

DIFFERENTIATION OF MICA STRUCTURES AND POLYTYPES BY DECONVOLUTION OF X-RAY POWDER DIFFRACTION PATTERNS

KRISTÁLY, F.

Institute of Mineralogy and Geology, University of Miskolc, Miskolc, Hungary

E-mail: askkf@uni-miskolc.hu

Mica group and related minerals are important rock-forming phases bearing information of petrogenesis and petrological evolution of numerous rock formations. Beyond metamorphic crystallization, processes of hydration and alteration and sedimentary transformations can be recognized by the detailed evaluation of X-ray diffraction patterns of complex rock powders. While talc-pyrophyllite, true micas and brittle micas can be routinely identified, there are quite a number of problems in interpreting species and solid solutions of the flexible and interlayer cation deficient micas – the most important from petrogenetic point of view. The commonly accepted view persists, according to which muscovite(s), biotite(s), illite(s) and related minerals may not be distinguished by XRPD. However, recent observations on large and various sample types show that even highly detailed differentiation is possible even on bulk rock analysis. The application of supporting methods like electron-beam microanalysis, rock chemistry and vibration spectroscopic methods must be applied.

Samples of clays, clastic and volcanic sedimentary rocks, shales and phyllites, schists, cataclastic and different magmatic, hydrothermal materials were investigated. Results serving as the base of this research are XRPD patterns recorded on Bruker D8 Advance (Vantec1 position sensitive detector) and Discover (LynxEye XE-T position sensitive detector) diffractometers with Cu-K $\alpha_{(1,2)}$ radiation and 40 kV with 40 mA generator settings. Step size, counting time and instrument geometry were chosen both with similar and different settings, to enhance possibilities of developing technical solutions. Observations and calculations were tested on high purity monomineralic samples and their mixtures.

As expected, several important peaks and angular regions can be delimited, which serve as the basis of recognizing and distinction between several mica phases present in one mixed sample: 4.5–4.2 Å, 3.4–3.2 Å, 2.6–2.3 Å and other special peaks for polytypes, but also (00 l) and (060) peaks are important. Beyond d -values of (00 l) peaks the shape and asymmetry are important parameters, however the information related to different structures can be extracted only through whole powder pattern deconvolution. The process also requires instrumental parametrisation either by Fundamental Parameters Approach, or by empirical profile convolution definition. Rietveld refinement is an optimal approach for such tasks, and it has the advantage that samples with complicated mineralogy can also be solved. It also handles the preferred orientation and anisotropic size distribution effects on peak intensity

and shape distortions. On the other hand, it offers the possibility to select those few mica-related entries from ICDD PDF database which can be trusted for Search/Match identification – always validated by deconvolution-based solutions.

Presence and ratio of muscovite and biotite series can be fixed by solving the fit of the 10 Å, 5 Å and ~2.5 Å peaks, while in the case of biotite-dominated mica fraction Mg vs. Fe²⁺ dominancy may be approximated on the (060) peak. Effects of interlayer cation substitution are detectable on the (00 l) peaks position, while cation deficiency can be tracked and approximated by occupancy related intensity refinement. Moreover, the presence and ratio of octahedral substitutions can be clarified. This way, transitions towards illite-group phases and glauconites can be observed and quantified, taking into account space group and lattice parameter constraints. While celadonites and paragonites are easily recognized, the Li-bearing phases poses more problems and less results do their scarcity and problems of chemical analysis. For polytype identification, after consulting the relevant literature it was also possible to select suitable ICDD PDF data entries and define starting structural models for deconvolution.

Crystallite size and strain effects are handled in the necessary manner that even nanocrystalline broadening does not obstruct the above possibilities. The measurement conditions were tested on grain size fractions of different samples obtained by sieving and sedimentation but also on nanocrystalline powders produced by milling. After testing the solution possibilities on high purity phases and their mixtures, investigations of multiphase known mixtures and rock specimens were also conducted. Results show that the presence of more than 2 mica types can be recognized even at ~2–3 wt% total mica fraction with ~0.5 wt% of detection limit, while for a mica fraction of > 10 wt% the presence of several types is recognized. Supporting results from additional analytical techniques is usually required to validate the solutions but improving diffractometer and software solutions provide significant potential for detailed mica characterization. Moreover, testing the effect of X-ray optics from improved towards lower angular resolution possibilities might facilitate mica differentiation in various application fields.

Acknowledgement

Supported by the Bolyai János research scholarship program (BO/00920/19/10) of the Hungarian Academy of Sciences.