Various redox conditions in Boda Claystone as reflected in the change of Fe$^{2+}$/Fe$^{3+}$ ratio in clay minerals

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Abstract. Fe$^{2+}$ and Fe$^{3+}$ species in layered clay minerals are analysed in samples obtained from two boreholes in Boda Siltstone Formation. In the first series occurrence of Fe$^{2+}$ components and Fe$^{2+}$ $\Rightarrow$ Fe$^{3+}$ oxidation is demonstrated in upper layers of a strata near to the surface. In the second series minerals are identified with iron present exclusively in ferrous form in a thin strata found in a borehole at 1050 m depth.

1. Introduction

Redox processes may influence the migration of certain radionuclides which are able to change their valency, and as a consequence, to change the charge of the migrating species. For example, reduction may proceed in the following processes: UO$_2^{2+}$ $\Leftrightarrow$ UO$_2$, $^{79}$SeO$_3^{2-}$ $\Leftrightarrow$ $^{79}$Se (0), $^{237}$NpO$_2^+$ $\Leftrightarrow$ $^{237}$NpO(OH)$_2$, $^{99}$TcO$_4^-$ $\Leftrightarrow$ $^{99}$TcO$_2$.

In turn, the opposite process of the previous reduction should also proceed in neighbouring media, first in pore water, then, in second stage, in host rock. In several cases the Fe$^{2+}$ $\Rightarrow$ Fe$^{3+}$ oxidation is considered as the possible counterpart of the previously mentioned reductions.

Boda Siltstone Formation (BSF) is considered as a perspective media for disposal of nuclear waste in Hungary. Thus, the ability of the constituting mineral components to participate in the redox processes may also be evaluated. In general, overwhelming part of the Boda Formation was formed under strong oxidation conditions in strong alkaline media at arid/semi-arid conditions. In correspondence, dominant part of the iron is present as hematite [1]. Thus, further oxidation can hardly be expected.

In the present study Fe$^{2+}$ and Fe$^{3+}$ components are studied with Mössbauer spectroscopy in BSF samples. Two examples are discussed in detail. In the first one the secondary oxidation of Fe$^{2+}$ to Fe$^{3+}$ is demonstrated in layered minerals in regions close to the upper boundary of the Boda Formation in a borehole driven from the ground. In the second example samples obtained from a deep drill crossing a reductive zone below the surface at 1050 m are analysed, and the iron containing minerals are identified.

With the present study we would like to demonstrate that minor amounts of iron can be present in ferrous form in spite of the predominance of the oxidative conditions governing the genesis of most of the BSF. Furthermore, it is also shown that Fe$^{2+}$ ions in layered clay minerals are accessible to Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ oxidation in natural environment. In addition, it is shown with the second case that regions may occur in the formation where iron exists exclusively in ferrous state.
2. Experimental

The studied samples were obtained from two different drills of the BSF. The first one, the vertical BAT-14 drill was bored from the ground. The claystone strata commences in 22.3 m depth. It is covered with Quaternary sediments (loess, redeposited loess and marl). The second set of samples was collected from another drill, Delta-9, bored in horizontal direction in a roadway at 1050 m depth below ground level. The mineral compositions of samples were analysed by X-ray diffraction or by thermogravimetry (TG) and differential thermal analysis. Only those minerals can be analysed with the latter methods which exhibit weight changes or thermal effects upon heating. The respective amounts of these thermally responding minerals can also be estimated as well. Iron-bearing minerals were analysed by Mössbauer spectroscopy as well.

3. Results

3.1. Fe$^{2+}$ and Fe$^{3+}$ bearing species in samples from top layers of a BSF strata

The relative amounts of thermally active minerals found in the studied samples are shown in table 1. Mössbauer spectra were collected in two velocity ranges on the samples. The spectra recorded in the wider velocity range ($\pm$ 12 mm/s) contain the contributions of all the iron bearing components, namely the whole sextet of hematite. The spectra recorded in the narrower range ($\pm$ 4 mm/s) provide better resolution for identifying the respective components, however they show only the two inner lines of the hematite sextet. The corresponding spectra are shown in figure 1, and data are collected in table 1.

![Figure 1](image1.png)  
**Figure 1.** Mössbauer spectra of samples taken from different depths of BAT-14 borehole. Spectra are collected in two velocity ranges. (H marks the positions of the two central peaks of the sextet of hematite)

![Figure 2](image2.png)  
**Figure 2.** Mössbauer spectra of samples taken from different distances in the Delta-9 borehole drilled horizontally in 1050 m depth. Spectra are collected in two velocity ranges.

Assignment of hematite, amounting to 64 – 66 % of iron, is unambiguous. Data published in the Mössbauer Mineral Handbook [2] can be considered for the identification of the components filling in the remaining 34 – 36 % spectral area. The IS = 1.1 and QS = 2.6 mm/s pair of data is reported for the characteristic Fe$^{2+}$ positions in chlorite in most cases. However, in several studies IS = 1.2 and QS = 2.4 pair of data is also specified. These data are also characteristic for some other layered clay minerals (illite, montmorillonite). Thus, adopting these values, the Fe$^{3+}$ doublet can probably be
attributed to ferrous ions located in chlorite or in other clay minerals. Several positions are available for iron in chlorite – both Fe\(^{2+}\) and Fe\(^{3+}\) may be located in it [3]. The assignment of the Fe\(^{3+}\) components is similar – the Fe\(^{3+}\) (a) and Fe\(^{3+}\) (b) doublets may attest either the presence of chlorite or illite-muscovite as well [2].

Thus, in short, it can be concluded from the relevant RI data that the Fe\(^{2+}\) portion decreases in the clay minerals from 14 % to c.a. 4 % as approaching the top few meters of the Boda Formation. This can probably be attributed to a secondary oxidation in the layered clay mineral (the amount of the other main constituting mineral, hematite, practically does not vary). This phenomena demonstrates that Fe\(^{2+}\) → Fe\(^{3+}\) oxidation may proceed under natural conditions in Boda Claystone which may influence occasional migration processes as well.

Table 1. Mineral composition and the corresponding Mössbauer data obtained on samples from different depths of BAT-14 drill.

| Depth (m) | Mineral composition (%) | Mössbauer data |
|----------|-------------------------|---------------|
|          | Chl. Ill/mus. Mont. Calc. | Component | IS | QS | MHF | RI |
| 1.1      | 0.5 24 7 35            | Fe\(^{2+}\) | 1.26 | 2.39 | 4.0 |
|          |                        | Fe\(^{3+}\) (a) | 0.19 | 0.85 | 3.2 |
|          |                        | Fe\(^{3+}\) (b) | 0.33 | 0.73 | 27.0 |
|          |                        | Fe\(^{3+}\) (hematite) | 0.40 | 0.22 | 50.7 | 65.7 |
| 2.4      | 33 10 15 8            | Fe\(^{2+}\) | 1.30 | 2.37 | 3.9 |
|          |                        | Fe\(^{3+}\) (a) | 0.12 | 0.81 | 2.3 |
|          |                        | Fe\(^{3+}\) (b) | 0.32 | 0.72 | 28.0 |
|          |                        | Fe\(^{3+}\) (hematite) | 0.37 | 0.22 | 50.7 | 65.6 |
| 6.1      | 8 10 10 12         | Fe\(^{2+}\) | 1.27 | 2.36 | 7.7 |
|          |                        | Fe\(^{3+}\) (a) | 0.21 | 0.79 | 15.1 |
|          |                        | Fe\(^{3+}\) (b) | 0.43 | 0.78 | 13.6 |
|          |                        | Fe\(^{3+}\) (hematite) | 0.37 | 0.23 | 50.6 | 63.6 |
| 11.5     | 13 13 5 7            | Fe\(^{2+}\) | 1.26 | 2.35 | 10.5 |
|          |                        | Fe\(^{3+}\) (a) | 0.19 | 0.76 | 8.5 |
|          |                        | Fe\(^{3+}\) (b) | 0.33 | 0.98 | 12.5 |
|          |                        | Fe\(^{3+}\) (hematite) | 0.38 | 0.22 | 50.6 | 68.5 |
| 57.8     | 27 25 1 5           | Fe\(^{2+}\) | 1.27 | 2.32 | 14.1 |
|          |                        | Fe\(^{3+}\) (a) | 0.18 | 0.76 | 12.9 |
|          |                        | Fe\(^{3+}\) (b) | 0.32 | 0.95 | 8.5 |
|          |                        | Fe\(^{3+}\) (hematite) | 0.38 | 0.22 | 50.7 | 63.6 |

\(a\)The depth is measured from the upper boundary of Boda Claystone, which is covered with loess and marl in thickness amounting together to 22.3 m.

\(b\) The listed minerals are: Chl. – chlorite, Ill/m. – illite/muscovite, Mont. – montmorillonite, Calc. – calcite

\(c\) The respective data are: IS: isomer shift, relative to metallic iron, mm/s; QS: quadrupole splitting, mm/s; MHF: magnetic hyperfine field, Tesla; RI: relative intensity, %

3.2. Crossing a strata formed under reductive conditions

Reductive conditions were prevailing during the genesis of the formation in exceptional periods. This is clearly reflected in the state of the iron in the respective samples collected from a horizontal bore drilled in a depth at 1050 m. The occurrence of the reductive zone is estimated in a layer positioned in between the 83 – 85 m distance from the commencement of the drill.
Table 2. Mössbauer data extracted from spectra of figure 2.

| Distance | Component          | IS    | QS    | MHF | RI |
|----------|--------------------|-------|-------|-----|----|
| 83.7 – 83.8 | Fe^{2+} (chlorite) | 1.13  | 2.62  | -   | 70 |
|          | Fe^{3+}            | 0.87  | 2.34  | -   | 7  |
|          | Fe^{2+} (pyrite)   | 0.34  | 0.63  | -   | 23 |
| 85.2 – 85.3 | Fe^{2+} (chlorite) | 1.13  | 2.62  | -   | 40 |
|          | Fe^{2+} (pyrite ?) | 0.37  | 0.59  | -   | 14 |
|          | Fe^{3+} (hematite) | 0.38  | 0.22  | 50.9| 45 |
| 91.8 – 91.9 | Fe^{2+} (chlorite) | 1.12  | 2.67  | -   | 15 |
|          | Fe^{2+}/Fe^{3+}    | 0.35  | 0.58  | -   | 24 |
|          | Fe^{3+} (hematite) | 0.38  | 0.22  | 50.9| 60 |

a The distance is measured from the commencement of the horizontal drill (in meters)

b The IS, QS parameters of Fe^{2+} in the pyrite (low spin state) and Fe^{3+} (high spin state) in silicate minerals can hardly be distinguished.

Data shown in table 2 and spectra of figure 2 attest that the Delta-9 boring crossed a zone which was primarily formed under reducing conditions. Hematite is not found by XRD at all in the sample taken from 83.2 m, and in correspondence, only ferrous iron is detected in the spectra of the sample taken from 83.7 m. (Reduction of hematite to form chlorite and pyrite in secondary diagenetic processes could hardly be assumed.) The IS, QS data in this sample are exactly the same as reported for chlorite [2], thus in this sample the presence of chlorite is evidenced. The overall Fe^{3+} / Fe^{2+} ratio characterizing the Boda Claystone is reversed in average by departing from this reductive layer located at 83 – 85 m, since the 60 % portion of ferric iron in hematite is restored in the sample taken at the ~92 m distance.

4. Conclusions
Two examples are presented to prove and analyse the occurrence of Fe^{2+} ions in minerals of Boda Claystone. In the first case presence of the Fe^{2+} is demonstrated in a vertical borehole driven near to the ground level. In this instance, Fe^{2+} is present in minor amounts beside the preponderance of the hematite. Fe^{2+} → Fe^{3+} oxidation in the topmost region is also evidenced. In the second case an example is shown to demonstrate the occasional occurrence of a strata formed under reducing conditions. In this region – similarly to the previous example - most of the ferrous iron is present in layered clay mineral (chlorite). Thus, it can be assumed that the Fe^{2+} → Fe^{3+} oxidation may provide the counterpart process for reduction of certain migrating radionuclides, provided the redox equilibrium is mediated by the pore water.

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