**Supplementary material**

**A. X-ray patterns decomposition**

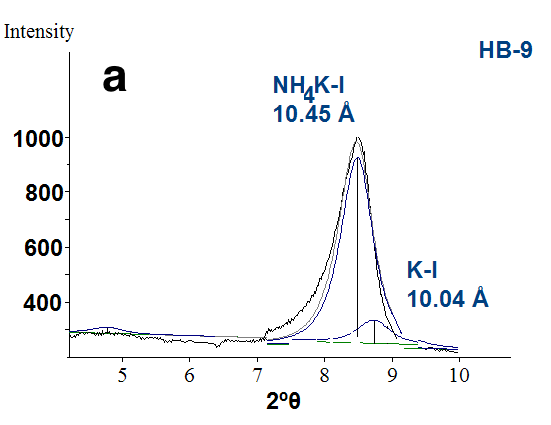
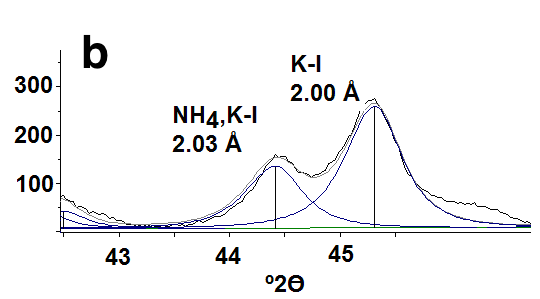
 

Fig. 1. Decomposition of the 001 and 005 peaks of sample HB-9

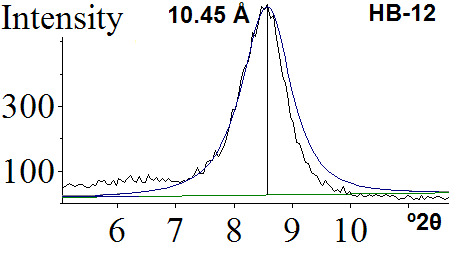


Fig. 2. Decomposition of 001 peak of sample HB-12

**B. Chemistry of the <2 μm clay fractions and Sr2+ saturated clay fractions**

**Introduction**

Sample HB-12 was revisited in terms of chemical composition, because a high amount of Na2O was measured by flame photometry in the <2 μm clay fractions. The TEM-AEM data obtained in this study confirmed the presence of Na+ as the third fixed or exchangeable interlayer cation. X-ray pattern of this sample was interpreted as NH4-I-S mixed layered with 12 %S. where the presence of NH4,K,Na-I was not recognized. Nevertheless, TEM-AEM data identified two distinct packets of NH4-I-S and NH4NaK-I. To clarify if the Na+ is exchangeable cation in smectite layers or fixed in illite layers, we saturated with 0.1M SrCl2 the <2 μm clay fractions of samples HB-12.

**Chemical analyses of the <2 μm clay fractions**

A combination of several analytical methods was used for obtaining the accurate chemical composition of the <2 µm clay fractions. Altotal, Fetotal, Mg2+, Mn2+ and Ca2+ were analyzed by atomic absorption spectroscopy, after dissolving the samples by HF-HClO4 digestion. Si4+ was determined gravimetrically, following decomposition by Na2CO3 fusion. Fe2+ was determined by dichromate titration. Na+ and K+ were analyzed by flame photometry. AlIV was calculated by its difference from SiIV, whereas AlVI = Altotal – AlIV. The H2O+ content was determined using the Penfield method (Sandell 1952).

Sr2+ saturation. The experiments were carried out by adding 1 gram of sample into the polypropylene centrifuge tubes with 100 mL of 0.1M SrCl2. Suspensions were shaken for 24 hours, then centrifuged, separated and the solutions resulted were preserved by adding HNO3 (65%) and stored at 4 ºC for subsequent chemical analyses. Most of the clay suspension was converted into Sr2+ form by four exchanges with 0.1M SrCl2. Prior to the analyses previously described, separate clay samples were subsequently washed and then dialyzed, so that Sr2+ would be the only exchangeable cation in the NH4-I clays selected. Sr2+ was analyzed in clay fractions by atomic absorption spectrometry.

After Sr2+ saturated clay fractions, the Ca2+ and Sr2+-aqueous solutions were analyzed by atomic absorption spectrometry, whereas a possible presence of Na+ in solution by flame photometry.

**Results**

Chemical compositions of the <2 µm clay fractions (samples HB-18, HB-12 and HB-9) not saturated and saturated with Sr2+ are shown in Table 1. The Ca2+ was exchanged with Sr2+in samples HB-12\* and HB-9, confirming that only Ca2+ is free exchangeable cation.

TABLE 1. Chemical compositions of the <2 μm clay fractions

|  |
| --- |
| Samples SiO2 TiO2 Al2O3 Fe2O3 MgO CaO Na2O K2O (NH4)2O SrO H2O Total |
| HB-18a 49.90 0.00 31.26 0.16 1.81 0.15 0.05 1.58 4.08 - 11.03 100.00 |
| HB-12 49.56 0.23 31,44 0.83 1.78 0.47 1.26 2.14 3.11 - 9.180 100.00 |
| HB-9 48.71 0.55 30.16 1.14 1.41 0.31 0.46 3.43 2.91 - 10.82 100.00 |
| HB-18\* 49.88 0.00 31.24 0.15 1.81 0.00 0.05 1.57 4.08 0.64 10.58 100.00 |
| HB-12\* 49.28 0.17 31,32 0.68 1.71 0.00 1.24 2.11 3.11 1.27 9.10 100.00 |
| HB-9 \* 48.68 0.51 30.10 1.11 1.38 0.00 0.55 3.41 2.91 0.83 10.42 100.00 |

a: from Bobos (2012); \*Sr2+ - saturated forms

Aqueous solutions after Sr2+ saturation clays were analyzed for Sr2+, Ca2+ and Na+ (**Table 2**).

TABLE 2. Amount of Sr2+ and Na+ measured in aqueous solution after saturation

Samples Ca2+ -solution Sr2+-solution %Sr2+ solution Na+ solution

HB-18 2.6786 x 10-6 mol 9.973 x 10-3 mol 99.63% 0

HB-12 8.382 x 10~6 mol 9.916 x 10-3 mol 99.16% 0

HB-9 5.529 x 10~6 mol 9.945 x 10-3 mol 99.45% 0

Crystal chemistry of NH4-I (sample HB-18) is given (**Table 3**) for comparison with the AEM data. The crystal chemistry formula for samples HB-12 and HB-9 was not calculated because both samples represent a mixture of two distinct illitic minerals.

**TABLE 3**. Crystal chemistry of NH4-I calculated on 11 oxygens

|  |
| --- |
| Si Ti Al Fe Mg Ca Na K NH4 Sr |
| HB-18\* 3.35 0.00 2.47 0.01 0.18 0.00 0.00 0.13 0.60 0.02 |
| HB-12\* - |
| HB-9\* - |

**Conclusion**

After Sr2+ saturation clay fractions was replaced only Ca2+ from smectite layers. Therefore, Na+ is a fixed interlayer cation in illite structure of samples HB-12 and HB-9.

References

Bobos, I. (2012) Characterization of smectite to NH4-illite conversion series in the

fossil hydrothermal system of Harghita Bãi, East Carpathians, Romania. *American Mineralogist****,* 97,** 5, 962–982.

Sandell, P. (1952) Micro determination of water by the Penfield method. *Micro­*

*chimica Acta*, **38,** 487–491.