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ORIGINAL ARTICLE

Application of the capillary method in micro X-ray diffractometry (μ-XRD): A useful technique for the characterization of small amounts of clay minerals

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ABSTRACT

The laboratory micro X-ray diffraction (μ-XRD) technique is a suitable method to study minerals *in-situ* in whole-rock specimens without any sample preparation or in polished thin sections, and even in small amounts in powdered form. The micro X-ray diffraction method uses the conventional, closed-tube X-ray generator, but modifications were needed in the diffraction column, sample holder and detector in order to achieve μ-XRD capability.

In this paper, we present a case study of the capillary method used in μ-XRD on hydrothermal clay mineral assemblages that formed in the Velence Mts (Hungary). The capillary method in μ-XRD has many advantages in the investigation of small amounts of clay minerals: (1) easy and rapid preparation of randomly oriented, powdered samples; (2) rapid measurements; (3) accurate diffraction patterns. By using the capillary method, the formation of preferred orientation can be eliminated; thus the (*hkl*) reflection of the clay minerals can be precisely measured. Illite polytype quantification and the investigation of (060) reflection of clay minerals can be used satisfactorily in μ-XRD.

Hydrothermal clay mineral assemblages are indicative of temperature and pH. Their examination can determine the physicochemical parameters of the hydrothermal fluids that interacted with the host granite in the Velence Mts. The analyzed hydrothermal clay minerals from the western part of the mountains suggest lower temperatures (150–200 °C) and intermediate pH conditions. In contrast, the clay mineral assemblages' characteristics for the eastern part of the mountains indicate more intense argillization and higher temperatures (~220 °C) and intermediate pH conditions.

KEYWORDS

micro-XRD, capillary method, clay minerals, illite polytype, Velence Mts

INTRODUCTION

X-ray diffraction (XRD) is a widely-used method to specify the mineralogical composition (phase identification) of natural as well as artificial materials. For a mineralogical study, if a sufficient amount material is available, conventional powder diffraction can be performed either on powdered mineral or rock samples which can be separated by various methods (hand-picking, gravitationally or by centrifugation) from their original host media. However, in many cases, due to technological reasons (similar density of mineral phases, e.g. feldspars), specific mineralogy (e.g. mixtures of clay minerals) or low quantity of the questionable mineral phases (e.g. results of low-grade alteration), preparation of the sample for

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conventional XRD analysis is difficult. Occasionally, due to the high value of the objects, no or only very limited sampling is permitted (e.g. archaeological artefacts or planetary materials). Structural characterization of clay minerals – e.g. illite polytypism – is also challenging, as the conventional sample preparation methods often result in preferred orientation in the sample. In order to overcome the weaknesses of the conventional XRD technique, the laboratory micro X-ray diffraction (μ-XRD) technique has been developed. The new method is suitable for examining minerals *in-situ* in (1) whole-rock specimens without any sample preparation or (2) in polished thin sections, and (3) even in small amounts of powdered form. Advantages of the *in-situ* μ-XRD method over conventional XRD has been demonstrated by a selected set of applications in geology and environmental sciences (see e.g. Tissot 2003; Flemming et al. 2005; Flemming 2007), in archaeometry (see e.g. Benedetti et al. 2004; Nel et al. 2006; Bontempi et al. 2008; Swider 2009; Mozgai et al. 2019) and in planetary sciences (see e.g. Round et al. 2010; Izawa et al. 2011).

Identification of mineralogy, polytypism, crystallinity and proportion of the components in clay mineral assemblages is indispensable in the studies of diagenetic and anchimetamorphic systems, as well as in the investigation of (ore-forming) hydrothermal systems. Clay mineral assemblages and the crystal structure (ordering, crystallinity, polytypism) of the individual clay species are indicative of the temperature, pH, as well as of the fluid-rock interaction. In spite of its significance, the link between the alteration product and the altered mineral can hardly be established by the combination of optical microscopy and conventional XRD.

In this paper, case studies are presented of the application of μ-XRD on hydrothermal clay assemblages that formed in a Permian granite intrusion during the Alpine cycle. First, we give an introduction into the μ-XRD technique; then we demonstrate the suitability of the capillary method of μ-XRD instrument in the investigation of clay minerals, when only a very limited amount of sample material is available or *in-situ* measurements are required.

The μ-XRD technique and the capillary method

The laboratory μ-XRD method uses the conventional, closed-tube X-ray generator, but in order to achieve μ-XRD capability, modifications were needed in the diffraction column, sample holder and detector. Microfocus tubes have been used for a long time to obtain transmission images, for which the focus size was set to a few μm in order to increase spatial resolution. In spite of these efforts, adequate X-ray output cannot be obtained with such settings, and the method is insufficient to use in X-ray diffraction (Takumi and Maeyama 2015). However, in the past decades, X-ray tubes with a few tens of μm focus have become available; this allows scientists to obtain a usable diffraction pattern from samples even in the 10 μm range.

In μ-XRD, a two-dimensional (2D) detector is used with a larger detection area, such as Imaging Plate (IP), Charge Coupled Device (CCD), Complementary Metal Oxide Semiconductor (CMOS) and Position Sensitive Proportional Counter (PSPC). All these types have their own advantages. The detector surface can be curved (IP) or flat (CCD, CMOS, PSPC). The curved detectors are normally designed for fixed sample-to-flat-detector distances, while flat detectors have the flexibility to be used at different sample-to-detector distances, so as to choose between higher resolution at greater distance or higher angular coverage at short distance. IP has a larger detection area than CCD, CMOS and PSPC. If the measurements are in fixed positions, they cannot be captured by a small area detector, and it is necessary to use a detector with a large detection area such as an IP (Takumi and Maeyama 2015).

A new RIGAKU D/MAX RAPID II diffractometer was purchased by the Institute for Geological and Geochemical Research (HAS), which is a unique combination of a MicroMax-003 third-generation microfocus, sealed-tube X-ray generator and a curved imaging plate detector. The diffractometer is operated with CuK_{α} radiation generated at 50 kV and 0.6 mA. Different types of collimators can be used (10, 30, 50, 100, 300, 500, 800 μm) depending on the size of the measured area. A built-in CCD camera was used to select the measurement area and for precise positioning of the sample at a downward angle of 45°. The detector system uses a curved IP, which is placed on the inner surface of a cylinder that surrounds the ω-axis at the center, allowing the recording of a 2D diffraction image over a broad 2θ range. The IP is read by a laser-scanning readout system in about 1 min. 2DP RIGAKU software is used to record the diffraction image from the laser readout and the operator can determine the area to integrate for a 2θ versus intensity plot. This plot is read into RIGAKU PDXL 1.8 software for data interpretation.

One of the disadvantages of the method is that due to the geometry of the instrument and the sample holder, the object/sample may cover certain areas of the imaging plate detector depending on its actual position in the diffraction geometry. Therefore, some higher d_{hkl} values cannot be detected, and to achieve the totally random orientation is often difficult. These limitations make the interpretation difficult in the case of some sample types (e.g. clay minerals). In order to overcome this limitation, the powdered samples for the micro-diffraction measurements are encapsulated in a borosilicate-glass capillary, with a diameter of 0.3 mm and wall thickness of 0.01 mm, by a vertical manual charging process. Then, the capillary is analyzed by the micro-diffractometer in transmission mode with a beam spot diameter of 100 μm. In each measurement, 0.5–1 mg of sample is placed in the funnel-end of the capillary and the sample is tapped into the narrow portion. The sample stage with the filled capillary is aligned before each measurement. The best technique for aligning is to adjust the X and Y axis on the sample stage and rotate the φ-axis. Orientation of the minerals can be prevented in the samples during the measurement by the rotation of the sample stage from 0° to 360° of the φ-axis, keeping the ω-axis fixed at 0° (Fig. 1). The

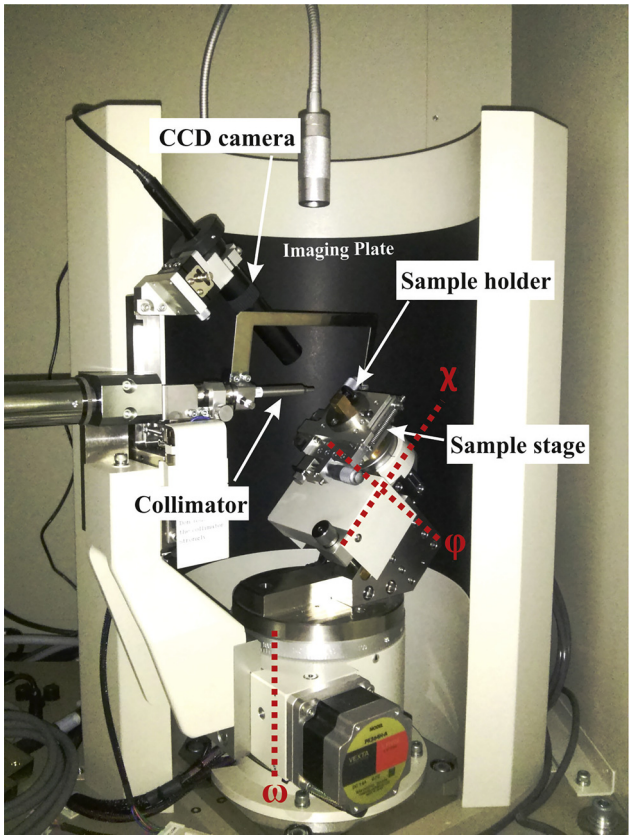

Fig. 1. RIGAKU D/MAX RAPID II micro X-ray diffractometer set-up

χ-axis is fixed at 45° relative to the ω-axis. The measurement time ranges between 3 and 10 min.

NEWMOD II and WIDFIRE software were used to analyze interstratified clay mineral samples and the illite polytypism.

CASE STUDY: HYDROTHERMAL CLAY MINERAL ASSEMBLAGES IN THE VELENCE MTS.

The Velence Mountains along the Periadriatic–Balaton Lineament in the western part of the Carpathian basin are a Permian, deeply eroded granite intrusion that have been affected by several hydrothermal processes during the Permian, Triassic and the Paleogene (Fig. 2a). The hydrothermal fluid-flow events can be characterized by different physicochemical properties (Molnár 1997, 2004; Benkó et al. 2012; Tóth 2017; Kovács et al. 2019). The alteration zones often overlap spatially, and the elder mineral assemblages are locally overprinted by the products of the younger hydrothermal systems.

Four localities, representing different argillic alteration assemblages, are examined in this study. Two localities in the western segment of the intrusion represent the low-temperature (80–150 °C), regional, Triassic hydrothermal event. The high-temperature (220–340 °C) Paleogene alteration zones are confined in some E–W structural zones in the eastern segment of the intrusion and are represented by two selected localities (Fig. 2b). In earlier studies (Benkó et al. 2012; Tóth 2017; Kovács et al. 2019), the mineralogical composition of bulk samples was determined by conventional XRD measurements and other petrographic methods, but with the conventional XRD technique we could not define the alteration of the single mineral particles. The granite affected by the Triassic hydrothermal alteration contains illite, kaolinite and smectite, while the granite affected by the Paleogene fluid flow contains only illite, based on conventional XRD measurements.

Several bulk samples were collected from the four areas, from which 3–4 cm-thick rock slices were made to facilitate further investigation. Each sample was divided into morphological components based on appearance (color, texture and the occurrence of argillization) under a binocular microscope. Plagioclase, alkali feldspar and clay minerals (in the fissure) were separated from each bulk sample. The capillary powder samples were prepared by hand-picked separation (scraped with a spatula) under a binocular microscope and homogenized using an agate mortar.

Units of the intrusion affected by the Triassic regional fluid flow

In both localities (Aranybulla Quarry and Karácsony Quarry) affected by the Triassic fluid flow, the alkali feldspar is macroscopically fresh, whereas the plagioclase and biotite are altered to greenish-white clay minerals (Fig. 3a and b). Intense and relatively broad peaks at 10 and 5 Å clearly indicate that illite is the predominating phase in these samples, based on the μ-XRD. Besides illite, there are peaks at 7.1 and 3.57 Å, which suggest the presence of kaolinite. The weak 15 Å reflection indicates the presence of some smectite and the asymmetric peak at 10 Å suggests randomly interstratified illite/smectite, containing a 15–20% swelling component based on the NEWMODE II calculation method. The peak position of the (060) reflection of smectite suggests the presence of dioctahedral smectite (beidellite, montmorillonite). Alkali feldspar from Karácsony Quarry contains wisps of illite (Fig. 3e and f).

Units of the intrusion affected by the Paleogene fluid flow

The structurally-controlled Paleogene hydrothermal alteration in the granite is much more intense than the regional pervasive Triassic hydrothermal circulation. Except for the rock-forming quartz and some remnants of alkali feldspar, yellowish-white and white fine-grained material replace the plagioclase and biotite (Fig. 3c and d). In a quarry that represents the distal zone of the hydrothermal system (Sukoró barite excavation), alkali feldspar is poorly altered, and the other minerals are replaced by illite (Fig. 3g). During illite polytype quantification, the measured μ-XRD diffraction patterns of the samples were compared to the WILDFIRE-calculated diffraction pattern. Several diagnostic polytype peaks of illite occur between 20–32° 2θ. The 1*M* character of the layers is suggested by the peak positions and

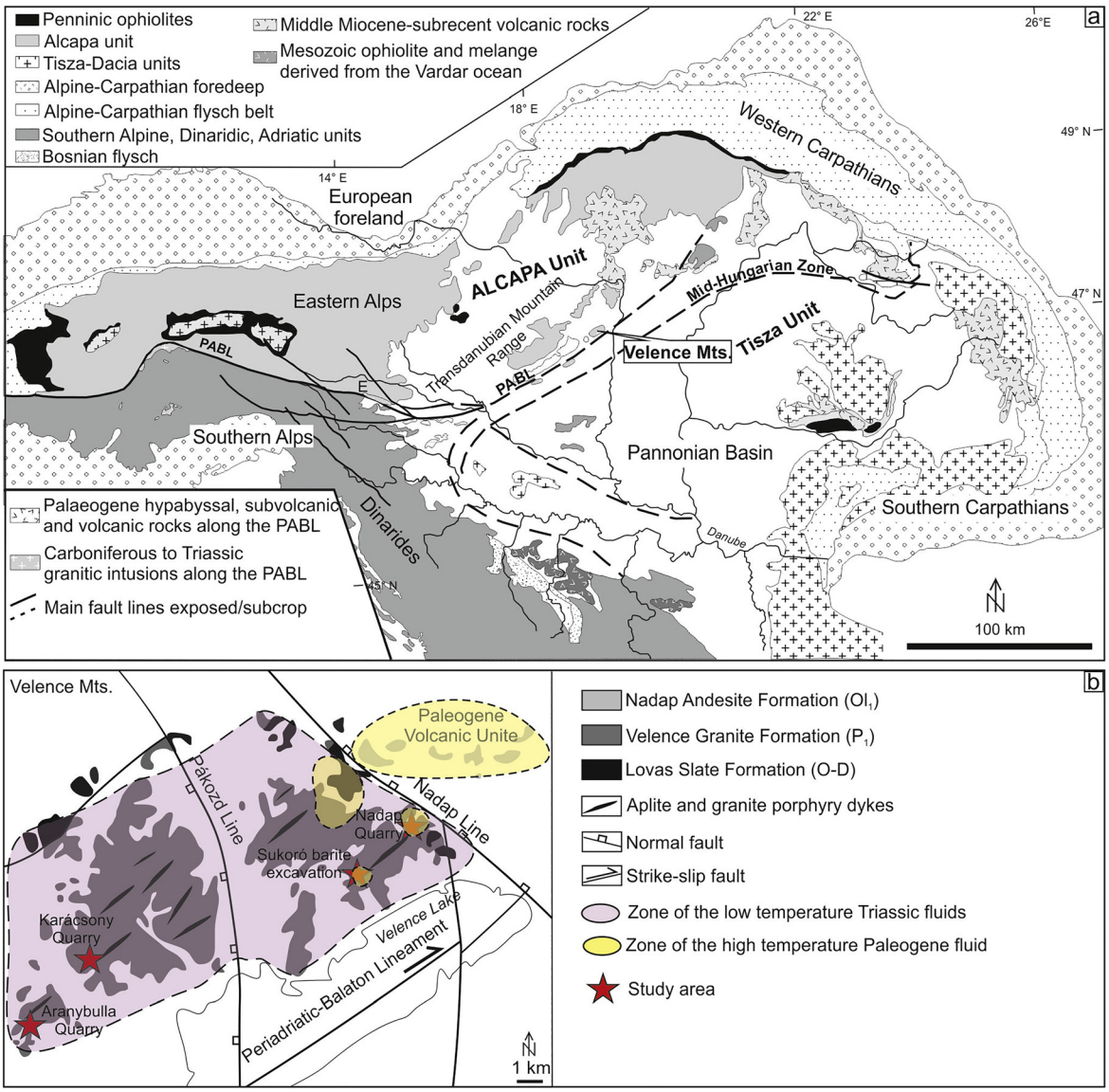

Fig. 2. (a) Location of the Velence Mts (Hungary) in the Alpine–Carpathian region after Csontos and Vörös (2004); (b) Geologic map of the Velence Mts. after Horváth et al. (2004)

the relative peak intensities of the reflections. The measured 11*l* reflections and intensity distributions are located between the pure 1M trans-vacant (*tv*) and 1M cis-vacant (*cv*) illite structures (Fig. 4 and Table 1).

According to Drits (2003) and Zviagina et al. (2007) this is represented by the possible interstratification of *tv* and *cv* layers.

Based on the μ-XRD results, the analyzed alkali feldspar pseudomorphs from the other quarry (Nadap Quarry) consist of smectite and illite, based on the intense peaks at 15 Å and 10 Å. However, the white material contains only illite (Fig. 3h). The μ-XRD pattern shows diagnostic reflections at 3.88 Å ($11\bar{3}$), 3.73 Å (023), 3.49 Å ($11\bar{4}$), 3.20 Å (114), 2.98 Å (025) and 2.86 Å (115), the appearance of which suggest the $2M_1$ character of the layers (Fig. 5).

Formation conditions of the hydrothermal clay minerals inferred from the mineral assemblages and the polytypism

The western samples can be characterized by the weakest argillization. According to White and Hedenquist (1990), illite indicates relatively high temperatures (>200 °C) and neutral to acidic conditions in hydrothermal environments. Kaolinite forms under acidic conditions (pH 2–7) and at temperatures between 100 and 220 °C (Reyes 1990; Hedenquist et al. 2000). Smectite forms at relatively low temperature (<150 °C) and neutral condition but beidellite is stable at a higher temperature than montmorillonite in hydrothermal environments (Yamada et al. 1991; Yamada and Nakazawa 1993). Based on the above-mentioned facts, the studied hydrothermal clay minerals represent a narrow

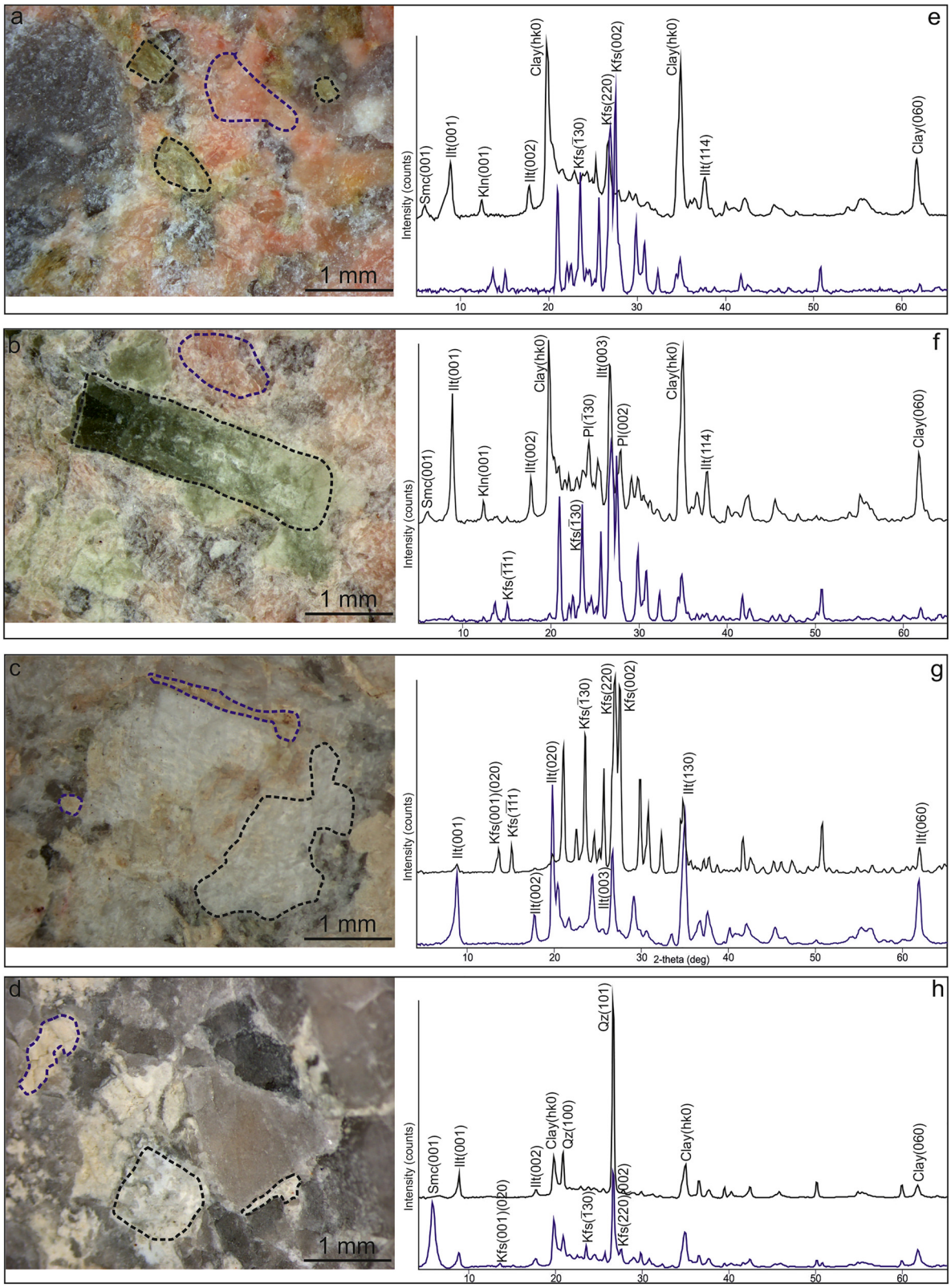

Fig. 3. (a–d) Macroscopic feature of the granite samples and the location of the sampling for μ-XRD (blue and black dotted shapes); (a) Aranybulla Quarry; (b) Karácsony Quarry; (c) Sukoró barite excavation; (d) Nadap Quarry; (e–h) Micro-XRD patterns of granite samples (Ilt – illite, Kln – kaolinite, Smc – smectite, Qz – quartz, Kfs – alkali feldspar, Pl – plagioclase)

stability field of formation. The analyzed clay minerals indicate low formation temperature (150–200 °C) and intermediate pH conditions.

In contrast to the western part, where only Triassic hydrothermal process caused argillic alteration, in the eastern part both the Triassic and Paleogene hydrothermal

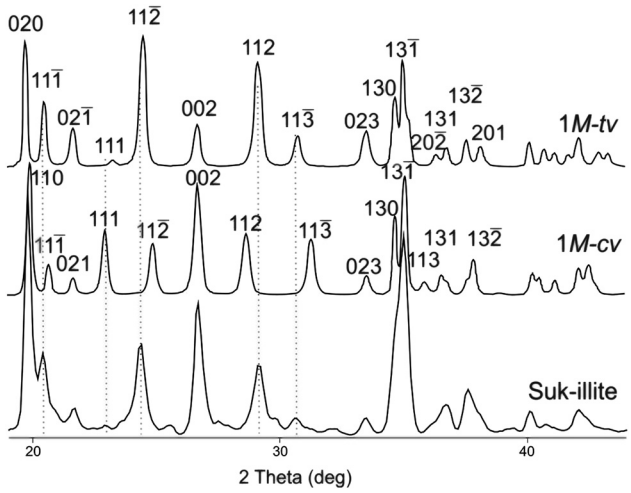

Fig. 4. Calculated XRD patterns of 1*M-tv*, 1*M-cv* illite and μ-XRD pattern of illite from the Sukoró barite excavation

processes developed clay mineral alteration paragenesis. Polytypism of illite may provide information about the thermodynamic conditions of the mineralizing fluid (Kraus et al. 1999; Bove et al. 2002). In hydrothermal systems, with increasing temperature and pressure, polytypism of illite shows the following sequence from 1*Md*, 1*M* to $2M_1$ (Inoue et al. 1988). However, the polytype determination can be difficult when measuring clay mineral assemblages because the (*hkl*) diffraction peaks interfere with other clay minerals and with the characteristic peaks of alkali feldspar and plagioclase (Velde and Hower 1963). Therefore, determination of the illite polytypism can only be performed with certainty in the eastern area. Polytypism of illite from the eastern part of the mountains can be characterized by 1*M* and $2M_1$ polytype. The analyzed clay minerals and the illite polytypism indicate higher formation temperature (~220 °C) than in the western part of the mountains. This result agrees with the findings of previous studies, which determined the physicochemical properties of the hydrothermal fluid flow systems (Molnár 1997, 2004; Benkó et al. 2012; Tóth 2017; Kovács et al. 2019).

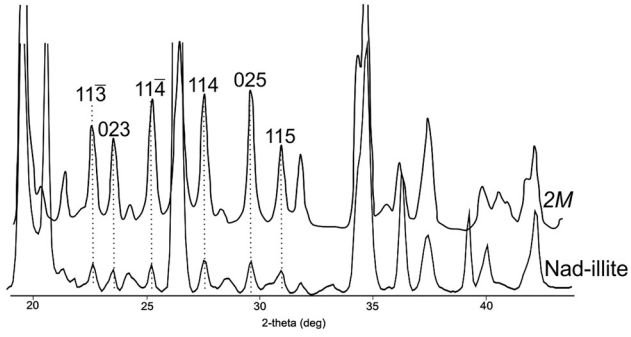

Fig. 5. Calculated XRD patterns of 2*M* illite and μ-XRD pattern of illite from the Nadap Quarry

Table 1. Reflection indices, d_{hkl} values and relative peak intensities in the simulated XRD pattern for structural models 1*M-tv* and 1*M-cv* (Zviagina et al. 2007) and the d_{hkl} values and relative peak intensities in the μ-XRD pattern of illite from Sukoró barite excavation (Suk-illite)

1*M-tv*			1*M-cv*			Suk-illite	
hkl	d_{hkl} (Å)	*I* (%)	*hkl*	d_{hkl} (Å)	I (%)	d_{hkl} (Å)	*I* (%)
020	4.502	97	110	4.460	100	4.480	100
11$\bar{1}$	4.337	50	11$\bar{1}$	4.299	21	4.343	35
021	4.106	29	021	4.104	11	4.100	3
111	3.823	4	111	3.879	49	3.874	1
11$\bar{2}$	3.638	100	11$\bar{2}$	3.580	39	3.646	54
022	3.344	32	022	3.343	82	3.339	62
112	3.067	80	112	3.119	43	3.069	43
113	2.910	21	11$\bar{3}$	2.862	41	2.915	2
123	2.676	26	023	2.675	12	2.676	1
130	2.588	51	130	2.589	56	2.583	24
131	2.567	81	131	2.561	88	2.561	88
220	2.550	36	113	2.506	9	2.481	4
20$\bar{2}$	2.474	9	131	2.460	13	2.445	11
131	2.446	13	13$\bar{2}$	2.379	27	2.390	19
13$\bar{2}$	2.396	21	11$\bar{4}$	2.317	1	2.357	3
201	2.361	13	22$\bar{1}$	2.243	14	2.243	6

CONCLUSIONS

X-ray diffraction is the basic technique for identification of clay minerals. The capillary method in μ-XRD has many advantages in the investigation of small amounts of clay minerals: (1) easy and rapid preparation of randomly oriented, powdered samples; (2) rapid measurements; (3) correct diffraction patterns. By using the capillary method, formation of the preferred orientation can be eliminated; thus the (*hkl*) reflection of the clay minerals can be measured. Illite polytype quantification and the investigation of (060) reflection of clay minerals can be performed satisfactorily by using μ-XRD. As proven by the samples of the Velence Mts, the capillary method in μ-XRD is a useful tool for identification of very small amounts of clay minerals analyzed *in-situ*. Since clay mineral assemblages and the crystal structure of the individual clay species are indicative of the temperature and pH, the μ-XRD method proved to be an excellent method for determining the physicochemical parameters of the hydrothermal fluids that interacted with the host granite in the Velence Mts. The analyzed hydrothermal clay minerals from the western part of the mountains suggest lower temperatures (150–200 °C) and intermediate pH conditions. The clay mineral assemblages indicate more intense argillization and higher temperatures (~220 °C) characteristic of the eastern part of the mountains.

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