



Selective dissolution of Fe–Ti oxides – Extractable iron as a criterion for andic properties revisited

C. Algoe^a, G. Stoops^a, R.E. Vandenberghe^b, E. Van Ranst^{a,*}

^a Department of Geology and Soil Science (WE13), Ghent University, Krijgslaan 281(S8), B- 9000 Gent, Belgium

^b Department of Physics and Astronomy, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium

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ABSTRACT

An important criterion used to determine andic properties in World Reference Base is Al + ½ Fe content (by ammonium oxalate) equal to 2% or more. Experiments have shown however that the acid–ammonium oxalate–extractable Fe (Fe_{ox}) value often does not only express the amorphous or short-range-order (SRO) Fe-constituents, typical for andic properties, but is influenced by the dissolution of Fe in magnetite and maghemite lattices. This paper discusses the influence of Fe–Ti oxides in particular titanomagnetite, a common constituent of many volcanic rocks, on Fe_{ox} values and proposes an alternative method for determination of SRO Fe-constituents. Mineralogical analyses of fresh dolerite, separated magnetic fractions and single titanomagnetite grains were carried out using scanning electron microscopy, electron microprobe, and Mössbauer spectroscopy. Iron was selectively extracted using acid–ammonium oxalate (Fe_{ox}), Na dithionite–citrate–bicarbonate (Fe_d) and Tiron (Fe_{tiron}). The concentrations of Fe_{ox} in all samples were higher than Fe_d and Fe_{ox}/Fe_d ratios progressively decreased from the strongly magnetic fraction to the weakly magnetic and non-magnetic fractions, proving the influence of titanomagnetite on Fe_{ox}. On the other hand, no notable difference was observed between Fe_{tiron} and Fe_{ox} in the different fractions, indicating the very limited influence of titanomagnetite on Fe extraction using Tiron. Consequently the Tiron extraction method is being recommended as a better alternative to the oxalate method to quantify amorphous/SRO Fe-constituents in soils and regoliths containing magnetic minerals, and especially to identify andic properties in soils on volcanic ash.

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1. Introduction

The first requirement formulated in WRB (IUSS Working Group WRB, 2007) for andic properties is an Al + ½ Fe content (by ammonium oxalate) in the fine earth (0–2 mm) fraction equal to 2.0% or more on an oven-dried (105 °C) basis (Blakemore et al., 1981), indicating the presence of amorphous or short-range-order (SRO) materials, such as allophane, imogolite, and ferrihydrite. The acid–ammonium oxalate–extractable Fe (Fe_{ox}) is supposed to be a reliable estimator of ferrihydrite and the Fe substituting Al in allophane, and not to extract other Fe oxides such as goethite and hematite to any significant extent (Schwertmann, 1964, 1973). The ½ in the formula is used because Fe has approximately twice the atomic weight of Al (Leamy et al., 1990). Thus by using one-half the weight of Fe, about the same amount of Fe and Al is required.

Over time, numerous methods have been developed or refined for the selective dissolution (extraction) of Fe oxides (Smith, 1994). The best known of these is the dithionite–citrate–bicarbonate (DCB)

method of Mehra and Jackson (1960). The DCB method takes advantage of the fact that most Fe(III) oxides are susceptible to reductive dissolution by Na-dithionite and as such the DCB-extractable Fe (Fe_d) provides an upper limit for the total amount of Fe oxides in a sample (Bigham et al., 2002). Methods targeting poorly crystalline phases (ferrihydrite, schwertmannite) take advantage of naturally accelerated dissolution rates associated with structural disorder. The most widely used approach involves an acid (pH = 3) medium in darkness with oxalate as the chelating agent. This dissolution reaction is strongly catalyzed both by light and by the presence of Fe(II); thus, magnetite, with Fe in mixed valence states, is also dissolved (Bigham et al., 2002).

Based on the assumption that the acid oxalate method only extracts poorly crystalline Fe oxides and DCB extracts all free Fe oxides, Fe_d should be always higher than Fe_{ox}, or formulated as the Schwertmann criterion (Schwertmann, 1964): $K_{Sch} = Fe_{ox} / Fe_d < 1$. In reality however, one observes commonly K_{Sch} values of soils exceeding 1 (Vodyanitskii et al., 2007). A critical study, for instance, of the precise analytical data for a series of volcanic ash soils by Meijer et al. (2007) shows that Fe_{ox} often exceeds Fe_d. For a few horizons this has an impact on them being considered as having andic properties. For instance sample Costa Rica Tc has the following

* Corresponding author. Tel.: +32 9264 4626; fax: +32 9264 4997.

E-mail address: eric.vanranst@ugent.be (E. Van Ranst).

extracted Fe contents: $Al_{ox} = 1.32\%$, $Fe_{ox} = 3.04\%$, $Fe_d = 1.10\%$; applying the formula $Al_{ox} + \frac{1}{2} Fe_{ox}$ one obtains a value of 2.84%, thus clearly andic properties. Using the Fe_d value the result would be only 1.87%, thus not sufficient to be characterised as andic properties. In much more of the analytical results of Meijer et al. (2007) Fe_{ox} is not higher than Fe_d , but almost equal, what means that, taking into account that crystalline Fe is present, more horizons suffer from an overestimation of Fe_{ox} , and probably do not have andic properties. There might be several explanations for this phenomenon. Vodyanitskii et al. (2007) for instance ascribe it to the catalysing effect of pyrite or siderite during the oxalate extraction. Although this might be true for some soils, a more plausible reason, mentioned by several authors (see below) is the possibility that magnetite or maghemite are attacked by the acid–ammonium oxalate procedure.

Few studies (Rhoton et al., 1981; van Oorschot and Dekkers, 2001; van Oorschot et al., 2002; Walker, 1983) assessed the effects of magnetite on oxalate and DCB extractable iron. It was demonstrated that oxalate extraction preferentially dissolved fine grained magnetic Fe oxides from both, synthetic and natural samples. DCB extractions were considered less specific and results obtained varied considerably. It was reported that DCB extraction did not attack primary magnetite, but did attack hematite in or on the magnetite grains (so-called martite) (Walker, 1983), that only pedogenic maghemite was dissolved (Fine et al., 1989; Singer and Fine, 1989; Singer et al., 1995), and that fine grained ($<1 \mu m$) magnetite was dissolved as well (Hunt et al., 1995). Although the results of different studies were difficult to compare because the extraction procedure was not always clearly specified (van Oorschot and Dekkers, 1999), the presence of magnetite in samples may confound the interpretation of Fe_{ox} data as representative of short-range-order forms of Fe (Gamble and Daniels, 1972; Rhoton et al., 1981).

Chemical extractants, including acid–ammonium oxalate and DCB, have also been used for studying the spatial distribution of Fe and other oxides in thin sections of undisturbed soil (Arocena et al., 1989, 1990; Bullock et al., 1975).

Tiron as a complexing agent to extract amorphous components in soils was first introduced by Biermans and Baert (1977) and their method was further calibrated by Kodama and Ross (1991). The alkaline (pH 10.5) Tiron solution was found to be equally effective as oxalate for extracting amorphous Fe oxides. Kodama and Ross (1991) compared the Tiron extraction with the oxalate extraction method on a wide range of reference minerals. They found that alkaline Tiron solution, like oxalate, dissolved allophanes and imogolite completely. The Tiron solution dissolved little magnetite compared with a substantial dissolution by oxalate. No significant dissolution was found for goethite, hematite, maghemite, and lepidocrocite, but some for akaganeite (Kodama and Ross, 1991).

Earlier studies focused mainly on magnetite and maghemite as such. Since in many cases more Ti-rich oxides are present in volcanic ejecta, especially in basaltic ones, the present study tries to contribute to the discussion by determining the influence of Fe–Ti oxides, in particular titanomagnetite, on the acid–ammonium oxalate, DCB and Tiron extractable Fe, experimenting with Ti-rich members of the spinel group.

2. Methods

2.1. Sample preparation

Fresh dolerite has been sampled in the village, Berg en Dal, situated about 90 km south of the capital Paramaribo in Suriname. The sample was ground and separated into different fractions based on magnetic properties using a hand magnet. The samples attracted to the magnet at a distance of 1 cm were classified as the strongly magnetic fraction (SMF), those attracted at a distance of 0.5 cm as the weakly magnetic fraction (WMF), and finally those not attracted

to the magnet in direct contact as the non magnetic fraction (NMF). Ten weight percent of the bulk sample consisted of SMF and another 10% of WMF. Chemical extractions were carried out on bulk samples, the separated fractions, thin sections and individual (titano)magnetite grains. Uncovered thin sections were prepared for scanning electron microscopy (SEM), microprobe analyses and chemical extractions on thin sections.

2.2. Selective dissolution analyses

The DCB extractions were carried out following the procedure outlined by Mehra and Jackson (1960). A 20 ml solution of Na citrate–bicarbonate buffer was added to 0.250 g of sample in a teflon centrifuge tube, which was then placed in a water bath at 75 °C. After the solution reached 75 °C, 0.75 g of sodium dithionite powder was added and the tube was kept at this temperature for 20 minutes while stirring continuously. After cooling, the mixture was centrifuged at 3000 rpm, decanted, washed, centrifuged again and decanted. The collected extraction solution was used for determining the concentrations of Fe, Al, Si and Mn by atomic absorption spectrophotometry (AAS). The same procedure was followed for DCB extractions on thin sections and on individual (titano)magnetite grains. In some cases multiple DCB extractions were carried out on the same thin section.

The acid–ammonium oxalate extractions were carried out following the modified procedure (Schwertmann, 1964, 1973) of the original method of Tamm (Tamm, 1922). A 0.2 M ammonium oxalate solution and a 0.2 M oxalic acid solution were prepared and mixed to obtain an ammonium oxalate and oxalic acid mixture with pH = 3. The sample weighing 0.250 g was placed in a plastic centrifuge tube to which 50 ml of 0.2 M ammonium oxalate mixture was added. This mixture was stirred in the dark for 4 hours at room temperature (20 °C) and centrifuged for 10 minutes at 2000 rpm. The clear supernatant solution was decanted into a 50 ml volumetric flask and the volume was made up to the mark with the oxalate mixture. This solution was used for the measurement of Fe, Al, Si and Mn by AAS. The same procedure was followed for treatments on thin sections, with extraction time of 4, 6, 8 and finally 8 hours, respectively. Extractions were also carried out on single (titano)magnetite grains.

The Tiron (catecholdisulphonic acid di-sodium salt, $C_6H_4Na_2O_8S_2$) extractions were done following the procedure of Biermans and Baert (1977), slightly adapted after Kodama and Ross (1991). A 0.1 M Tiron solution (a maximal value within practical limits following Biermans and Baert (1977)) was prepared by dissolving 16.61 g Tiron (Acros organics, CAS nr 149-45-1, $C_6H_4Na_2O_8S_2 \cdot H_2O$, molecular weight: $332.21 \text{ g} \cdot \text{mol}^{-1}$) in approximately 400 ml of H_2O in a plastic beaker. A Na_2CO_3 solution was prepared by dissolving 2.65 g of Na_2CO_3 in 50 ml H_2O and added to the Tiron solution. The pH was adjusted to 10.5 with 15 M NaOH and the volume made up to 500 ml in a plastic volumetric flask. In order to extract Fe, Al, Si and Mn, 60 ml of the extraction solution was added to 50 mg sample in teflon centrifuge tubes, and heated for 1 hour in a water bath at 80 °C while stirring continuously. The samples were then cooled, filtered and the filtrate was used for measuring the concentrating Fe, Al, Si and Mn by AAS.

2.3. Mineralogical analyses

The chemical composition of the opaque minerals was determined by wavelength dispersive spectrometry (WDS) microprobe analyses on uncovered thin sections and energy dispersive spectrometry (EDS) microprobe analyses on magnetic grains. The opaque grains in thin sections were also studied using scanning electron microscopy (SEM) and a back-scattered electron scanning image (BESI) was obtained. In addition, SEM images were obtained of the surfaces of untreated (titano)magnetite grains, as well as of DCB, oxalate and Tiron treated grains.

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