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ILMENITE AND MAGNETITE OF A THOLEIITIC BASALT

Key Words—Basalt, Ilmenite, Iron oxides, Magnetic soil, Magnetite, Mössbauer.

In a recent paper, Goulart *et al* (1994) reported the existence of a ferric ilmenite, $(0.85)FeTiO_3$, $(0.15)Fe_2O_3$, in a soil developed from basalt. At that time, it was not clear whether the solid solution was directly inherited from the parent rock, dominantly, a tholeiitic basalt, or was somehow formed during pedogenesis. Some (Al, Ti)-maghemite and hematite were also reportedly detected in this soil (Goulart 1994). In the present work, a magnetic extract of a basalt sample from the same geological domain was studied in detail, and its mineralogy is described.

Firstly, a piece of the basalt was collected in a cut just aside the highway BR 452, 37.2 km northwest from Tupaciguara (Minas Gerais State, Brazil), from a rock block 4 m below the surface, underlying a dusky red magnetic Alfisol (saturation magnetization – $\sigma_s \approx 2$ JT^{-1} kg^{-1}). Then, the rock sample ($\sigma_s < 1$ JT^{-1} kg^{-1}) was powdered in a mortar and sieved to 250 mesh. Part of this powdered sample was dissolved in a concentrated HCl-HNO_3-HF mixture, and the solution was chemically analyzed by the standard titration method using potassium dichromate (Jeffery 1981), with minor modifications, to quantify Fe, and with a Spectroflame (Analytical Instruments) plasma emission spectrophotometer for the other elements, given the following results in mass%: Fe_2O_3, 15.20; Al_2O_3, 12.00; TiO_2, 3.70; MnO, 0.18; SiO_2, 49.8, CaO, 6.81; MgO, 3.77; K_2O, 2.88; Na_2O, 2.23; LOI, 2.25. From the chemical composition, the rock was classified as a high-Fe tholeiitic basalt, according to the Jensen (1976) plot. The powdered rock was also analyzed by X-ray diffraction (XRD), in a Rigaku Geigerflex diffratometer with a graphite, diffracted beam monochromator using Co(Kα) radiation, and by Mössbauer spectroscopy with a constant acceleration transmission spectrometer and a Co^{57}/Rh source.

The silicates were selectively removed to concentrate the iron oxides by placing the powdered basalt sample in 5 M NaOH solution for six hours at 80°C, then centrifuging, washing with diluted hydrochloric acid, and centrifuging again to separate the solid phase. This procedure was repeated 3 or 4 times, until the magnetization of the treated sample reached a constant

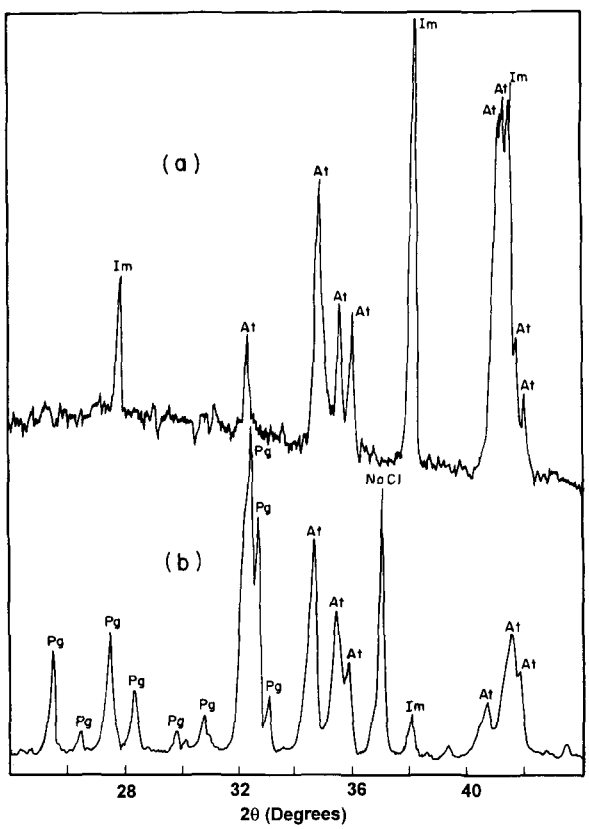


Figure 1. Powder X-ray patterns of the (a) residue remaining after 5 M NaOH extraction and (b) fresh basalt. At = augite, Im = ilmenite and Pg = plagioclase. NaCl is the internal standard.

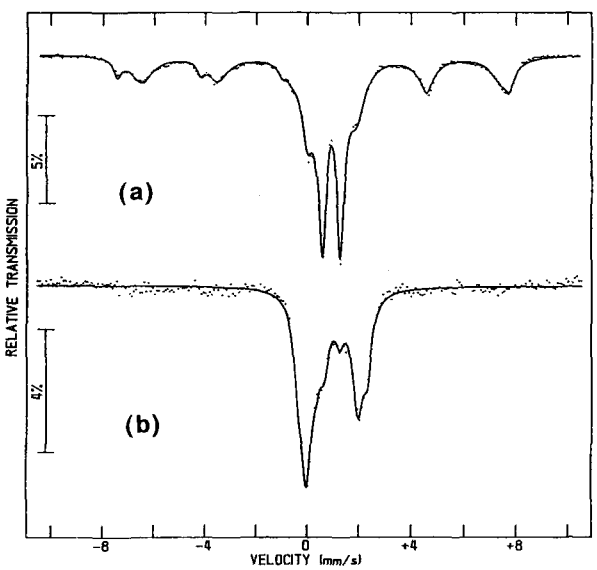


Figure 2. Room temperature Mössbauer spectra of (a) residue remaining after 5 M NaOH extraction and (b) the fresh basalt.

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Table 1. Least-square fitted Mössbauer parameters for the residue remaining after 5M NaOH extraction from the basalt sample. The Mössbauer spectrum is presented in Figure 2a.

Mineral	Site	δ^1/ mm s^{-1}	ϵ,Δ^2/ mm s^{-1}	B_{eff}^3/T	RA[4]/%
Magnetite	$Fe^{2.5+}$	0.59	−0.02	43.3	35
	Fe^{3+}	0.28	−0.06	47.2	8
Ilmenite	Fe^{2+}	1.06	0.68		34
	Fe^{3+}	0.30	0.35		5
Silicates	[5]	1.09	1.90		18

[1] Isomer shift relative to αFe.
[2] Quadrupole splitting.
[3] Hyperfine magnetic field.
[4] Relative area of the subspectrum.
[5] Unresolved doublet (Figure 2b). The resolved parameters for this subspectrum are presented in Table 2.

Table 2. Least-square fitted Mössbauer parameters for the central doublets of the chemically untreated basalt sample. The Mössbauer spectrum (not shown here) was obtained in a Doppler velocity full scale ranging from −4 mm s^{-1} to +4 mm s^{-1}.

Mineral	Site	δ^1/ mm s^{-1}	Δ^2/ mm s^{-1}	RA[3]/%
Augite	Fe^{2+} in M1	1.15	2.71	19
	Fe^{2+} in M2	1.02	2.00	49
	Fe^{3+} in M1	0.44	0.58	19
Ilmenite	Fe^{2+}	1.07	0.68	10
	Fe^{3+}	0.30	0.35	3

[1] Isomer shift relative to αFe.
[2] Quadrupole splitting.
[3] Relative area of the subspectrum.

value. This selective chemical treatment reduced the sample quantity to about 1% of the whole initial mass, and the saturation magnetization increased to 12 JT^{-1} kg^{-1}. The XRD pattern of the chemical separate showed only the characteristic reflections of ilmenite and augite (Figure 1a), indicating the effectiveness of the chemical treatment in preferentially removing plagioclase minerals (compare with the XRD pattern of the untreated sample presented in Figure 1b).

Ilmenite (determined lattice parameter, a = 0.5082 nm and c = 1.4070 nm), augite and plagioclase (albite and/or anorthite) were the main mineralogical phases identified by XRD in the whole rock sample. No magnetite or maghemite could be unequivocally detected as most of the diagnostic reflections overlap with those of augite. However, the room temperature Mössbauer spectrum of the chemically-treated basalt revealed the existence of two relatively asymmetric sextets (Figure 2a and Table 1) of magnetite (43% of the spectral area), along with ilmenite (39%) and silicates (18%). A spectral analysis of the untreated sample in a narrower range of velocity, from −4 mms^{-1} to +4 mms^{-1} (spectrum not shown here), unveiled five central doublets, three of them due to the augite and two due to the ilmenite (Table 2). A full scale spectrum of the untreated sample is presented in Figure 2b.

Reported hyperfine (Fe^{3+} : δ/Fe = 0.28 mm/s, Δ = 0.35 mm/s; Fe^{3+} : δ/Fe = 1.03 mm/s, Δ = 0.66 mm/s) and lattice (a = 0.5082 ± 0.0001 nm; c = 1.398 ± 0.001 nm) parameters for the soil-ilmenite characterized by Goulart *et al* (1994) are close to those found for the basalt-ilmenite in this work, indicating its relatively high stability during pedogenesis. On the other hand, magnetite seems to be rather unstable under weathering, in this lithology, as it was not detected in the transitional horizon C/R of the overlying soil (B. A. Ferreira 1994, unpublished data). A similar result is reported by Goulart (1994), based on a detailed mineralogical analysis of the magnetic extract from the B horizon sand fraction. Thus, the soil-ilmenite is directly inherited from the parent rock, whereas the soil-maghemite is somehow formed from the basalt-magnetite.

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REFERENCES

Goulart. A. T. 1994. Structural and magnetic properties of iron oxides occurring in magnetic soils derived from basalt and tuffite. D.Sc. thesis. Federal University of Minas Gerais (Brazil) (in Portuguese).

Goulart, A. T., M. F. de Jesus Filho, J. D. Fabris, and J. M. D. Coey. 1994. Characterization of a soil ilmenite developed from basalt. Hyperfine Interactions **91**: 771–775.

Jeffery, P. G. 1981. *Chemical Methods of Rock Analysis,* 3rd ed. London: Pergamon Press, 375 pp.

Jensen, L. S. 1976. A new cation plot for classifying subalkalic volcanic rocks. Ontario Department of Mines, Miscellaneous Paper 66.

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