Determination of accurate $^{41}\text{Fe}^{3+}$, $^{60}\text{Fe}^{3+}$, and $^{61}\text{Fe}^{2+}$ site populations in synthetic annite by Mössbauer spectroscopy

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ABSTRACT

We report accurate $^{41}\text{Fe}^{3+}$, $^{60}\text{Fe}^{3+}$, and $^{61}\text{Fe}^{2+}$ site populations in synthetic annite. They are achieved by detailed analysis of high-quality Mössbauer spectra collected at room temperature, liquid $\text{N}_2$ temperature, and liquid $\text{He}$ temperature. The experimental difficulties related to (1) site-specific recoilless fractions, (2) absorber thickness and polarization effects, and (3) absorber texture effects are rigorously addressed. A new quadrupole splitting distribution method that allows arbitrary shape distributions for each site is used for the spectral analysis. It resolves the three sites in accordance with visible spectral features and reveals a needed defect $^{61}\text{Fe}^{2+}$ site.

Whereas subspectral areas are generally believed to have optimal accuracies of a few percent of total spectral areas, we obtain site population to $\pm 0.2\%$ for Ni + NiO buffered synthetic annite: $^{41}\text{Fe}^{3+}/\text{Fe} = 4.00 \pm 0.15\%$, $^{60}\text{Fe}^{3+}/\text{Fe} = 7.00 \pm 0.20\%$, and $^{61}\text{Fe}^{2+}/\text{Fe} = 89.00 \pm 0.20\%$. These populations suggest that 16.50% of the H in the ideal structural formula, $\text{KFe}_2\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, is missing because of charge-balance requirements: $^{61}\text{Fe}^{2+} + \text{OH}^- = ^{60}\text{Fe}^{3+} + \text{O}^{2-} + \text{H}^+$.

INTRODUCTION

Several recent advances in the methodology of Mössbauer spectroscopy have a direct bearing on the accuracy with which site populations can be determined in Fe-bearing minerals. These include (1) thickness effect evaluations for absorbers with intrinsically broad lines (Ping and Rancourt, 1992; Rancourt et al., 1993), (2) ideal absorber thickness determinations (Long et al., 1983; Rancourt et al., 1993), (3) analytic methods for removing the spectral distortions of the thickness effect (Rancourt, 1989), (4) Voigt-based spectral line shapes for absorbers with quadrupole splitting distributions (QSD) (Rancourt and Ping, 1991; Ping et al., 1991), (5) criteria for identifying distinct spectral contributions (Rancourt et al., 1992; Rancourt, 1993), and (6) methods for determining site-specific recoilless fractions (Royer, 1991). Here, we report the first application of these methods in an attempt to obtain the best possible accuracy of site populations in an Fe-bearing mineral. We demonstrate that an accuracy of 0.2% of $\text{Fe}_{\text{tot}}$ is possible, whereas the generally accepted limit is 2–5% of $\text{Fe}_{\text{tot}}$.

We choose annite because of the predominant role of Fe in its overall crystal chemistry, with $^{61}\text{Fe}^{2+}$, $^{60}\text{Fe}^{3+}$, and $^{41}\text{Fe}^{3+}$ populations being controlled by both structural constraints and thermodynamic conditions (Hazen and Wones, 1972). Better site populations here give an improved evaluation of early annite crystal-chemistry models.

In applying the above methods to annite, we illustrate one of the major difficulties in obtaining site populations using Mössbauer spectroscopy: a given fitting model applied to a given spectrum does not, in general, produce unique populations. This is an intrinsic limitation of non-linear least-squares minimization problems that is often not recognized by spectroscopists. Instead of a unique solution, one obtains a domain of possible values in the space of the resolved site populations. Spectra collected at different temperatures give rise to solution domains that may have relatively small intersections, thereby significantly constraining the possible site populations.

We have obtained four solution domains from (1) model fits to the room-temperature (RT) spectrum, (2) model
fits to the liquid N\textsubscript{2} temperature (LNT) spectrum, (3) analysis independent of line-shape model of the RT dimensionless, intrinsic-absorber, resonant cross section, and (4) analysis independent of line-shape model of the liquid He temperature (LHeT) spectrum. Since the Fe\textsubscript{3+} is known, combining any two of the above solution domains gives unique [Fe\textsuperscript{3+}] [Al\textsuperscript{3+}] and [Fe\textsuperscript{2+}] populations, with different associated errors. In this sense, the site populations have been obtained by several independent methods. In particular, we stress that the LHeT evaluation is a truly independent measurement because annite is magnetically ordered at LHeT (Christie et al., 1991), and the hyperfine structure of the spectrum collected at this temperature is magnetically resolved.

The structural formula unit for ideal annite (including formal charges and 2:1 layer coordinations) is

\[
\text{K}^{+} \text{[Fe}_{3}^{2+} [\text{Al}_{3}^{3+}] 2 \text{Si}_{4}^{4+} \text{O}_{10}^{5-} (\text{OH})_{2}. \quad (1)
\]

Although the ideal analogue end-members in which [Fe\textsuperscript{2+}] is replaced by [Ni\textsuperscript{2+}, Mg\textsuperscript{2+} (phlogopite end-member), Cu\textsuperscript{2+} or Co\textsuperscript{2+} are believed to occur, Hazen and Wones (1972) argued that the ideal annite end-member does not occur because of structural constraints involving the mismatch of tetrahedral and octahedral sheets. They argued that in annite this mismatch is primarily alleviated by the oxanionate reaction

\[
\text{[Fe}_{2}^{2+} + \text{OH}^{-} \rightarrow \text{[Fe}_{3}^{3+} + \text{O}^{2-} + \text{H} \uparrow \quad (2)
\]

which replaces relatively large [Fe\textsuperscript{2+}] cations by [Fe\textsuperscript{3+}]. They stated that this theory was supported by a subsequent study employing Mössbauer spectroscopy (Wones et al., 1971) and that the latter study "confirmed that at least 10 mole percent of octahedral iron in all synthetic annites is in the trivalent state." Our synthetic annite contains 7.3 mol\% of [Fe\textsuperscript{3+}] in the trivalent state.

An earlier Mössbauer study (Häggström et al., 1969) had already observed a large amount of Fe\textsuperscript{3+} in a synthetic annite sample, and the only other Mössbauer study of synthetic annite (Ferrow, 1987a, 1987b) also clearly observes Fe\textsuperscript{3+} (both [Fe\textsuperscript{3+}] and [Fe\textsuperscript{3+}]) in a room-temperature spectrum. The presence of [Fe\textsuperscript{3+}] was not explained in the latter study, and accurate site populations were not attempted. Dyar and Burns (1986) studied three annite samples, with the most Fe-rich of these having 84\% of the amount of Fe contained in a synthetic annite sample. They reported [Fe\textsuperscript{3+}]/Fe = 0-10\% and Fe\textsuperscript{3+}/Fe = 11-55\%.

If a tetrahedral-octahedral mismatch is a major factor controlling site populations in annite, then the Fe\textsuperscript{3+}/Al\textsuperscript{3+} exchange

\[
[\text{Fe}_{3}^{3+} + [\text{Al}_{3}^{3+} \rightarrow [\text{Al}_{3}^{3+} + [\text{Fe}_{3}^{3+} + \text{Cl}_{2}^{3+} \quad (3)
\]

is a more effective mechanism for reducing the relatively large lateral extension of the [Fe\textsuperscript{2+}] sheet than the oxanionate reaction alone. That suggests that once the structural constraints are satisfied, the relative amounts of [Fe\textsuperscript{3+}] and [Fe\textsuperscript{3+}] depend on the reducing ability of the environment at synthesis. The essential step in testing these and other ideas concerning the cause of site populations in annite is to obtain accurate [Fe\textsuperscript{3+}] and [Fe\textsuperscript{3+}] populations.

**SAMPLE SYNTHESIS AND CHARACTERIZATION**

The synthesis was performed by J.-L. Robert at Orléans and was achieved in the following way.

The starting material was a fine mechanical mixture of a specially prepared silicate gel and metallic Fe powder. Such a mixture allows fast and reproducible equilibration under the experimental conditions used (Juliet et al., 1987).

The gel contained half of the Fe\textsubscript{3+} and was prepared by the method of Hamilton and Henderson (1968) using the following reagents: high-grade K\textsubscript{2}CO\textsubscript{3} transformed into KNO\textsubscript{3} by reaction with HNO\textsubscript{3}, a titrated nitrate solution of Al, a titrated nitrate solution of Fe, and tetraethylhydroxysilicate (T.E.O.S.), for silica.

The starting mixture and 20 wt\% of distilled H\textsubscript{2}O were sealed into a Pt tube by arc welding. The synthesis was performed at 600 ± 5 °C and P\textsubscript{HSo} of 2.00 ± 0.05 kbar, in a cold-seal Tuttle-type externally heated pressure vessel, with an experiment duration of 3 weeks.

The f\textsubscript{0} was controlled by the Ni + NiO buffer, using the double capsule (Au-Pt) method devised by Eugster (1957). Under our experimental conditions, this buffer sets an f\textsubscript{0}, of 10-19.1 bars (Hubner and Sato, 1970). This f\textsubscript{0}, is approximately that set by the alloy constituting the pressure vessel.

Powder X-ray diffraction (XRD) indicated that the experiment product was entirely a single phase of mica. The data were consistent with the 1\textit{M} polytype structure having unit-cell parameters of \(a = 5.393(2), b = 9.342(1), c = 10.332(3) \text{ Å}, \beta = 100.1(2)°, V = 512.5 \text{ Å}^3\). These are similar to those given by Hazen and Burnham (1973) for annite from Pikes Peak (\(a = 5.3860, b = 9.3241, c = 10.2683 \text{ Å}, \beta = 100.63°, V = 506.8 \text{ Å}^3\)).

Fe-bearing impurities were not detected in any of the Mössbauer spectra or in any of the Squid (superconducting quantum interference device) magnetometry measurements performed between 4.2 and ~250 K. In addition, no signs of impurities were seen in any of the scanning electron microscope (SEM) pictures. These show that the synthetic annite is very fine grained, with the largest crystals having typical dimensions of 1-2 µm and the smallest crystals being typically ~0.1 µm (Fig. 1).

Several low-field Squid magnetometry measurements (0.5-30 G) revealed a magnetic ordering temperature at \(T_c = 58 ± 1 \text{ K}\). This is the highest ordering temperature ever observed in any layer silicate and possibly in any magnetically two-dimensional material. It is indicative of a large Fe\textsuperscript{2+} loading of the octahedral sheets.

The Squid data on the 30 G susceptibility of the powder follow the Curie-Weiss law at \(T \gtrsim 60 \text{ K}\). Analysis of these data in the range of 100-150 K yields a Curie-Weiss temperature \(\theta_{CW} = 60 ± 2 \text{ K}\) and a Curie constant \(C = 0.020 ± 0.002 \text{ emu·K/g}\). The predicted value of C for
ideal annite ($^{57}$Fe$^{2+}$/Fe = 100%) having the cell volume $V = 512.5 \, \text{Å}^3$ and corresponding ideal density $\rho = 3.317 \, \text{g/cm}^3$ is $(6/V)(\mu_\mu n\mu)^2/3k_B = 0.021 \, \text{emu-K/g}$, where $\mu_\mu$ is the Bohr magneton, $k_B$ is the Boltzmann constant, and $p_{eff} = 5.4$ is the effective Bohr magneton number for an Fe$^{3+}$ ion (Ashcroft and Mermin, 1976). Letting 11% of the Fe be Fe$^{3+}$ implies $p_{eff} = 5.46$ and gives a predicted $C = 0.022 \, \text{emu-K/g}$. The Squid magnetometry results therefore give an upper limit for Fe$^{3+}$/Fe of ~10%.

Infrared absorption in the OH-ion stretching mode region showed the expected dominant N band at 3665 cm$^{-1}$, with a full width at half maximum of 30 cm$^{-1}$. The N band arises from OH ions for which the three immediately neighboring octahedral sites are filled with divalent ions (Vedder, 1964), here Fe$^{2+}$-Fe$^{2+}$-Fe$^{2+}$. In addition, two small bands of comparable intensity having widths of ~30 cm$^{-1}$ are present at 3580 and 3545 cm$^{-1}$. We interpret these as I bands, which are caused by OH ions having one of the three closest octahedral sites occupied by a trivalent ion (Vedder, 1964), and refer to them as I$_a$ and I$_b$, respectively. This assignment is supported by the fact that I$_a$ grows dramatically (remaining at 3545 cm$^{-1}$) and becomes comparable in intensity to the N band when the annite sample is oxidized by heating in air (Christie et al., 1993). We therefore attribute I$_a$ and I$_b$ to Fe$^{2+}$-Fe$^{2+}$-Al$^{3+}$ and Fe$^{2+}$-Fe$^{3+}$-Fe$^{3+}$ configurations, respectively. Their relative intensities are consistent with the amounts of $^{57}$Al$^{3+}$ and $^{57}$Fe$^{3+}$ obtained by Mössbauer spectroscopy in the present study. When V bands (caused by OH ions close to octahedral vacancies) are present, they occur at lower frequencies than I bands (Vedder, 1964). No other distinct bands are present down to 3000 cm$^{-1}$ that might be attributed to V bands. Thus, the infrared absorption spectrum indicates the presence of $^{57}$Al$^{3+}$ and $^{57}$Fe$^{3+}$ and the relative absence of octahedral vacancies.

**Experimental Methods and Analysis**

**Collection and Calibration**

Transmission $^{57}$Fe Mössbauer spectra were obtained, calibrated, and folded in the usual way (e.g., Rancourt et al., 1992). Folding is essential to produce flat backgrounds with parameters that do not trade off with those of the absorption patterns when least-squares fitting is performed.

The RT center shifts (with RT = 22 °C) are referenced to metallic Fe at RT; however, the center shifts at LNT and LH$_T$ depend on the $^{57}$Fe center shifts of the $^{57}$Co-Rh source at LNT and LH$_T$, respectively, and are therefore not known accurately.

All the spectra except one were collected at Ottawa. Two LH$_T$ spectra were collected: one at $T = 7.0 \, \text{K}$ was collected at Ottawa, and one at $T = 4.2 \, \text{K}$ was collected at Technische Universität München by Murad. The München data were collected in the sine mode rather than in the constant acceleration mode of the transducer. No significant difference can be seen between these two LH$_T$ spectra, and both were analyzed for the present study.

The low-temperature experiments were done in a He exchange gas cryostat, with the source and absorber at the same temperature, although the source temperature was not measured directly.

The cryogenic absorber was prepared as follows and was also used at RT in the cryostat. A Cu holder with ultra-pure Al windows 1.40 cm in diameter was uniformly loaded with 81.5 mg of the annite powder. The powder was hand pressed between the two Al windows to ensure mechanical stability and thermal contact. The holder is not gas-tight and allows exchange gas to penetrate.

Rancourt (1989) recently described all of the factors that need to be considered when accurate site populations from Mössbauer spectroscopy are required. We next address each of these that are relevant to the present case.

**Spectrum Quality: Signal to Noise Ratio**

Fitting models must rely on distinct observed spectral features. Therefore, the best possible statistics should be...
obtained. To achieve this we use the ideal absorber thickness for annite. This thickness gives the largest signal to noise (S/N) ratio in a given accumulation time and is ~50 mg/cm² for annite (Rancourt et al., 1993; Long et al., 1983). RT spectra were also collected at 35, 61, and 90 mg/cm² to gauge the impact of thickness effects on fitted spectral areas.

Absorber thickness effects

At a given absorber thickness, thickness effects are particularly severe for spectra containing small numbers of intrinsically thin absorption lines but are much less significant when the absorption is divided into many and intrinsically broad lines. New methods for calculating the expected thickness attenuation of intrinsically broad lines have recently been developed (Rancourt et al., 1993; Ping and Rancourt, 1992). These suggest that, for annite, significant thickness attenuation should occur at the thicknesses we have used. This implies that a full thickness correction procedure (Rancourt, 1989) should be applied to yield the intrinsic absorber cross section.

We have applied this procedure to our 53-mg/cm² RT spectrum and have analyzed the extracted intrinsic absorber cross section. We find that the site-specific relative subspectral areas are the same within uncertainties as those from fitting the raw 53-mg/cm² spectral data. It seems therefore that, in this case, the non-negligible thickness-related spectral distortions and main peak attenuations do not significantly affect the extracted subspectral relative areas with the fitting model line shapes that we have used. This is true despite the noticeable thickness distortions that are shown to increase systematically with thickness in Figure 2. The simulated spectrum for the thin-sample limit is also shown for comparison. Representative extracted Fe³⁺/Fe values are 11.0–11.2% at 0–53 mg/cm², ~11.5% at 61 mg/cm², and ~11.7% at 90 mg/cm².

That we are effectively in the thin limit for those quantities that interest us is supported by the additional facts that (1) the LN⁷ spectrum (53 mg/cm² absorber) is thicker because of larger recoilless fractions and has a different line shape because of larger quadrupole splittings (QS), yet it gives the same relative subspectral areas as the RT spectra; and (2) the LHe⁷ hyperfine spectra are magnetically split and consist of very broad lines from hyperfine field distributions coupled with quadrupole splitting distributions, yet they also give the same subspectral areas. The latter point is significant because such a hyperfine structure should dramatically reduce the effective absorber thickness.

Polarization effects

Polarization effects can occur in addition to ordinary thickness effects when the Mössbauer radiation is polarized, as it is resonantly absorbed on traversing the finite thickness absorber. This, in general, can occur in single-crystal or textured absorbers but will not occur in sufficiently fine and nontextured absorbers (see section on absorber texture below).

For a given amount per squared centimeter of a polarizing material or mineral, a textured or single-crystal sample gives rise to greater spectral distortions than a nontextured fine powder absorber of the same material. For this reason, an absorber that is expected to be thin on the basis of calculations of the effect of ordinary thickness (e.g., Ping and Rancourt, 1992) may, in fact, be thick if it contains polarizing material.

These considerations are important to the present application because (1) all materials that give rise to quadrupole doublets are Mössbauer polarizing materials, and (2) no general and practical procedure presently exists to correct for polarization effects arising from real absorbers with intrinsically broad absorption lines, such as those found in all Fe-bearing silicate minerals.

Fortunately, our annite is a very fine powder (a clay in fact, see Fig. 1) and our absorbers are nontextured (next section) such that polarization effects are negligible in this application. This is supported by the fact that exact ordinary absorption corrections of the RT spectrum gave consistent results (previous section).

Absorber texture

A nontextured absorber is a powder or polycrystalline sample in which all of the crystal orientations are represented with equal probabilities. If there is a preferred orientation, then the absorber is textured.

If the Goldanskii-Karyagin effect and dynamic line shape effects are barred, nontextured absorbers have
spectra composed of elemental quadrupole doublets that have equal intensities of their high- and low-energy Lorentzian line components. This supplies welcome constraints for the fitting models that are applied to the spectral data. In this study, these constraints were essential.

Texture is particularly difficult to avoid in layer silicates where the cleavage gives rise to flakes that prefer the plane of the absorber. However, with the claylike nature of our annite (Fig. 1), using a relatively thick absorber (of near ideal thickness 53 mg/cm²) gave a complete absence of texture.

We checked this by rotating our 53-mg/cm² absorber by 30 and 54°, which gave thicknesses of 61 and 90 mg/cm², respectively. All of the spectral changes (Fig. 2) can be attributed to thickness effects alone, with no change in intrinsic doublet symmetries. Furthermore, our fitting models that assume complete absence of texture gave statistically ideal and physical fits and no evidence of systematic differences that could be attributed to a small amount of texture.

The 35-mg/cm² absorber also showed a total absence of texture; however, a 6.2-mg/cm² absorber showed obvious signs of texture. Using the near ideal thickness of 53 mg/cm² therefore has the double advantage of giving good spectrum quality and ensuring that, with this claylike sample, there is no texture. Having to account for thickness effects is a worthwhile compromise in view of these advantages.

**Quadrupole splitting distributions (QSD)**

In modeling the spectra, it is advantageous to use as many physical constraints as can be rigorously justified. Here, the choice of the model line shape is the first consideration. Although elemental lines that are due to single groups of identical probe environments must, in the absence of thickness effects and other artifacts, be Lorentzian lines, absorption lines that are made up of several overlapping Lorentzians are not Lorentzian in shape.

A given species in a given anion coordination, Fe³⁺, Fe²⁺, etc., say, has many different local environments that are defined by local distortions, local charge distributions, the types and positions of nearest neighbor anions, next nearest neighbor cations, etc. Each local environment gives rise to a single elemental quadrupole doublet such that a continuous distribution of quadrupole splittings can be used to model the overall absorption doublet.

A powerful new method for fitting with distributions has been developed (Rancourt and Ping, 1991) and has been applied to quadrupole splittings recently (Ping et al., 1991). We use this method here and therefore briefly describe it.

Each local environment has its own quadrupole splitting (Δ) and also has its own center shift (δ). Since, for a given species and anion coordination, Δ depends much more strongly on the local environment than does δ, we assume that δ and Δ are linearly coupled:

\[ \delta = \delta_0 + \delta_1 \cdot \Delta \]  

and distribute only Δ. That is, by optimization we obtain a distribution, \( P(\Delta) \), of quadrupole splittings that automatically has an associated distribution of δ through Equation 4.

The coupling parameters δ₀ and δ₁ are characteristic of a particular group of probe ions (e.g., of a particular species or of a particular species and anion coordination, etc.). Rancourt and Ping (1991) referred to such a group, one that has its own P(Δ) and its own values of δ₀ and δ₁, as a site. In the present applications to annite at RT and LNT (above the magnetic ordering temperature), it turns out that only three such sites with independent Δ distributions are required and that these correspond to ⁴⁴Fe³⁺, ⁴⁴Fe²⁺, and ⁴⁴Fe²⁺, that is, only the valence state and coordination number give rise to distinct spectral components. All other information concerning more subtle structural features [e.g., cis and trans octahedral sites, FeO³⁻ and FeO²⁺OH⁺ coordinations rather than FeO³⁻ (OH⁻)₂ at octahedral sites, etc.] is taken into account by the Δ distributions. Rancourt (unpublished manuscript) has established that quantitative populations for cis and trans ⁴⁴Fe²⁺ sites cannot be obtained by Mössbauer spectroscopy in trioctahedral micas. The cis and trans sites are not resolved but only contribute to the overall QSD, \( P(\Delta) \).

We assume that a true \( P(\Delta) \) can be expressed as a sum of Gaussian components:

\[ P(\Delta) = \sum_{i=1}^{N} p_i G_i(\Delta_i, \sigma_{\Delta_i}) \]  

where the \( p_i \) is a weight factor such that \( \sum p_i = 1 \) and each Gaussian, \( G_i \), is normalized to an area of 1. Each Gaussian has a center position, \( \Delta_i \), and a Gaussian half-width, \( \sigma_{\Delta_i} \). Only as many Gaussians, \( N \), as are required by the data are used: most often \( N = 1 \) or \( N = 2 \) is sufficient. This is because the Gaussians are intrinsically suitable for describing real distributions.

The power of the technique lies in that the corresponding line shape, \( Q(\nu) \), for a given site can be shown analytically to be a sum of Voigts (Rancourt and Ping, 1991):

\[ Q(\nu) = \sum_{i=1}^{N} p_i \sum_{k=\pm 1} V_k(\delta_0 + \delta_i \Delta_i + k\Delta_i/2, |\delta_0 + \gamma/2|\sigma_{\Delta_i}, \gamma, h_i; \nu) \]  

where \( \gamma \) is the underlying Lorentzian full width at half maximum (FWHM) and \( h_i \) is the underlying Lorentzian height. For non textured thin absorbers we should have \( h_i = h \) (symmetric elemental doublets) and \( \gamma = 0.194 \) mm/s (Heisenberg value for ⁵⁷Fe).

Using this line shape \( Q(\nu) \) in a configuration of one site and one component \( (N = 1) \) with \( h = h_1 \) and \( \gamma = 0.194 \) mm/s requires six free parameters: \( h, \delta_0, \delta_i, \Delta_0, \sigma_0, \) and a flat background level, BG. By comparison, two equal-area Lorentzian lines that are allowed to have different widths [the two Voigt lines in the \( N = 1 \) \( Q(\nu) \) have different widths through \( \delta_i \)] also require six free parameters: two centers, two \( \gamma's, \) one area, and a BG.
The $Qy$ line shapes in a one-site, $N$-component configuration with $h_\gamma = h_\gamma$. and free $\gamma$ require $4 + 3N$ free parameters. Our final fits to RT and LNT spectra require three sites attributable to $^{57}$Fe$^{3+}$, $^{57}$Fe$^{3+}$, and $^{60}$Fe$^{2+}$. Each site gives distinct, characteristic, visible features in the spectra (e.g., Rancourt et al., 1992). Both $^{57}$Fe$^{3+}$ and $^{60}$Fe$^{3+}$ require only $N = 1$; however, the $^{60}$Fe$^{2+}$ site requires $N = 3$. The resulting model is referred to as a 1-1-3 model. For the Fe$^{3+}$ sites, we always set $\delta_i = 0$, and the $\gamma$ is always common to all sites. This gives a maximum of 21 free parameters in our 1-1-3 model fits.

**Parameter tradeoffs**

As mentioned above, even for a given fitting model that uses physically correct line shapes and that introduces only as many free parameters as are required to obtain statistically acceptable fits, a fundamental problem persists: the solution obtained by minimization is usually not unique. Entire regions in the parameter space give equally good and acceptable fits. This problem is particularly severe in cases like the present one, where considerable line overlap occurs.

Since we are mainly concerned with subspectral (i.e., site-specific) areas to obtain site populations, we examine how these areas trade off with each other. We find that the Mössbauer solution, for, say, 1-1-3 fits to the RT spectrum, corresponds to an entire line segment of finite length in the three-dimensional space of the populations $^{57}$Fe$^{3+}$, $^{60}$Fe$^{3+}$, and $^{60}$Fe$^{2+}$.

All the points on this line segment give equally good 1-1-3 fits at RT by changing (i.e., trading off) the values of several of the fitting parameters that are dependent on each other through the spectrum shape. Such a solution domain (Rancourt et al., 1985) of equivalent Mössbauer solutions can always be mapped out completely by imposing fixed values on some of the dependent parameters.

The LNT spectrum yields its own solution domain. If the latter intersects the RT domain, then the Mössbauer solution can be significantly reduced, in our case to a single point in the population space. A third measurement, such as a very different LiHe$T$ spectrum, can further reduce the solution or, in our case, corroborate the already unique solution.

That is the main idea. Once a line shape model has been carefully chosen based on physical and statistical considerations, we identify the solution domains and attempt to reduce the Mössbauer solution by using several measurements.

**Recoilless fractions**

In the absence of thickness and polarization effects, the subspectral area, $A_i$, for site $i$ is related to the corresponding site population as

$$A_i = \frac{\eta_i \, f_i \, \Gamma_0 \, f_o \, n_{\text{as}}}{1 - f_o}$$

where $\eta_i$ is the part of the BG level that corresponds to Mössbauer (14.4 keV) $\gamma$-rays, $f_i$ is the recoilless fraction of the source, $\sigma_0$ is the cross section at resonance for the Mössbauer transition, $\Gamma_0$ is the natural FWHM of the Mössbauer transition ($\Gamma_0 = 0.097$ mm/s), $f_o$ is the sitespecific recoilless fraction of the absorber, and $n_{\text{as}}$ is the number of $^{57}$Fe nuclei in site $i$ per unit area of the uniform thickness absorber.

The total spectral area is then a sum over all sites

$$A_{\text{tot}} = \sum_j A_j$$

such that the relative site populations are given by

$$\frac{Fe}{Fe} = \frac{n_{\text{as}}}{n_{\text{as}}} = \frac{f_o}{f_o A_{\text{tot}}}$$

where

$$n_{\text{as}} = \sum_j n_{\text{as}}$$

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**Table 1. RT spectrum fit parameters**

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<th>Fit</th>
<th>$\beta$</th>
<th>BG</th>
<th>$A_{\gamma}$</th>
<th>$\delta_i(3+)$</th>
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Note: symmetric elemental doublets are assumed ($h_\gamma = h_\gamma$) for all sites. Parameters $\gamma$, $\delta_i$, $\Delta_0$, and $\sigma_i$ are in millimeters per second. The (3+), (3+), and (2+) refer, respectively, to $^{57}$Fe$^{3+}$, $^{57}$Fe$^{3+}$, and $^{60}$Fe$^{2+}$-specific parameters. BG is in kilocounts. The total absorption area

$$A_{\text{tot}} = \frac{\eta_i \, f_i \, \Gamma_0 \, f_o \, n_{\text{as}}}{1 - f_o}$$

(Eq. 6) is in kilocounts times millimeters per second. Parameter $\delta_i$ (Eq. 4) is dimensionless. The site- and component-specific areas ($a_{3+}$, etc.) are in percentages of $A_{\text{tot}}$. Except in the 1-1-2 fit, $a_{3+}$ and $a_{3+}$ are frozen parameters that are not adjusted in the fitting process.
and the average recoilless fraction is given by

$$\bar{f} = \frac{1}{n_a} \sum_{j} n_{a_j} f_{a_j}. \quad (9)$$

Equation 8 shows that even relative site populations can only be obtained from spectral areas if site-specific absorber recoilless fractions are known. These recoilless fractions depend on local bonding strengths and configurations and must be measured. They also depend on temperature.

Royer (1991) has made an extensive study of site-specific recoilless fractions in Fe-bearing trioctahedral micas and found that, whereas all the biotite samples studied had larger Fe³⁺ recoilless fractions than Fe²⁺ recoilless fractions in varying degrees, the same synthetic annite sample as studied here had recoilless fractions that were equal for all sites, within experimental accuracy. This finding is corroborated by our study, which finds the same Fe³⁺/Fe²⁺ spectral area ratios at RT, LNT, and LHeT.

## RESULTS AND DISCUSSION

### RT spectrum

The Fe²⁺ spectral contribution has sufficient structure to require at least two Gaussian components in its QSD. The best 1-1-2 fit that resolves the ⁵⁷Fe³⁺, ⁸⁷⁹Fe⁺, and ⁵⁹Fe²⁺ sites is shown in Figure 3, and the corresponding fit parameters are given in Table 1.

The two Fe²⁺ Gaussian components should not simply be ascribed to cis and trans sites. They are part of one continuous distribution that cannot be unambiguously resolved into cis and trans contributions. Indeed, equivalent fits can be obtained for an entire range of cis-trans population ratios that actually correspond to essentially identical QSD. This topic will be the subject of a future publication.

The difference spectrum (Fig. 3) of the 1-1-2 fit shows significant discrepancies in the region of the visible Fe³⁺ features (0.1-1.1 mm/s) and, most notably, at ~1.7 mm/s. The latter discrepancy is also seen in other Fe-bearing trioctahedral micas (e.g., Hargraves et al., 1990) and suggests the existence of a small family of Fe²⁺ sites that have relatively small QS. This, in turn, suggests that a 1-1-3 fitting model is appropriate. If so, it should also remove the other discrepancies.

The discrepancy observed at ~1.7 mm/s (Fig. 3) is real and does not disappear when the spectrum is corrected for thickness (e.g., Hargraves et al., 1990). It is essential that this inconsistency be resolved since, in our annite, it represents a spectral area comparable in magnitude with the Fe³⁺-specific subspectral areas. A 1-1-2 fit overestimates Fe³⁺/Fe, especially ⁷⁷⁹Fe³⁺/Fe.

The 1-1-3 model is successful in that it eliminates all previous systematic differences, and it yields a statistically ideal reduced chi-squared of $\chi^2_{red} \approx 1$. This means that the 1-1-3 model may be the correct physical model; it cannot be ruled out on statistical grounds, as in the case of the 1-1-2 model with $\chi^2_{red} \approx 3$. As mentioned above, however, there remains a fundamental problem of non-uniqueness.

A typical 1-1-3 fit is shown in Figure 4, and the fit parameters for several 1-1-3 fits are given in Table 1. The worst 1-1-3 fit considered is shown in Figure 5.

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<th>$a(3+]</th>
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Fig. 3. The solid line running through the spectral data represents the best 1-1-2 fit to the RT spectrum that resolves the three Fe sites. The difference spectrum for this fit is shown with the same vertical scale at the top of the figure, where the solid horizontal line indicates the zero-difference level. The subspectral contributions corresponding to ⁷⁷⁹Fe³⁺ (narrow doublet) and ⁵⁹Fe²⁺ (broad doublet) are shown on a shifted BG level for clarity. The corresponding fit parameters are given in Table 1.
Table 2. LNT spectrum fit parameters

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Note: symmetric elemental doublets are assumed ($h, = h, ) for all sites. Parameters $\gamma$, $\delta_{0}$, $A_{wo}$, and $\sigma_{0}$ are in millimeters per second. The $(3+)$, $(2+)$, and $(3+)$ refer, respectively, to $^{57}$Fe$^{3+}$, $^{57}$Fe$^{2+}$, and $^{57}$Fe$^{3+}$-specific parameters. BG is in kilocounts. The total absorption area

$$A_{wo} = \sum_{i=1}^{3} \sum_{k=1}^{n} \sum_{i=1}^{3} p_{ik}$$

(Eq. 6) is in kilocounts times millimeters per second. Parameter $\delta_{0}$ (Eq. 4) is dimensionless. The site- and component-specific areas ($a(3+)$, etc.) are in percentages of $A_{wo}$. Except in the 1-1-2 fit, $a(3+)$ and $\sigma_{0}(3+)$ are frozen parameters that are not adjusted in the fitting process.

The 1-1-3 fits differ in the partitioning of the spectral area among the three sites of interest. We illustrate these tradeoff effects by plotting $^{57}$Fe$^{3+}$/Fe vs. $^{57}$Fe$^{2+}$/Fe for acceptable 1-1-3 fits of the RT spectrum (Fig. 6). This figure also shows the analogous tradeoff curve for 1-1-3 fits of the LNT spectrum and the Fe$^{3+}$ constraint obtained from both the LHeT spectra and the thickness-corrected RT spectrum, as explained below.

On both the RT and LNT trade-off curves shown in Figure 6, the $\chi^2$ remains ideal within approximately 2 s.d. of its statistically predicted mean value for a correct fitting model.

As we move on these trade-off curves, we also observe some trade-off between the Fe$^{3+}$ and the Fe$^{2+}$. For example, on the RT curve we go from Fe$^{3+}$/Fe = 11.9% at the low $^{57}$Fe$^{2+}$ end to Fe$^{3+}$/Fe = 11.0% at the high $^{57}$Fe$^{2+}$ end (Table 1). The LNT trade-off curve has a more constrained behavior, with Fe$^{3+}$/Fe varying between 11.25 and 10.89% (see below).

LNT spectrum

Figure 7 shows that, at LNT (= 80 K), a 1-1-2 model works better than at RT (Fig. 3). The fit (Table 2), however, is again statistically unacceptable ($\chi^2 > 1 + 2\sigma$) and again shows a significant systematic discrepancy on the low-energy side (here at ~2 mm/s) of the high-energy component of the Fe$^{2+}$ absorption. This again suggests the existence of a family of Fe$^{2+}$ local environment sites that have relatively small QS and leads us to 1-1-3 fits.

A typical 1-1-3 fit to the LNT spectrum is shown in Figure 8, and the fit parameters for all the 1-1-3 fits considered are given in Table 2. The relevant trade-off curve for $^{57}$Fe$^{3+}$/Fe vs. $^{57}$Fe$^{2+}$/Fe at LNT is plotted in Figure 6, along with the corresponding RT curve.
On examining these curves (Fig. 6) and the corresponding data (Tables 1 and 2), we note that the LNT curve gives a relatively narrow range of possible populations compared with the range given by the RT curve alone. This situation arises because the site-specific contributions are better resolved in the LNT spectrum. In particular, the visible $^{57}$Fe$^{3+}$ contribution goes from being a shoulder at RT (0.4 mm/s in Fig. 3) to being a distinct peak at LNT (0.6 mm/s in Fig. 7).

We also note that if these RT and LNT tradeoff curves are plotted (not shown) in the full three-dimensional population space of $^{57}$Fe$^{2+}$ vs. $^{56}$Fe$^{2+}$ and $^{56}$Fe$^{3+}$, then they continue to be represented by line segments, and these line segments come closest to intersecting at their large $^{57}$Fe$^{3+}$ ends, where $^{57}$Fe$^{3+}$/Fe = 11.0%. This is in contrast to the plot of $^{57}$Fe$^{3+}$/Fe vs. $^{56}$Fe$^{3+}$/Fe, where the projections of the true tradeoff curves appear as almost parallel line segments.

This shows that, in the present application, combining RT and LNT results leads to a unique solution. This solution is corroborated by the LHeT measurements and by an independent method that gives a measurement of Fe$^{3+}$/Fe from a thickness-corrected spectrum.

The thickness-corrected RT spectrum

The RT spectrum was corrected for thickness using procedures that have been described elsewhere (Rancourt, 1989; Royer, 1991). In this way, the dimensionless intrinsic absorber resonant cross section, $\sigma'_0(E)$, is obtained from the measured absorption spectrum by deconvoluting the transmission integral.

This cross section has an area of $\int dE \sigma'_0(E) = \frac{\gamma_0}{\Gamma_0} \eta_0$, and is free of the artifacts from (1) thickness effects and (2) source line width. This means that the spectral features in $\sigma'_0(E)$ are much narrower than the corresponding features in the absorption spectrum, by at least $\Gamma_0$. This is seen in Figure 9, where the RT $\sigma'_0(E)$ is plotted.

Here we see that the visible Fe$^{3+}$ contributions are much more resolved than in the raw data and that the high-energy Fe$^{2+}$ line is much sharper. The level at 1.55 mm/s is close to the zero-resonance BG level such that the cross section can be clearly divided into two areas, irrespective of any fitting model. These are a low-energy area, $A_L$,
at $E < 1.55$ mm/s and a high-energy area, $A_H$, at $E > 1.55$ mm/s.

Clearly then,

$$\frac{Fe^{3+}/Fe}{A_L - A_H}/(A_L + A_H)$$

(10)

and, since the dividing energy has a maximum uncertainty of $\pm 0.07$ mm/s, we conclude that $Fe^{3+}/Fe = 11.19 \pm 0.25\%$.

This is a rigorous constraint that is devoid of any error caused by thickness effects and that does not depend on any assumed fitting model. Fitting $\sigma(E)$ with a 1-1-3 model does, of course, give the same result. This constraint reduces the $RT$ tradeoff line (Fig. 6) to only half of its original length (preserving the high-$T$ end) and leaves the $LT$ tradeoff line intact.

**LHeT spectra**

The spectrum at $T = 4.2$ K is shown in Figure 10, and the spectrum at $T = 7.0$ K has been shown elsewhere (Christie et al., 1991). These two LHeT spectra are virtually identical and show magnetic hyperfine splitting, as expected from the high magnetic ordering temperature.

As described previously (Christie et al., 1991), a paramagnetic $Fe^{2+}$ contribution (labeled P in Fig. 10) may persist down to these temperatures, although most of the $Fe^{2+}$ is magnetically split and gives rise to the main absorption lines at $-1.4$, $+1.0$, and $+4.6$ mm/s.

The small absorption lines at the outside edges of the spectrum (at $E \lessapprox -6.0$ and $E \geq 7.0$ mm/s) are entirely due to the outer lines (lines 1 and 6) of $Fe^{3+}$ sextet contributions.

By fitting just these outer $Fe^{3+}$ lines, without requiring that the complicated middle part ($-6 \lessapprox E \lessapprox +7$ mm/s) of the spectrum be fitted, we can obtain populations of $Fe^{3+}$ that contribute to these outer lines. We assume $3:2:1:1:2:3$ sextet ratios and find $Fe^{3+}/Fe = 10.99 \pm 0.17$ and $11.0 \pm 0.3\%$ for the spectra at $T = 4.2$ and $T = 7.0$ K, respectively. The same results are obtained independently of line shape by simply adding channel counts in appropriate ranges. The data at $T = 4.2$ K must first be linearized, since they were collected in sine rather than constant acceleration mode.

These numbers show that all of the $Fe^{3+}$ spectra in the sample are magnetically hyperfine at LHeT. In a preliminary study, Christie et al. (1991) concluded that this was not the case. This error occurred because, at that time, the higher temperature spectra (LNT and $RT$) were not fully understood and had not been completely and correctly analyzed.

In addition to $Fe^{3+}$ components being unambiguously resolved in the LHeT spectra, we note that these resolved features show a bimodal structure suggesting two families of $Fe^{3+}$ sextets, denoted A and B in Figure 10 and corresponding to line 1 to line 6 splittings of 14.5 and 17.5 mm/s, respectively.

It is possible to estimate populations for these A and B $Fe^{3+}$ sites by the same methods described above. The results are given in Table 3, where the $Fe^{3+}/Fe$ numbers are also summarized. The main source of error in all these values is area tradeoff between $Fe^{3+}$ and $Fe^{2+}$ for the $A$ and $B$ populations.

The values of the $Fe^{3+}$ and $Fe^{3+}$ populations (Table 3) strongly suggest that $Fe^{3+}$ should be assigned to $^{57}Fe^{3+}$ and that $Fe^{3+}$ should be assigned to $^{57}Fe^{3+}$. We therefore conclude that, in annite, the mean saturation $Fe^{3+}$ hyperfine fields are $\sim 45.6$ and $\sim 55.0$ T for octahedral and tetrahedral sites, respectively, and that these two sites are well resolved at LHeT because their hyperfine field distribution widths are sufficiently small.
Site populations and spectral interpretation

We summarize the above results and discussion by giving final site populations: 

$^{56}\text{Fe}^{3+}/\text{Fe} = 4.00 \pm 0.15\%$,

$^{56}\text{Fe}^{2+}/\text{Fe} = 7.00 \pm 0.20\%$, and

$^{56}\text{Fe}^{3+}/\text{Fe} = 11.00 \pm 0.20\%$ (or $^{56}\text{Fe}^{2+}/\text{Fe} = 89.00 \pm 0.20\%$). These are consistent within the RT and LNT fit results illustrated in Figure 6, the $^{56}\text{Fe}^{3+}/\text{Fe}$ number obtained from the thickness-corrected RT spectrum, and the LHe$T$ results. They are the only numbers that simultaneously satisfy all of the model-dependent and model-independent constraints that follow from the RT, LNT, and LHe$T$ spectra.

The final site populations for our Ni + NiO buffered synthetic annite correspond to $x = 0.210 \pm 0.006$ and $y = 0.120 \pm 0.004$ in the general structural formula for annite, assuming no octahedral vacancies:

$$K_{2}[\text{Fe}^{2+}_{x-y}, \text{Fe}^{3+}_y \text{Al}^{3+}_{z-y}](\text{Al}^{3+}_{y} \text{Fe}^{3+}_y \text{Si}_2^{4+})$$

where square brackets represent octahedral sites and angle brackets represent tetrahedral sites. The populations imply that 16.5% of the H in the ideal structural formula is absent.

That different analysis procedures used on a given spectrum and very different spectra collected at different temperatures all lead to a unique set of site populations helps to set various aspects of the spectral interpretation.

For example, it gives us confidence in the physical correctness of the 1-1-3 fitting model used with spectra collected above $T_c$. This suggests that the needed defect Fe$^{2+}$ site is indeed real and should be explained, as attempted in the next section.

Also, it helps to unravel the very complicated LHe$T$ spectrum in that (1) this spectrum is understood not to contain a paramagnetic Fe$^{3+}$ contribution, and (2) the magnetic hyperfine patterns of$^{56}\text{Fe}^{3+}$ and $^{56}\text{Fe}^{2+}$ are identified. That is important because the spectra collected at $T < T_c$ contain an enormous amount of information concerning both Fe$^{2+}$ and Fe$^{3+}$, their local environments, and their cooperative magnetic behavior, provided the spectra can be decoded.

Finally, consider the temperature dependencies of the average quadrupole splittings between LNT and RT (Tables 1 and 2). For $^{56}\text{Fe}^{3+}$, with a significant increase in the splitting from 2.40 to 2.88 mm/s as the temperature is lowered, the change is real and is as expected. For $^{56}\text{Fe}^{2+}$, having a small decrease from 0.53 to 0.47 mm/s, the splitting is essentially constant at the expected value of $\sim 0.50$ mm/s (Rancourt et al., 1992). For $^{56}\text{Fe}^{2+}$ (large decrease from 0.95 to 0.66 mm/s) the values are anomalous in that changes of this magnitude are not expected for Fe$^{2+}$ ion unless substantial structural transformations occur. The anomaly is not significant, however, because the extracted Fe$^{3+}$ quadrupole splitting values themselves are not significant. This insignificance arises from line position tradeoffs when, as is the case here, the low-energy components of relatively weak Fe$^{2+}$ doublets are buried under the low-energy component of a strong Fe$^{3+}$ doublet (Rancourt et al., 1992; Rancourt, 1993). Both $^{56}\text{Fe}^{3+}$ values (0.95 and 0.66 mm/s) are reasonable and illustrate the possible range that is consistent with the spectral data.

Defect site Fe$^{2+}$

In this section we propose a crystal-chemical model that explains both the measured population of the defect Fe$^{2+}$ site ($^{56}\text{Fe}^{2+}$) and its small QS.

We note (Tables 1 and 2) that $^{56}\text{Fe}^{2+}/\text{Fe} \approx \frac{1}{2}(\text{Fe}^{3+}/\text{Fe}) = \frac{1}{2}(0.5 \text{Fe}^{3+} + 0.45 \text{Fe}^{3+})/\text{Fe} \approx 6\%$. If we accept the Al$^{3+}$/Fe$^{3+}$ exchange idea mentioned in the introduction and Equation 11, then $^{56}\text{Fe}^{2+}/\text{Fe} = ^{56}\text{Al}^{3+}/\text{Fe}$, and $\sim 11\%$ of the octahedral sites are occupied by trivalent cations that are either Fe$^{3+}$ or Al$^{3+}$. The remaining $\sim 89\%$ of the octahedral sites are occupied by Fe$^{2+}$. This suggests that $^{56}\text{Fe}^{2+}$ and the trivalent octahedral cations might tend to form defect structures with 1:2 stoichiometry, with a missing H atom for each trivalent octahedral cation.

Consider the model illustrated in Figure 11, where two of 19 octahedral sites (2/19 = 10.5%) are occupied by either Fe$^{3+}$ or Al$^{3+}$. Here, the 3+ ions are positioned on opposing cis sites separated by a trans site. The missing H occurs at the OH sites of the central trans site, which is the $^{56}\text{Fe}^{2+}$ site.

Table 3. Fe$^{2+}$ populations from the RT thickness-corrected spectrum and LHe$T$ spectra

<table>
<thead>
<tr>
<th>T</th>
<th>$^{56}\text{Fe}^{2+}/\text{Fe}$</th>
<th>$^{56}\text{Al}^{3+}/\text{Fe}$</th>
<th>$^{56}\text{B}^{3+}/\text{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 K</td>
<td>11.19 ± 0.25%</td>
<td>7.4 ± 0.4</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>4 K</td>
<td>10.99 ± 0.17</td>
<td>7.3 ± 0.3</td>
<td>3.7 ± 0.3</td>
</tr>
</tbody>
</table>
Fig. 11. Representation of the proposed octahedral layer defect structure that we associate with the *Fe\(^{3+}\)\ defect Fe\(^{3+}\) site spectral contribution. Here, a patch of the octahedral layer is shown in which two of 19 of the octahedral sites (2/19 = 10.5%) are occupied by 3+ ions (Fe\(^{3+}\) or Al\(^{3+}\)) instead of by Fe\(^{2+}\). The positions of the 3+ ions are indicated by 3+. Apex OH groups represented by small solid circles. Two apex sites that, in the ideal structure, would be occupied by OH groups but that instead are occupied by O\(^{2-}\) to conserve charge balance are represented by large open circles. The location of the *Fe\(^{2+}\)\ ion is indicated by an asterisk. The ion occupies a trans site position, whereas the 3+ ions are on opposing cis sites.

This defect structure (Fig. 11) is plausible in terms of local charge requirements and bonding rules. The central trans site may be distorted in such a way as to result in a relatively small *Fe\(^{2+}\)\ QS.

We only propose this model as a starting point for further study. It suggests that, at low Fe\(^{3+}\) concentrations in annite, the 3+ octahedral cations prefer cis sites in opposing pairs and form cis-trans-cis complexes.

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