

TEMPORAL STABILITY OF A FINE-GRAINED MAGNETITE

Key Words—Electron microscopy, Magnetic properties, Magnetite, Mössbauer spectroscopy, Oxidation.

The oxidation state of a magnetite synthesized under alkaline conditions at ambient temperature (series IV, sample 0, of Schwertmann and Murad, 1990) was monitored by Mössbauer spectroscopy over a period of >8 years. The sample had a unit-cell dimension of 0.83852(3) nm, which is noticeably lower than that of stoichiometric magnetite (0.83967 nm, according to JCPDS card #19-629), and indicates partial oxidation. Electron microscopy showed the sample to consist of a mixture of small (<100 nm), almost spherical, particles and up to 300 nm large, euhedral crystals (Figure 1).

Room-temperature Mössbauer spectra of stoichiometric magnetite consist of two sextets. Thermally activated electron delocalization between Fe^{3+} and Fe^{2+} in the octahedral sites causes the nuclei to sense an average iron valence of 2.5 and produces a sextet with an isomer shift intermediate between those of Fe^{3+} and Fe^{2+} and a hyperfine field of about 46 T. The second sextet results from Fe^{3+} in the tetrahedral sites, which gives a magnetic hyperfine field of about 49 T. Upon gradual oxidation of Fe^{2+} , electron delocalization becomes inhibited, and the former sextet gives way to an Fe^{3+} sextet with parameters that differ only slightly from those of Fe^{3+} in the tetrahedral sites. A distinction between these spectral components requires spectra to be taken under an externally applied magnetic field.

EXPERIMENTAL METHODS

The sample synthesis has been described by Schwertmann and Murad (1990). Mössbauer spectra were taken using a $^{57}\text{Co}/\text{Rh}$ source moved either in a sinusoidal or a triangular mode. To reduce possible orientation effects, the sample was mixed with 2 parts sugar or boron nitride. Measurements were carried out on absorbers that had Fe concentrations between 7.2 and 8.3 mg/cm². Spectra were taken in velocity ranges between ± 10.4 and ± 11.9 mm/s at room temperature and between 200 and 78 K cooling both source and absorber in a bath cryostat. The transmitted radiation was recorded with a proportional counter and stored in a 1024 channel analyzer until $0.7\text{--}1.7 \cdot 10^6$ counts had been accumulated. A metallic iron foil was used for velocity calibration. The mirror halves of the spectra were folded and Lorentzian line fits carried out by

a computer procedure, constraining corresponding lines of every sextet to have equal widths and intensities.

RESULTS AND DISCUSSION

A chemical analysis performed 3 months after synthesis showed the magnetite to have an $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of 0.20 rather than the ideal 0.33, indicating partial oxidation. The first Mössbauer spectrum (Table 1 and Figure 2, top) was taken 3 months later and indicates the same $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio, thus corroborating the chemical analysis.

Additional room-temperature spectra of the magnetite were taken 61 and 99 months after synthesis. The contribution of intermediate valence iron in the octahedral sites to the total spectrum showed a marked decrease within this period (Table 1 and Figure 2). This is particularly evident in a decreasing intensity of the peaks at -6.8 and -3.7 mm/s (marked with arrows in Figure 2). On the basis of the relative areas of the sextets due to total Fe^{3+} and intermediate valence Fe, structural formulae were calculated. These formulae show that a gradual oxidation of Fe^{2+} has taken place (Table 1). If the proportion of Fe^{2+} is correlated with the time elapsed since synthesis, this variation indicates oxidation of about 0.3% of the original Fe^{2+} per month.

The hyperfine fields for the total (i.e., tetrahedral plus octahedral) Fe^{3+} component showed a minor but consistent increase from 49.3 to 49.7 T during the period of study. The hyperfine fields due to intermediate valence iron in the octahedral sites, in contrast, showed only insignificant (<0.1 T) and unsystematic variations. The hyperfine field for octahedral Fe^{3+} in magnetite is known to be higher than that for tetrahedral Fe^{3+} (Coe *et al.*, 1971). The observed increase in the Fe^{3+} hyperfine field thus can be ascribed to a progressive oxidation of Fe^{2+} in the octahedral sites with time.

Mössbauer spectra of the sample taken at 160 K under longitudinally applied external magnetic fields of 1 T and 6 T showed an incomplete suppression of the $\Delta m_1 = 0$ (i.e., the 2nd and 5th) peaks (Murad *et al.*, 1990). The average spin canting angle, calculated from the relative intensities of the $\Delta m_1 = 0$ peaks, was 18°. Such non-collinear magnetic structures are characteristic for fine-grained ferrites that, because of a

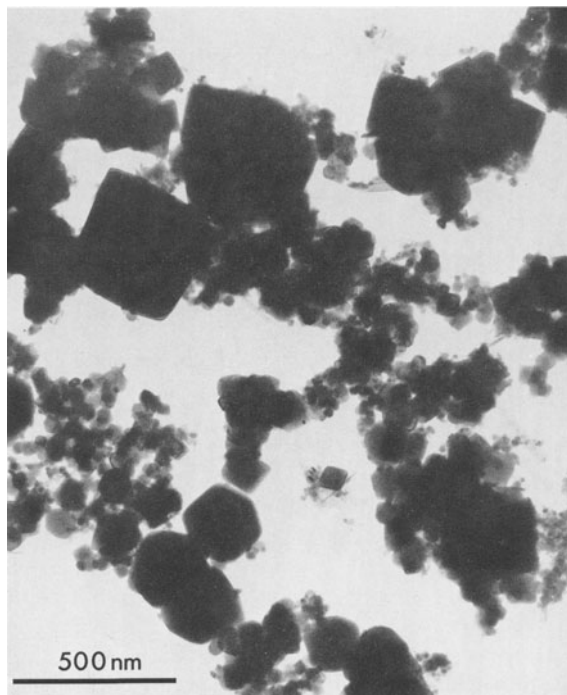


Figure 1. Transmission electron micrograph of the magnetite studied.

large proportion of surface-near atoms, tend to be highly disordered (Morrish and Haneda, 1983) and, thus, in line with the other properties of the studied magnetite.

CONCLUSIONS

Low-temperature Mössbauer data show that small particle size has a pronounced effect on the magnetic properties of the magnetite. The susceptibility of the sample to oxidation can also be ascribed to its small particle size. Thus $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios that have been determined for fine-grained magnetites will only be valid for a limited period if no precautions are taken to prevent oxidation (e.g., storage under a non-oxidizing medium or in a vacuum). Correlations of such $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios with other properties require all mea-

Table 1. Compositions of the magnetites deduced from room-temperature Mössbauer spectra.

Time ¹	$A(2.5)/A(3)^2$	$\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})^3$	Composition ⁴
6	0.67	0.200	$\text{Fe}^{3+}[\text{Fe}_{1.28}^{3+}\text{Fe}_{0.57}^{2+}\square_{0.14}]\text{O}_4$
61	0.48	0.160	$\text{Fe}^{3+}[\text{Fe}_{1.36}^{3+}\text{Fe}_{0.45}^{2+}\square_{0.18}]\text{O}_4$
99	0.41	0.146	$\text{Fe}^{3+}[\text{Fe}_{1.39}^{3+}\text{Fe}_{0.41}^{2+}\square_{0.20}]\text{O}_4$

¹ Months elapsed since sample synthesis.

² Ratio of areas of the sextets due to mixed-valence and trivalent iron. For stoichiometric magnetite, this ratio is 2.0.

³ Derived from the ratio $A(2.5)/A(3)$.

⁴ Octahedral cations in brackets.

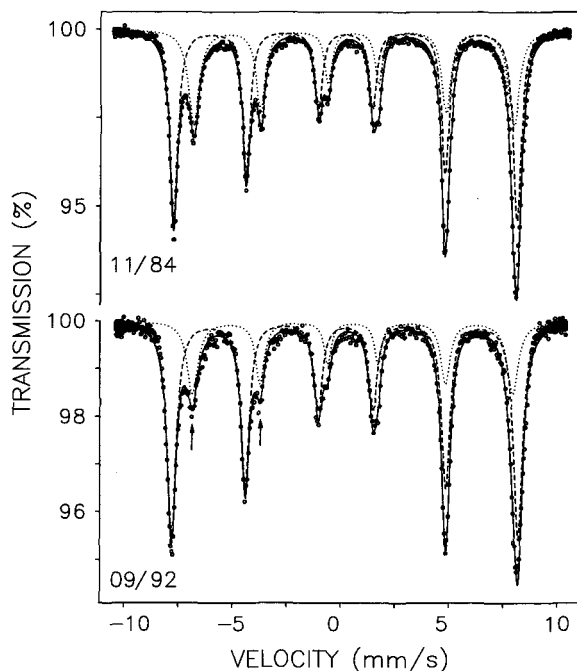


Figure 2. Room-temperature Mössbauer spectra of the studied magnetite taken 6 months (top) and 99 months (bottom) after synthesis. The spectra have been fitted with two sextets to account for total Fe^{3+} (broken subspectrum) and iron of mixed valence in the octahedral sites (dotted subspectrum).

surements to be made within a reasonably short period of time.

The susceptibility of fine-grained magnetites to oxidation could offer an explanation for the observation that magnetites found in soils are generally coarse-grained and of detrital origin. The formation of biogenic magnetites in a gley soil has recently been documented by Faßbinder *et al.* (1989). Such magnetites would generally be of smaller particle size than their detrital counterparts, and consequently—because of a higher susceptibility to oxidation—less stable.

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