57Fe Mössbauer, XRD, FT-IR, FE SEM Analyses of Natural Goethite, Hematite and Siderite

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Abstract: Natural goethite, hematite and siderite were analysed with 57Fe Mössbauer, XRD and FT-IR. FE SEM images of samples were also taken. The Mössbauer spectra of limonite (α-FeOOH·nH2O) from Budapest (Hungary), Ljubija (Bosnia and Herzegovina) and Korçë (Albania) showed the same type of spectrum, indicating low crystallinity and broad particle size distribution. All goethite particles from these three locations were one-dimensional (1D), but with different nano/microstructures. A very early precursor of limonite from Budapest and Ljubija locations was assigned to FeS2 (pyrite and/or marcasite) which oxidised upon ventilation (oxygenation) under hydrogeothermal conditions, thus producing FeSO4 and Fe2(SO4)3. In the next step limonite deposits were formed. The similarity between this limonite formation under hydrogeothermal conditions and the chemical precipitation of goethite from FeSO4 or Fe2(SO4)3 solutions at laboratory level was briefly discussed. The deposition of lateritic goethite at the Korçë location is presumed to be due to the chemical weathering (tropical conditions) of ultramafic rocks. Under the same conditions and a proper pH the transformation of goethite to hematite is possible. Alternatively, the oxidation of Fe2+ in magnetite and its transformation to hematite via maghemite (γ-Fe2O3) as an intermediate could have taken place. The Mössbauer spectrum of siderite from the Ljubija location showed a quadrupole doublet with asymmetric spectral lines. This asymmetry could be assigned to the Goldanskii-Karyagin effect, however, the contribution of the crystallite texture to this asymmetry cannot be excluded. Hematite and a small fraction of siderite at the Vareš location (Bosnia-Herzegovina) are of metasomatic origin deposited in limestone that now form a series of greatly metamorphosed sedimentary rocks. Hematite particles were deposited in the form of laminates (2D).

Keywords: iron ores, goethite, hematite, siderite, 57Fe Mössbauer.

INTRODUCTION

Goethite (α-FeOOH), hematite (α-Fe2O3) and siderite (FeCO3) are widespread minerals in nature (soils, sediments, rocks, water systems). This is not surprising if we remember that iron is the fourth most abundant element after oxygen, silicon and aluminium in the Earth’s crust. Generally, knowledge about the phase composition, microstructure and chemical composition of these minerals helps us to better understand the geochemical history of the Earth and possibly Mars. Historically, iron ores were exploited by ancient people to produce raw iron using charcoal as a reducing agent for Fe3+ and Fe2+ ions. Natural goethite, hematite and siderite also found applications as inorganic pigments in protective coatings as well as in artistic paints in a variety of colours. Natural goethite is often described with the term limonite (α-FeOOH·nH2O). However, limonite is not considered as separate crystal structure, it may contain variable fractions of hydrated iron oxides (goethite and hematite).

There are certain similarities between the geochemistry of natural goethite, hematite and siderite and their precipitation chemistry at laboratory level. However, the properties of natural iron oxides and siderite may differ from those compounds synthesised in a chemical laboratory since the exact parameters of geochemical formation of these minerals are not known. Such differences are mainly due to different stoichiometry, crystallinity, presence of associated minerals and structural impurities in natural minerals. Moreover, hydrogeothermal conditions existing during the formation of natural minerals can be determined on the basis of hydrothermal parameters in
laboratory synthesis. Musić et al.[1–8] systematically investigated the precipitation chemistry of iron oxides at the laboratory level. Iron oxides and their properties were discussed in a classic book by Cornell and Schwertmann.[9]

The aim of the present work was to investigate the 57Fe Mössbauer effect in selected iron ores from Hungary, Bosnia-Herzegovina and Albania. 57Fe Mössbauer spectroscopy is a very useful method in the determination of alloys and compounds containing iron atoms (ions). Iron ores are natural inorganic materials of complex microstructural properties, including crystal substitution, associated phases, etc. Therefore, additional instrumental methods such as XRD and FT-IR as well as FE SEM imaging were also used to monitor the nano/microstructure of the investigated ores. The experimental results will be correlated with the chemistry of iron oxides and siderite and the available geological data.

EXPERIMENTAL

Iron ores from four locations were investigated, declared as (a) limonite from a Budapest, Hungary (HU1) location, (b) limonite and siderite from Ljubija, Bosnia and Herzegovina (BH1 and BH2) locations, (c) hematite from a Vareš, Bosnia and Herzegovina (BH3) location, and (d) goethite from a Korčë, Albania (AL1) location (Table 1).

57Fe Mössbauer spectra were recorded using the standard Mössbauer instrumentation by WissEl GmbH (Starnberg, Germany). 57Co in the Rh matrix was used as a source of 14.4 keV gamma rays. Raw spectra were evaluated using the MossWinn computer program.

XRD patterns were recorded using the APD 2000 diffractometer manufactured by ItaStructures (GNR-Analytical Instruments Group, Italy). The CuKα wavelength of 0.15406 nm, 40 kV high voltage and 30 mA current were applied.

FT-IR spectra were recorded using a spectrometer manufactured by Bruker.

Samples were also inspected with a thermal field emission scanning electron microscope (FE SEM, model JSM 7000F manufactured by Jeol Ltd.). FE SEM was linked with the EDS spectrometer (INCA 350) manufactured by Oxford Instruments.

Table 1. Origin of iron ores.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin of the samples</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>HU1</td>
<td>Limonite</td>
<td>Budapest, Hungary</td>
</tr>
<tr>
<td>BH1</td>
<td>Limonite</td>
<td>Ljubija, Bosnia and Herzegovina</td>
</tr>
<tr>
<td>BH2</td>
<td>Siderite</td>
<td>Ljubija, Bosnia and Herzegovina</td>
</tr>
<tr>
<td>BH3</td>
<td>Hematite</td>
<td>Vareš, Bosnia and Herzegovina</td>
</tr>
<tr>
<td>AL1</td>
<td>Goethite</td>
<td>Korčë, Albania</td>
</tr>
</tbody>
</table>

RESULTS

Figure 1 shows the RT Mössbauer spectra of HU1, BH1, BH2, BH3 and AL1 iron ores. The Mössbauer spectrum of limonite from the Budapest location (sample HU1) shows a hyperfine magnetic splitting spectrum with very broadened spectral lines which deviate from the theoretical ratio 3 : 2 : 1 : 1 : 2 : 3. Distribution of hyperfine magnetic fields was used in the fitting procedure and the corresponding Mössbauer parameters are given in Table 2. This spectrum can be assigned to the goethite phase. It is known that the shape of goethite’s Mössbauer spectrum is influenced by low crystallinity, metal cation substitution for iron and particle size distribution. The Mössbauer spectrum of limonite from the Ljubija location (sample BH1) showed a superposition of two sextets (Figure 1). The inner sextet of this spectrum is similar to the spectrum of sample HU1 and can be assigned to the goethite phase, whereas the outer sextet (6.1 % of the relative spectral area) can be assigned to the hematite phase. The Mössbauer spectrum of siderite ore from the Ljubija location (sample BH2) showed a quadrupole doublet with parameters $\Delta = 1.27$ mm s$^{-1}$ and $\lambda = 1.83$ mm s$^{-1}$ (Figure 1; Table 2). Figure 2 also shows the Mössbauer spectrum of siderite from the Ljubija location recorded at Lehigh University, Bethlehem, 1980. The asymmetry of the quadrupole doublet was well visible and this spectrum was fitted as a superposition of two single lines. The line corresponding to the ±3/2 → ±1/2 transition (right-hand side peak, higher energy) showed a larger area than the line of the ±1/2 → ±1/2 transition (left-hand side peak). The origin of this asymmetric doublet is often assigned to the Goldanski-Karyagin effect (G.K.E).[11] However, the texture effect can also contribute to the asymmetry of the FeCO$_3$ quadrupole doublet. Nagy et al.[12] critically reinvestigated G.K.E. and concluded that, without measuring the angular dependence of spectral lines’ intensities, noticed asymmetry cannot be assigned exclusively to the G.K.E. The Mössbauer spectrum of hematite ore from the Vareš location (sample BH3) showed a well developed sextet with HMF = 51.4 T which corresponds to hematite mineral. In the same spectrum a quadrupole doublet (8.4 %) was also found with parameters corresponding to siderite (Figure 1; Table 2). The Mössbauer spectrum of sample AL1 from the Korčë location showed a superposition of two sextets (one collapsing) and a central quadrupole doublet. The spectrum of AL1 sample recorded at 4.3 K (Figure 3) showed the superposition of two sextets with parameters corresponding to a mixture of goethite (inner sextet) and hematite (outer sextet). Since the central quadrupole doublet disappeared in this spectrum, it can be inferred that the collapsing sextet and central quadrupole doublet in the spectrum recorded at RT are due to broad particle size distribution in goethite as well as to the fraction of superparamagnetic particles present in the same iron ore.
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Figure 1. RT Mössbauer spectra of iron ores, (a) limonite (HU1) from Budapest, (b) limonite (BH1) from Ljubija, (c) siderite (BH2) from Ljubija, (d) hematite (BH3) from Vareš, limonite/hematite (AL1) from Korčë.

Table 2. $^{57}$Fe Mössbauer parameters calculated for the recorded samples and phase identification.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectral component</th>
<th>$\delta / \text{mm s}^{-1}$</th>
<th>$2\varepsilon / \text{mm s}^{-1}$</th>
<th>$\Delta / \text{mm s}^{-1}$</th>
<th>$B_H / \text{T}$</th>
<th>$\Gamma / \text{mm s}^{-1}$</th>
<th>Area / %</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>HU1</td>
<td>sextet</td>
<td>0.36</td>
<td>-0.27</td>
<td>-</td>
<td>29.7(a)</td>
<td>0.26</td>
<td>100.0</td>
<td>$\alpha$-FeOOH</td>
</tr>
<tr>
<td>BH1</td>
<td>sextet</td>
<td>0.37</td>
<td>-0.27</td>
<td>-</td>
<td>32.3(a)</td>
<td>0.27</td>
<td>93.9</td>
<td>$\alpha$-FeOOH</td>
</tr>
<tr>
<td>BH2</td>
<td>doublet</td>
<td>1.27</td>
<td>-</td>
<td>1.83</td>
<td>-</td>
<td>0.30</td>
<td>100.0</td>
<td>FeCO$_3$</td>
</tr>
<tr>
<td>BH3</td>
<td>sextet</td>
<td>0.37</td>
<td>-0.19</td>
<td>-</td>
<td>51.4</td>
<td>0.29</td>
<td>91.6</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>BH3</td>
<td>doublet</td>
<td>1.23</td>
<td>-</td>
<td>1.77</td>
<td>-</td>
<td>0.31</td>
<td>8.4</td>
<td>FeCO$_3$</td>
</tr>
<tr>
<td>AL1</td>
<td>sextet</td>
<td>0.36</td>
<td>-0.26</td>
<td>-</td>
<td>24.6(a)</td>
<td>0.31</td>
<td>50.9</td>
<td>$\alpha$-FeOOH</td>
</tr>
<tr>
<td>AL1</td>
<td>doublet</td>
<td>0.36</td>
<td>-</td>
<td>0.59</td>
<td>-</td>
<td>0.36</td>
<td>8.4</td>
<td>Fe$^{3+}$ phase</td>
</tr>
</tbody>
</table>

(a) average value of $B_H$ distribution. Isomer shift is given relative to $\alpha$-Fe. Errors: $\delta \pm 0.01$ mm s$^{-1}$, $2\varepsilon \pm 0.01$ mm s$^{-1}$, $\Delta \pm 0.01$ mm s$^{-1}$, $B_H \pm 0.2$ T.

Figure 2. RT Mössbauer spectrum of siderite from the Ljubija location recorded at Lehigh University, Bethlehem, Pennsylvania.

Figure 3. Mössbauer spectrum of AL1 iron ore recorded at 4.3 K.
The XRD patterns of these ores (Figures 4 and 5) showed agreement with Mössbauer spectroscopy in determination of iron phases. The HU1 iron ore showed significantly broadened diffraction lines which can be generally assigned to low crystallinity and broad particle size distribution of goethite. On the other hand, the BH1 iron ore showed sharper XRD lines, thus manifesting a better crystallinity and increased particle size of goethite. The presence of a small amount of quartz was also detected in this sample. The BH2 iron ore showed in the XRD pattern the presence of siderite and small amounts of calcite and ankerite as associated minerals. The XRD pattern of BH3 iron ore showed the hematite phase as well as small intensity lines of siderite. A small amount of quartz as an associated mineral was also visible in the same sample. The XRD pattern of AL1 iron ore showed a mixture of goethite and hematite as well as the presence of calcite and traces of quartz. The XRD line of quartz (α-SiO₂) of 100% relative intensity is positioned at 2θ = 26.62°, whereas the second strongest line of 21.8% is positioned at 2θ = 20.82°.

The FT-IR spectra of selected iron ores are shown in Figures 6 and 7. The spectrum of HU1 limonite sample is typical of a goethite phase (Figure 6). The main IR bands at 896 and 798 cm⁻¹ are usually used in the identification of goethite.[14–16] These IR bands were assigned to the Fe–O–H in-plane bending (δOH) and out-of-plane bending (γOH) vibrations, respectively. The broad IR band at 3436 cm⁻¹ was due to the stretching −OH vibrations of adsorbed H₂O molecules, whereas the IR band at 1636 cm⁻¹ was due to the bending −OH vibrations. The IR band at 3117 cm⁻¹ was due to the stretching vibrations of structural −OH groups in goethite. The FT-IR spectrum of BH1 limonite sample also showed IR bands typical of goethite. Weak IR bands between 1109 and 996 cm⁻¹ can be related to the presence of a small amount of quartz.[17] The FT-IR spectrum of BH2

![Figure 4](image4.png)

**Figure 4.** XRD patterns of HU1, BH1, BH2, BH3 iron ores. Q stands for quartz, A for ankerite, S for siderite and C for calcite.

![Figure 5](image5.png)

**Figure 5.** XRD pattern of AL1 iron ore. Q stands for quartz and C for calcite.

![Figure 6](image6.png)

**Figure 6.** FT-IR spectra of HU1, BH1, BH3, AL1 iron ores.
(siderite sample) in Figure 7 shows four pronounced IR bands at 735, 865, 1415 and 1809 cm$^{-1}$. Huang and Kerr$^{[18]}$ recorded IR bands for FeCO$_3$ at 737, 866, 1422 and 1818 cm$^{-1}$ that are in good agreement with our data. The FT-IR spectrum of BH3 sample in Figure 6 can be assigned to hematite as the main phase and siderite as an associated phase. The IR spectrum of hematite shows six active vibrations, two $A_{2u}$ ($E||C$) and four $E_u$ ($E\perp C$)$^{[19–21]}$. In the case of BH3 sample the following IR bands corresponding to hematite were recorded: 644 cm$^{-1}$ ($A_{2u}$), 532 cm$^{-1}$ ($E_u$), 455 cm$^{-1}$ ($E_u$) and 397 cm$^{-1}$ ($A_{2u}$). Furthermore, the FT-IR spectrum of BH3 sample showed a shoulder at 737 cm$^{-1}$ and two IR bands at 866 and 1420 cm$^{-1}$ which can be assigned to a small amount of FeCO$_3$. The FT-IR spectrum of AL1 sample showed IR bands at 545 and 460 cm$^{-1}$ corresponding to hematite and IR bands at 909, 801 and 3164 cm$^{-1}$ corresponding to goethite. The IR band at 1418 cm$^{-1}$ can be assigned to calcite and those at 1070 and 1008 cm$^{-1}$ to quartz as associated phases.

The FE SEM images of samples HU1, BH1 and AL1 (Figure 8. a, b and c) showed the presence of one-dimensional (1D) goethite particles. However, differences in the nano/microstructure of these 1D goethite particles were noticed. 1D goethite particles in sample HU1 consisted of much smaller primary goethite particles, whereas goethite particles in sample BH1 were in the form of very long laterally arrayed fibres. Nanorods of goethite were noticed in sample AL1 (Figure 8. c). In the same FE SEM image of sample AL1 an amorphous-like fraction was visible which can be assigned to aggregates of very fine (superparamagnetic) $\alpha$-FeOOH particles. The FE SEM images of sample BH2 (Figure 9. a, b) showed big aggregates of siderite, whereas the particles of sample BH3 (Figure 9. c and d) showed a two-dimensional (2D) microstructure.

**DISCUSSION**

The Budapest limonite site is situated in Central Europe, where in the far history of Earth had been the Pannonian Sea as part of the Paratethys Sea. When the Carpathian Mountains rose up, the Pannonian Sea became isolated...
and linked to the Paratethys Sea only through the Đerdap Strait. Then the rivers filled the Panonian Sea with fresh water and due to this natural activity the original salinity was decreasing and finally a freshwater lake was formed. The rivers brought along gravel, sand and mud from the surrounding mountains and the process of filling the Panonian Sea was completed 5 to 6 million years ago forming the Pannonian Plateau. Magyar et al. [22] investigated oxygen-related facies in Lake Pannon deposits (Upper Miocene) at the Budapest-Kőbánya location. The authors concluded that oxygen availability had been a major factor in shaping the sedimentary facies and biofacies during Late Miocene (8 to 8.5 million years ago). Lake Pannon sequence contains blue clays deposited in low-oxygen conditions. The strong ventilation (oxygenation) caused by storms and lake waves promoted bioturbation, as indicated by the presence of trace fossils belonging to the Arenicolites ichnofacies or a lacustrine equivalent to the marine Skolithos ichnofacies. Fully bioturbated sand layers with the infaunal Dreissenomya and other littoral molluscs indicate longer periods of bottom ventilation, and this can be corroborated with the presence of limonite-cemented sandstones. Görög and Török [21] investigated clay pits in Budapest. The lower clay layer is grey and impermeable whereas the upper layer is yellow due to the presence of limonite and has a limited permeability. The origin of limonite from the Budapest location can be related to the chemical weathering of FeS\textsubscript{2} under oxygenation conditions. This can be corroborated by the fact that at the Budapest location FeS\textsubscript{2} crystals (pyrite and/or marcasite) can also be found. Iron sulphide, considered a precursor of HU1 limonite, underwent oxygenation and in the presence of moisture yielded hydrated FeSO\textsubscript{4} and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}. Under hydrogeothermal conditions these iron sulphates precipitated in the form of hydrated goethite (limonite). Hydronium jarosite (H\textsubscript{3}OFe\textsubscript{3}(OH)\textsubscript{6}(SO\textsubscript{4})\textsubscript{2} can also be formed under specific precipitation conditions. At present the Budapest location is rich in hot springs and some of them have the temperature of up to ~ 95 °C. Certain similarities can also be derived between the geochemical formation of limonite and laboratory precipitated goethite by controlled oxygenation of FeSO\textsubscript{4} solutions. Gotić and Musić [2] investigated the precipitation of iron.

Figure 9. FE SEM images of (a), (b) siderite (BH2) and (c), (d) hematite (BH3).
oxides, including goethite, by controlled oxygenation of FeSO₄ solutions. Musić et al.[6] monitored the hydrolysis of Fe₂(SO₄)₃ solutions at 90 or 120 °C. The conditions were determined for the precipitation of α-FeOOH and H₂OFe₃(OH)₆(SO₄)₂ at 90 °C, and additionally for basic iron sulphate, Fe₄(OH)₆SO₄, at 120 °C.

The origin and time-frame of limonite-siderite deposits at the Ljubija location have been a subject of interest among geologists for a long time.[24] Grubić and Protić[25] distinguished two minerals formation, an older siderite-limonite and a younger ankerite-limonite. According to these researchers, siderite is present in lenses and alternating with black argillaceous schist in the siderite-limonite formation, originated as primary non-magnetic hydrothermal marine sediments in the Lower to Middle Carboniferous. The first evidence of the synsedimentary origin of these siderite deposits was reported by Jurković.[26] Smrtić-Palinkaš et al.[27] recognised three textures of Ljubija siderite deposits: (a) marine dark siderite and ankerite, (b) siderite with zebra texture, and (c) siderite veins. A marine origin of the host carbonates and a hydrothermal metasomatic origin of iron mineralisation were indicated. The texture differences in siderite deposits were assigned to physico-chemical changes of the mineralising media. Sulphur isotope ratios suggested the Permian seawater or Permian evaporates as the main sulphur reservoir. Sulphides and sulphates played an important role in the mineralisation of limonite and siderite. This can also be confirmed by the presence of sulphates in the form of barite (BaSO₄) veins at the Ljubija location and broader. The mineralisation of limonite and siderite at the Ljubija location was assisted by hydrothermal conditions in this region.[28] EDS analysis showed the presence of up to ~2 % manganese in iron ores from the Ljubija location. Very probably in limonite Mn is present as Mn³⁺ which is substituted for Fe³⁺ in goethite crystal structure, whereas in siderite it is supposed to appear as Mn²⁺. Hematite/siderite ore from the Vareš location near Sarajevo are of metasomatic origin deposited in limestones that now form a series of greatly metamorphosed rocks.[29] The metasomatic deposits of siderite had been formed primarily in carbonate rocks in the presence of mineralising solution in line with the reaction:

\[ \text{CaCO}_3 + \text{Fe(HCO}_3\text{)}_2 \rightarrow \text{FeCO}_3 + \text{Ca(HCO}_3\text{)}_2 \]

The oxygenation of FeCO₃ under hydrogeochemical conditions produced hematite. Hematite at the Vareš location is often associated with smaller amounts of siderite due to an incomplete oxidation of Fe³⁺, as confirmed by present investigation.

In the case of goethite/hematite ore (AL1 sample) from the Korçë location in Albania we presume different genesis in relation to the previously discussed iron ores. The formation of goethite and hematite at this location could be considered as result of intensive chemical weathering (tropical conditions) of the ultramafic rocks. Generally, in this geochemical process we can suppose that a primary precursor was olivine (Mg₃Fe²⁺⁴⁺SiO₄). As a result of this process laterites rich in iron oxides (group name) had been formed. During the chemical weathering of ultramafic rocks, chlorite, kaolinite, lizardite and some other minerals could also be formed. Lateritic goethites in a broader location may contain 1–2 % of nickel. In the present case in AL1 sample a small amount of chromium was found with EDS, which is not surprising because ultramafic rocks typical of Albania are also rich in chromium, for example chromite. Hematite can crystallise from goethite under tropical conditions and a proper pH. Hematite can also form by oxidation of magnetite (Fe₃O₄) via the maghemite (γ-Fe₂O₃) phase. Our Mössbauer investigation of magnetite ore from a close location (Demir Hisar, Macedonia) showed that this ore consisted of substoichiometric magnetite and hematite as an associated phase. Santana et al.[30] investigated magnetic minerals by Mössbauer spectroscopy to identify their pedogenic transformation on a stelate-forming soil in Minas Gerais in Brazil. The authors concluded that magnetite transforms to hematite during pedogenesis through a progressive oxidation of Fe²⁺ to Fe³⁺ in magnetite. It was also suggested that in mafic geological systems the transformation of highly substituted magnetite to hematite occurs via the maghemite phase.

Mössbauer spectroscopy has also made a significant contribution in the analysis of the minerals and soils at Mars surface.[31–35] After landing the Mössbauer instrumentation along with other spectroscopic and imaging techniques on the Mars surface the presence of goethite and jarosite minerals was detected. This can be taken as strong evidence of water presence in far history of Mars. On the other hand, the presence of hematite at Martian surface can be explained by precipitation processes from water medium containing sulphates and/or by oxidation of Ti-magnete. Mössbauer spectroscopy also revealed the presence of other Fe-bearing minerals, such as olivine and pyroxene on the Mars surface. Olivine is a typical mineral formed by crystallization of magma, which further undergoes chemical weathering under the presence of water. Mechanical weathering of olivine by wind and streaming waters accelerated its chemical weathering. In addition, the analysis of Mars surface and meteorites showed the presence of iron sulphides (FeS) which may be taken as precursors of iron hydrous oxides. Comparing the results of the present study with those obtained by in-situ analysis of Mars surface as well as Martian meteorites it can be concluded about similarities in geochemical/geological development of the Earth and Mars in their far history.
CONCLUSION

Investigation of the $^{57}$Fe Mössbauer effect in goethite, hematite and siderite ores from Hungary, Bosnia and Herzegovina and Albania showed the capabilities of this spectroscopic method in analysing these iron ores. The Mössbauer spectra of all limonite samples were typical of low crystalline FeOOH$n$H$_2$O with broad particle size distribution. The limonite phase in all cases consisted of 1D particles, but of different nano/microstructures. Siderite sample from the Ljubija location showed a quadrupole doublet with asymmetric spectral lines. The mechanism of geochemical formation of limonite started with ventilation (oxygenation) of FeS$_2$ and FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ formation. In the next step, under hydrogeothermal conditions and a proper pH. There is also an alternative to this mechanism, i.e., the chemical weathering and oxidation of Fe$^{2+}$ in magnetite and formation of hematite via maghemite ($\gamma$-Fe$_2$O$_3$) as an intermediate phase. The presence of chromium traces in iron ore from the Korčić location indicates that ultramafic rocks at this location also contained chromium minerals, for example chromite (FeCr$_2$O$_4$).

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