Effect of Annealing and Gamma Irradiation on Clay Mineral Properties

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The effect of annealing and gamma irradiation on the structural and magnetic properties of some green and grey clay minerals collected from different sites of Moldavia (Bradicesti, Frumoasa) is investigated. X-ray diffraction evidenced a multiphase mineralogical composition, where muscovite is the predominant phase. The annealing (at 500°C for 4h) and gamma irradiation procedures (0.126 mGy/h) induced an increase in quartz content and a diminution in the content of some impurity phases like clinohlor, and montmorillonite. Some changes in the 40K radioactivity were evidenced by gamma spectrometry and were related to the decomposition and oxidation processes. Electron paramagnetic resonance spectra of studied samples suggest that the used procedures induce oxi-do-reduction processes and a migration process of Fe(III) and Mn(II) species in places with different environments.

Keywords: clay minerals, annealing, gamma irradiation, EPR, structure

Clays are naturally occurring materials, typically containing minor to significant amounts of other mineral impurities. The variability of the clay particles chemistry is often related to the geochemical environment of their formation [1-3].

Based on their structures and chemical compositions, the clay minerals can be divided into four main classes: Kandites 1:1 layered clays (Kaolinite); Smectites 2:1 layered clays (Montmorillonite); Illites/Micas 2:1 layered clays (Muscovite, fig.1), Chlorites 2:1:1 layered clays (Clinochlore).

Due to their ion exchange properties, clays have many advanced applications and for this reason it is very important to investigate carefully their structural properties [4, 5]. These properties are mainly governed by the interaction of the interlayer materials with the environment. The stability of interlayer materials with respect to temperature and gamma irradiation and the consequent changes in their structure and physical properties are of great importance for their use.

Iron is the most common weathering impurity in clay minerals and is found in substitutional structural sites as well as in iron compounds adsorbed on surface. The magnetic properties of these materials stem mainly from these iron impurities.

The aim of this work is exploring the effect of annealing and gamma irradiation on the structural and magnetic properties of some green and grey clay minerals collected from different Romanian sites.

Experimental part

Natural mineral clays where collected from two Romanian occurrence sites located in Moldavia region (Bradicesti-sample B, Frumoasa-sample F). The samples collected from a depth of 10 m were dried during 6 days, at room temperature and then crushed and sieved with a 0.5 mm mesh. The powdered samples were annealed at 500°C for 4h (samples BC, FC) and submitted to a gamma irradiation procedure by using a 152Ir radioactive source with a gamma dose of 0.126mGy/h (samples BI, FI, BCI, FCI). The sample source distance was fixed at 1m.

Clay morphology and elemental chemical composition were analyzed by using a VEGA II LSH scanning electron microscope, equipped with EDX - QX QUANTAX.

X-Ray diffraction studies (XRD) were performed by using a SHIMADZU LAB XRD 6000 diffractometer (CuKα, λ = 1.54059 Å). Crystalline phases were identified by using Crystallographica program. Unit cell parameters of crystalline phases were determined with XLAT-Cell Refinement program. Grains sizes were determined by using Debye-Scherrer relation [6]:

\[
D = \frac{0.92}{w \cos \theta}
\]  

where w is full width of XRD peak at half height, expressed in radians, λ is the wavelength of X-ray radiation, θ is Bragg angle.

Sample radioactivity was investigated by using a Canberra Packard HR GAMMA SPECTROMETER, with an HpGe detector, in the range of 30 keV to 1.8 MeV with a standard electronic chain and 8192 channels multichannel. Energy calibration was performed with a 153Eu source. The specific activity of natural radionuclides was calculated with a GENIE 2000 program.

The radionuclide activity, A, corresponding to a photpeak in gamma spectra is defined by the formula [7]:

\[
A(Bq) = \frac{M (cps)}{I \times \varepsilon_{geom} (\gamma / Bq) \times \varepsilon_{det} (cps / \gamma)}
\]

where A is the activity in Bq, M the peak net area in counts per second (cps), \(\varepsilon_{geom}\) the geometrical efficiency in gamma rays per Bq, \(\varepsilon_{det}\), the detector efficiency in cps per

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gamma ray and \( I \) is the probability of emission of a gamma ray per disintegration (in %).

Electron paramagnetic resonance spectra were registered, at room temperature, on a continuous wave CMS 8400 Spectrometer (X band, 6000Gs). From the resonance condition, \( g \) factor was expressed by the formula [8]:

\[
g = \frac{h \nu}{\mu_B B} = 0.71447 \frac{\nu(\text{Hz})}{B(\text{Gauss})}
\]  

(3)

where \( B \) is the resonance magnetic field and \( \nu \) is 9.402 GHz.

**Results and discussion**

**Structural investigations**

Scanning electron microscopy evidenced for powdered natural mineral samples, collected from the two Moldavian sites, have quite similar morphologies, characteristic to muscovite phase (fig.1).

X-Ray energy dispersive spectra (EDX) gave information about the chemical elemental composition (fig.2c). As is shown in Table 1, the chemical compositions of natural clay minerals from Bradicesti and Frumoasa are almost the same. There are some small differences, especially in carbon contents [9]. The obtained chemical composition is typical for muscovite with impurity phases, like quartz, calcite, etc. Samples have important iron contents and also some transitional elements, like Mn, or sulfur and carbon. They can be found as cations in aluminosilicate structures or as oxides or sulfates impurities.

XRD patterns of natural clay minerals in comparison with those registered for gamma irradiated and annealed samples are shown in figure 2 a) and b).

Crystallographica program was used for identification of crystalline phases. It was established that natural clay minerals are a mixture of crystalline phases: muscovite-1M (K\(_{0.5}\)Mg\(_{1.5}\)Al\(_2\)Si\(_3\)O\(_{10}\)(OH)\(_2\), C2/m, \( a = 0.521 \) nm, \( b = 0.901 \) nm, \( c = 1.007 \) nm, Ms1), muscovite H.K.(Al\(_{0.5}\)Fe\(_{0.5}\))Si\(_3\)O\(_{10}\)(OH)\(_2\), C2/c, \( a = 0.518 \) nm, \( b = 0.902 \) nm, \( c = 2.004 \) nm; Ms2), quartz, Q (SiO\(_2\); hexagonal; \( a = 0.491 \) nm, \( c = 0.541 \) nm; P3121), small quantities of clinochlor (\((\text{Mg, Fe})_6\text{Si}_4\text{Al}_2\text{O}_{10}\text{(OH)}_8\); Chl), montmorillonite (CaMg\(_2\)Al\(_3\)Si\(_4\)(OH)\(_8\)\(\cdot\)4H\(_2\)O, hexagonal, \( P\); \( a = 0.517 \) nm, \( c = 1.502 \) nm, Mt) and very small contents of metal oxides (cristobalite, C; hematite, H; rutile, R)(fig 2).

The crystalline phases content, as determined from XRD pattern, and their grain sizes, \( D \), and peak values of \( 2 \theta \), are shown in table 2 [10].

XRD investigations evidenced that there are no significant differences between the two clay mineral samples from Bradicesti and Frumoasa. As compared to Frumoasa sample, sample from Bradicesti has lower muscovite and clinochlor contents and higher contents in quartz and montmorillonite respectively.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si at.%</th>
<th>Al at.%</th>
<th>O at.%</th>
<th>Na at.%</th>
<th>Ca at.%</th>
<th>K at.%</th>
<th>Mg at.%</th>
<th>Fe at.%</th>
<th>Mn at.%</th>
<th>S at.%</th>
<th>Ti at.%</th>
<th>C at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>22.10</td>
<td>8.00</td>
<td>59.10</td>
<td>0.21</td>
<td>3.60</td>
<td>1.99</td>
<td>1.76</td>
<td>2.29</td>
<td>0.22</td>
<td>0.18</td>
<td>0.45</td>
<td>0.16</td>
</tr>
<tr>
<td>F</td>
<td>21.00</td>
<td>7.80</td>
<td>58.80</td>
<td>3.61</td>
<td>3.60</td>
<td>1.90</td>
<td>1.89</td>
<td>2.12</td>
<td>0.16</td>
<td>0.91</td>
<td>0.32</td>
<td>0.48</td>
</tr>
</tbody>
</table>
The annealing and irradiation procedures induce changes in sample crystallinity and phases contents. XRD analyses evidenced that magnesian muscovite is thermo resistant and some damages occur when it is submitted, in its natural form, to gamma irradiation. It seems that under these conditions muscovite decomposes in quartz and other silicate phases. This process is accomplished by the increase in grain sizes.

The detection of iron oxides or oxyhydroxides by means of XRD is very difficult due to the fact that many peaks are superposed on XRD peaks of other phases (muscovite, quartz, clinochlor, etc) [10]. Some small XRD peaks observed in XRD patterns suggest the presence of cristobalite, C, hematite, H and rutile, R, impurity phases.

Muscovite is a part of the main dioctahedral mice. The unit cell parameters are mainly influenced by the nature of ions, which are in their tetrahedral and octahedral coordinative. Some changes in XRD peak positions are evidenced for the sample annealed, FC, suggesting changes in unit cell parameters, as a consequence of a possible ion migration and oxidation processes.

Clinochlore is a phyllosilicate mineral, with layered structure of 2:1 (tetrahedral-octahedral-tetrahedral). Cations Mg(II), Mn(II) and Fe(III) can move between the aluminosilicate layers. Exposure to radiation can influence substitution between Fe(III) and Mn(II) Mg(II) in octahedral layers [11 - 13]. Some substitution in the crystal structure can be detected by changes in XRD peak intensities, and shifts in 2θ values. Thermal treatment can induce micro-cracks, which extend along the basal layer and nanometer microcrystals are formed.

**Gamma spectroscopy**

For gamma spectroscopy (GS), the clays were properly accommodated in a standard box, sealed and kept for nearly three weeks before analysis, in order to achieve the secular equilibrium. The spectra were acquired by accumulation during 12 h.

It is known that the thermal treatment of carbonates, hydro silicates involves removal of hydroxyl radicals from the layered structures and also can involve the removal of some radionuclides species, descendentes of naturele of series of 238U and 232Th, which can be found in clay minerals as consequence of natural radioactivity. In order to investigate the influence of thermal annealing (performed at 500°C in air for 4 h), on the sample content in natural radionuclides (Bradicesti, samples B and BCI; Frumoasa, Fig. 2. Effect of gamma irradiation and annealing on XRD pattern: a) sample from Bradicesti (B, BI) ; b) sample from Frumoasa (F, FC)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Muscovite</th>
<th>Muscovite</th>
<th>Quartz</th>
<th>Clinohlor</th>
<th>Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ms1</td>
<td>Ms2</td>
<td>Q</td>
<td>Chl</td>
<td>Mt</td>
</tr>
<tr>
<td>B</td>
<td>Phase, %</td>
<td>56.40</td>
<td>8.60</td>
<td>19.40</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>D, nm</td>
<td>75</td>
<td>17</td>
<td>57</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>20, deg.</td>
<td>26.61</td>
<td>26.62</td>
<td>26.54</td>
<td>12.40</td>
</tr>
<tr>
<td>BIR</td>
<td>Phase, %</td>
<td>54.60</td>
<td>10.00</td>
<td>27.80</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>D, nm</td>
<td>77</td>
<td>18</td>
<td>61</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>20, deg.</td>
<td>26.63</td>
<td>26.64</td>
<td>26.57</td>
<td>12.43</td>
</tr>
<tr>
<td>F</td>
<td>Phase, %</td>
<td>58.90</td>
<td>14.40</td>
<td>17.20</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>D, nm</td>
<td>77</td>
<td>27</td>
<td>44</td>
<td>27</td>
</tr>
<tr>
<td>FC</td>
<td>Phase, %</td>
<td>67.00</td>
<td>6.60</td>
<td>19.50</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>D, nm</td>
<td>65</td>
<td>49</td>
<td>32</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>20, deg.</td>
<td>26.64</td>
<td>26.87</td>
<td>26.55</td>
<td>6.35</td>
</tr>
</tbody>
</table>

Table 2

**STRUCTURAL CHARACTERIZATION OF ANALYZED SAMPLES**
sample F and FC), we have investigated the descendentes of naturale series of 238U and 232Th by using a high resolution gamma spectrometer. The main results of this study are shown in table 3.

The results obtained for the radioactivity of radionuclides of descendental natural series of 238U and 232Th evidenced that radionuclides suffer some changes. The small increase in the radioactivity of sample BC and the small decrease in the radioactivity of sample FC can be related to decomposition and oxidation processes that induce changes in radionuclide concentration.

The sample weight mean activity may be enhanced by the trapping of radionuclides by the associated iron oxides or by the organic matter. Intense irradiation of clay minerals may imply not only severe modifications of the structural state of these materials, but may also modify the chemical properties, such as cation sorption or ion exchange. For instance, significant changes in the cation distribution coefficient of clay soils due to γ-irradiation may directly affect the migration of radionuclides [13].

The repartition of transitional metals in the natural mineral clay and the effect of annealing and gamma irradiation on their interaction with the neighbors were investigated by using electron paramagnetic resonance (EPR) technique. The EPR spectra of samples from Bradicesti and Fruamoasa were registered in X-band, at room temperature and are shown in figure 3 a), b). EPR signals evidence strong differences between Bradicesti and Fruamoasa samples, in good correlation with XRD patterns, gamma spectrometry and elemental chemical analysis. It is well known that EPR signal of Mn (II) is easily observed at room temperature, even if it is present in minute levels, compared to other ions. EPR spectra of Bradicesti sample clearly indicate the presence of isolated Mn (II) species [14]. This signal was poorly affected by annealing or irradiation procedures.

EPR signals of Bradicesti and Fruamoasa samples show different Fe(III) species in different coordinations. The EPR spectrum of natural mineral clay from Bradicesti shows three signals belonging to Fe (III) species: \( g = 2, \Delta B = 523 \text{ Gs} \); \( g = 2.72, \Delta B = 1049 \text{ Gs} \) and \( g = 5 \) which can be attributed to isolated and clustered iron species in muscovite and clinohlor phases. The irradiation process affects drastically the EPR signal at \( g = 2.72 \), favors the apparition of some new EPR signals at \( g = 2.57 \) and \( g = 3.20 \). The annealing process also causes the disparition of

![Fig. 3. Effect of gamma irradiation and annealing on EPR spectra: a) sample from Bradicesti (B, BI, BCI); b) sample from Fruamoasa (F, FC, FI)](image-url)
the signal observed at $g = 2.72$, and the increase in the signal at $g = 5.02$, $\Delta B = 119$ Gs. Some authors evidenced similar EPR signals at $g = 9.0, 5.0, 4.3, 3.5$ and $2.8$ in kaolinit. They considered that these signals result from the $-\frac{5}{2} \rightarrow \frac{-3}{2} \gamma''$, $-\frac{1}{2} \rightarrow \frac{1}{2} \frac{\pi}{2}$, $-\frac{1}{2} \rightarrow \frac{1}{2} \frac{\pi}{2}$, $-\frac{1}{2} \rightarrow \frac{1}{2} \frac{\pi}{2}$, $-\frac{1}{2} \rightarrow \frac{1}{2} \frac{\pi}{2}$, electronic spin transitions [15-17].

The large signal, evidenced in the natural mineral clay from Frumoasa, at $g = 2.26$, $\Delta B = 1209$ Gs, can be attributed to some different Fe(III) - O - Fe(III), or Fe(III) - O - Fe(II) species. The irradiation procedure destroys this signal and a new signal at $g = 3.21$, $\Delta B = 1091$ Gs was evidenced. The annealing procedure determines a strong increase in the signal at $g = 2.00$, $\Delta B = 729$ Gs. When irradiation procedure is applied after the annealing one (BCI and FCI samples) the EPR signals remain similar with those observed for the annealed samples. This means that the annealing procedure increases the sample resistance to gamma irradiation.

It is known that clays minerals have octahedral sites with different environments. Some of these are adjacent to hydroxyl groups, which are bound by hydrogen bonds to the next silicate sheet, other are located between the apical oxygens of two silicate sheets. This different environment of the octahedral sites leads to different lattice distortions and to different crystal fields that act on the iron impurities. The joint action of crystal fields and applied magnetic fields should explain the dissimilar anisotropies found in these layered minerals. EPR studies show that sites occupied by Fe(III) have a more or less symmetrical axial symmetry.

These results allowed us to conclude that the used procedures induce iron species migration in sites with higher or lower symmetry and that some oxido-reduction processes occur.

Conclusions

XRD, SEM and EDX investigations suggest that clay minerals are mixtures of muscovite, quartz, clinoclore and montmorillonite phases. If in Bradicesti sample the paramagnetic species are adjacent to hydroxil groups, in Frumoasa sample they are adjacent to layer oxygens. These differences explain some of the observed differences in sample properties.

All the obtained results evidenced that the annealing (at 500°C for 4h) and gamma irradiation procedures (0.126mGy/h) induce structural changes. When irradiation procedure is applied to annealed samples no other structural changes were observed, samples being resistant to gamma irradiation.

EPR technique is a powerful tool in evidencing paramagnetic centers and can be used to differentiate the electronic environments of Fe(III) and Mn(II) ions.

References


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