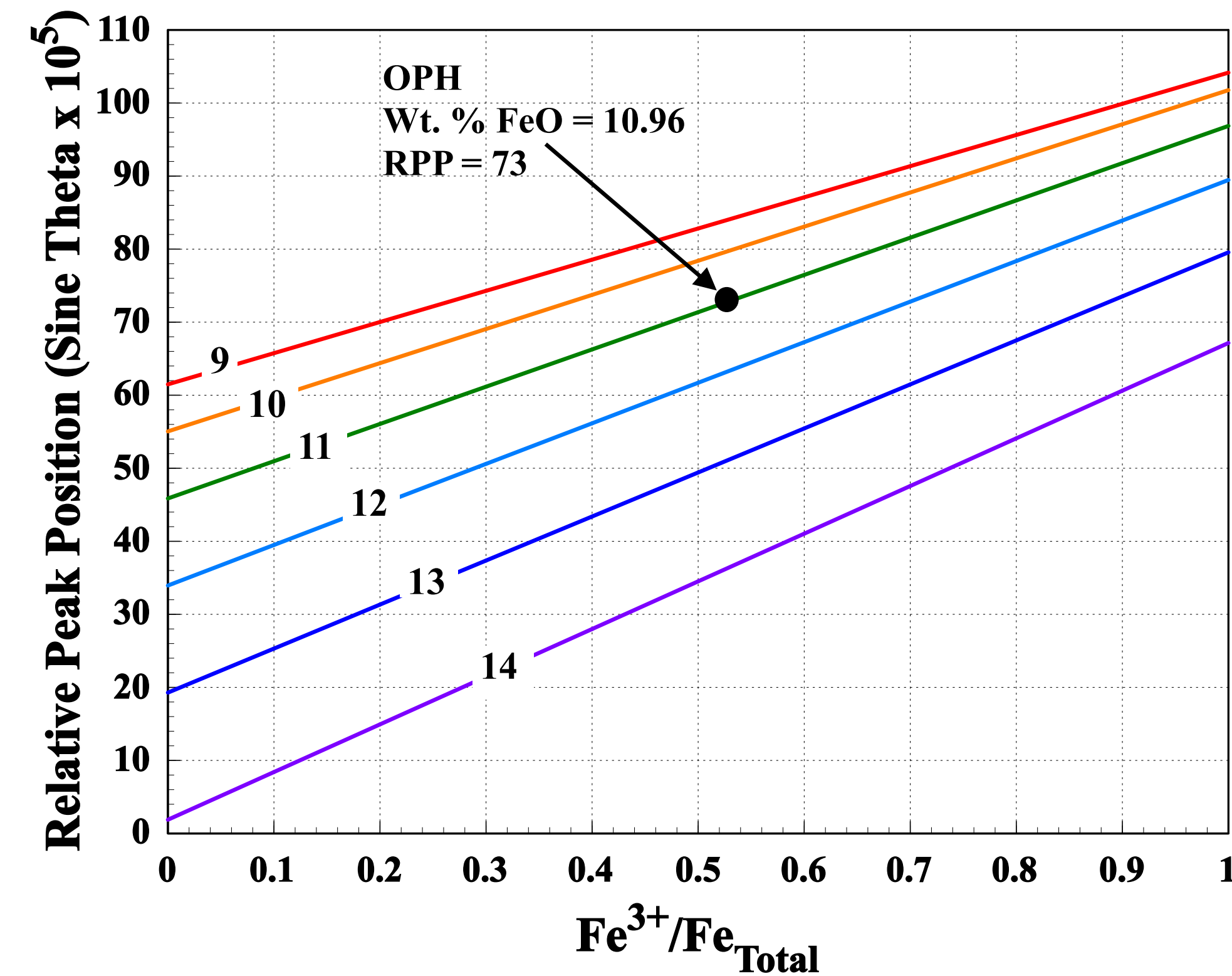
8. Discussion

The calibration presented here, based on three suites of experimentally treated amphiboles, reproduces the measured values of Fe^{3+}/Fe_{Total} to within ± 0.07.

Given the empirical nature of this calibration additional verification would be warranted for amphiboles with Fe contents that differ significantly from the amphiboles used in our calibration (i.e., weight % FeO > 7 and < 13).

All amphiboles used in this calibration were Al-rich calcic amphiboles with significant Na and variable amounts of Ti. This calibration may be applied to other amphiboles with similar chemical characteristics (e.g., most amphiboles that have formed in the Earth's mantle). However, without additional testing, caution should be exercised when dealing with amphiboles whose crystal chemistry differs significantly from those examined in this study.

References

Fialin, M., Wagner, C., Metrich, N., Humler, E., Galoisy, L., and Bezos, A. (2001) $Fe^{3+}/\sum Fe$ vs. FeLα peak energy for minerals and glasses: Recent advances with the electron microprobe. American Mineralogist, 86, 456-465.

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