

A WARNING ON THE USE OF MÖSSBAUER SPECTROSCOPY IN SEMIQUANTITATIVE ANALYSIS OF SOILS

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It is usual in Mössbauer spectroscopy analysis to take the subspectra areas as a measure of the concentration of the Fe compounds that generate them. In soils, the presence of different-size particles of different nature makes the semiquantitative Mössbauer studies difficult, and some handling of the sample must be carried out in order to get reliable area results (Bowman et al. 1967; Muir 1968; Williamson et al. 1981).

In performing an investigation (Saragovi et al. 1994) about the effect of Fe dissolution treatments on different-size particles of an Argentinian Mollisol (Muzzi soil, Ap horizon, suborder Ustoll, Haplustoll petrocalcic), we found results that seemed to depend on the size of the treated soil. Compared to the more commonly studied soils, the amount of Fe is very small and the amount of clays (montmorillonite-illite) is very large. Since, when sieving, a significant proportion of the Fe remains in the coarse fractions, it is important to look at the different soil sizes. In this Note, we present the results obtained when $<2\ \mu\text{m}$, $<50\ \mu\text{m}$ and $<2\ \text{mm}$ samples were subjected to the usual preparation procedure as well as a milling preparation procedure, to call attention to the importance of sample preparation. We have dispersed, air-dried and passed the soil sample through a 2-mm and a 50- μm stainless-steel sieve. The $<2\ \mu\text{m}$ size was then obtained by settling a soil sieve. We treated all of these samples with the following Fe dissolution methods: ammonium oxalate (AO) (McKeague et al. 1966; Schwertmann 1973), dithionite–citrate–bicarbonate (DCB) (Mehra et al. 1960) and dithionite–ethylenediaminetetra–acetic acid (D–EDTA) (Rueda et al. 1992). Then we produced 4 samples for each one of the sizes ($<2\ \text{mm}$, $<50\ \mu\text{m}$, $<2\ \mu\text{m}$): the untreated, the AO-treated, the DCB-treated and the D–EDTA-treated samples.

For Mössbauer spectroscopy, we prepared all of the absorbers using approximately $8\ \text{mg cm}^{-2}$ of Fe (Long et al. 1983) in powder form. We made 2 sets of samples: the non-milled and the milled ones. For the 1st set, we carefully ground and mixed each of the 12 above-mentioned samples (that is, 4 for $<2\ \text{mm}$ size, 4 for $<50\ \mu\text{m}$ size and 4 for $<2\ \mu\text{m}$ size) with non-refined sugar, trying to avoid the preferred orientation of the powder crystallites. For the 2nd set, we milled the 8 samples in a ball miller, then prepared the ab-

sorbers using the previous procedure. Also, to be safe with respect to the texture effect, we checked the measurements using the magic angle (Ericsson and Wäppling 1976) in all samples. We tried different milling times and chose the final interval as the one in which the total area of the Mössbauer spectrum remained almost the same for 2 consecutive intervals. This was achieved in 12 min. We did not mill the clay fractions to avoid undesirable changes in the mineralogy of this fraction. As an example, Torres Sanchez (1996) has reported major changes in the mineralogy of natural maghemite under only 10 min of grinding.

We measured the spectra at 300 K (room temperature, RT) and fitted them with the Dist3e program (Vandenberghé 1992). We obtained the best fits using 2 distributions of quadrupole doublets (D1 and D2) and 2 distributions of hyperfine fields (S1 and S2), except for some cases where only 1 S distribution was enough. For the purpose of this Note, we are only interested in the “magnetic contribution” (S1 + S2) and the “paramagnetic contribution” (D1 + D2). In Figure 1, we show the spectra for the AO-treated soil of size $<2\ \text{mm}$ in which the fitted and experimental points are indicated.

Turning to the spectral areas, we took notice of the fact that, for each sample, the total areas increased their values with the milling interval up to an almost constant value. Also, we measured the background correction (B) in all of the absorbers, using the filter method (Housley et al. 1964, Williamson et al. 1981), finding a value of ~ 1.3 for B . This value was practically independent of the absorber sizes, in spite of being high. We should mention that we are not interested in knowing the recoilless fraction, f_r , values (Greenwood and Gibb 1971), since we compare the same samples under different treatments.

In Table 1 we show the relative normalized subspectral areas in percentiles for each particle size under the different treatments used for the non-milled samples and for the milled ones. For each sample, we computed the relative “magnetic” (S1 + S2) and “paramagnetic” (D1 + D2) populations from their areas, and for each size the treated sample areas were normalized to the untreated ones. The extracted Fe columns, showing the extracted area, were derived

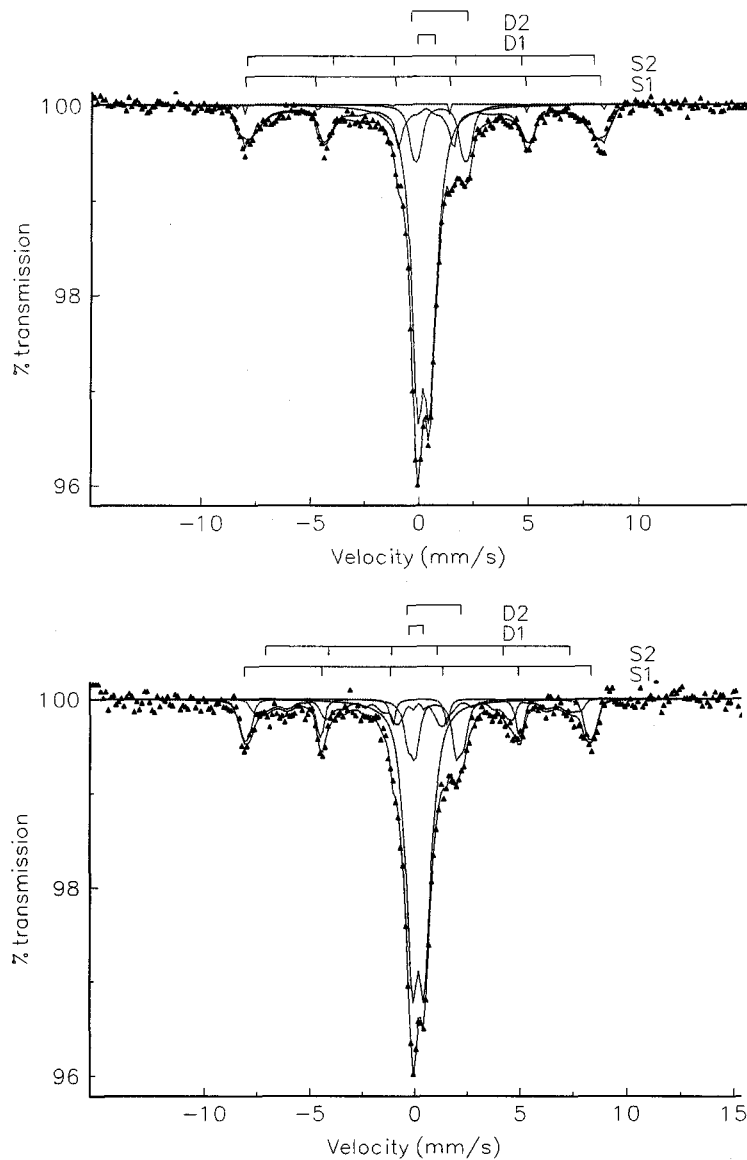


Figure 1. Mössbauer spectrum for soil size <2 mm at room temperature treated with AO: a) (top) non-milled sample and b) (bottom) milled sample.

from subtraction of the magnetic and paramagnetic populations from 100.

Considering the total amount of extracted Fe, the data corresponding to the different treatments for the <2 μm -size particles shows an expected trend, that is, an improvement in the Fe-extraction rate with the D-EDTA treatment, which is better than the DCB one, which in turn is better than the AO treatment. This trend is coincident with those observed in all fractions when analyzing the extracted Fe after the treatments using atomic absorption. On the contrary, the Mössbauer data corresponding to the other sizes show an unclear behavior at variance with the trends revealed with the milled samples. When milling, the Fe-extrac-

tion rates exhibit the same trend for all particle sizes, showing that the D-EDTA procedure is the most efficient for all sizes as compared to DCB and AO. In turn, the DCB treatment is more efficient than AO for all sizes.

We would like to mention that we also measured the samples at 15 K, and the same trends are observed as at RT.

In conclusion, we have shown that the use of the Mössbauer spectral areas in a soil semiquantitative analysis has to be considered very carefully, especially in Fe-poor soils. Even in the case where the texture effect and the background radiation corrections are taken into account, it is possible to obtain misleading

Table 1. Relative normalized areas in percent at room temperature for non-milled and milled samples.

Sample	S1 + S2	D1 + D2	Extract- ed Fe	S1 + S2	D1 + D2	Extract- ed Fe
<2 mm						
non-milled			<2 mm milled			
Nontreated	39	61	0	38.3	61.7	0
AO-treated	23	40.3	36.7	30.4	61.6	8
4 DCB-treated	20.3	44.3	35.4	27.7	54.8	17
D-EDTA-treated	13	40.6	46.4	20	43.8	36
<50 µm						
non-milled			<50 µm milled			
Nontreated	30.2	69.8	0	29	71	0
AO-treated	26	61.6	12	20	61	19
4 DCB-treated	15.6	48.2	36.2	20.6	54.3	25
D-EDTA-treated	15	57.6	27.4	8.9	59.1	32
<2 µm non-milled			<2 µm non-milled			
Nontreated	15.9	84.1	0	15.9	84.1	0
AO-treated	17.6	79	3.5	17.6	79	3.5
4 DCB-treated		83.8	16.1		83.8	16.1
D-EDTA-treated		52	48		52	48

results, even wrong trends, unless the homogeneity of the samples is assured.

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