Mössbauer spectra of white micas from the Central Western Carpathians Mountains

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Abstract. Potassium white micas from the rocks included into Cretaceous deformation zones (ca. 100-70 Ma in age) of the Central Western Carpathians were investigated by Mössbauer spectroscopy. White micas formed during a polystage evolution and changing P-T conditions of their crystallization in crustal-scale shear zones. We found criteria for distinguishing generations of celadonite-poor (muscovitic) and celadonite-rich (phengitic) white micas using Mössbauer spectroscopy. This method revealed contrasting spectra characterized by typical quadrupole doublets corresponding to Fe$^{2+}$ and Fe$^{3+}$ contents in white micas. They are in the range of 2.9-3.0 mm/s for phengite, and 2.6-2.7 mm/s for muscovite. Mössbauer spectra reflect well the chemical changes in white mica aggregates, especially of those close to the end-member muscovite and (alumino-)celadonite compositions.

1. Introduction

Tectonic shear zones of the central Western Carpathians are located in basement/cover structural complexes subjected to Mesozoic and/or Tertiary metamorphism and deformations. These shear zones are analogous to those within the Austroalpine complexes of the Eastern Alps. The Central Western Carpathian are dissected by a few major shear zones. Here, a crustal shortening by underthrusting of some basement/cover complexes was accompanied by crystallization of celadonite-rich muscovite (phengite). This kind of phyllosilicates, besides the other associating minerals like pumpellyite, zoisite, grossular-rich garnet, chloritoid and kyanite, belongs to the group of white micas which often occur in higher-pressure zones. The studied zones fall into varying pressure interval of 300 – 1000 MPa. We specified chemical and spectroscopic characteristics [1],[2],[3], which allow distinction between celadonite-poor (muscovitic) and celadonite-rich (phengitic) white micas. White mica generations formed during a polystage evolution and changing P-T conditions from the very low to medium temperatures at medium pressure within the Alpidic Central Western Carpathians orogenic wedge.

The main goal of this study was to document the correlation between chemical composition of a natural white mica [1],[4] and its Mössbauer characteristics, respectively. These data should enhance identification of different white mica aggregates in blastomylonitic rocks. Mössbauer spectroscopy is a very efficient tool for the white mica investigation, because it provides information on relative abundance of Fe$^{2+}$ and Fe$^{3+}$, which are not distinguishable by electron microprobe. Moreover, it also allows identification of all iron containing phases, when characterized by different hyperfine parameters. Celadonite poor muscovite and celadonite rich muscovite (phengite) are distinguished in presented Mössbauer spectra by the superposition of several quadrupole doublets corresponding to Fe$^{2+}$ or Fe$^{3+}$ contents.
We separated original grain-size aggregates to avoid crushing of larger muscovite or phengite flakes during separation procedure. Ms porphyroclasts were separated from roughly crushed samples, nearly in original grain-size. White mica aggregates were separated from representative samples, containing more than 90% of newly-formed white mica aggregates, concentrated in foliation planes. The samples containing fine-grained micas were gently crushed after removal of the weathered parts. Subsequently, they were ground with pestle and mortar, sieved under 0.16 mm, soaked in distilled water and ultrasonically disaggregated. For the Mössbauer spectroscopy, samples were powdered and measured at room temperature by a standard transmission geometry Mössbauer spectrometer using a Co(Rh) source. Isomer shifts are given relative to the source. Spectra were evaluated by NORMOS program. Polished sections of samples were analysed by using a CAMECA SX100 and JEOL JXA-8100. Beam diameter varied from 2-10 μm and current from 20 to 10 nA according to size of the white mica flakes.

3. Results and discussion

Mössbauer spectra of celadonite-poor muscovite are shown in Fig.1. The spectra consist of two quadrupole doublets. The higher one corresponds to Fe$^{2+}$ with QS = 2.63 – 2.73 mm/s and IS = 1.01-1.20 mm/s and the lower one to Fe$^{3+}$ with QS = 0.66 – 0.73 mm/s and IS = 0.24 mm/s. Experimental error of QS values in all investigated samples is 0.01 mm/s. The relative amount of each component was determined from the area of the subspectra and is given in Tab. 1. The chemical composition of studied samples is documented in Tab. 2. Our results indicate that part of measured samples (MF-84, MF-KU) represent celadonite-poor muscovite with different ratio of Fe$^{2+}$/Fe$^{3+}$. For a comparison, the Mössbauer spectra of a typical celadonite-rich muscovite (phengite) are reported in Fig. 2 and Tab.1 (MK-237, PI-17HZ, MK-P1) with parameters Fe$^{2+}$ (QS = 2.95 – 3.00 mm/s, IS=1.01 mm/s) and Fe$^{3+}$ (QS = 0.71 mm/s, IS = 0.23 mm/s).

Table. 1 Mössbauer parameters of white micas from the Tatric tectonic unit.

| sample     | Fe$^{2+}$ (%) | QS Fe$^{2+}$ (mm/s) | Fe$^{3+}$ (%) | QS Fe$^{3+}$ (mm/s) |
|------------|---------------|---------------------|---------------|---------------------|
| MK-237     | 21            | 2.95                | 79            | 0.73                |
| PI-17HZ    | 48            | 3.00                | 52            | 0.71                |
| MK-P1      | 57            | 2.99                | 43            | 0.66                |
| MF-84      | 90            | 2.63                | 10            | 0.70                |
| MF-KU      | 77            | 2.66                | 23            | 0.71                |

Table. 2 EMPA chemical analysis of white micas from Tatric tectonic unit.

| mass % ox. | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | Cr$_2$O$_3$ | FeO | MnO | MgO | CaO | Na$_2$O | K$_2$O | F | Cl | NiO | Total |
|------------|---------|---------|-------------|-------------|-----|-----|-----|-----|---------|-------|---|----|-----|--------|
| MK-237     | 48.65   | 0.39    | 27.60       | 0.00        | 5.68| 0.02| 1.56| 0.05| 0.09    | 10.70 | 0.04| 0.00| 94.78|
| MK-P1      | 50.67   | 0.37    | 26.96       | 0.00        | 4.06| 0.06| 1.60| 0.02| 0.06    | 10.90 | 0.01| 0.02| 94.71|
| MF-84      | 49.31   | 0.08    | 31.80       | 0.00        | 1.43| 0.03| 1.98| 0.01| 0.21    | 10.98 | 0.00| 0.00| 95.82|
| MF-KU      | 46.66   | 0.36    | 36.20       | 0.05        | 0.93| 0.00| 0.74| 0.01| 2.02    | 8.37  | 0.00| 0.00| 95.35|

| Mol. Frac. (11 O) | Si | Al$^{3+}$ (IV) | Al$^{3+}$ (VI) | Ti | Cr | Fe | Mn | Mg | Ca | Na | K | Total |
|-------------------|----|----------------|----------------|----|----|----|----|----|----|----|----|-------|
| MK-237            | 3.35| 0.65           | 1.59           | 0.02| 0.00| 0.33| 0.00| 0.16| 0.00| 0.01| 0.94| 7.10  |
| MK-P1             | 3.46| 0.54           | 1.62           | 0.02| 0.00| 0.23| 0.00| 0.16| 0.00| 0.01| 0.95| 7.04  |
| MF-84             | 3.26| 0.74           | 1.74           | 0.00| 0.00| 0.08| 0.00| 0.19| 0.00| 0.03| 0.93| 7.02  |
| MF-KU             | 3.09| 0.91           | 1.91           | 0.02| 0.00| 0.05| 0.07| 2.05| 0.00| 0.26| 0.71| 7.05  |
Mössbauer spectra well reflect the chemical changes in white mica aggregates, especially close to the end-member muscovite and (alumino-)celadonite composition, respectively. For a practical aspect and for distinguishing of muscovite from phengite we utilize Fe$^{2+}$ parameter, grouped into two different, but quite narrow intervals, with a “gap” of relevant values between them (see Tab. 1).

Similarly, the micro-Raman spectra indicate clear differences between muscovite porphyroclasts and newly formed phengite aggregate [3].

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References

[1] Rieder M, Cavazzini GD, Yakonov Y, Frank-Kamanetskii V, Gottardi G, Guggenheim S, Koval PV, Mülle, G, Neiva AMR, Radoslovich EW, Robert JL, Sassi FP, Takeda H, Weiss Z, Wones D.R. 1998. Nomenclature of micas American Mineralogist 36 (3), 905-912.

[2] Sitek J., Sulák M, Putiš M, Tóth I 2007. Chemical changes of Wmca across the West-Carpathian tectonic shear zones, registered by electron microprobe and Mössbauer spectroscopy. In: Pudiš D, Martinček I, Jannický I, (Eds.), APCOM 2007, Conference Proceedings, Bystrá, Slovakia.

[3] Sulák M., Kaindl R., Putiš M., Sitek J., Krenn K., Tóth I., 2009: Chemical and spectroscopic characteristics of potassium white micas related to polystage evolution of the Central Western Carpathians orogenic wedge. Lithos, 113, 709-730.

[4] Tischendorf G, Rieder M, Förster H-J, Gottesmann B, Guidotti CV, 2004. A new graphical presentation and subdivision of potassium micas. Mineralogical Magazine 68 (4), 649-667.