

DICKITE AND KAOLINITE AS ALTERATION MINERALS WITHIN THE Pb-ZN-AG SULFIDE DEPOSITS ON NORTHERN KOSOVO

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INTRODUCTION

The kaolin group of minerals is represented by kaolinite, dickite and nacrite. Identification of three polytypes with chemical formula $Al_4Si_4O_{10}(OH)_8$ can be achieved by combination of X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Kaolinite occurs in hydrothermal ore veins, in hot springs deposits and as authigenic vermicular crystals in sediments. It is a common weathering product and is a major component of soils, residual clays, bauxites and certain sedimentary deposits. Dickite is generally related to the conditions of higher temperature and pressure and mainly occurs in hydrothermal environments. Nacrite is the rarest polytype among them and is mostly related to the hydrothermal systems.

Kaolin minerals are recorded within two hydrothermal Pb-Zn-Ag sulfide deposits in the Northern Kosovo, related to the Late Palaeogene, post-collisional volcanism (Cvetković et al., 2004). Dickite occurs in the Trepča deposit and kaolinite is found in the Crnac deposit (Fig. 1).

This publication deals with genesis of dickite and kaolinite and presents their mineralogical characteristics. The geochemical conditions for the formation of dickite and kaolinite in Pb-Zn-Ag sulfide deposits in Kosovo are estimated on the basis of fluid inclusions data obtained from cogenetic quartz, spatially associated with the kaolin minerals.

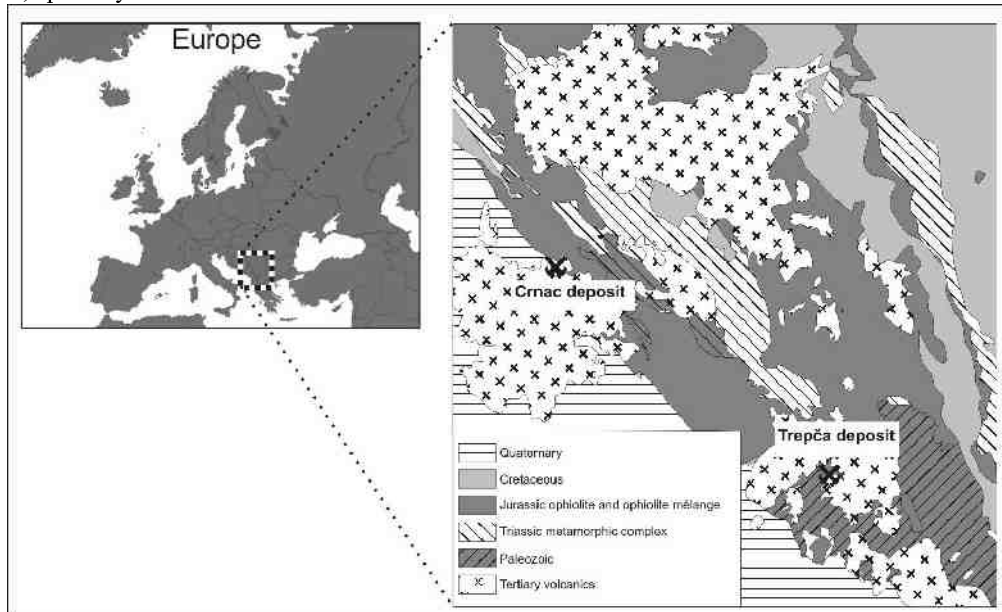


Figure 1. Geographical and geological setting of the Trepča and Crnac mineral deposits.

GEOLOGICAL SETTING

STARI TRG HYDROTHERMAL-METASOMATIC ORE DEPOSIT

Stari Trg hydrothermal-replacement and skarn ore deposit is located 40 km NW from Priština, Kosovo. The mine is placed within the Kopaonik block of Western Vardar zone in the easternmost part of Dinarides (Dimitrijević, 1997).

Mineralization is represented by galena, sphalerite, pyrite, arsenopyrite and pyrrhotite, and hosted by marbleized limestones with inherited paleokarst features, under the screen of schists. The paleokarst phenomena played important role in the ore deposit genesis as conduits for ore-forming fluids. Mineralization is controlled structurally. The steeply deeping pipe-shape structure, with a volcanic semi-circular trachyte plug surrounded by volcanic breccia, on the contact between schists and carbonates, controls geometry of the ore body. The major gangue minerals are carbonates and quartz. Common skarn minerals (ilvaite, hedenbergite, garnet) precede sulfide mineralization (Schumacher, 1954).

Breccia is composed of subangular fragments of the country rocks, rounded clasts of trachyte and contains mostly pyrite mineralization. The common size of clasts ranges from tens centimetres to several meter. In the deeper levels lateral branches cut limestones and assume characteristics of fluidized breccia with milled matrix and jigsaw-fit texture. Dominant minerals are carbonates, various silicates, mostly sericite and feldspar, and quartz. Carbonates are occasionally replaced by pyrite.

There are two modes of dickite occurrences within Stari Trg deposit, and both of them are associated with the breccia. (1) Dickite in the form of monomineral aggregates as a vug-filling cluster within Fe-carbonate fragments. Carbonate is represented by siderite enriched in Ca and Mn. It is occasionally impregnated by pyrite and replaced by microcrystalline quartz. Quartz also occupies cavities in the form of euhedral crystals. (2) Dickite occurs as alteration product of silicate minerals mostly sericite and K-feldspar in milled matrix of fluidized breccia.

CRNAC PB-ZN-AG HYDROTHERMAL-METASOMATIC DEPOSIT

Crnac vein type hydrothermal deposit is situated in the Western Vardar zone, at the northernmost border of the Kosovo region. It consists of two types of mineralization: a vein type and metasomatized listwaenites. The vein type mineralization is hosted by Jurassic amphibolites, amphibolite schists and gabbroidic rocks. The Jurassic amphibolite hosts are overlain by serpentinite and serpentinitized peridotites. The entire geological section is cross-cut and intruded by a succession of trachyte dykes in Miocene time. The trachyte dykes are accompanied or enveloped by vein type mineralization. The mineralization consists of a series of steeply dipping massive ore veins, thick between 1 and 5 m. Ore petrography suggests 3 vein formation stages: pre-mineralization stage, with pyrite-quartz-kaolinite; major mineralization stage with galena-sphalerite-chalcopyrite; and post-mineralization stage, with prevailing carbonates, siderite-ankerite-calcite-dolomite-cerussite.

Listwaenite is a silica-carbonate rock produced by hydrothermal alteration of serpentinite. Listwaenite type of mineralization occurs in the upper-most level of the deposit, at the contact between amphibolites and overlying serpentinite. Silicification followed by lesser pyritization is a pre-mineralization stage, the next stage is base metal formation terminating with carbonatization, sericitization and illitization. Some of the listwaenite samples are grading into hydrothermal breccias, with increased fraction of rounded particles from pre-mineralization phase, cemented afterwards during the major mineralization phase.

Kaolinite occurs in the three different parageneses within Crnac Pb-Zn-Ag deposit: (1) kaolinite associated within vein type mineralization, following pre-mineralization stage with large masses of open-space grown euhedral quartz and pyrite. (2) Kaolinite associated with listwaenite type of mineralization occurs as rounded clasts up to three centimetres in size. (3) Kaolinite associated with the trachyte dykes as alteration of feldspars.

The kaolinite type (1) occurs as milky-white irregular masses, few millimetre to centimetre in size. It is more abundant at the lowermost level of the deposit, decreasing upwardly in quantity. At some places kaolinite is associated with carbonates, assumed to be introduced during post-mineralization phase. The purity of kaolinite also decreases upward, where is often found as a mixture of kaolinite-ankerite-illite-chlorite-montmorillonite phases.

SAMPLES AND METHODS

Dickite in the form of monomineral aggregates was separated from vug-fillings in the fragments of Fe-carbonates within breccia (Fig 2). Size of the aggregates, up to 5 mm, allows separation of dickite without contamination by the host rock.

Milky-white kaolinite, associated within vein type mineralization, is separated from the VI level in the Crnac deposit (Fig. 2). Kaolinite, appears as irregular masses of vug-fillings, up to centimeter in size, together with corresponding quartz-pyrite pre-mineralization assemblage.

X-ray diffraction (XRD) analyses were performed using a Philips diffractometer PW 3040/60 X'Pert PRO (45 kV, 40 μ A) with CuK α monochromatised radiation ($\lambda=1.54056$ Å) and $\theta-\theta$ geometry. Sample was scanned between 4 and 63° 2 θ with 0.02° step per 0.5 minute and between 48 and 78°2 θ with 0.02° step per 1 minute. The goniometer was calibrated against quartz standard.

The textural features of the sample were examined by Tescan scanning electron microscope (SEM) equipped by INCA 250 analysing system and Oxford detectors (20 kV, 10 nA, counting time of 200 seconds).

Raman spectroscopy was performed by Jobin Yvon T64000 system working in micro Raman, triple monochromatic mode. An argon ion laser (Coherent, Innova 400, Santa Clara, CA) operating at 514.5 nm with a laser power of 20 mW at the samples for excitation.

A fluid inclusion studies were carried out on primary fluid inclusions within doubly polished, wafers of quartz associated with dickite and kaolinite. Measurements were performed at Linkam THMS 600 stage mounted on an Olympus BX 51 microscope. The precision of the system was $\pm 2.0^\circ\text{C}$ for homogenization temperature, and $\pm 0.2^\circ\text{C}$ in the temperature range between -60 and $+10^\circ\text{C}$.

Solute chemistry analyses were conducted using a crush-leach procedure (Nesbitt & Prochaska, 1998). Anions (Cl⁻, SO₄²⁻ and F⁻) and cations (Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺) of the leachates were analyzed by ion chromatography using a Dionex DX – 500 system with a micromembrane suppressor.

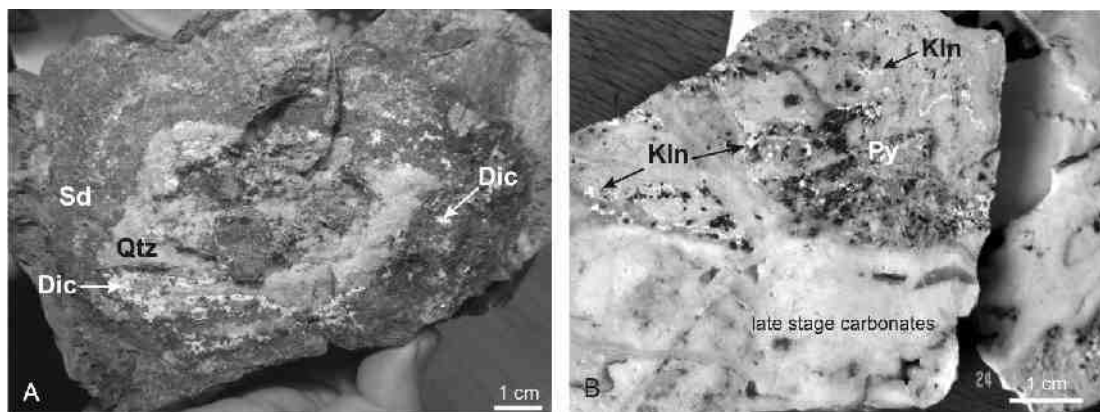


Figure 2. Macroscopic view of a) dickite clusters within breccia fragments from the Trepca deposit; b) vein type mineralization from the Crnac deposit with milky white irregular masses of kaolinite.

RESULTS AND DISCUSSION

DICKITE

The XRD patterns are shown in Figure 3. According to Brindley & Brown (1980), Chen et al. (2001) and Zotov et al. (1998) all diagnostic diffraction lines for dickite are present. No crystalline impurity is observed. The results of least-squares refinement of the dickite structure using the present powder XRD data are $a = 5.147(1)$ Å, $b = 8.932(1)$ Å, $c = 14.421(3)$ Å, $\beta = 96.86(2)^\circ$ and $V = 658.2(1)$ Å³.

Scanning electron microscopy shows that dickite aggregates consist of 1-2 μm thick hexagonal crystals ranging from 5 to 20 μm in diameter (Fig. 4). The major chemical elements determined by EDX detector are aluminum, silicon and oxygen.

Raman spectra of dickite are characterized by six bands in the $\nu(\text{OH})$ stretching region shown in Figure 5. Bands at 3623, 3686 and 3697 cm^{-1} are indicative for dickite polycrystals (Wiewora et al., 1979). Sharp band at 3623 cm^{-1} is indicative for dickite single crystals (Johnson et al., 1998). Shoulder

at 3686 cm^{-1} points to the presence of diffusely adsorbed water. The bands within $50\text{-}1800\text{ cm}^{-1}$ region are in accordance with published data for dickite (Wiewora et al., 1979; Johnson et al., 1998).

Fluid inclusions from quartz associated with dickite are two-phase (L+V) at room temperature and homogenise to a liquid phase between 285 and 320°C . Their salinities range between 6.0 and 8.5 wt.% NaCl eqv.

The bulk leachate data of fluid inclusions in quartz associated with dickite suggest Cl^- as major anion and Ca^{2+} and Na^+ as dominant cations.

Fluid inclusion density, in the range between 0.7595 and 0.8482 g/cm^3 , was determined by combination of the microthermometric and bulk leachate data.

Isochores were calculated using the computer program ISOC (Fig. 7; Bakker, 2003) from the equation of state by Zhang & Frantz (1987) and a correction for the volumetric properties of quartz. Homogenization pressure (pH) is estimated in the range between 6.5 and 10.8 MPa.

Alkali geothermometres applied on bulk leachate data reveal formation temperature in the interval from 290 (K-Na-Ca; Fournier & Truesdell, 1973) to 330°C (Na-K; Can, 2002). Formation pressure between 12 and 60 MPa is estimated by combination of fluid inclusion and geothermometric data (Fig. 6).

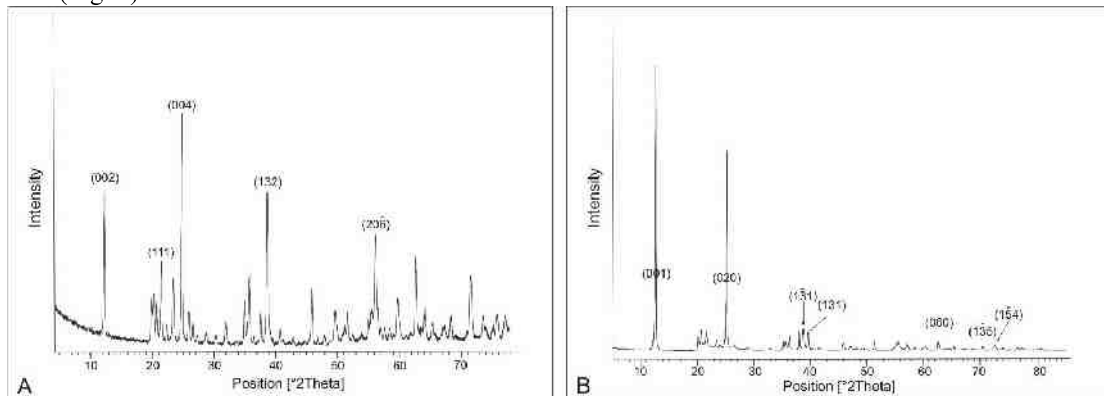


Figure 3. X-ray diffraction patterns of a) dickite from the Trepca deposit; b) kaolinite from the Crnac deposit.

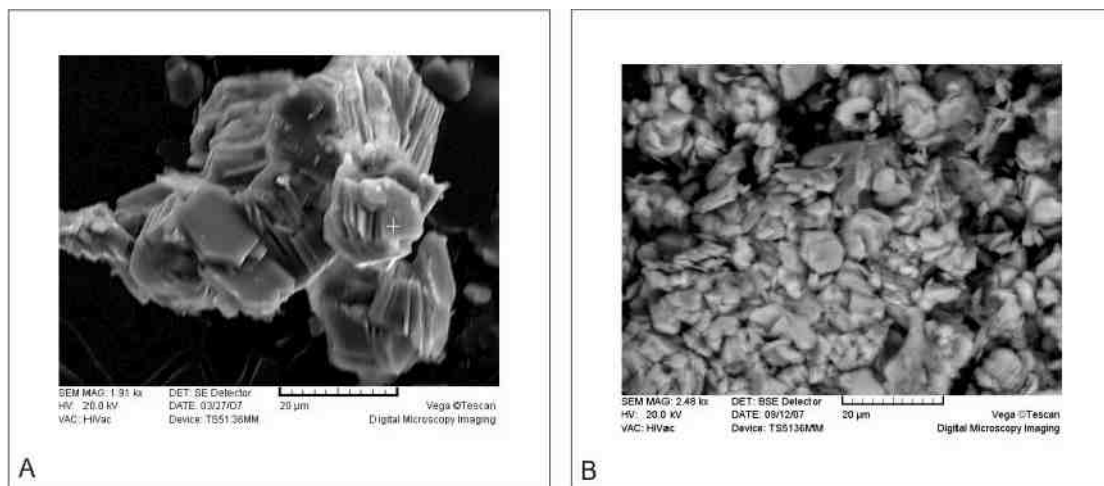


Figure 4. Scanning electron microphotographs supplemented by EDS spectra for a) classic book-like dickite packets composed of $5\text{-}15\text{ }\mu\text{m}$ wide minerals; b) pseudo-hexagonal kaolinite plates, 3 to $5\text{ }\mu\text{m}$ wide, slightly elongated in shape and associated in $5\text{-}15\text{ }\mu\text{m}$ thick packages.

KAOLINITE

The powder XRD pattern of kaolinite is plotted in Figure 3. Determined cell parameters of kaolinite are $a = 5.13(3) \text{ \AA}$, $b = 8.94(6) \text{ \AA}$, $c = 7.52(5) \text{ \AA}$, and $V = 335(3) \text{ \AA}^3$, while $\alpha = 93.2(7)^\circ$, $\beta = 103.5(7)^\circ$ and $\gamma = 90.1(7)^\circ$.

SEM microphotographs of kaolinite samples show a number of large pseudo-hexagonal plates, slightly elongated in shape. They frequently appear as 5-15 μm thick packages, with plates diameters varying from 3 to 5 μm . Partially, they formed rose-shaped aggregates (Fig. 4). Element analyses reveal no presence of impurities, while Al peak is almost equal in height to Si peak.

The unit cell of kaolinite is C centered, and according to Bish (1993) corresponds to C1 space group. It contains four OH-groups, therefore Raman spectra of well crystallized samples display four low-frequency bands. Raman spectra of kaolinite presented at Figure 5. According to the experimental study performed by Balan et al. (2005) within well ordered kaolinite samples this band is shifted to a slightly lower frequency. Two weaker bands at 3655 and 3669 cm^{-1} are attributed to the two out-of-phase stretching modes of the inner-surface OH groups. The bands within low-frequency region are in concordance with published data for kaolinite (Wiewora et al., 1979; Johnson et al., 1998).

Fluid inclusions microthermometry was performed on quartz wafers, from quartz-kaolinite-pyrite assemblage from the VI level. Primary two-phase inclusions are situated within quartz growth zones. Salinities vary between 4.6 and 5.1 wt% NaCl equ., and they all homogenized to the liquid state in temperature ranging from 210 to 250°C. Primary fluid inclusions assemblage is overprinted by the pseudosecondary inclusions, forming clusters that nearly reach the grain boundaries. These fluids contain bivalent cations and various amount of CO_2 beside H_2O , and are interpreted as a late stage fluids evolved via water-rock reactions (homogenization varies from 131 to 176°C, and salinities from 0.6 to 6.9 wt% NaCl equ.).

Due to deficiency of quartz, bulk leachate data are obtained on pyrite associated with kaolinite (Table 3). Applied alkali geothermometers suggest unreliable high temperature in the range from 360 (K-Na-Ca; Fournier and Truesdell, 1973) to 380°C (Na-K; Can, 2002).

Isochores were calculated using the computer program ISOC (Fig. 6; Bakker, 2003) from the equation of state by Zhang & Frantz (1987) and a correction for the volumetric properties of quartz.

Homogenization pressure is estimated in the range between 1.7 and 3.7 MPa.

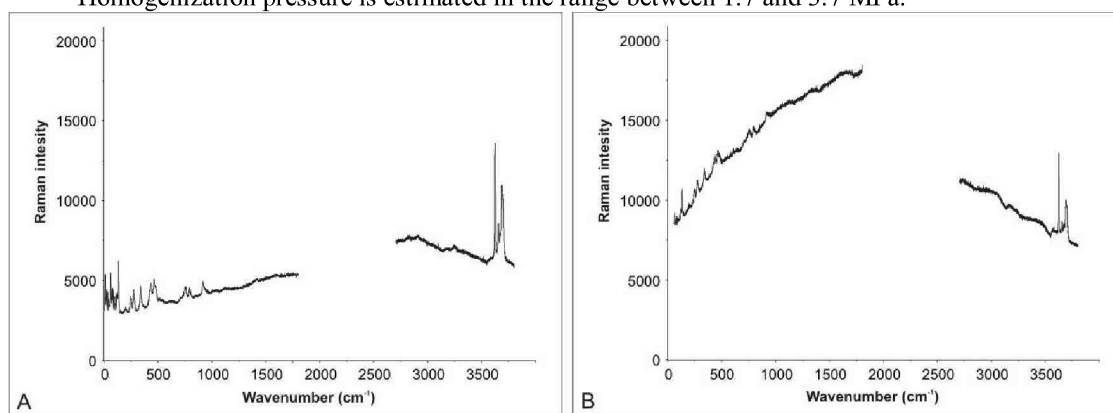


Figure 5. Raman spectra for low frequency and hydroxyl stretching region of a) dickite from the Trepca deposit; b) kaolinite from the Crnac deposit.

CONCLUSION

Combination of applied methods allows identification and distinction of dickite and kaolinite.

The first record of dickite in the Trepca deposit consists of the micrometer size crystals and is the only present kaolin phase. In the Trepca deposit dickite occurs mainly as vug-filling clusters within Fe-carbonate fragments of breccia. It is related to the pre-mineralization phase in the deposits. Dickite is precipitated from high temperature (290-330°C), moderate saline (6.0 and 8.5 wt.% NaCl equiv.) fluids under pressure between 12 and 60 MPa.

Investigated kaolinite is grown in the vein type mineralization of the Crnac deposit. Kaolinite occurs as milky-white irregular masses of vug-fillings and belongs to the paragenesis quartz-pyrite-kaolinite. According to fluid inclusion data kaolinite is precipitated at moderate temperature ($T_H = 210 - 250^\circ\text{C}$) and low pressure ($p_H = 1.7 - 3.7 \text{ MPa}$) from low saline fluid (4.6 - 5.1 wt% NaCl equ.).

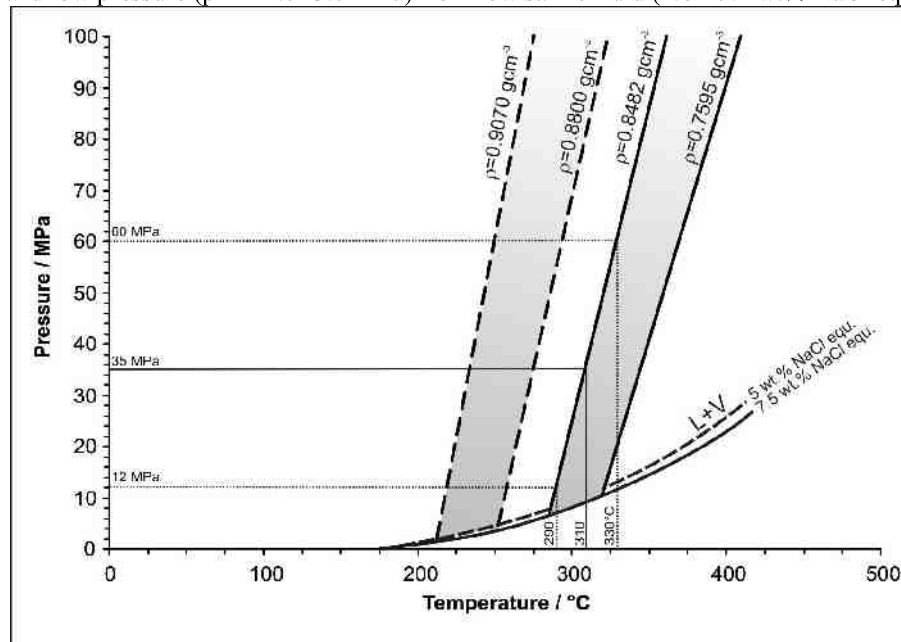


Figure 6. P-T diagram shows isochores constructed on basis of microthermometric data for fluid inclusions in the quartz associated with dickite from the Trepca deposit (solid lines) and with kaolinite from the Crnac deposit (dashed line). The trapping temperatures are calculated from Na/K, and K/Mg/Ca geothermometer equations applied on bulk leachate data obtained on quartz associated with dickite from the Trepca deposit.

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