

# Microstructural Properties of Natural Allophane/Gibbsite from a White Bauxite Deposit in Montenegro

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**Abstract:** Microstructural properties of white bauxite from Montenegro were investigated. XRD analysis showed the presence of allophane ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ) and gibbsite ( $\gamma\text{-Al}(\text{OH})_3$ ). The allophane phase showed very broadened diffraction lines, thus indicating poor crystallinity as well as very fine nanoparticles in this phase. Upon heating of natural allophane/gibbsite at 1000 °C mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) was formed, but with a lower degree of crystallinity. FT-IR spectra of allophane, gibbsite and mullite were interpreted. FE-SEM images of natural allophane/gibbsite showed a dominantly amorphous-like morphology. Upon heating of natural allophane/gibbsite two-dimensional (2D) microstructure was visible. EDS analysis showed traces of calcium, potassium, magnesium and iron. The  $^{57}\text{Fe}$  Mössbauer spectrum of iron traces showed a small relative intensity magnetic splitting component due to the presence of hematite and a central quadrupole doublet due to the presence of  $\text{Fe}^{3+}$  ions substituted for  $\text{Al}^{3+}$  in octahedral positions and/or a superparamagnetic fraction of hematite particles. The possible geochemical mechanism of white bauxite formation in Montenegro is discussed.

**Keywords:** allophane, gibbsite, white bauxite, Montenegro.

## INTRODUCTION

**A**LLOPHANE is a poorly crystalline hydrous aluminosilicate which is often present in volcanic ash soils. Discoveries of natural allophanes are common in Japan and New Zealand, USA, Canada, Indonesia, Sweden as well as in South America and Africa. In dependence on the geological history and environmental conditions natural allophanes show different degrees of crystallinity with a varying Si/Al ratio. Generally, allophane consists of aggregates of very fine hollow spheres with diameters ~ 3.5 to 5 nm.

Yoshinaga *et al.*<sup>[1]</sup> reported on the formation of imogolite and allophane in association with soil derived from sedimentary rock such as sandstone. Wada<sup>[2]</sup> investigated structural properties of soil allophanes with two end-members of the compositions  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , and the structure of these allophanes was proposed. Allophane with the Si/Al ratio 1/1 consists of a silica tetrahedral chain and an alumina octahedral chain

sharing a corner of the tetrahedron and octahedron, respectively. With the addition of another alumina octahedral chain to the silica tetrahedral chain allophane with the Si/Al ratio 1 : 2 was formed. The XRD pattern of poor crystalline allophane was explained as a consequence of the differences in alignment of the above mentioned structural chains. Van der Gaast *et al.*<sup>[3]</sup> also investigated the structure of allophane samples (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio from 1.12 to 1.68) using small angle XRD and high-resolution electron microscopy.

The thermal treatment of allophanes caused structural changes due to condensation of SiO<sub>4</sub> tetrahedra probably induced by a breakdown of Si–O–Al linkages and dehydroxylation of Si–OH groups.<sup>[4]</sup> Kitagawa<sup>[5]</sup> also investigated dehydration of adsorbed water and structural hydroxyl groups in two natural allophane samples.

The functional groups (Si–OH and Al–OH) in allophane particles are responsible for their acid/base surface properties. Allophane and imogolite roles in soil

biogeochemical processes were reviewed by Parfitt.<sup>[6]</sup> In allophane soils phosphate anions are specifically and very strongly adsorbed and therefore the presence of allophane adsorbent in soils decreases the phosphorus uptake by plants. On the other hand, allophane can be used to remove high concentrations of phosphates from meat processing industry which make problems in water systems due to the eutrophication role of phosphates.<sup>[7]</sup> Boron<sup>[8]</sup> and arsenate<sup>[9]</sup> adsorptions by allophane were also investigated.

In the present work we focused on the properties of natural allophane/gibbsite found in a deposit of white bauxite from Montenegro. Near this location there are high quality deposits of red bauxites (low Si content). The coexistence of red and white bauxites at the same geographical area is unique in the geochemical sense.

## EXPERIMENTAL

The natural allophane/gibbsite from Vonjin Do, Trubjela, Montenegro was investigated.

XRD patterns were recorded using an APD 2000 diffractometer manufactured by *ItalStructures* (GNR-Analytical Instruments Group, Italy). The  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm), 40 kV high voltage and 30 mA current were applied. ICDD cards for allophane No. 38-0449, for gibbsite No. 33-0018 and for mullite No. 15-0776 were used.

FT-IR spectra were recorded using a FTIR-ATR 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 an EDS spectrometer (INCA-350) manufactured by *Oxford Instruments*.

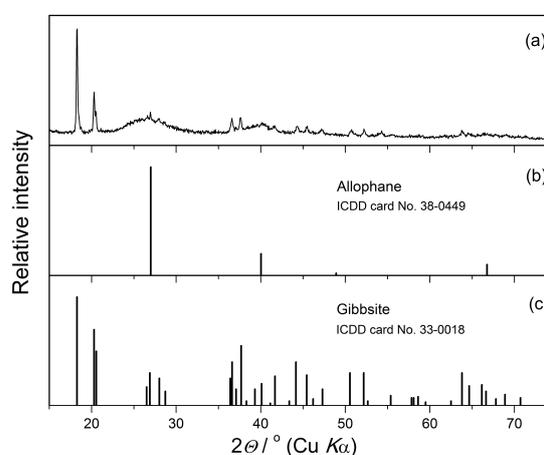
The RT Mössbauer spectrum of natural allophane / gibbsite sample was recorded using a spectrometer set-up from *WissEl* modules (Starnberg, Germany). The  $^{57}\text{Co}$  in the Rh matrix was used as a Mössbauer source.

## RESULTS AND DISCUSSION

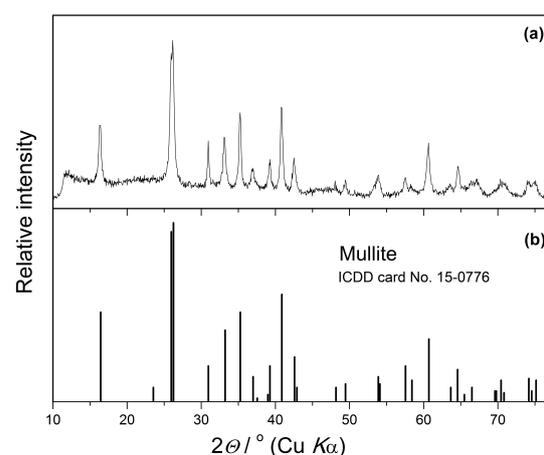
Figure 1 shows the XRD pattern of natural allophane / gibbsite minerals found in a white bauxite deposit in Montenegro. Three main diffraction peaks of allophane ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ) in line with the ICDD card No. 38-0449 are positioned at  $2\theta = 26.997^\circ$  (100 %),  $40.041^\circ$  (20 %) and  $66.763^\circ$  (10 %). In the present case these are very broad peaks thus indicating poor crystallinity or/and the presence of very fine particles of allophane. In the same XRD pattern the gibbsite phase peaks are visible and they are in line with the ICDD card No. 33-0018. Figure 2 shows the XRD pattern of sample produced by heating natural allophane/gibbsite from Montenegro at  $1000^\circ\text{C}$ . The XRD pattern of this

thermal decomposition product was assigned to mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) in line with the ICDD card No. 15-0776.

Figure 3a shows the FT-IR spectrum of natural allophane/gibbsite sample. This spectrum shows IR bands (shoulders) which can be assigned to these phases, but overlapping of the corresponding bands is evident. Ming *et al.*<sup>[10]</sup> discussed a possible presence of allophane on Mars and the relation to the thermal infrared (TIR) spectra of synthetic allophane. According to them, Si-rich allophanes have two broad absorption bands centred near  $1080\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$  from Si(Al)–O stretching and Si(Al)–O bending vibrations, respectively, whereas Al-rich allophanes show three broad IR bands at  $950$ ,  $540$  and  $430\text{ cm}^{-1}$ . Reinert *et al.*<sup>[11]</sup>



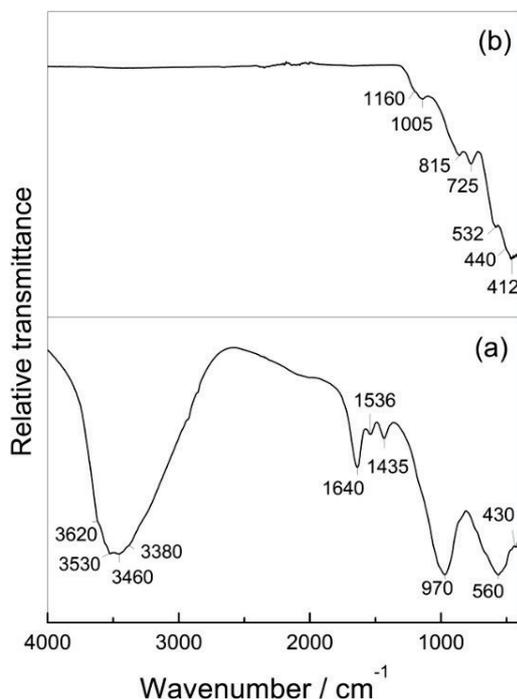
**Figure 1.** The XRD pattern of (a) natural allophane/gibbsite minerals from a white bauxite deposit in Montenegro, (b) allophane standard ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ) and (c) gibbsite standard ( $\gamma\text{-Al}(\text{OH})_3$ ).



**Figure 2.** The XRD pattern of (a) mullite produced upon heating of natural allophane/gibbsite at  $1000^\circ\text{C}$  and (b) mullite standard ( $\text{Al}_2\text{Si}_6\text{O}_{13}$ ).

recorded a broad IR band at  $\sim 3500\text{ cm}^{-1}$  due to stretching  $\nu_{(\text{OH})}$  vibrations of adsorbed water and corresponding bending  $\nu_{(\text{OH})}$  vibrations at  $1638\text{--}1639\text{ cm}^{-1}$ . Allophane with the ratio Si/Al = 0.5 showed a prominent IR band at  $978\text{ cm}^{-1}$  with the shoulder at  $858\text{ cm}^{-1}$  which was assigned to Si–O–(Si) and Si–O–(Al) stretching vibrations. For the ratio Si/Al = 1 the IR band at  $978\text{ cm}^{-1}$  was shifted to  $995\text{ cm}^{-1}$ . The IR bands at  $\sim 422$  and  $570\text{ cm}^{-1}$  for the Si/Al = 0.5 ratio and  $452$  and  $553\text{ cm}^{-1}$  for the Si/Al = 1 ratio were assigned to the vibration of the allophane crystal framework. Nampi *et al.*<sup>[12]</sup> synthesised aluminosilicates with varying  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2$  molar ratios (3 : 1, 3 : 2, 3 : 3 and 3 : 4) and treated them at different temperatures up to  $1400\text{ }^\circ\text{C}$ . The FT-IR spectra showed broadening and shifts of IR bands for samples prepared at  $800\text{ }^\circ\text{C}$  and this was assigned to the restructuring of octahedral and tetrahedral positions of Al and Si atoms before mullite crystallization. The IR band at  $560\text{ cm}^{-1}$  can be assigned to allophane, whereas Kitagawa<sup>[5]</sup> noticed the same IR band at  $570\text{ cm}^{-1}$ .

Single-crystal Raman and FT-IR spectra of gibbsite were combined with the factor group analysis and it was concluded that six  $\nu_{(\text{OH})}$  stretching bands can be expected to appear in the corresponding spectra.<sup>[13]</sup> The interlayer hydrogen-bonded OH groups oriented along the *c*-axis of gibbsite crystals showed bands at  $3433$ ,  $3370$  and  $3363\text{ cm}^{-1}$ , whereas the interlayer hydrogen-bonded OH groups



**Figure 3.** The FT-IR spectra of (a) natural allophane/gibbsite minerals and (b) mullite obtained upon heating of allophane/gibbsite at  $1000\text{ }^\circ\text{C}$ .

oriented nearly parallel to the (001) plane showed IR bands at  $3623$ ,  $3526$  and  $3519\text{ cm}^{-1}$ . Typical Raman bands of gibbsite<sup>[14,15]</sup> were positioned at  $3617$ ,  $3522$ ,  $3433$  and  $3364\text{ cm}^{-1}$ . In the present work the shoulders in the FT-IR spectrum (Figure 3a) were noticed at  $3620$ ,  $3530$ ,  $3460$  and  $3380\text{ cm}^{-1}$  and these IR positions can be assigned to the gibbsite phase. Moreover, in this spectrum the typical IR bands corresponding to gibbsite were overlapped by stretching  $\nu_{(\text{OH})}$  vibrations of  $\text{H}_2\text{O}$  molecules as well as with Si–OH and Al–OH groups from allophane. The IR band at  $1640\text{ cm}^{-1}$  is due to the bending  $\nu_{(\text{OH})}$  vibrations of  $\text{H}_2\text{O}$  molecules. The IR band at  $1435\text{ cm}^{-1}$  is a  $\nu_3$  fundamental vibration of adsorbed carbonate ion, while the IR band located at  $1536\text{ cm}^{-1}$  can be assigned to a degenerate fraction of the  $\nu_3$  vibration.<sup>[16]</sup> Su and Suarez<sup>[17]</sup> noticed IR absorption bands of adsorbed carbonates on amorphous aluminium hydroxide ( $\text{Am-Al}(\text{OH})_3$ ) at  $1420$  and  $1490\text{ cm}^{-1}$ . In the same work gibbsite adsorbed much less  $\text{CO}_3^{2-}$  than  $\text{Am-Al}(\text{OH})_3$  and the  $\nu_3$  vibration splitting was not noticed for the experimental conditions. Guckel *et al.*<sup>[18]</sup> recorded two IR absorption bands at  $1500$  and  $1421\text{ cm}^{-1}$  which were assigned to the  $\nu_{3,\text{as}}$  and  $\nu_{3,\text{s}}$  vibration modes of carbonate ions adsorbed on gibbsite.

Figure 3b shows the FT-IR spectrum of sample obtained by heating natural allophane/gibbsite. This sample was assigned to mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) on the basis of the XRD pattern as shown in Figure 2. The FT-IR spectrum shows IR band at  $1005\text{ cm}^{-1}$  with a shoulder at  $1160\text{ cm}^{-1}$  and those positioned at  $815$ ,  $725$ ,  $532$ ,  $440$  and  $412\text{ cm}^{-1}$ . Beran *et al.*<sup>[19]</sup> investigated dehydration and the structural development of mullite precursors using FT-IR spectroscopy. Mullite precursors were prepared from alkoxides  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and  $\text{Al}(\text{OC}_4\text{H}_9)_3$  by the sol-gel procedure. The molar ratio of these precursors corresponded to  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . In line with the work by Beran *et al.*<sup>[19,20]</sup> the IR bands at  $1160$  and  $1005\text{ cm}^{-1}$  can be assigned to the Si–O stretch ( $\text{SiO}_4$ ), the one at  $815\text{ cm}^{-1}$  to the Al–O stretch ( $\text{AlO}_4$ ) in plane, at  $725\text{ cm}^{-1}$  to T–O–T ( $\text{TO}_4$ ; T=Si,Al) in plane, at  $532\text{ cm}^{-1}$  to the Al–O stretch ( $\text{AlO}_6$ ) and at  $440\text{--}412\text{ cm}^{-1}$  to the O–Si–O band ( $\text{SiO}_4$ ) and Al–O–Al band ( $\text{AlO}_6$ ). Generally, IR bands recorded for mullite prepared around  $1000\text{ }^\circ\text{C}$  (proto mullite) can be shifted in relation to mullite ceramics fired at  $1350$  to  $1450\text{ }^\circ\text{C}$ . These IR band shifts are caused by the small crystallite size, a structural disordering and a local deviation in stoichiometry in proto-mullite.

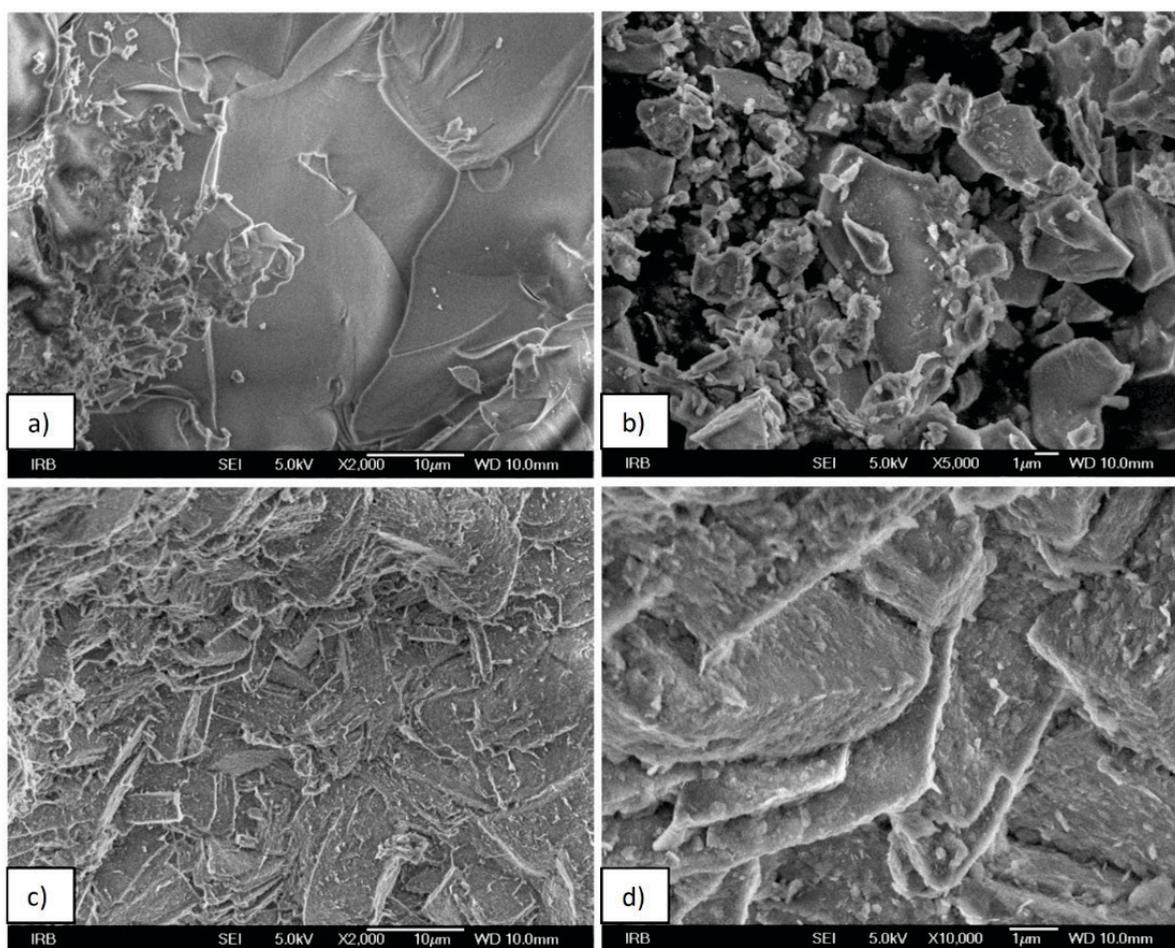
Figure 4 shows the FE-SEM images of (a,b) natural allophane/gibbsite, and (c,d) mullite produced by heating this natural composite at  $1000\text{ }^\circ\text{C}$ . The FE SEM images of (a,b) allophane/gibbsite sample showed a dominantly amorphous-like morphology. On the other hand, mullite (or proto-mullite) produced at  $1000\text{ }^\circ\text{C}$  showed dominant two-dimensional (2D) microstructures. The EDS analysis of this sample showed traces of Ca (0.18 %), K (0.40 %) and Mg

(0.44 %). Natural allophane/gibbsite also showed about less than 1 % of iron in tiny veins of the iron containing phase(s). The  $^{57}\text{Fe}$  Mössbauer spectrum of this brown/red tiny vein was recorded (Figure 5) and showed the superposition of central quadrupole doublet and sextet. The sextet showed the hyperfine magnetic field (HMF) value of 48.9 T which is a value smaller than that from literature data (51.8 T)<sup>[21]</sup> for a well defined hematite. In the present case this can be explained by a possible substitution of trace elements into the hematite crystal structure or the presence of very fine particles (collapsing sextet). Central quadrupole doublet can be assigned to iron substituted for aluminium at octahedral sites and/or a small fraction of superparamagnetic hematite particles.

The origin of bauxites in Mediterranean countries was the subject of many discussions. It is generally accepted that Mediterranean red bauxites are of the boehmite-type. For example, one analysis of red bauxites from Montenegro showed the following mineralogical composition:<sup>[22]</sup> boehmite (65–67 %), gibbsite (5–6 %),

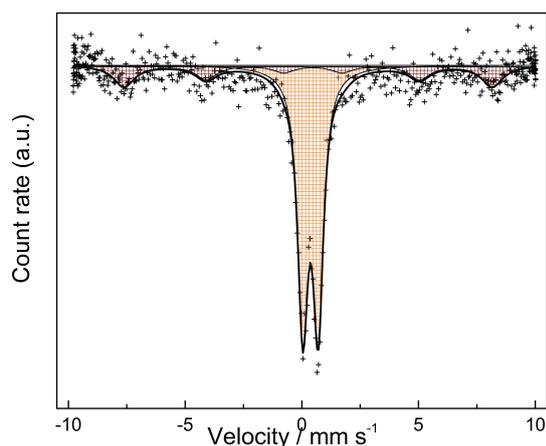
hematite (17–18 %), rutile (3 %), kaolinite and halloysite (7–8 %) and calcite (0.3 %). Bárdossy<sup>[23]</sup> discussed broadly the theory of *terra rossa*, *i.e.*, the formation of bauxite deposits on carbonate rocks. The idea of *terra rossa* theory is based on weathering of limestone and dolomite rocks and a preconcentration of red bauxite. This theory was also considered by Burić<sup>[24]</sup>. On the other hand, Pajović<sup>[25]</sup> proposed a volcanogenic theory which takes into account the Al-Si parent material from volcanic ash (tuff) or Al-Si dust from lateritic weathering of rocks and soils. Our structural/microstructural analysis of white bauxite from Vonjin Do (geographic map No. 6 in Ref. [24]) showed the phase composition of allophane and gibbsite and this finding can support the volcanogenic theory<sup>[25]</sup> of the formation of white bauxites as found at the above mentioned location.

Generally, the transformation of allophane and imogolite minerals to gibbsite occurs as a result of desilications in an open and strongly leaching environment. The associations of allophane and gibbsite are found in many volcanic ash soils and pumice beds.



**Figure 4.** FE-SEM images of (a,b) natural allophane/gibbsite minerals (different magnifications), and (c,d) of mullite produced upon heating natural allophane/gibbsite at 1000 °C (different magnifications).

Allophane and imogolite precipitate preferentially in a weathering environment where the water phase has pH ~ 5 to 7. Chemical weathering and the corresponding phase transformations of volcanic ash (tuff) can be generally shown in several sequences, as follows: allophane/imogolite → halloysite → kaolinite → (gibbsite, goethite, hematite) → laterite. Intensive chemical weathering of volcanic glasses and ashes is primarily induced by the gaseous emission of anhydrides of chloride, nitrate and sulphate acids during the volcanic activity. Gardner<sup>[26]</sup> concluded that gibbsite does not precipitate as a result of the dissolution of kaolinite unless quartz is absent from the geological system. This conclusion is in line with the fact that bauxites do not readily form on quartz-rich rocks. It has also been established that for gibbsite crystallization from amorphous Al(OH)<sub>3</sub>, the minimum pH ~ 5.6 and the maximum initial concentration of total dissolved silicon less than 10<sup>-6.3</sup> moles per liter are needed. In nature and in the laboratory mutual coagulation of fine gibbsite and silica particles (or corresponding Al- and Si-hydroxy polymers) is possible. pH<sub>Iep</sub> values at pH ~ 8 to 10 were measured for gibbsite particles<sup>[27]</sup> of different origin and for silica at pH between 1.7 and 3.5<sup>[28]</sup>. Musić *et al.*<sup>[29]</sup> synthesised amorphous SiO<sub>2</sub> nanoparticles and measured their pH<sub>PZC</sub> = 1.7 using microelectrophoresis. Macias Vazquez<sup>[30]</sup> investigated the presence of gibbsite in soils and saprolites of Galicia, NW Spain, and its formation by weathering of various aluminosilicates, especially plagioclases. The presence of gibbsite in deeper layers of deposits was explained by complexing Al<sup>3+</sup> with biomolecules, thus increasing Al<sup>3+</sup> mobility.



**Figure 5.** The RT Mössbauer spectrum of a tiny brown/red vein from natural allophane/gibbsite (sextet (25,9 %); IS = 0.37 mm s<sup>-1</sup>, QS = -0.20 mm s<sup>-1</sup>, HMF = 48.9 T, LW = 1.09 mm s<sup>-1</sup>; doublet (74.1 %); IS = 0.37 mm s<sup>-1</sup>, QS = 0.66 mm s<sup>-1</sup>, LW = 0.53 mm s<sup>-1</sup>).

## CONCLUSION

The microstructural properties of natural allophane/gibbsite from a white bauxite deposit in Montenegro were investigated using XRD, FT-IR, FE SEM/EDS and <sup>57</sup>Fe Mössbauer spectroscopy. Very broad XRD lines were assigned to the allophane phase of poor crystallinity, consisting of very fine nanoparticles. Three main diffraction lines can be assigned to allophane with the formula Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 3H<sub>2</sub>O. Gibbsite (γ-Al(OH)<sub>3</sub>) was identified as an additional crystalline phase to allophane. Heating at 1000 °C of natural allophane / gibbsite from Montenegro yielded mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>) which was not well crystallized (proto-mullite). The formation of well crystallized mullite ceramics can be obtained at 1350 to 1450 °C. The FT-IR spectra confirmed the results obtained from XRD. The FE-SEM images of natural allophane/gibbsite showed a dominantly amorphous-like morphology, whereas upon heating at 1000 °C the two-dimensional microstructure was visible. EDS showed traces of calcium, potassium, magnesium and iron. The RT <sup>57</sup>Fe Mössbauer spectrum recorded for a preconcentrated thin vein (brown/red in colour) from allophane/gibbsite sample showed the superposition of one sextet and central quadrupole doublet. The sextet was due to the presence of a hematite phase, whereas the central quadrupole doublet was assigned to Fe<sup>3+</sup> ions substituted for Al<sup>3+</sup> at octahedral positions and/or a fraction of superparamagnetic hematite particles. In spite of the fact that there are some uncertainties concerning the formation of allophane/gibbsite minerals, the volcanogenic origin of these minerals in white bauxite deposits from Montenegro can be generally presumed.

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