

Iron Mineralogy of Venus' Surface Investigated by Mössbauer Spectroscopy

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We discuss the use of Mössbauer (MB) spectroscopy to study Fe-bearing minerals on Venus' surface. At present, there is no direct information about the mineralogy of Venus' surface, although *in situ* chemical analyses by X-ray fluorescence (XRF) spectroscopy have been done by the Venera 13, 14, and Vega 2 spacecraft at three landing sites. The XRF elemental analyses are sensitive to major rock-forming elements heavier than sodium and show the presence of several mass percent iron. Normative mineralogical calculations model the Fe mineralogy at the Venera 13, 14, and Vega 2 landing sites, but the actual Fe minerals present are unknown. We calculate synthetic MB spectra for the normative Fe minerals at the Venera 14 and Vega 2 landing sites. Some calculations include several mass percent of the Fe oxides (magnetite, hematite) and sulfides (pyrite, pyrrhotite) that are frequently discussed in the literature as being present on Venus' surface. Our results indicate that the normative iron minerals at the different landing sites can be identified, quantitatively measured, and distinguished from each other using MB spectroscopy. We also find that about 1 mass percent of any of the different iron oxides and sulfides considered in our modeling should be detectable using MB spectroscopy. This is significant because the loaded dielectric model for low radar emissivity regions on Venus requires several mass percent of Fe-bearing phases. The temperature dependence of the MB spectra is also calculated. Finally, the implications of these results for future spacecraft missions to Venus using MB spectroscopy are discussed. © 2000 Academic Press

Key Words: Venus; Mössbauer spectroscopy; mineralogy; geochemistry; pyrrhotite; pyrite; olivine; fayalite; ferrosilite; clinopyroxene; orthopyroxene; magnetite; hematite; Venera 13 and 14; Vega 2.

INTRODUCTION

At present, there is no direct information about the mineralogy of Venus' surface. Instead, our knowledge of the surface mineralogy is derived from chemical analyses and radar ob-

servations of the surface, and thermodynamic calculations and laboratory studies of atmospheric weathering reactions (Fegley *et al.* 1997a). Gamma ray analyses by five landers (Venera 8, 9, 10 and Vega 1 and 2) give elemental abundances for U, Th, and K. X-ray fluorescence (XRF) analyses by three landers (Venera 13, 14, and Vega 2) give elemental abundances for major elements heavier than sodium. All the analytical data are summarized and discussed in Fegley *et al.* (1997a), and descriptions of the gamma ray and XRF experiments are given in file CDP4C4A1 on the companion CD-ROM.

Iron is one of the most abundant elements detected by the XRF analyses of Venus' surface. The theoretical mineral compositions of the three landing sites analyzed by X-ray fluorescence have been calculated by Barsukov *et al.* (1982, 1986) and are given in Table I. These theoretical mineral compositions are called normative compositions (or normative mineralogies) and are indicated, but not proved, by the elemental analyses. The computational method is called the CIPW norm, after the four geologists who devised the method, and it is described in detail by Johannsen (1939) and in other petrology texts.

Table I shows that the normative minerals at the Venera 13, 14, and Vega 2 landing sites include three Fe-bearing phases (fayalite Fe_2SiO_4 dissolved in olivine, ferrosilite FeSiO_3 dissolved in pyroxene, and ilmenite FeTiO_3). Laboratory studies and theoretical models predict that other Fe-bearing minerals such as magnetite (Fe_3O_4), hematite (Fe_2O_3), and pyrrhotite (nonstoichiometric Fe sulfide with the general formula Fe_{1-x}S , where x is less than or equal to 0.125) may also be present on Venus' surface, even though they are not predicted by the normative calculations for these three landing sites.

Why is information about Fe-bearing minerals on Venus' surface important? First, Fe-bearing minerals are involved in chemical reactions with C-, O-, H-, and S-bearing gases in Venus' atmosphere. These reactions include oxidation-reduction reactions (Fegley *et al.* 1995a, 1997a,b) and production of reduced

TABLE I
Normative Mineral Compositions

Mineral	Venera 13	Venera 14	Vega 2
Orthopyroxene (En ₇₅ Fs ₂₅)	—	18.2	25.4 ^a
Clinopyroxene (Wo ₄₈ En ₃₆ Fs ₁₆)	—	—	2.5 ^b
Diopside (CaMgSi ₂ O ₆)	10.2	9.9	—
Olivine (Fo ₇₅ Fa ₂₅)	26.6	9.1	13.9 ^c
Anorthite (CaAl ₂ Si ₂ O ₈)	24.2	38.6	38.3
Albite (NaAlSi ₃ O ₈)	3.0	20.7	18.9
Orthoclase (KAlSi ₃ O ₈)	25.0	1.2	0.5
Nepheline (NaAlSi ₃ O ₄)	8.0	—	—
Ilmenite (FeTiO ₃)	3.0	2.3	0.5
Total	100.0	100.0	100.0

Note. Barsukov *et al.* 1982, 1986.

^a The orthopyroxene is 75 mol% enstatite (En = MgSiO₃) and 25 mol% ferrosilite (Fs = FeSiO₃).

^b The clinopyroxene is 48 mol% wollastonite (Wo = CaSiO₃), 36 mol% enstatite, and 16 mol% ferrosilite.

^c The olivine is 75 mol% forsterite (Fo = Mg₂SiO₄) and 25 mole% fayalite (Fa = Fe₂SiO₄).

sulfur gases in the Venus sulfur cycle (Fegley and Treiman 1992, Fegley *et al.* 1995b, Fegley 1997, Hong and Fegley 1997, 1998). Thus, determination of the nature and the abundance of Fe-bearing minerals in rocks and soil will provide important information about atmospheric weathering processes. Second, percent levels of Fe-bearing sulfides such as pyrite (FeS₂) have been suggested to explain low radar emissivity regions on Venus (Pettengill *et al.* 1982, 1988). Other materials, such as volatile compounds of trace metals with high dielectric constants, have been proposed to explain the low radar emissivity (Brackett *et al.* 1995, Pettengill *et al.* 1996). However, it is still important to consider analytical methods to detect and distinguish Fe sulfides such as pyrrhotite and pyrite that may be present at abundances of several mass percent. Finally, knowledge of the nature and abundance of Fe-bearing minerals in basaltic rocks will provide important information about igneous processes inside Venus.

Iron Mössbauer (MB) spectroscopy is an excellent method to determine the Fe-mineralogy and the relative abundance of Fe-bearing minerals on the surface of a rocky body such as a planet, satellite, or asteroid (e.g., Klingelhöfer *et al.* 1995, 1996, Klingelhöfer 1999). The key feature of MB spectroscopy is that the Fe minerals present, their relative abundances, and the oxidation state(s) of Fe in the different minerals are determined directly. This information cannot be obtained from XRF spectroscopy which, unlike MB spectroscopy, measures the total elemental abundance of Fe in all minerals present in the sample (e.g., total Fe in metal, oxide, sulfide, and silicate). MB spectroscopy is useful for *in situ* analyses of planetary surfaces because no sample preparation is required if a back scattering geometry is used.

Several books such as Bancroft (1973) give good descriptions of the theory and technique of MB spectroscopy, and we only briefly review the essential points here. Iron MB spectroscopy uses resonance absorption of 14.41 keV γ -rays (the Mössbauer

effect) by ⁵⁷Fe nuclei in a solid to investigate the splitting of nuclear energy levels that is produced by interaction of the Fe nuclei with the surrounding electronic environment. The γ -ray source is normally ⁵⁷Co, which decays to the 14.41 keV excited Mössbauer nuclear state of ⁵⁷Fe. In general, the nuclear energy level structure of the Fe-bearing sample is different than that of the ⁵⁷Co source (because of different oxidation states, chemical environments, and/or magnetic order). Thus, the energy of the source γ -rays must be modulated to achieve resonance. This is done using the Doppler effect by mounting the ⁵⁷Co source on a velocity transducer and moving it with respect to the sample. A MB spectrum is the relative number of γ -rays per second re-emitted from (back scattering geometry) or absorbed by (transmission geometry) a sample as a function of the relative velocity of the source and sample. Although MB spectra for transmission and backscattering geometry are mirror images (i.e., downward and upward peaks, respectively), the MB pattern is the same in the two cases. This is illustrated in Fig. 5 of Klingelhöfer *et al.* (1996), which shows transmission and backscattering MB spectra for a Hawaiian palagonite.

The different Fe-bearing phases in a sample and the oxidation state(s) of Fe atoms in each phase are determined from peak locations in the MB spectrum. The peak areas give the relative abundances of Fe atoms in the corresponding phases. If Fe atoms (perhaps with different oxidation states) occur in different crystallographic sites in a mineral, the relative abundances of Fe atoms in the different sites can also be measured. If the properties of the absorber vary with temperature, the MB spectrum will depend on the measurement temperature. This is the case for the Fe minerals expected to be present on Venus, and therefore temperature effects have to be considered. Spacecraft MB spectrometers flown to Venus will probably be operated at, or near, room temperature because the solid state detectors currently used do not work at higher temperatures. However, the sample itself can remain at high temperature.

Each Fe mineral has its own characteristic fingerprint in a MB spectrum. Figure 1 illustrates this point and shows the characteristic room temperature (backscattering) spectra for some of the minerals plausibly present on Venus. The calculated MB spectrum at the bottom of Fig. 1 is a composite of all the subspectra shown, with the relative areas of the different components being proportional to the relative amounts of the different iron bearing phases. The apparent complexity of the composite MB spectrum may lead to the question of how such a measured spectrum can be deconvolved to give information about the Fe-bearing minerals present and their abundances. This is routinely done using computer programs that fit the observed MB spectrum with spectra of individual component minerals. The choice of component minerals is normally guided by the type of sample being studied. For example, Fe-bearing minerals that are only stable at and below room temperature may be included in fits to MB spectra of martian surface samples, but probably would not be included in fits to MB spectra of venusian surface samples. Independent information such as an elemental analysis is also useful for deciding whether or not to include Fe-bearing minerals containing

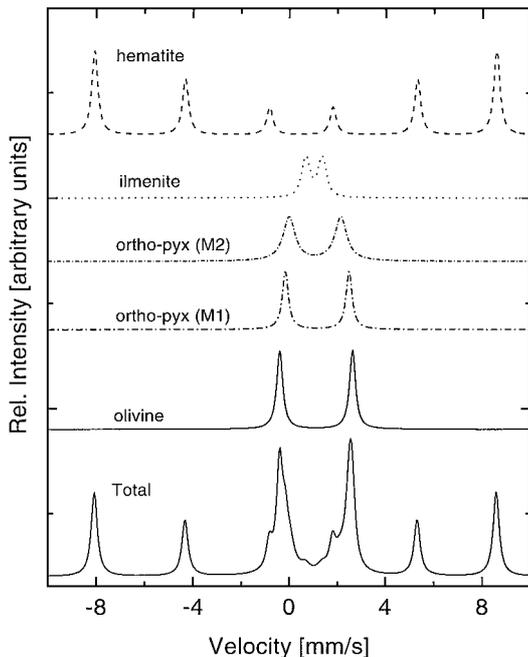


FIG. 1. An example of a calculated backscattering Mössbauer spectrum showing the characteristic subspectra of the different Fe bearing phases and the total spectrum, which is the composite of the subspectra. The same types of lines are used for these minerals in subsequent figures except in the case of the dashed line, which is also used for pyrite and pyrrhotite as noted in the figure captions. See the text for more details.

a particular element. The computer fits are varied such that the sum of all subspectra gives the best match to the data as defined by a statistical criterion such as chi squared. Examples of MB data analyses for natural samples are given in some of our other papers (e.g., Fegley *et al.* 1995a,b, Klingelhöfer *et al.* 1995, 1996).

In this paper, we consider the use of spacecraft MB spectroscopy for studying the Fe mineralogy of Venus' surface. We do this by calculating synthetic MB spectra for the Fe minerals present in the normative mineralogies at the Venera 14 and Vega 2 landing sites. We then illustrate changes to the MB spectrum of the Vega 2 landing site due to the addition of small amounts of Fe oxides and sulfides. Then, we examine the effects of high temperature on some calculated MB spectra. We conclude by discussing the use of *in situ* MB spectroscopy on future spacecraft missions to Venus. Preliminary results of this work were presented earlier (Klingelhöfer and Fegley 1996).

CALCULATION OF MÖSSBAUER SPECTRA

We calculated Mössbauer spectra for the normative Fe-bearing minerals at the Venera 14 and Vega 2 landing sites. Table I summarizes the normative mineral compositions calculated by Barsukov *et al.* (1982, 1986) from the XRF elemental analyses. Other authors have also calculated normative mineralogies from the XRF data, but we use the Russian results because they made the XRF analyses on Venus and are presumably more familiar

with the data. The CIPW normative calculations use ideal mineral formulae such as FeTiO_3 for ilmenite, Fe_3O_4 for magnetite, and Fe_2O_3 for hematite. By analogy with terrestrial geology, we expect that on Venus these minerals will also exist as solid solutions containing other components (e.g., titanomagnetite instead of pure magnetite). These solutions are not modeled in the CIPW norms or in our calculated MB spectra. However, elsewhere we discuss our experimentally measured MB spectra of tholeiitic basalts (Fegley *et al.* 1995a, Klingelhöfer *et al.* 1996). These papers show that MB spectra of basalts can be used to identify and measure the relative abundances of the constituent Fe-bearing minerals in basalts and also show that MB spectroscopy can tell the difference between pure phases (e.g., ilmenite, magnetite) and their solid solutions.

The synthetic MB spectra discussed here were calculated using a data analysis program developed at the University of Darmstadt (Klingelhöfer *et al.* 1992, Gellert *et al.* 1993). It calculates the spectra as a superposition of a number of individual and characteristic mineral subspectra which can be singlets (single line spectra), doublets (quadrupole split two line spectra), and sextets (magnetically split six line spectra), respectively. The resonance lines are modeled using a Voigt profile, which is a convolution of a Lorentzian line and a Gaussian line (Rancourt *et al.* 1991).

Mössbauer parameters (i.e., the isomer shift, the quadrupole splitting, and the magnetic hyperfine splitting) that are characteristic of different Fe-bearing minerals are taken from the literature. The isomer (or center) shift is a measure of the electron density at the Fe nucleus and gives information about the oxidation state of the Fe atom. The quadrupole splitting is caused by an electric field gradient (at the Fe nucleus) originating either from an asymmetric electronic configuration in the neighborhood of the Fe nucleus or from a non-cubic crystal structure, or from both effects. The magnetic hyperfine splitting of the nuclear energy levels is caused by a magnetic field at the Fe nucleus that is present only in magnetic fields such as Fe metal or hematite. In all cases we have selected the most typical parameter sets (see Table II). We used linewidths (the full width at half maximum, FWHM) that are typically found for terrestrial minerals. We do not expect significant line broadening effects (i.e., an increase in the FWHM) at Venus ambient temperatures

TABLE II
MB Parameters Used in the Calculations

Component	Isomer shift (mm/s) relative to Fe	Quadrupole splitting (mm/s)	Relative intensity (mass%)	
			Venera 14	Vega 2
Orthopyroxene	+1.16	2.60 (M1)	61.42	60.05
		2.14 (M2)		
Clinopyroxene	+1.17 +1.05	2.30 (M1)	—	5.9
		2.14 (M2)		
Olivine	+1.12	2.98	30.71	32.86
Ilmenite	+1.07	0.68	7.86	1.2
Total			100	100

(660–740 K) for the minerals under consideration. For example, significant line broadening effects due to Fe diffusion in olivine have been observed only at temperatures of about 1400 K (Wißmann *et al.* 1996).

The relative intensities, A_k , of the different Fe mineral phases were calculated from their relative amounts (g_k values), taking into account the different Debye–Waller (f) factors and the corresponding stoichiometric factors S (see Fegley *et al.* 1995b, Meisel *et al.* 1990). Average values for the f factors of the different phases at room temperature were taken from the literature (De Grave *et al.* 1991, Fegley *et al.* 1995b). The formula used is

$$A_k = g_k \times (\sum_i A_i \times S_i \times \varepsilon_i^k) / S_k, \quad (1)$$

where g_k is the weight percentage of component k , ε_i^k is the ratio of the Debye–Waller factors of components k and i (f_k/f_i), and g_k is normalized to the sum of all Fe-bearing components.

RESULTS AND DISCUSSION

Mössbauer spectra for the Venera 14 and Vega 2 landing sites. Figure 2 shows the calculated room temperature (300 K)

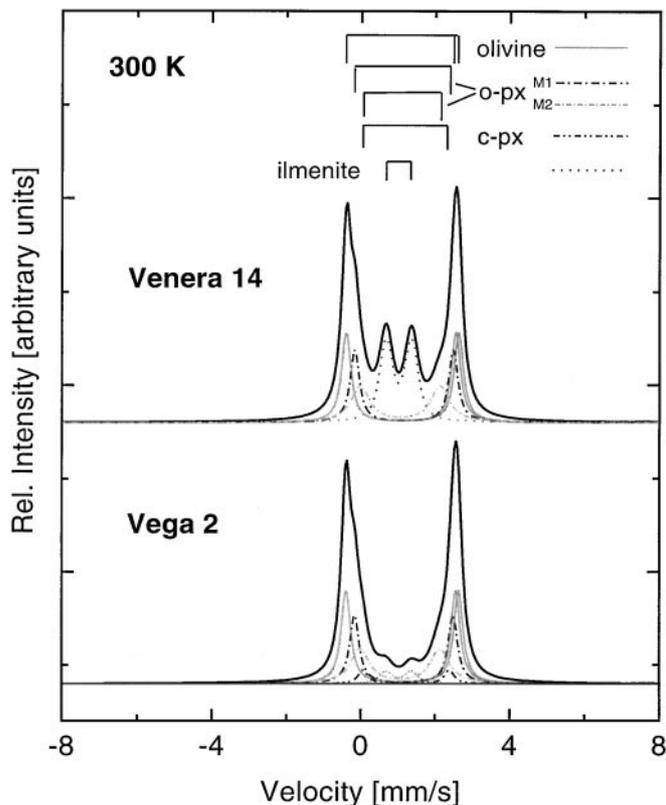


FIG. 2. Calculated room temperature (300 K) backscattering Mössbauer (MB) spectra for the iron-bearing minerals calculated to be present at the Venera 14 and Vega 2 landing sites. The CIPW normative mineralogies were calculated by Barsukov *et al.* (1982, 1986) from the XRF elemental analyses and are listed in Table I. The vertical lines at the top of the figure show the positions of MB peaks for the different minerals.

backscattering MB spectra for the normative Fe minerals at the Vega 2 and the Venera 14 landing sites. The subspectra of the individual minerals, which are olivine, orthopyroxene, clinopyroxene, and ilmenite, as well as the sum of the subspectra, are shown in each case. The sum of the subspectra shows what experimentally measured MB spectra at each landing site would look like. The spectra clearly show the difference in mineralogy between the two landing sites. The most pronounced difference is due to the higher ilmenite content at the Venera 14 landing site, which gives rise to the double-peaked structure in the center of the MB spectrum (at velocities from about +1 to +2 mm s⁻¹). The shape of the outer, main resonance lines, which are a superposition of the olivine and pyroxene lines, is also different, but not as pronounced as for the inner part of the spectrum. The main difference is the linewidth, which can be extracted by the MB data analysis program. These calculations show that Mössbauer spectroscopy would be able to determine the Fe mineralogy at each landing site and to determine the differences in mineralogy between the two landing sites. As will be discussed later, the high temperatures on Venus' surface might enhance the spectral resolution, but in any case would not decrease the resolution with respect to the 300 K spectra displayed in Fig. 2.

Detectability of Fe sulfides. The XRF elemental analyses detected percent levels of sulfur at the Venera 13, 14, and Vega 2 landing sites (Surkov *et al.* 1984, Barsukov *et al.* 1986). Although the XRF analyses report sulfur as SO₃, this does not necessarily mean that sulfate minerals are present because XRF gives elemental, not mineralogical, information. As discussed by Fegley *et al.* (1997a), the S-bearing minerals that may be present on Venus include anhydrite (CaSO₄), pyrrhotite (Fe_{1-x}S), and pyrite (FeS₂). By analogy with terrestrial petrology, Fe-bearing sulfides containing other metals may also be present on Venus (e.g., Fe–Ni sulfides such as pentlandite (Fe,Ni)₉S₈, and Fe–Cu sulfides such as chalcopyrite CuFeS₂). There is very little discussion of such sulfides in the literature about Venus' geochemistry and mineralogy. However, Ni and Cu are less abundant than Fe (in chondritic material, and in the Earth's crust), and neither was detected in the XRF analyses, so we can reasonably expect that Fe–Ni and Fe–Cu sulfides may be less abundant than Fe sulfides on Venus. We thus focus here on pyrrhotite and pyrite. These two minerals are easily identified and measured in MB spectra of laboratory samples (e.g., see the transmission MB spectra of Fig. 6 in Fegley *et al.* 1995b).

To indicate the sensitivity of MB spectroscopy for these Fe sulfides, we calculated spectra by adding different amounts of pyrite and pyrrhotite (with the formula Fe_{0.875}S or Fe₇S₈) to the Vega 2 landing site mineralogy. For example, Fig. 3 shows calculated spectra at 300 K for the Vega 2 nominal mineralogy with 0–9 mass% pyrite added. The results in Fig. 3 indicate that about 1 mass% of pyrite is easily detectable. This is significant because, as noted earlier, percent levels of Fe-bearing sulfides have been suggested to explain low radar emissivity regions on Venus (Pettengill *et al.* 1982, 1988).

Similar results have been obtained for pyrrhotite, which is also detectable at about the 1 mass% level. Iron-poor pyrrhotite

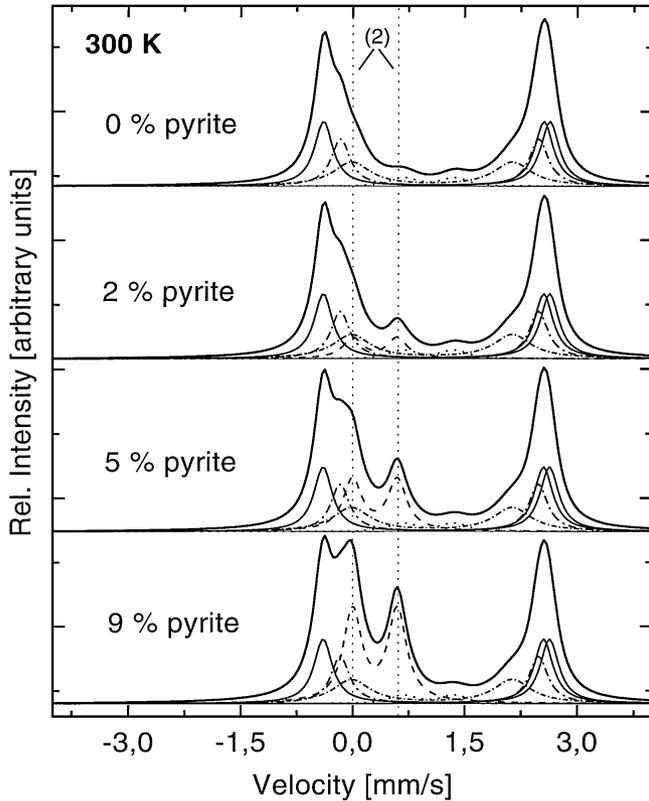


FIG. 3. Calculated room temperature (300 K) backscattering Mössbauer spectra for the Vega 2 landing site normative Fe mineralogy plus different amounts (mass%) of pyrite (FeS_2). Pyrite (represented by the dashed line) shows up as a doublet component with a center shift of $+0.30 \text{ mm s}^{-1}$ and a quadrupole splitting of 0.6 mm s^{-1} (room temperature values). The positions of the two pyrite MB peaks are indicated by the vertical dotted lines labeled (2). Following European convention, the comma is used as the decimal point on the x -axis in this and subsequent figures.

(Fe_7S_8) has a Curie temperature (T_C) of 578 K so the MB spectra have a different appearance above and below this temperature. This behavior is illustrated in Fig. 4. At 300 K, below the Curie temperature, the MB spectrum of pyrrhotite displays a superposition of three magnetically split sextets. However, at higher temperatures, above the Curie temperature, pyrrhotite appears as a broad doublet with a small splitting value.

Detectability of Fe oxides. Magnetite is commonly present in basaltic rocks on Earth and by analogy may also be present in basaltic rocks on Venus. Laboratory experiments, Venera lander observations, and theoretical models suggest that hematite is present and presumably forms by atmospheric weathering on Venus' surface (Pieters *et al.* 1986, Fegley *et al.* 1995a,b, 1997b). Transmission MB spectra of terrestrial tholeiitic basalt before and after thermal oxidation show that MB spectroscopy can easily detect percent levels of magnetite and hematite and distinguish between the two oxides (Fegley *et al.* 1995b, 1997a, Klingelhöfer *et al.* 1996).

We calculated room temperature (300 K) MB spectra for the Vega 2 landing site mineralogy where we added different amounts of hematite or magnetite. The results indicate that these

Fe oxides can be detected clearly at the percent level. Examples of the calculations for hematite are given in Fig. 5. The arrows in the figure point to one of the outer lines of the six resonance lines of hematite.

Calculated MB spectra at Venus surface temperatures. Up to this point we have discussed spectra calculated for room temperature (about 300 K). However, surface temperatures on Venus range from about 740 K in the lowlands to about 660 K at the top of Maxwell Montes. We now discuss temperature effects on the calculated MB spectra for Fe oxides, silicates, and sulfides.

Our calculations of temperature effects used the available high temperature MB parameters in the literature (e.g., Mitra 1992, Burns 1993, Cornell and Schwertmann 1996), but only a few MB experiments have been done at Venus surface temperatures. Thus, in several cases we had to extrapolate the available data to the temperature range of interest. Below we summarize briefly the temperature dependent spectral characteristics of the minerals which were included in our calculations. In all cases we assumed that the isomer shift is temperature independent, which is

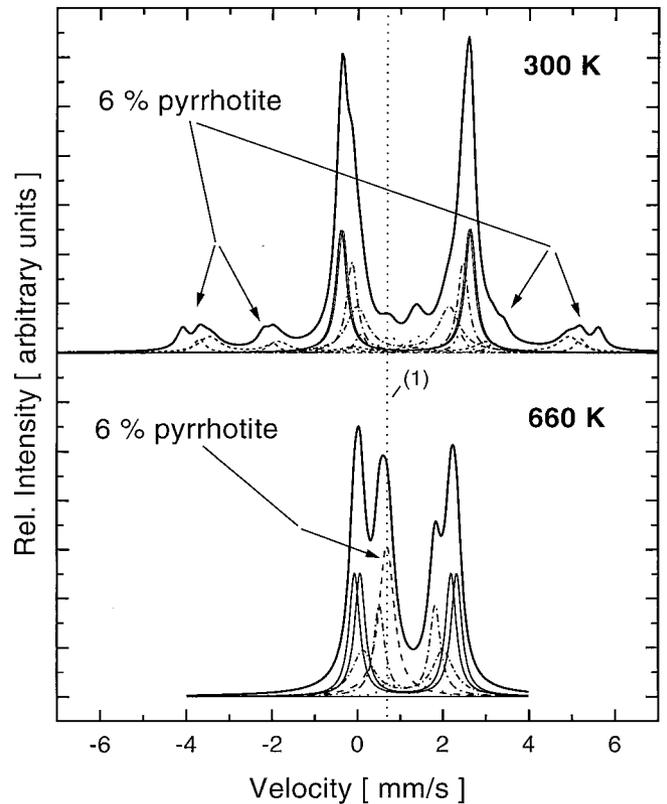


FIG. 4. Calculated backscattering Mössbauer spectra at 300 and 660 K (top of Maxwell Montes) for the Vega 2 landing site normative Fe mineralogy plus 6 mass% pyrrhotite (Fe_7S_8). In the 300 K spectrum pyrrhotite appears as a superposition of three magnetically split sextets. The arrows in the top panel show the position of the outer MB peaks of the three pyrrhotite subspectra. At 660 K pyrrhotite is paramagnetic and its MB spectrum appears as a narrow doublet at about $+0.65 \text{ mm s}^{-1}$. The doublet looks like a single peak and is marked by an arrow and a vertical dotted line. The pyrrhotite MB spectrum is represented by a dashed line in both panels.

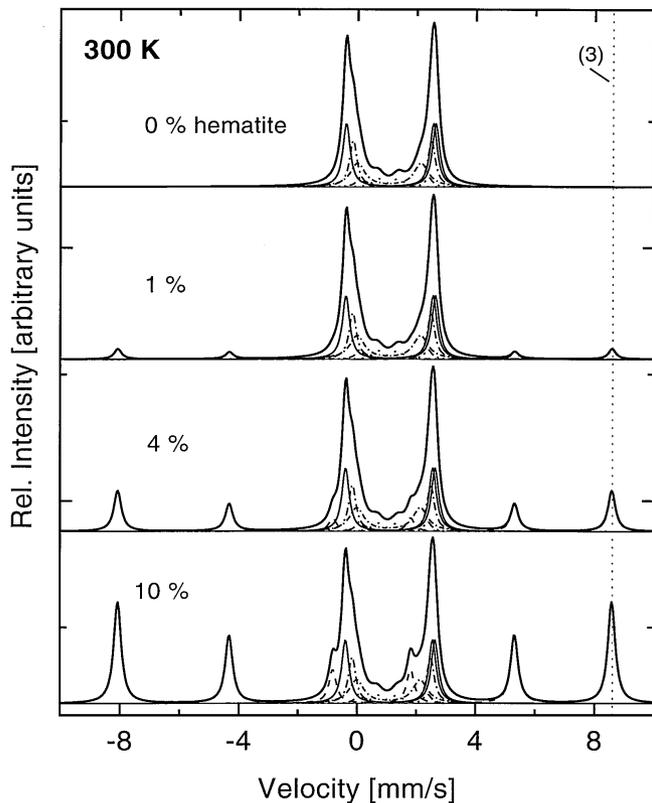


FIG. 5. Calculated room temperature (300 K) backscattering Mössbauer spectra for the Vega 2 landing site normative Fe mineralogy plus different amounts (mass%) of hematite (Fe_2O_3). Hematite shows up as a magnetically split sextet component (six MB peaks) with a center shift of about $+0.37 \text{ mm s}^{-1}$, a magnetic hyperfine field splitting of 16.67 mm s^{-1} , and a quadrupole splitting of about -0.2 mm s^{-1} (295 K values). The vertical dotted line (3) marks one of the outer hematite peaks. This is easily distinguished at a hematite abundance of 1 mass percent. The outer four hematite MB peaks coincide with the solid line for the total spectrum while the inner two hematite MB peaks appear as a dashed line.

a reasonable assumption taking into account the expected energy (i.e., velocity) resolution of a spacecraft MB spectrometer. The second order Doppler effect is not considered in the calculations.

Pyroxene. The pyroxenes are single-chain silicates with two distinct Fe^{2+} sites (M1 and M2) appearing in the MB spectrum as two ferrous quadrupole split components (see Fig. 1). No magnetic splitting is observed at room temperature and above. The temperature dependence of two different orthopyroxenes was experimentally and theoretically studied by Van Alboom *et al.* (1994) up to a temperature of 490 K. The quadrupole splitting linearly decreases with increasing temperature for temperatures above about 250 K, and we used a linear extrapolation of the splitting values for temperatures up to 750 K. The values used in our calculations are given in Table III. No high temperature data are available for clinopyroxene and we used the same linear behavior as for the orthopyroxenes, but with different starting values at 300 K. We also used only one doublet (M1) in the calculations for clinopyroxene, because at the Vega 2 landing site the abundance of the clinopyroxene component is only

TABLE III
Quadrupole Splitting (QS) Values (mm/s)

	QS	300 K	650 K	700 K	750 K
Orthopyroxene ^a	M1	2.60	1.31	1.08	0.93
	M2	2.14	1.88	1.81	1.76
Clinopyroxene	M1	2.30	1.00	0.80	0.65
Olivine ^b	M1	2.93	2.13	2.03	1.92
	M2	3.03	2.39	2.28	2.19

^a Extrapolated values according to Van Alboom *et al.* (1994).

^b Measured and extrapolated values for natural olivine after Stanek *et al.* (1986).

about 6 mass%, so neglecting the less intense second doublet does not affect the results significantly.

Olivine. The crystal structure of olivine is orthorhombic, and there are two nearly octahedral sites, M1 and M2, which can be occupied by Fe atoms. Below about 300 K, the two paramagnetic Mössbauer doublets overlap completely and have nearly identical parameters. At higher temperatures, the quadrupole doublets of the M1 and M2 sites in natural olivine can be resolved, and a linear dependence of the quadrupole shift with temperature is observed (Mitra 1992, Stanek *et al.* 1986). We used values given by Stanek *et al.* (1986) for temperatures up to 623 K (see also Mitra 1992), extrapolating them to a slightly higher temperature of 740 K in our calculations (see Table III).

Hematite. Pure hematite ($\alpha\text{-Fe}_2\text{O}_3$) is weakly ferromagnetic at room temperature, and the corresponding Mössbauer spectrum consists of a sextet (six resonance lines) with a small quadrupole splitting of -0.20 mm s^{-1} and a magnetic hyperfine field splitting of about 16.67 mm s^{-1} equivalent to 51.8 Tesla (T). The magnetic hyperfine field and therefore also the splitting of the MB spectrum is temperature dependent and follows an approximate Brillouin curve (Cornell and Schwertmann 1996). The Curie temperature T_C of pure hematite is 956 K and therefore well above the maximum surface temperature on Venus. Hematite shows a structural change at the Morin temperature, T_M , which is at about 260 K. Below T_M , hematite is antiferromagnetic. At the high temperatures on Venus' surface, the magnetic hyperfine field splitting is reduced, compared to a 300 K spectrum, according to a Brillouin curve behavior. The values obtained from this relation and used in our calculations are given in Table IV.

TABLE IV
Magnetic Hyperfine Splitting (HFS) (mm/s)

	HFS	300 K	650 K	700 K	750 K
Magnetite	A	15.78	12.23	11.20	10.38
	B	14.81	11.48	10.52	9.74
Hematite Pyrrhotite	I	16.67	14.11	13.55	12.89
	II	9.71	—	—	—
	III	8.90	—	—	—
		8.40	—	—	—

Magnetite. Pure magnetite (Fe_3O_4) is ferrimagnetic at room temperature and has a Curie temperature of 850 K, which is significantly less than for hematite (see above). There are two different Fe sites in the crystal structure giving rise to two magnetically split sextets in the magnetite MB spectrum. The temperature dependence of the magnetic hyperfine fields for both sites is the same as for hematite. The magnetic hyperfine field splittings for different temperatures (i.e., different elevations) on Venus' surface can be obtained from this (see Table IV). In general, the temperature dependence of the magnetic hyperfine fields for magnetite are very similar to those obtained for hematite and they will not be discussed further in this paper. However, as noted earlier, the MB spectra of magnetite and hematite are quite different and the two phases can be easily distinguished from one another.

Pyrite. Montano and colleagues studied pyrite thermal decomposition at temperatures up to 713 K and found that the isomer shift changed slightly due to the second order Doppler effect and the quadrupole splitting at high temperatures was almost the same as at room temperature (Bommannavar and Montano 1982, Montano and Vaishnav 1981, Montano *et al.* 1981). Based on their data, we assume that the sensitivity of MB spectroscopy to pyrite at high temperatures is similar to the sensitivity at room temperature (see Fig. 3). We also note that the kinetic data obtained by Montano and Vaishnav (1981) for pyrite thermal decomposition support our laboratory data showing that pyrite will decompose rapidly on Venus' hot surface (Fegley 1997, Fegley *et al.* 1995b, 1997a, Hong and Fegley 1997, 1998).

Pyrrhotite. Pyrrhotite is unstable but decomposes very slowly on the surface of Venus (Fegley and Treiman 1992, Fegley *et al.* 1995b). At room temperature (300 K) the MB spectrum is composed of three magnetically split subspectra (see Fig. 4) which can be attributed to the three different Fe sites in the structure of Fe_7S_8 . If more Fe-rich pyrrhotites are present they will exhibit more than three magnetically split subspectra (e.g., see Fegley *et al.* 1995b). Because the Curie temperature is 578 K for Fe_7S_8 (Burns 1993), pyrrhotite is paramagnetic at Venus surface temperatures and produces a doublet in the MB spectra. Figure 4 displays calculated spectra at 300 and 660 K for the Vega 2 landing site mineralogy and a pyrrhotite content of 6 mass%. Goncharov *et al.* (1970) studied pyrrhotite MB spectra up to 463 K and found only a small increase in the quadrupole splitting and a small change in the isomer shift (due to the second order Doppler effect). Their results do not extend above the Curie temperature, but the small variations observed for the MB parameters up to 463 K are consistent with our use of room temperature MB parameters for pyrrhotite.

Temperature effects on MB spectra for the Vega 2 landing site. Using the data discussed above, we calculated MB spectra for the normative Fe mineralogy at the Vega 2 landing site at three different surface temperatures: (a) 740 K in the plains, (b) 705 K at about 5-km elevation where the low radar emissivity regions

begin (e.g., Theia Mons, Ozza Mons), and (c) 660 K at the top of Maxwell Montes. For reference, the Vega 2 landing site is 1.2 ± 0.2 km above the modal radius of 6051.4 km and is at a temperature of 730 K.

In the calculations, we assumed that the relative Debye–Waller factors are temperature independent over the 300–740 K range. The absolute values of the Debye–Waller factors decrease exponentially with increasing temperature (e.g., see De Grave *et al.* 1991, Mitra 1992), and for simplicity we assume that the decrease is about the same for different Fe phases. The decreasing Debye–Waller factors result in decreasing intensity of back scattered MB radiation. The implications of this effect for *in situ* measurements at high temperatures on Venus will be discussed next.

Figure 6 shows the change in the shape of the MB spectra (i.e., the outer curves) with temperature (and elevation). At 740 K, corresponding to the temperature of the venusian plains, the different components are actually better resolved than at 660 K (top of Maxwell Montes) or even at 300 K. This improved resolution will compensate partially for the decrease in intensity due to decreased Debye–Waller factors.

We are also interested in the sensitivity of MB spectroscopy to minor components such as Fe sulfides and Fe oxides at these high

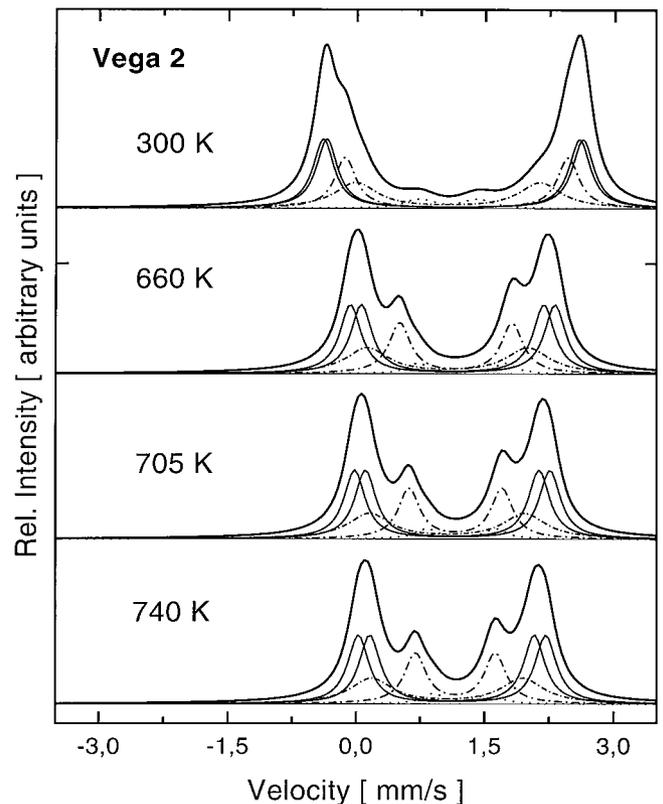


FIG. 6. Calculated backscattering Mössbauer spectra for the Vega 2 landing site normative Fe mineralogy as a function of temperature. The calculated spectrum is composed of five Fe-bearing components: olivine (M1 and M2 sites), the M1 site in pyroxene, the M2 site in pyroxene, and ilmenite. The types of lines used for these five components are the same as in Fig. 1.

temperatures. We therefore calculated spectra at Venus ambient temperatures for the Vega 2 Fe mineralogy plus minor amounts of Fe sulfides or oxides. As an example, Fig. 7 shows MB spectra at 660 K for the Vega 2 Fe mineralogy plus different amounts of pyrrhotite. The position where the pyrrhotite line shows up is marked by an arrow. These calculations suggest that MB spectra measured at high temperature are sensitive to Fe sulfides and Fe oxides at the 1% level, just as found for MB spectra at 300 K.

As described above, the magnetic properties of hematite (and of other magnetic minerals such as pyrrhotite and magnetite) are temperature dependent. Figure 8 shows calculated spectra at different temperatures for the Vega 2 Fe mineralogy plus 4 mass% hematite. The positions of the hematite resonance lines change significantly with temperature, as indicated by the arrows. But even at the highest temperature the hematite signal is still clearly resolved. The results for magnetite are very similar, even though the Curie temperature of pure magnetite is about 100 K lower than that for hematite. As mentioned earlier, titanomagnetites, instead of pure magnetite, may be present on Venus. Titanomagnetites have lower Curie temperatures than pure magnetite, and titanomagnetite with sufficiently large Ti contents becomes paramagnetic at Venus surface temperatures. Paramagnetic ti-

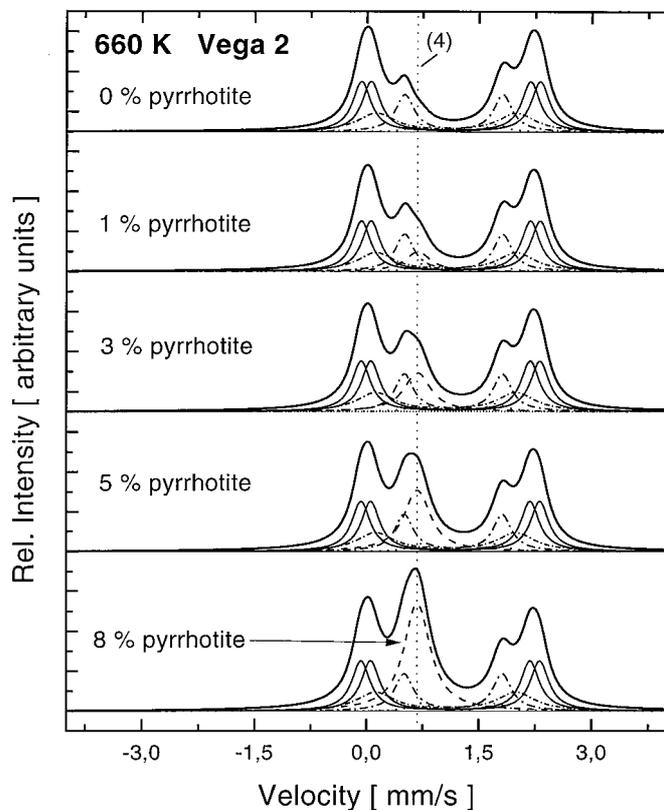


FIG. 7. Calculated backscattering Mössbauer spectra at 660 K for the Vega 2 landing site normative Fe mineralogy and different amounts (mass%) of pyrrhotite (Fe_7S_8), which is shown as a dashed line in this figure. The arrow marks the narrow pyrrhotite doublet, which looks like a single broad MB peak. Also see Fig. 4 for pyrrhotite MB spectra at 300 and 660 K.

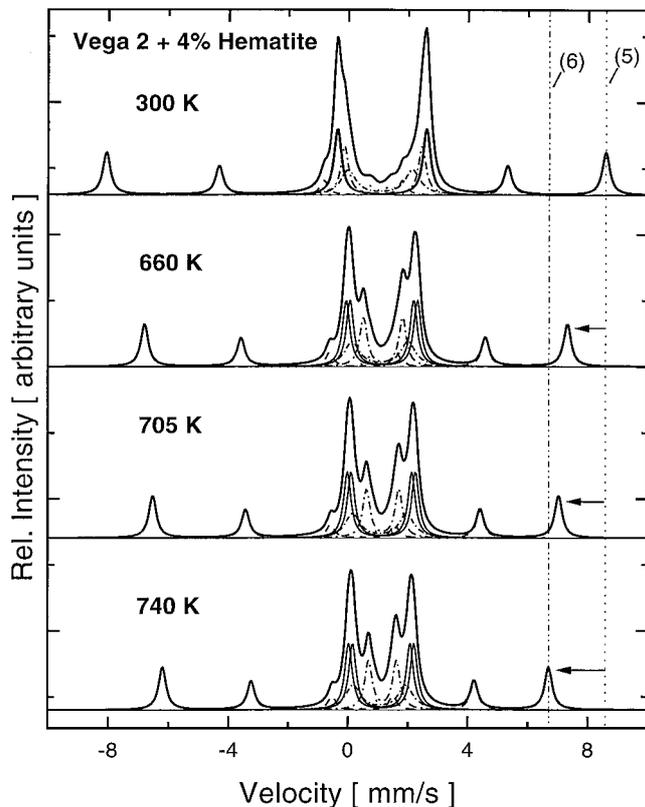


FIG. 8. Calculated backscattering Mössbauer spectra at different temperatures for the Vega 2 landing site normative Fe mineralogy plus 4 mass% hematite, which is shown by a dashed line. The position of the hematite MB peaks changes with temperature because of the temperature dependence of the magnetic properties of hematite. This movement is illustrated by the vertical lines (5) and (6), which mark the 300 and 740 K positions, respectively, for one of the outer hematite MB peaks.

titanomagnetite will appear as doublets in the MB spectra (e.g., see Fegley *et al.* 1995a).

CONCLUSIONS AND IMPLICATIONS

Each Fe mineral has its own characteristic MB spectrum, which is a fingerprint for the identification of Fe minerals. The synthetic MB spectra computed for the normative Fe mineralogies at the Vega 2 and the Venera 14 landing sites indicate that MB spectroscopy can identify the Fe minerals at each site and can distinguish the different Fe mineralogies of the two landing sites. The different ilmenite abundances at the Venera 14 site ($\sim 8\%$) and the Vega 2 site ($\sim 1\%$) are easily distinguished in the MB spectra. Furthermore, the calculated spectra for the two landing sites show that Fe-bearing olivine and pyroxene are easily seen and that hematite, magnetite, pyrite, and pyrrhotite could be detected at the 1% level. The calculations also show that high temperature MB spectra are useful for mineral identification. Therefore, *in situ* MB spectroscopy would be very useful for identifying and measuring the relative abundances of Fe-bearing minerals present on Venus' surface.

The harsh environmental conditions on Venus' surface constrain the operation of a spacecraft MB spectrometer on Venus. We now consider briefly some of these constraints taking the design of the Mössbauer backscattering spectrometer on the Mars Surveyor 2001 (APEX payload) and 2003 (ATHENA rover payload) missions as a guide (Klingelhöfer 1999, Klingelhöfer *et al.* 1996).

A Mössbauer spectrometer for a Venus mission would have a mass similar to the APEX instrument (about 500 g). This instrument would operate in backscattering geometry and therefore no special sample preparation is needed. The sample has to be positioned a few millimeters in front of the instrument because the intensity of backscattered MB radiation decreases and the necessary integration time increases with increasing distance between the sample and detectors. The sample is separated from the detectors by a window which can sustain the high temperature and high pressure of Venus' lower atmosphere. Beryllium is a suitable window material because it can withstand the physical conditions on Venus and is very transparent to Mössbauer radiation. During operation the temperature of the detectors (Si-PIN diodes, which are Si diodes with very thin P- and N-doped layers at the front and back sides, respectively, and a thick intrinsic part in between) should not exceed ~ 310 K because the detector noise increases significantly for temperatures above this. Thus, the detector (but not the whole instrument) has to be kept below this temperature during the time spectra are measured. Measurement times are typically a few hours and depend on the Fe content of the sample, the Mössbauer source activity, and the total numbers of detectors (or the total sensitive detector area). Thus, operation of a MB spectrometer on the surface of Venus would probably require cooling by phase change materials and/or active refrigeration. Other analytical instruments such as XRF spectrometers, X-ray diffractometers, and visible-IR spectrometers using solid state detectors have similar operating constraints that are imposed by the need to maintain the detectors at low temperatures relative to ambient conditions on Venus.

Another possibility might be to operate the MB spectrometer at higher altitudes where it is much cooler. This could be done as part of a balloon mission where samples would be taken during a short excursion close to the surface (e.g., by a sampling snake) and then be brought to higher altitudes for analyses of the rock and soil samples. One concept for a balloon mission envisions floating at altitudes of 40 to 60 km, corresponding to ambient temperatures of about 410 to 260 K (Campbell *et al.* 1999). The advantages of high altitude (i.e., low temperature) operation would be a reduction in the detector noise level and an increase in signal intensity because of increased Debye–Waller factors. Longer integration times would also be possible because cooling of the detectors and associated electronics is not an issue. All of these factors lead to MB spectra with better statistical quality. The sample handling would also be easier at higher altitudes because of the lower temperatures and the lower pressure. Sample handling on Venus' surface would be more complex, as demonstrated by the sample handling equipment on the Venera

and Vega landers. However, this problem is common to many analytical instruments (XRF, XRD, UV, visible, IR spectrometers).

We recommend that further laboratory work should be done to measure MB parameters for Fe minerals at Venus surface temperatures. In particular, variation of the Debye–Waller factors as a function of temperature should be investigated for several common Fe minerals for temperatures up to about 800 K. The temperature dependence of the quadrupole splitting, in particular for pyrrhotites, has not been studied for the relevant temperature range and should be done. Finally, the issues involved in design of mechanical equipment for sample acquisition and handling at high temperatures and high pressures for a MB spectrometer and other analytical instruments also need to be studied.

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