Voltammetric Identification of Pedogenic Iron Oxides in Paleosol and Loess

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Abstract
Voltammetry of immobilized microparticles was used to detect low concentrations of goethite and hematite in paleosol and loess samples. The total content of Fe oxides in the natural samples was below 2 wt% and below the detection limit of X-ray powder diffraction. Goethite was distinguished from hematite due to the different electrochemical reactivity of the product of thermal dehydroxylation of goethite (very fine crystalline hematite). The voltammetric analysis was tested using synthetic samples of ferrihydrite, goethite, hematite, magnetite, or Mg-ferrite with SiO2 and a natural sample of smectite with an admixture of goethite. The detection is most sensitive for goethite and hematite (detection limit about 0.1 wt%), and approximately an order of magnitude better than X-ray powder diffraction analysis.

Keywords: Goethite, Hematite, Paleosol, Loess, Voltammetry of microparticles

1. Introduction
Pedogenic (formed in soil) ferrihydrite, Fe2O3·n H2O, goethite α-FeOOH, and hematite α-Fe2O3 play an important role in the chemistry of iron in soils [1]. Ferrihydrite is a metastable product of fast hydrolysis of dissolved iron. Goethite and hematite are the final products of aging of ferrihydrite and other metastable ferric oxides, and their ratio reflects the conditions under which the soil was formed, such as rainfall, temperature, and Al/Fe ratio [1, 2]. Generally, hematite prevails over goethite in soils formed in warmer and drier climate. The identification of small amounts of these minerals is, however, not an uncomplicated task [1]. Ferrihydrite and sometimes also goethite are poorly crystalline minerals and/or present in small amounts only. Therefore, they cannot be easily identified by X-ray diffraction analysis. Similarly, the success of Mössbauer spectroscopic analysis is complicated by non-stoichiometry, Al-for-Fe substitution, and the small particle size of these species [3, 4]. Diffuse reflectance spectroscopy is sufficiently sensitive and specific to determine soil ferric oxides [5, 6], but it is not very common in analytical practice. Rock magnetic methods [7] can detect ferrimagnetic magnetite Fe3O4 and maghemite γ-Fe2O3 with extraordinary sensitivity, but the contribution of imperfectly antiferromagnetic goethite and hematite to the overall magnetic properties is usually insignificant compared to the signal of magnetite even when the magnetite content is small. In addition, ferrihydrite is paramagnetic at room temperature so it cannot be detected by remanent magnetic measurements.

The total content of ferric oxides is routinely evaluated by chemical extraction techniques, such as dithionite-citrate-bicarbonate or oxalate extractions [1]. The dissolution is based on the increase of the dissolution rate of ferric oxides after their reduction to Fe2+, that is finally converted to soluble Fe2+ by action of acids and/or ligands

$$\text{Fe}_2\text{O}_3(s) + 2e^- + 6\text{H}^+ \rightarrow 2\text{Fe}^{2+}(aq) + 3\text{H}_2\text{O}$$

(1)

The source of electrons is a chemical agent, such as dithionite or ferrous oxalate. The interpretation of extraction techniques is not so straightforward as was believed after introducing them in the 1960’s and 1970’s. Not only phase composition, but also particle size and Al-for-Fe substitution significantly affect the dissolution reactivity of ferric oxides [5, 8, 9]. A reliable but comparatively laborious approach to ferric-oxide analysis is a combination of chemical extraction with other method such as Mössbauer spectroscopy [3], elemental analysis and diffuse-reflectance spectroscopy [5], or elemental analysis and X-ray diffraction [8]. The aim of the present work was to test whether the combination of magnetic characterization methods and chemical and electrochemical dissolution can lead to a successful identification of the mineralogical composition of natural samples.

Voltammetry, usually employing redox dissolution reactions, was proposed several times as an analytical tool for powdered solids, for which traditional analysis is not convenient, or should be shortened, simplified, and/or done with a small amount of samples available [10–14]. In the last decade, the technique referred to as voltammetry of microparticles has been applied to analysis of metals, metal oxides and chalcogenides [15, 16], including ferric oxides [17–19]. Electrochemical dissolution of ferric oxides proceeds analogous to the chemical reaction described by Equation 1 but the electron is supplied by the working
electrode. Voltammetry of microparticles has not yet been used to characterize the ferric oxides in natural samples except for a few cases of laterites [18, 20], in which well-crystalline iron oxides, easily detectable by X-ray diffraction, form one of the major components. In the present study, we focused on early Quaternary loess containing ferric oxides in concentration of about 1 wt%, i.e., below the detection limit of X-ray diffraction analysis. To distinguish goethite from hematite of a similar reactivity we propose to heat the samples to 300 °C which causes transformation of goethite to poorly crystalline hematite, which is more reactive in dissolution [17].

2. Experimental

We sampled a well-developed loess section with several palaeosols just North of the village of Borœtice, South Moravia, Czech Republic. This site contains four palaeosols, each developed at a different time. The top of the section has been partly disturbed by solifluction, therefore we only sampled the lowermost, oldest palaeosol. The top part of the documented section consists of an earthified Rotlehm, which formed from the loess during the Lower-Middle Pleistocene (ca. 0.9–0.5 Ma ago), it has been identified as belonging to soil complex PK VII. The lower part of the section contains the original loess and dates from the Lower Pleistocene [22]. The A-horizon of the palaeo-loess has been eroded prior to the new deposition of loess. The magnetic susceptibility is enhanced paleosol compared to that of the loess, which is consistent with the observation that all central European palaeosols have enhanced susceptibility compared to the original loess [23]. The average carbonate content in the palaeo-loess is ca. 0.5 wt%, the loess horizon has an average carbonate content of ca. 26 wt%. Bulk samples were taken at 30-cm interval over the entire length of the section, samples were dried and stored in a laboratory refrigerator prior to use. The samples are labeled as Bx, with x the level in centimeter at which the sample was taken. The zero level was set at the top of the palaeo-loess. The loess is located at the bottom of the section, around 240 cm. Between approximately 190 and 230 cm there is a gradual change from palaeo-loess to loess, which is not only reflected in a gradual change in color, but also by changes in magnetic signal as well as mineralogical composition.

To evaluate the total amount of chemically reactive ferric oxides and Al-for-Fe substitution, the samples were extracted by the citrate-bicarbonate-dithionite (CBD) procedure in three steps [9] and after each step the concentration of Al, Fe, and Si in the extracts was analyzed by ICP. X-ray diffraction analysis (Siemens D5005, CuKα radiation) was performed to characterize the mineralogical composition of natural samples.

Bulk susceptibility was measured with a KLY-2 susceptibility-bridge (AGICO, sensitivity 4 × 10⁻⁸ SI, susceptibility of the samples was at least two orders of magnitude higher). Subsamples were mixed with epoxy resin and used for isothermal remanent magnetization (IRM) acquisition analysis. The IRM was induced by a PM4 pulse magnetizer and measured with a JR5A spinner magnetometer (AGICO). A review on rock magnetic measurements and their analytical applications can be found in [7] with a more detailed discussion of the methodology and analytical implications.

To test the voltammetric analysis we used sample VZS-6 characterized in [3] (here denoted Smectite-1). Smectite-1 is natural aluminosilicate containing admixture of goethite in the concentration 0.82 wt% (by Mössbauer spectroscopy) or 1.2 wt% (by chemical dissolution). In addition to natural samples, some synthetic samples were analyzed for two main reasons: 1) to be able to directly compare the electrochemical response to more crystalline synthetic material to supposedly less crystalline solid material, and 2) to look for the most suitable internal standard. Commercially available pigments Bayferrox 306 (magnetite) and 140 (hematite-1) were used without further pretreatment. Hematite-2 and goethite-1 were prepared by oxidative hydrolysis of a ferrous sulfate solution. Hematite-3 and Al-doped hematite-4 were prepared by evaporation of a solution of Fe₃O₄ (hematite-3) and Al- and Fe-nitrates (hematite-4), with citric acid (NO₃-C₆H₅O₇·3H₂O) citric acid in molar ratio 1.5:1 and calcination of the dry foam at 600 °C. Hematite-4 contained 10 mol% Al. Goethite-2, 3, and 4 were obtained by aging ferrihydrite in strongly alkaline solution at 70, 4, and 70 °C, respectively. Goethite-4 contained 8 mol% Al. Hematite-2 and goethites have been used previously for voltammetric studies [17, 18]. Ferrihydrite was the product of forced hydrolysis of ferric nitrate solution. Mg ferrite was prepared by solid-state synthesis from MgO and Fe₂O₃ at 1100 °C. β-MnO₂ was prepared by thermal decomposition of Mn(II) nitrate, and birnessite (K₀.₂₅MnO₂) by the sol-gel procedure from potassium permanganate and glucose [21]. Electrochemical dissolution of the manganese oxides was also reported in [21]. The phase purity of synthetic samples was checked by powder X-ray diffraction. Before the voltammetric experiments, synthetic ferric and manganese oxides were carefully mixed with SiO₂ (particle size 13 μm) in an agate mortar to dilute the analyte to a level similar to that in natural loess and palaeo-loess samples.

For the electrochemical study, a N₂-deaerated acetate buffer (acetic acid: acetate ratio 1:1, total acetate 0.2 M) was used as supporting electrolyte. A paraffin-impregnated graphite working electrode was used. All potentials are referred to saturated calomel reference electrode (SCE). Voltammetric analysis of the pure synthetic Fe oxides was described in [17–19].

3. Results and Discussion

The natural samples were mainly composed of common clay minerals (smectite, kaolinite, mica-illite) and relic minerals (quartz, feldspars). The overall amount of kaolinite was relatively low. As for the actual feldspars and clay minerals, B0, B30, and B90 were similar in composition. B60, B120
and B150 exhibited the largest diffraction lines of various feldspars and less developed clay minerals. The content of smectite and kaolinite continuously increased from B150 to B240 (the loess sample). B240 contained a significant amount of calcite, which is typical of loess, and the highest amount of kaolinite and mica-illite. No free iron oxides (hematite, goethite, magnetite-maghemite) were detected by powder X-ray diffraction. The sum of reactive Fe represented approximately 2% of the sample mass as follows from the results of CBD extraction given in Table 1. The considerable amount of extracted Si showed that clay minerals were also partially dissolved, and so not all Al (and maybe Fe) extracted was bound in the ferric oxides.

Magnetic characterization revealed that all natural samples contained two magnetic components. One component, with low coercivity and high saturation isothermal remanent magnetization (SIRM), was most likely pseudo single-domain magnetite, i.e., with particle size close to 1 μm [7]. The other component had very high coercivity and its contribution to the SIRM was in the order of 10%. This second component was most likely fine-grained (single-domain) hematite, i.e., with particles <1 μm, which is typical for pedogenic iron oxides. Because the SIRM of magnetite is about three-orders of magnitude higher than that of hematite, magnetite will dominate the signal even if it is present in ten-times smaller concentration than hematite. Hence, the rock-magnetic methods revealed fine-grained pedogenic hematite with a substantially smaller amount of slightly larger magnetite (of lithogenic as well as pedogenic origin). Goethite would not be detected under these conditions due to very small remanent magnetism (antiferromagnetic structure) and the relatively low magnetic field used for IRM acquisition. The rock magnetic behavior of these samples will be detailed in a separate contribution.

Voltammetry was applied in the same manner as reported previously [17–19]. Scanning started at open circuit potential and continued to negative potentials at scan rate 4 mV/s. An example of a typical voltammetric curve of natural sample is shown in Figure 1 (B60). Each scan was repeated three times and the difference between the first and second one, and the second and the third scan are shown as well in Figure 1. Obviously, the background current was very high with respect to the net current of ferric oxide dissolution. The subtraction of two subsequent scans solved this problem and resulted in clear voltammograms of ferric oxides in all natural samples (Fig. 2, Table 2). Differential pulse voltammetry could also be used to suppress the large background, but the interpretation of the resulting voltammograms is not so straightforward as in the case of common linear-sweep measurement – for example, it requires empirical calibration plots [11]. We therefore preferred linear sweep voltammetry although we were not successful in decreasing the background current by changing scan rate or solution pH. All voltammograms discussed in this article were obtained by the subtraction of the first two scans.

| Table 1. Percentage of Fe, Al, and Si extracted by CBD of natural samples. |
|-----------------|-------|-------|-------------|
|                 | 1st step |       | Total of three steps |
|                 | Fe     | Al    | Fe       | Al    | Si  |
| B0              | 2.12   | 0.14  | 2.30     | 0.23  | 0.32 |
| B30             | 1.48   | 0.09  | 1.63     | 0.14  | 0.13 |
| B60             | 1.58   | 0.10  | 1.72     | 0.19  | 0.30 |
| B90             | 1.01   | 0.07  | 1.13     | 0.10  | 0.12 |
| B120            | 1.32   | 0.13  | 1.32     | 0.12  | 0.13 |
| B150            | 2.07   | 0.15  | 2.23     | 0.21  | 0.30 |
| B180            | 1.25   | 0.08  | 1.37     | 0.12  | 0.12 |
| B210            | 1.49   | 0.09  | 1.63     | 0.15  | 0.24 |
| B240            | 0.75   | 0.04  | 0.82     | 0.06  | 0.11 |

Fig. 1. Voltammetric curves of paleosol B60. Upper part: 1st, 2nd, and 3rd linear-sweep voltammetric scans; lower part: subtraction of 1st minus 2nd, and 2nd minus 3rd scans.
orders magnitude lower than that of the $\alpha$-phases. This is in general agreement with the results of rock magnetic measurements.

To discriminate between the two $\alpha$-phases, we used the method of Grygar [17], which is based on the fact, that at relatively low temperatures goethite is dehydrated to reactive, defect-rich hematite, of which VA peak is shifted anodically with respect to its parent goethite. This phenomenon is demonstrated in Figure 2 with natural Smectite-1 and synthetic Goethite-3 heated at 300°C for 15 minutes in air. We also processed the other natural samples in this way, and evaluated the changes of the voltammetric peaks caused by the heating. In the majority of the samples, such as B0 and B90, the only effect of heating was 'activation' of ferric oxides, leading to sharper VA peaks at similar potentials as in the original samples. In such cases, we can identify

Table 2. Voltammetric peak potentials $E_p$ (V vs. SCE) of loess samples as received and after heating at 300°C for 15 minutes. Start at OCP (about 0.25 V), 4 mV/s. A possible minor peak or shoulder is denoted (sh). Iron oxide denotation: h hematite, g goethite, sp magnetite or ferrite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As received</th>
<th>After heating</th>
<th>Iron oxide present</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>-0.46</td>
<td>-0.49, -0.9 (sh) h, sp (?)</td>
<td></td>
</tr>
<tr>
<td>B30</td>
<td>-0.60, -0.95 (sh)</td>
<td>-0.48, -0.8 (sh) g, sp (?)</td>
<td></td>
</tr>
<tr>
<td>B60</td>
<td>-0.55, -0.7 (sh)</td>
<td>-0.48, -0.8 (sh) h</td>
<td></td>
</tr>
<tr>
<td>B90</td>
<td>-0.48, -0.6 (sh)</td>
<td>-0.47 h</td>
<td></td>
</tr>
<tr>
<td>B120</td>
<td>-0.45</td>
<td>-0.48 h</td>
<td></td>
</tr>
<tr>
<td>B150</td>
<td>-0.45</td>
<td>-0.48 h</td>
<td></td>
</tr>
<tr>
<td>B180</td>
<td>-0.47</td>
<td>-0.46 h, g (?)</td>
<td></td>
</tr>
<tr>
<td>B210</td>
<td>-0.4 (sh), -0.61, -0.45, -0.8 (sh) h, g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B240</td>
<td>-0.60, -0.9 (sh)</td>
<td>-0.44, -0.85 (sh) g, sp (?)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Voltammetric curves of paleosols B0, B90, B210, B240 and Smectite-1 and synthetic Goethite-3. The original samples and the samples heated to 300°C for 15 min are shown.
hematite as the main α-phase. In samples B240 and B210 and possibly in B180 and B30, the anodic shift of the voltammetric peak was indicating the presence of goethite. Samples B180 to B240 were similar from mineralogical point of view, moreover they exhibited increased degree of weathering of feldspars, and an increased amount of pedogenic goethite could hence be expected in these samples.

The amount of Al extracted by the first step of CBD (Table 1) corresponded to about 12 mol% Al in dissolved ferric oxides, which is common for soil hematites [1]. Such a level of substitution could possibly affect the dissolution reactivity of ferric oxides. For example, Al-for-Fe substitution was found to decrease dissolution reactivity of goethite, and above 10 mol% of Al, goethite looses its electroactivity [18]. Cr- and Mn-substitution in hematite have a similar effect [24, 25], but Al-doped hematite has not yet been subjected to voltammetric analysis. We hence prepared and tested a series of Al-doped hematites with Al content up to 10 mol%. Electrochemical properties of pure hematites 1–3 and 10 mol% Al doped hematite-4 are also given in Table 3. All Al-doped hematites were electroactive and yielded well-defined voltammetric peaks without a significant change of peak potential. However, the peak area of Al-doped Hematite-4 was decreased. We can therefore confirm that Al-for-Fe substitution found in the soil and loess samples does not endanger voltammetric detection of hematite.

The semi-quantitative evaluation of VA curves is complicated by the fact that the actual overall amount of deposited sample is not known. We hence tested the possibility to use additions of an internal standard for a quantitative evaluation. To avoid peak overlap of the standard and Fe oxides, we chose Mn oxide additions. Mn(III,IV) oxides are dissolved reductively under similar conditions as Fe oxides [21] but at potentials by at least 0.5 V more positive. β-MnO₂ (pyrolusite) and K₀.₂₅MnO₂ (birnessite) were tried as internal standards, yielding peaks at +0.30 and +0.41 V, respectively. The tests performed with synthetic samples surprisingly showed that the charges of Mn- and Fe-oxide reductive dissolution were not in the proportion expected on the base of the oxide weight and the stoichiometry of the corresponding dissolution reaction. The areas of the Fe oxide peaks were 2 to 10 times larger than theoretically expected (Table 3, column ‘sensitivity’). Magnetite and ferrihydrite were increased the least, while the peaks of both α-phases were enhanced 7 to 10 times. It is probably related to a catalytic reaction, either hydrogen-evolution side reaction [26] or reduction of oxygen [27]. The ‘sensitivity’ did not depend substantially on the particle size of ferric oxides.

We used an internal standard to examine the limit of voltammetric detection of ferric oxides. In synthetic physical mixtures of Fe and Mn oxides with SiO₂, samples with a concentration of goethite and/or hematite larger than 0.1 wt% yielded clear VA peaks with the charge ratios of Mn- and Fe-oxide dissolution not affected by dilution. In Figure 3, the charges of the dissolution peaks of goethite or hematite in synthetic mixtures were plotted against their concentration, showing the lower concentration range suitable for the detection of the α-phases. The plot also indirectly shows reproducibility of the sample deposition on the working electrode. At concentrations below 0.1%, the voltammetric peaks of α-phases disappeared.

In addition we tried to use the internal standard to estimate the total amount of reactive ferric oxides in loess samples. Because the quantitative analysis of Fe oxides in loess by X-ray diffraction was impossible, we can consider the amount of Fe dissolved by CBD (Table 1) as the upper estimate of the ferric oxide content. For this experiment we used the natural samples heated at 300 °C that improved the peak shape of the ferric oxides, and mixed the subsamples of preheated samples with the internal standard (about 1 wt% β-MnO₂). We compared the charge ratio of Mn and Fe oxide dissolution assuming that enhancement of the Fe response was equal to those of synthetic Al-doped hematite-4 (Table 3). This yielded an amount of Fe in ferric oxides in soil and loess samples between 0.6 wt% (B240) and 1.2 wt% (B0). X-ray diffraction is able to detect more than about

![Fig. 3. The areas of voltammetric peaks of ferric oxides in synthetic mixtures of α-phases with SiO₂. The concentration of FeOOH was expressed as Fe₂O₃.](image)
1 wt% crystalline phases, and the detection limit of diffuse reflectance spectroscopy is below 0.5 wt% of ferric oxides [6].

4. Conclusions

An assemblage of α-phases (goethite and hematite) was found in the paleosol and loess samples. The overall content of ferric oxides was below 2 wt%, probably close to 1 wt%. To distinguish goethite and hematite, the samples were heated at 300 °C and the voltammograms of the original and heated samples were compared. Hematite was identified to be the major component of the ferric oxide assemblage. In the loess sample (about 0.5 wt% of Fe in ferric oxides) we found a significant amount of goethite. The limit of voltammetric detection of these two phases in synthetic samples was about 0.1 wt%, which is sufficient for detection of pedogenic ferric oxides in soils and loess. The sensitivity of voltammetry to detect microparticles of goethite and hematite is hence comparable to that of diffuse reflectance spectroscopy and it is about an order of magnitude better than that of X-ray powder diffraction analysis. The voltammetric detection of goethite and hematite is enhanced by a catalytic side reaction that, on the one hand, excludes exact quantitative determination by using an internal standard, but on the other hand, enables to detect several tenths % of the electroactive species in a mixture without further sample pretreatment.

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6. References