

Geochemistry and electron spin resonance of hydrothermal dickite (Nowa Ruda, Lower Silesia, Poland): vanadium and chromium

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Abstract: Geochemical analyses for trace V and Cr have been done on a representative sample of a typical hydrothermal dickite/kaolinite filling vein at Nowa Ruda. The mineralogy of the sample is comparatively simple, dickite being the principal component (ca. 91 % of the total sample). Geochemical fractionation and inductively coupled plasma-optical emission spectrometry (ICP-OES) indicate that most (>90 % of total metal) of the V and Cr reside in the dickite. Electron Spin Resonance (ESR) shows that most (>70 %) of the V in the dickite structure is in the form of vanadyl (VO^{2+}) ions. A high concentration of Cr^{3+} is also detected in this structure by ESR. The combination of geochemical and spectroscopic tools applied to VO^{2+} and Cr^{3+} allow one to specify the Eh (>0.4 V, highly oxidizing) and pH (≤ 4.0 , highly acidic) of the solution during the formation of dickite from the Nowa Ruda Basin. Substantial proportions of the V and Cr (as well as VO^{2+} and Cr^{3+}) in the dickite structure were probably contained in an original hydrothermal acid water. We suggest that hot hydrothermal waters leached the surrounding varieties of gabbroids enriched in V and Cr for the dickite-forming solution. The results of this work have shown V and Cr are potentially reliable indicators for geochemical characterization of the physicochemical conditions of their formation. The bulk-rock V/Cr ratio in hydrothermal dickites and kaolinites from Nowa Ruda, Sonoma (California, USA), Cigar Lake (Saskatchewan, Canada) and Teslić (Bosnia and Hercegovina) is also briefly explored here as a potential tracer of redox state during their formation.

Key words: electron spin resonance, kaolinite, dickite, chromium, vanadium.

Introduction

The kaolinite group minerals include kaolinite, dickite, nacrite and halloysite. Acid alteration in magmatic hydrothermal systems is often represented by minerals such as kaolinite and dickite (Izquierdo et al. 2000, and references therein). Hydrothermal kaolinite and dickite are mainly formed in situ through alteration of source minerals (mainly K-rich feldspars and other aluminosilicates) by hydrothermal acid waters.

V and Cr are elements of significance in geochemical cycles as well as important trace elements in biochemistry. The oxidation states of V in the geosphere correspond to V^{3+} , V^{4+} and V^{5+} . V is present in natural waters, where redox conditions, pH, adsorption and complexation are the main controlling parameters of the solubility of this transition metal element. In oxygenated natural waters, V is predicted to occur in the +5 oxidation state, primarily as highly soluble and mobile vanadate ions: $\text{H}_n\text{VO}_4^{n-3}$ ($n=0$ to 4), and as NaHVO_4^- (Turner et al. 1981). As a consequence, the V species involved in incorporation processes appear anionic, resulting in a relatively low affinity for the negatively charged colloidal clay particles (Whitfield & Turner 1987).

Vanadyl ion (VO^{2+}) shows a strong tendency to interact with the surface of Al and other metal hydrous oxides and is

thus capable of becoming specifically bound within the colloidal clay particles (Wehrli & Stumm 1989).

Geochemical studies indicate that Cr occurs in natural aquatic environments in two oxidation states: Cr(III) and Cr(VI). In low (suboxic/anoxic) Eh natural environments, the main aqueous Cr(III) species are Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$. Under oxidizing conditions, aqueous Cr is present in a Cr(VI) anionic form, HCrO_4^- and/or CrO_4^{2-} , depending on the pH. Cationic Cr(III) species are rapidly and strongly adsorbed by colloidal clay particles, but adsorption of anionic Cr(VI) species onto these particles is expected to be minimal (Rai et al. 1986, 1987).

Physicochemical conditions during the formation of a non-hydrothermal kaolinite are usually deduced from field data as well as experimental/thermodynamic data. The stability of this mineral is often expressed in plots using pH and ion activities. The hydrothermal kaolinites/dickites are not frequently studied and our knowledge of the physicochemical conditions necessary for their formation is still limited. One way to get an objective evaluation of the nature of solutions during the formation (precipitation) of kaolinites/dickites is to examine components that were undoubtedly introduced into their lattice by these solutions. Such components certainly include VO^{2+} and Cr^{3+} ions.

Indeed, VO^{2+} and Cr^{3+} in natural aquatic environments are characterized almost entirely by the pH and oxidation reduc-

tion potential (Eh) of the environment. These two parameters also have a strong influence on the mobility and complexation of VO^{2+} and Cr^{3+} ions. These two ions, therefore, are sensitive geochemical indicators of the geochemistry of the clay-forming solutions and may provide clues to the origin of the clay deposits of the past. This has led us to study VO^{2+} and Cr^{3+} in dickite from Nowa Ruda (NR), a hydrothermal mineral enriched in V and Cr (Morawiecki 1956). After a mineral characterization of the sample using X-ray diffraction, Fourier transform infrared spectroscopy, differential thermal analysis, and scanning electron microscopy, selective leaching procedures were performed to establish specific mineral hosts for V and Cr by inductively coupled plasma-optical emission spectrometry (ICP-OES). To support the speciation study, we quantitatively determined the VO^{2+} concentration in dickite using a new experimental calibration with a principle derived from a previous study of clays (Premović et al. 2011).

Experimental

Geological setting

The Nowa Ruda Basin is located in the Sudetes Mountains (southwestern Poland), near the city of Wrocław (Fig. 1). The geology and mineralogy of this basin were extensively studied by Morawiecki (1956), Kowalski & Lipiarski (1973), and Borkowska (1985). The gabbro-diabasic massif of the Nowa Ruda Basin, which spreads over 15 km², is composed of rocks of probable Proterozoic age (Oberc 1960) and is represented by olivine gabbros, olivine-free gabbros with diorite, troctolites and plagioclases. Most of these rocks reveal postmagmatic alteration. The upper part of the gabbroic rocks is weathered.

The regolith covering the gabbroic rocks, composed mainly of bauxites, argillites, and gabbros, breccias and conglomerates, is of Carboniferous age (Wiewióra 1967). These formations are overlain by a thick series of shales of Westphalian A age, which are followed by sandstones and carbon-bearing kaolinitic shale of the Upper Carboniferous formation. The Upper Carboniferous is represented by carbon-free sandstones and conglomerates and is overlain by the clastic formation of Rotliegendes. Quaternary clays, gravels and sands represent the youngest rocks. The general stratigraphic succession of the Nowa Ruda Basin is shown in Fig. 2.

Dickite/kaolinite occurs mainly as veins within the gabbro weathering products, or is associated with the dark grey kaolinitic shale. The mineral is usually light green or bluish-green (Fig. 3). Apart from these veins, kaolinite at the Nowa Ruda location also occurs in the form of large lenses. According to Kowalski & Lipiarski (1973) kaolinite and dickite from the Nowa Ruda Basin may have originated in the hydrothermal solutions genetically related to the magmatism of the Late Carboniferous.

Sample location and description

Kaolinite and dickite are found throughout the abandoned coal mine Piast near the town of Nowa Ruda. These minerals



Fig. 1. Geographical location of Nowa Ruda.

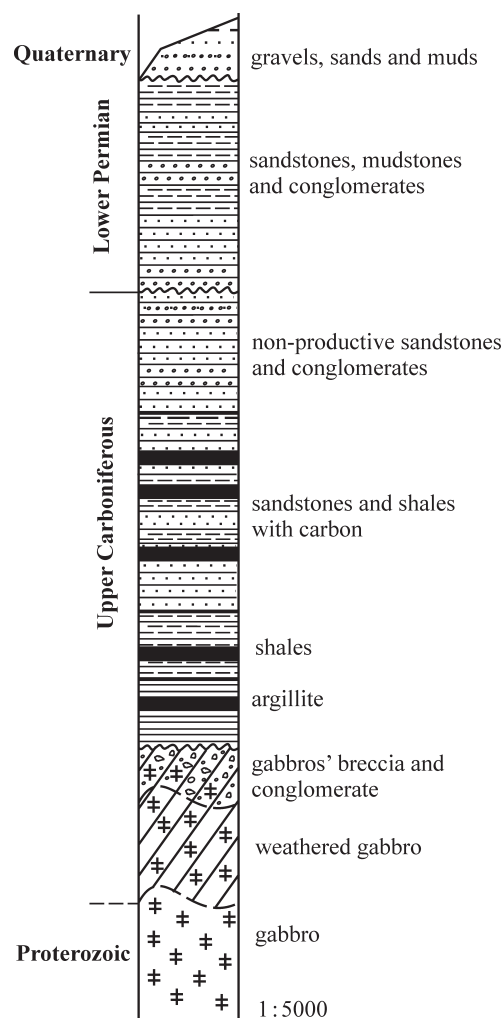


Fig. 2. General stratigraphic section of the NR region, modified after Morawiecki (1956) and detailed Geological Map of Sudetes Mts, 1:25,000, sheet Nowa Ruda, (Wójcik 1956) and sheet Jugów, (Gawróński 1958).

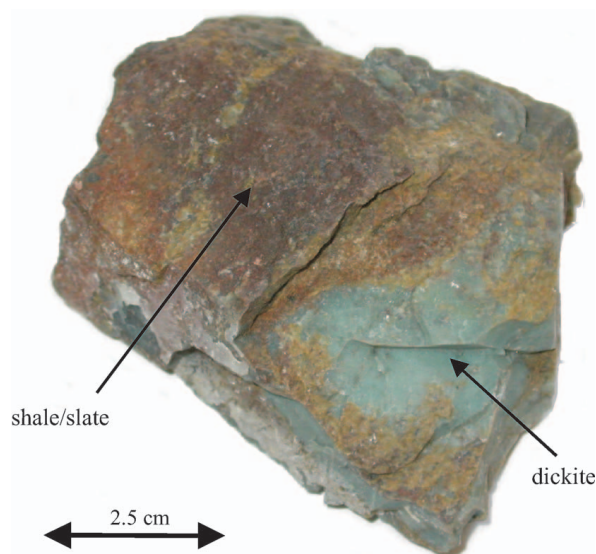


Fig. 3. Example of blue dickite filling the veins within black shales/slates from the dump of the abandoned coal mine Piast. Sample size: 7×10 cm.

are generally believed to be the most common product of a hydrothermal alteration (Morawiecki 1956). A representative blue dickite sample (hereafter DS) was collected by L. Stoch in a vein of kaolinitic shale at the Piast mine. Nine samples of dickite from Nowa Ruda were also collected by J.C.

Analytical methods

ICP-OES Spectrometry. V and Cr of the whole-rock sample and leaching fractions were analysed by ICP-OES. A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas. Total uncertainty (including accuracy error) of the analysis ranges from 5 % to 20 % for V and Cr.

For purpose of Cr(VI) detection, DS was digested using 0.28 M Na_2CO_3 /0.5 M NaOH solution heated at 90–95 °C for 1 h to dissolve Cr^{6+} and stabilize it against reduction to Cr^{3+} . Subsequently, Cr(VI) could be identified colorimetrically at 540 nm with diphenylcarbazide in acid (pH 2) solution (Bartlett & James 1979); ≤ 1 ppm can be detected. However, no Cr(VI) could be identified in DS using this method.

X-ray Diffraction (XRD) Analysis. XRD patterns were obtained with the Philips PW 1729 and 3710 diffractometers using $\text{CoK}\alpha$ radiation (35 and 45 kV, 30 mA). Powder diffractograms were acquired in the 3–90° 2θ range, with 7–20 s counting per 0.01° and 0.04° 2θ step. Samples were prepared using the back-loading procedure according to Moore & Reynolds (1989), providing significant disorientation of clay layers.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra were recorded, in absorbance mode, with a BOMEM Michelson Series MB FTIR spectrometer. The resolution was 4 cm^{-1} in the 400–4000 cm^{-1} analysed range. Spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of a clay sample with 150 mg of KBr.

Differential Thermal Analysis (DTA). The DTA curve was obtained from 20 mg sample in a Pt crucible on a Perkin-Elmer 7 Series Thermal Analysis System heated at 10 °C min^{-1} .

Scanning Electron Microscope (SEM). The morphology and the semiquantitative chemical analyses were performed by scanning electron microscopy (scanning microscope Philips XL 30 ESEM/TMP) coupled to an energy-dispersive spectrometer (EDAX type Sapphire). The backscattered electron (BSE) mode was done before microprobing. Analytical conditions were as follows: accelerating voltage 15 or 20 kV, probe current 60 nA, working distance ca. 10 mm, counting time 100 s. Individual parameters are printed on photos: acceleration of electron beam and magnification. Samples were coated with gold and stuck to a carbon tape.

Electron Spin Resonance (ESR) Spectroscopy. The ESR measurements were performed on fine powder samples that were transferred to an ESR quartz tube. The ESR spectra were recorded at room temperature using a Bruker ESP 300E spectrometer at X-band bridges with a standard 100 kHz field modulation. The measurements were made at 9.3 GHz utilizing a rectangular TE cavity.

In order to accomplish maximum accuracy and precision it was necessary to focus attention on the following: a sample tube was always kept inside the ESR cavity with an approximate magnetic field uniformity; and the reproducibility of the sample positioning was achieved by using the same sample tube with a fixed holder. Tests verified that all spectra for the standard measurements were obtained with instrumental parameters which gave no instrumental effects on peak height/shape/width. Most of the measurements were run at 2 mT modulation amplitude, 100 ms time constant, 16 min scan time. The field was scanned on 200 mT when the entire spectrum was desired. The instrument was carefully tuned according to the manufacturer's directions.

Analysis and fractionation

The fractionation procedure was similar to that used by Premović (1984). The flow chart in Fig. 4 outlines the major steps in preparing the four fractions. These are:

Powdered dickite (1 g) was treated (room temperature, 12 h) with acetate buffer: acetic acid/sodium acetate (1 M, 12 h) solution at pH 5.0 to remove most of the carbonates. This solution also removes other soluble minerals. The soluble material constitutes the carbonate fraction.

The insoluble residue (I) was demineralized further by repeated treatment with cold HCl (6 M). This acid solution removes mostly metal hydroxides and oxides, including V- and Cr-hydroxides and -oxides. The soluble part constitutes the cold HCl-fraction.

The insoluble residue (II) was demineralized with boiling HCl (6 M, 80 °C, 12 h). This treatment removes most of the soluble silicates. The soluble part constitutes the boiling HCl-fraction.

The insoluble residue (III) was demineralized with boiling mixture of HF (22 M)/HCl (12 M) (3:1 v/v, 80 °C, 12 h). This acid mixture removes SiO_2 and Al_2O_3 . SiO_2 and Al_2O_3 removal was checked by FTIR/EDS analyses. The soluble part constitutes the dickite fraction.

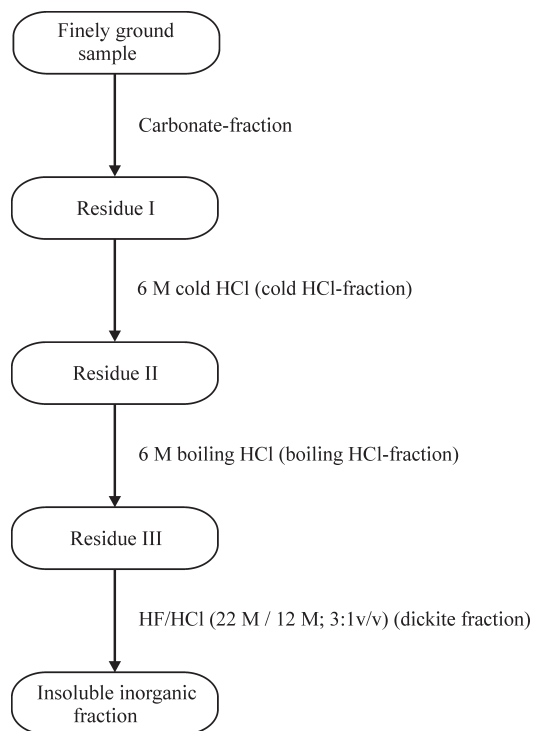


Fig. 4. Flow chart of fractionation procedure.

The final residue from (III) is the acid insoluble fraction.

Results

Chemical and ICP-OES analyses

The acetate buffer/HCl demineralizing steps remove only 7 % of DS. This is due to the total dissolution of carbonates and other soluble minerals [acetate buffer: 3 %], the dissolution of metal hydroxides and oxides (e.g. V- and Cr-hydroxides and -oxides) [cold-HCl: 1 %] and the destruction of some silicate minerals [boiling HCl: 3 %] (Table 1). SiO_2 and Al_2O_3 , the dominant constituents of dickite, seem to be unaffected by these demineralization steps. The leaching experiment indicates that more than 97 % of the dickite fraction is removed by the HF/HCl step, Table 1.

Table 1 shows the distributions of V and Cr among the four components of DS. These results show that the HF/HCl fraction contains >98 % and <97 % of the total V (175 ppm) and

Table 1: Geochemical distributions of V [ppm] and Cr [ppm] from selective leaching experiments of DS from Nowa Ruda.

Fraction	Sediment (± 5 wt. %)	V	Cr
Acetate buffer	3	35	35
Cold-HCl	1	70	190
Boiling-HCl	3	40	340
Dickite*	91	190**	435
Insoluble residue	2	–	–
Total sample	100	175	410

*V/Cr = 0.4. ** VO^{2+} concentration: 160 ± 20 ppm.

Cr (410 ppm), respectively, indicating that the bulk of V and Cr reside primarily within the dickite structure. In addition, acetate buffer/cold-HCl leaching removed less than 1% of total V and Cr. This result indicates that a negligible amount of V and Cr is in the form of hydroxides and/or oxides that can be specifically adsorbed on the colloidal clay particles or precipitated (Evans 1978).

XRD analyses

Indicative peaks for distinction between dickite and kaolinite lie in the range of angles 2θ 43° – 47° , where dickite generates two main peaks: 2.387 Å and 2.324 Å of intensity 50 and 90, respectively (Joint Committee on Powder Diffraction Standards (JCPDS) 10–430) whereas kaolinite gives three peaks: 2.386 Å (intensity $I=25$), 2.338 Å ($I=40$) and 2.293 Å ($I=35$) (JCPDS 14–164). We performed XRD analyses for nine representative samples of dickite from Nowa Ruda to check which mineral of the kaolinite group is dominant. In most of these samples XRD patterns show the predominant presence of dickite (Fig. 5A) which confirms the results of Morawiecki (1956). Only a few of them show a minor presence of kaolinite-1Tc (Fig. 5B). In almost all the investigated samples traces of talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] were noticed.

FTIR analyses

An accurate distinction between kaolinite and dickite can be achieved by using FTIR, assessing the position and relative intensities of the OH-stretching bands in the 3600 – 3700 cm^{-1} region (Russel 1987). The FTIR spectrum of DS is shown in Fig. 6 and is characteristic of dickite. Dickite shows strong absorption at 3621 cm^{-1} and two medium-strong absorption bands at 3704 and 3654 cm^{-1} , whereas absorption bands for kaolinite are at 3697 , 3620 , 3669 and 3652 cm^{-1} . FTIR analysis also showed that dickite is the only kaolinite mineral present in DS, confirming the XRD analysis. Our XRD and FTIR data for DS are in a good agreement with a previous spectroscopic study of DS by Balan et al. (2002).

Differential thermal analysis (DTA)

The DTA curve of DS presents a dehydroxylation peak at ca. 670 $^\circ\text{C}$ and an exothermic peak at about 1000 $^\circ\text{C}$, Fig. 7. This is in agreement with a typical curve of dickite (Mackenzie 1970). However, the position of the dehydroxylation peak towards the high-temperature limit (dehydroxylation peak generally found in the region 500 – 700 $^\circ\text{C}$), as well its sharpness, are in accord with a well-ordered dickite structure (Bish & Duffy 1990).

SEM/EDS analyses

Under the SEM, green or bluish-green DS from Nowa Ruda have the morphology of well-formed, uniform vermicular aggregates of large (≤ 10 μm) blocky dickite crystals (Fig. 8A,B). EDS analyses show that these crystals mainly consist of O, Al and Si (Fig. 8C); minor K, Fe and Ti were also detected. This elemental composition is indicative of

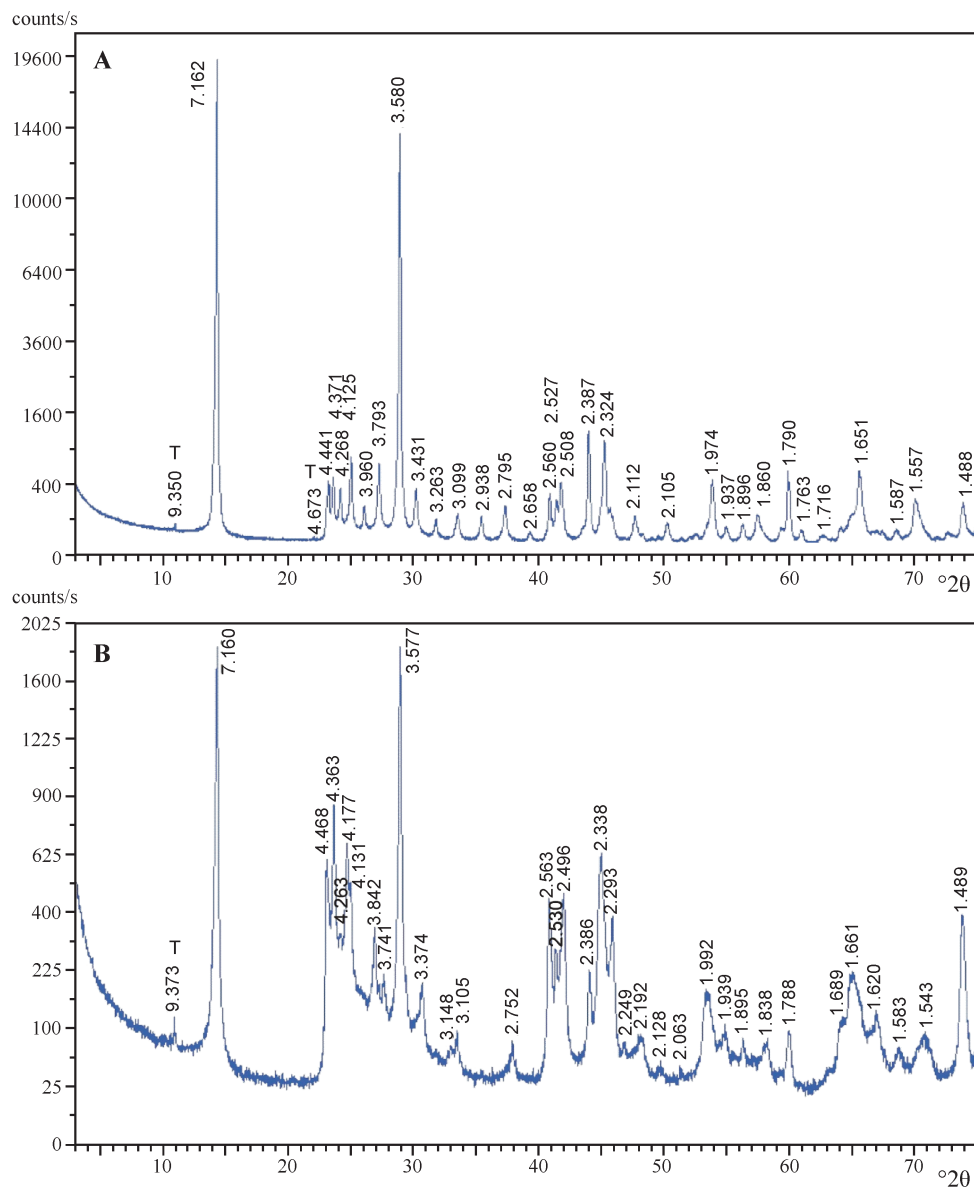


Fig. 5. XRD patterns of dickite (A) and kaolinite-1Tc (B) from Nowa Ruda. T — traces of talc.

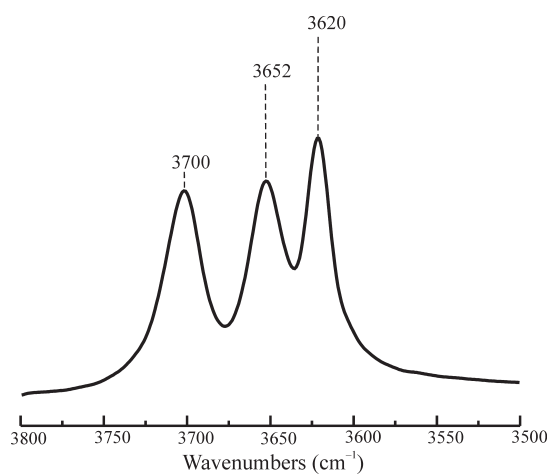


Fig. 6. FTIR spectra in the OH stretching vibrations zone of dickite.

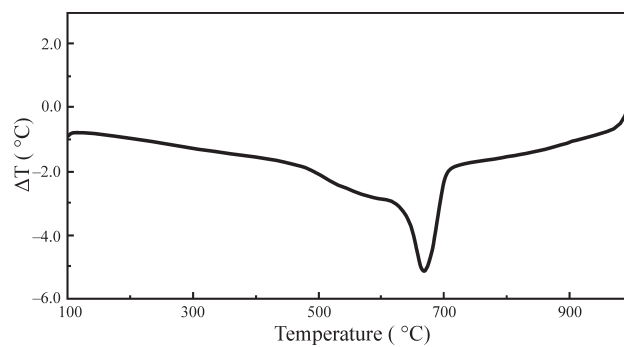


Fig. 7. DTA curve of DS.

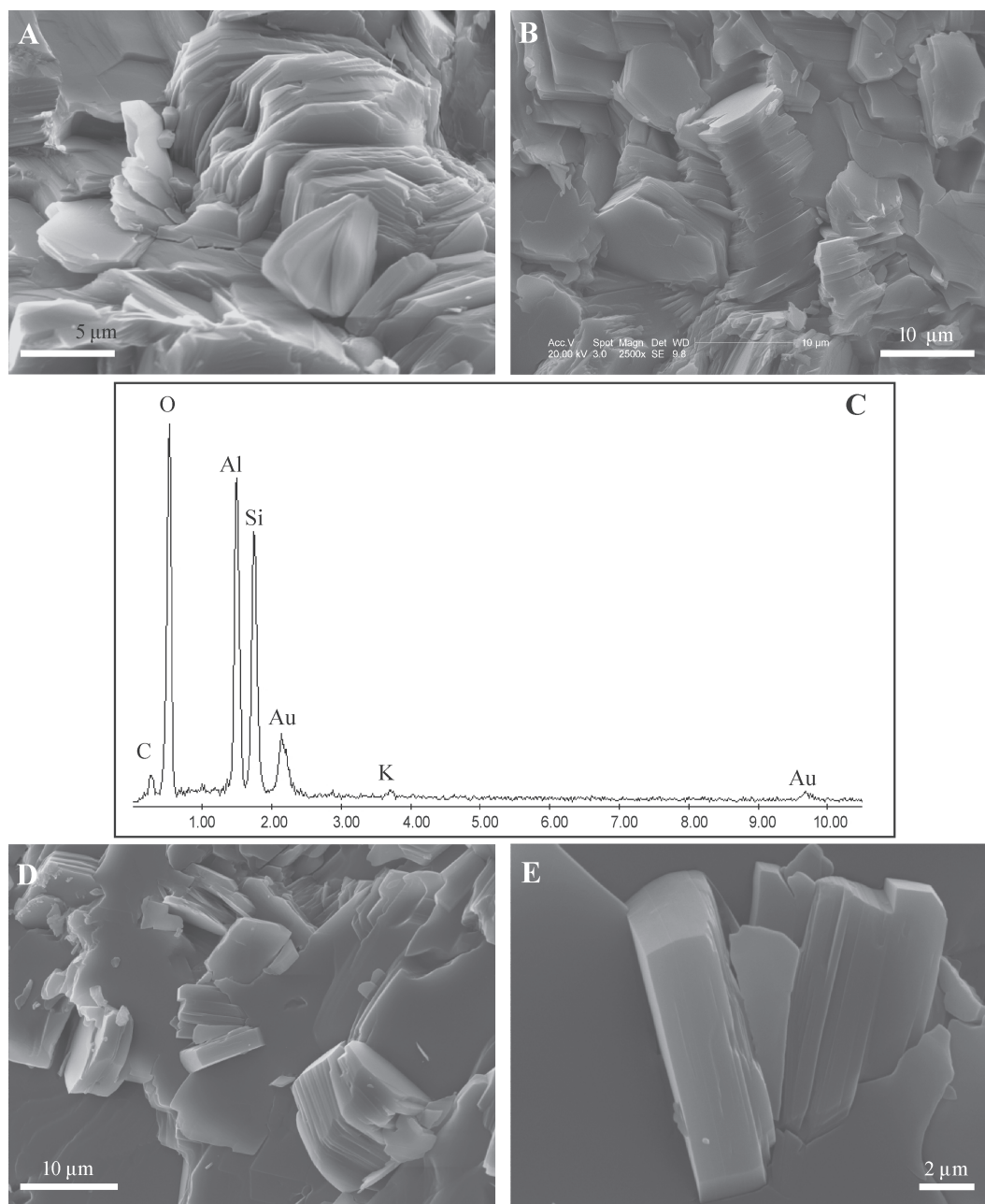


Fig. 8. SEM view of the crystals of the kaolinite group of minerals from Nowa Ruda: vermicular dickite flakes (A, B); EDS spectrum of dickite (C); and, well-shaped kaolinite crystals (D, E). SEM Photos by Ewa Teper & Justyna Ciesielczuk.

minerals of the kaolinite group. Fig. 8D,E also shows well-shaped kaolinite crystals.

ESR analyses of VO^{2+}

Two main sets of transitions can be distinguished in a high magnetic field in the total ESR spectrum of untreated DS, around 3400 G and in a low magnetic field around 1500 G, corresponding to VO^{2+} and Cr^{3+} , respectively (Balan et al. 2002). In high magnetic fields, the untreated DS shows a multiline spectrum (Fig. 9A) similar to the spectrum of VO^{2+} ions incorporated into the lattices of some kaolinites (Premović

1984; Muller & Calas 1993). The spectrum shows an anisotropic spectrum signal pattern typical of an axially symmetrical hyperfine coupling.

The ESR method employed to quantify VO^{2+} as previously described by (Premović et al. 2011) is given by the following equation:

$$[C_c] = (S_c/S_{st}) [C_{st}]$$

where C is the concentration of VO^{2+} , c indicates the clay sample and st indicates the standard. S is the specific signal intensity (the integrated area under the corresponding ESR absorption per g of the sample).

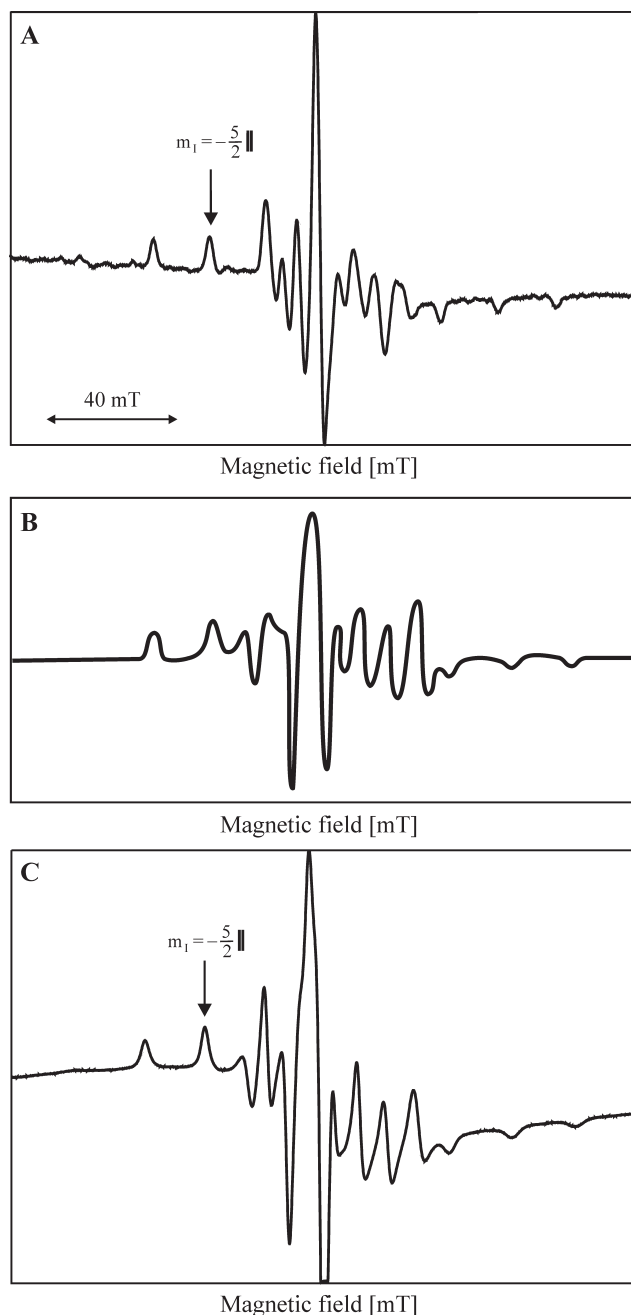


Fig. 9. First derivative, room temperature, anisotropic VO^{2+} ESR spectrum of: untreated DS (A); an initial glycerol solution containing 8000 ppm of VO^{2+} (B); and, a standard containing 400 ppm of VO^{2+} in the KGa-2/glycerol mixture (C).

A glycerol solution was prepared by first dissolving known amounts of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ in a solution containing 1.5 ml of concentrated H_2SO_4 + 0.5 ml of deionized H_2O and then diluting it with glycerol to the desired VO^{2+} concentration (8000 ppm) with thorough agitation. Changes in the loading Q-factor of the ESR cavity can result in samples with different dielectric properties. The above glycerol solution has a high dielectric constant (about 56 D) and cannot be used as a reliable comparison of relative VO^{2+} concentrations of clays. For this reason, standards were prepared by mixing/diluting small

amounts of the glycerol solution with kaolinite to the desired VO^{2+} concentrations. Preparing this mixture has the effect of maintaining the dielectric medium of standards close to the clay samples, keeping the Q similar. The standards prepared in this way covered the range of 50 to 400 ppm of VO^{2+} . The kaolinite used in these standards was KGa-2 (Georgia, USA), which contains very low amounts of VO^{2+} (<5 ppm).

Figure 9 also illustrates the anisotropic ESR spectrum of: (B) an initial solution of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ compound dissolved in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ and diluted with glycerol and (C) a standard containing 400 ppm of VO^{2+} . These spectra are typical of those previously reported for VO^{2+} in either powder (polycrystalline) solids or extremely highly-viscous liquids (Goodman & Raynor 1970).

Only one line of the VO^{2+} anisotropic hyperfine pattern is considered for obtaining the integrated area. Consequently, just a narrow part of the VO^{2+} spectrum needs to be recorded. For this purpose, we select the first derivative ^{51}V hyperfine line marked with $m_l = -5/2 \parallel$ in the spectra of DS (Fig. 9A) and the standard (Fig. 9C). This line was chosen in order to keep the linewidth and lineshape similar and to minimize interferences from both neighbouring VO^{2+} resonance lines and the lines of other ESR active species present. In addition, from our continuing study of VO^{2+} in various clay materials, we have found that the anisotropy of the ESR parameters of VO^{2+} in various clays has little or no effect on linewidth and lineshape of the $-5/2 \parallel$ line. The area under the $-5/2 \parallel$ line was evaluated taking into account baseline corrections, multiplying or dividing it by factors required to put the areas of the $-5/2 \parallel$ line of both the standards and DS on the same setting. A study of the intensity and width of the $-5/2 \parallel$ line of both the standards and the DS versus the square root of microwave power showed no saturation. Consequently, a high power of 100 mW was selected for measurement, ensuring a high absolute intensity of the $-5/2 \parallel$ line.

We computed the integrated area of the $-5/2 \parallel$ line for five standard samples containing 400 ppm of VO^{2+} prepared on five different days. Repeatability of results was generally very good, usually better than $\pm 5 \%$.

Although the DS was not collected from freshly exposed mine faces, repeated ESR analyses over the course of several months showed no change in its VO^{2+} content. Similar experiments on the VO^{2+} standards showed that after several weeks no oxidation had occurred. After six weeks of exposure to air the VO^{2+} concentration was virtually unchanged from its initial value.

If the specific intensities of the $-5/2 \parallel$ lines of the standards are simply plotted against the VO^{2+} concentration a linear calibration curve is obtained. Fig. 10 shows this plot in the 50–400 ppm range. Using this plot as the calibration curve, DS was recorded for the VO^{2+} spectrum and the specific intensity of the $-5/2 \parallel$ line was determined to obtain the concentration of VO^{2+} . The vanadyl concentration obtained for DS is 160 ± 20 ppm, corresponding to more than 70 % total V (Table 1).

The demineralizing steps with the acetate buffer/HCl do not affect the concentrations of the VO^{2+} ions in DS. However, the VO^{2+} ions disappear (checked by ESR), completely during HCl/HF demineralization. Therefore it is reasonable to assume

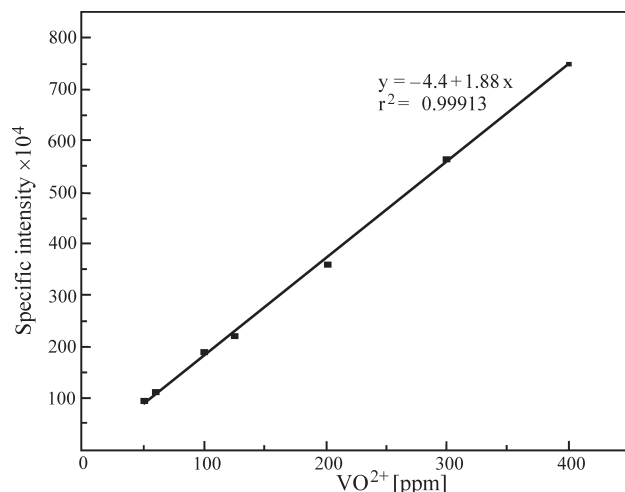


Fig. 10. The glycerol/KGa-2 mixture as a standard for the VO²⁺ concentrations range from 50 to 400 ppm.

that these ions are incorporated into the dickite structure. Indeed, a negligible contribution of dipolar magnetic broadening arising from interactions between VO²⁺ and the neighbouring VO²⁺ and/or other V ions (as expected from the low V content of dickite, Table I) is consistent with this notion. The lack of change of the ESR signals attributed to VO²⁺, even upon prolonged (10 h) laboratory heating of the dickite at 500 K and in the presence of air, indicates that this ion is strongly bound to the dickite structure.

ESR analyses of Cr³⁺

The representative ESR spectra of Cr³⁺ within the dickite lattice are shown in Fig. 11 in low (A) and high (B) magnetic fields. According to Balan et al. (2002), these ESR spectra can be attributed to the isolated Cr³⁺ ions in the diamagnetic matrix of the dickite structure. These authors showed that Cr³⁺ substitutes for Al³⁺ in the octahedral sheet.

In the present study, we show that like VO²⁺, Cr³⁺ is completely removed by HCl/HF demineralization. The corresponding concentration of Cr is 435 ppm. This confirms that Cr³⁺ (like VO²⁺) ions are located within the dickite structure of DS and are probably present in significant amounts. To quantify Cr³⁺ employing a similar method to that described above would create almost insurmountable experimental problems.

Discussion

Gabbros as a source of V and Cr in NR dickite

As mentioned earlier, the hydrothermal kaolinite and dickite of the Nowa Ruda Basin are probably related to magmatism of the Late Carboniferous period. Kraynov & Ryzhenko (1992), who made a thorough study of Eh/pH in many geochemical water types, reported that the acidity of the hydrothermal waters (in areas of contemporary magmatism) is within the pH range of ca. 0–4 and that the Eh values vary from 0.4–0.8 V. The field of these waters is marked in Fig. 12 as shaded.

Geochemical data suggest that the geological conditions under which dickite formed must have been relatively rich in V and Cr (i.e. VO²⁺ and Cr³⁺), and they were introduced into dickite during formation aided by an invasive hydrothermal water. The fact that >95 % of V and Cr (Table I) resides within the dickite structure indicates that most V and Cr in dickite-forming solution was in a dissolved form. We suggest that most of these two metals were introduced into dickite by this solution already enriched in V and Cr.

An extensive geochemical study of the gabbro massifs in Nowa Ruda Basin was carried out by Białowolska (1973). According to this author, V in gabbroic rocks of the basin occurs mainly in disseminated form replacing iron and is mostly concentrated in pyroxenes (300 ppm) but it is much less abundant in olivines (10 ppm). Among the Nowa Ruda gabbros, the highest Cr content of 635 ppm is concentrated in the olivine type. Diabase gabbros and troctolites contain about 300 ppm of Cr. Chromium occurs in disseminated form, replacing the trivalent iron in minerals according to diadochy. It also forms its own minerals, namely chromite and Cr-spinel associated with serpentinized pyroxenes. For this reason, we propose that hot hydrothermal waters leached the surrounding gabbros, providing V and Cr for mineralizing solutions.

Initial hydrothermal waters were probably mixed with groundwaters in the Nowa Ruda Basin, and this probably significantly decreased the concentrations of V and Cr. We believe that the final contents of V and Cr in dickite-forming

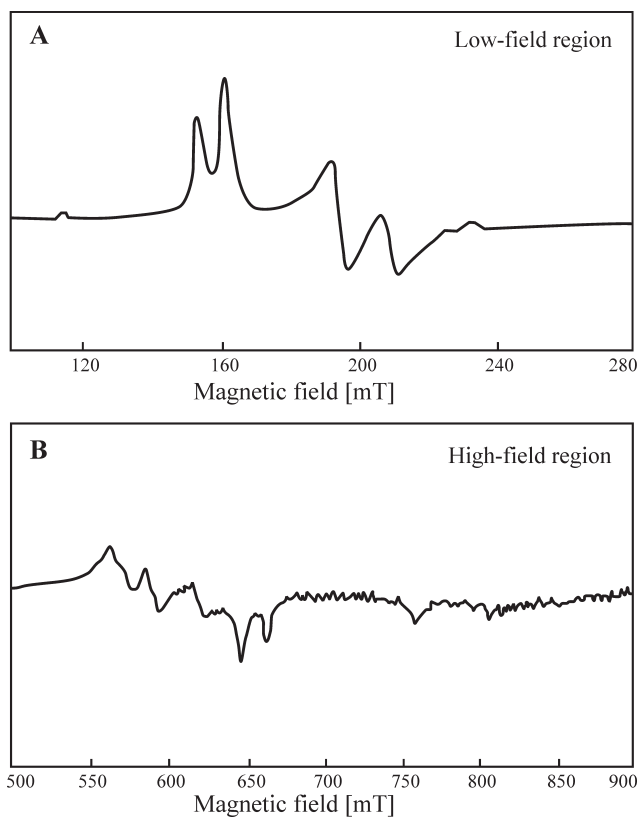


Fig. 11. First derivative, room temperature, anisotropic ESR spectrum of Cr³⁺ of untreated DS: in low magnetic field region (A); and high magnetic field region (B).

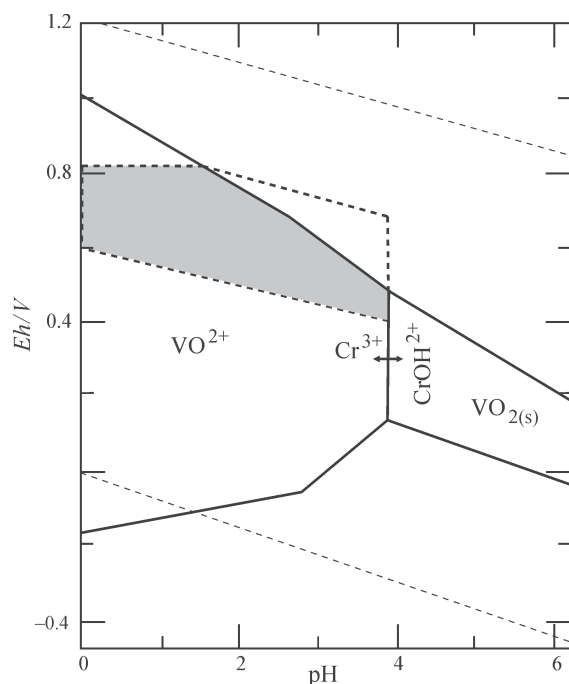


Fig. 12. Eh-pH diagram for VO_2^+ and Cr^{3+} at 300 K and 1 atm for formation of dickite. The assumed total V concentration is 5 ppm. The shaded area represents Eh/pH region of the hydrothermal waters defined by Kraynov & Ryzhenko (1992). Probable physicochemical conditions of dickite are represented by the hatched area.

solution depended less on their initial values than on the degree of subsequent mixing of these two waters.

Morawiecki (1956) carried out geochemical analyses of two samples of almost pure dickite and one sample of nearly pure kaolinite from NR veins. The dickite samples (on a whole-rock basis) contained V (55 and 80 ppm) but Cr (250 ppm) was found only in one of these minerals. Such Cr discordance can only be explained in terms of the difference between the dickite-forming solutions. The fact that NR kaolinite studied by Morawiecki (1956) contained high V (430 ppm) but not Cr is in line with this interpretation. The variability in V and Cr concentrations associated with kaolinite and dickite in the Nowa Ruda Basin probably represents a difference in dissolved V and Cr in their precipitating solutions as they were a mixture of the original hydrothermal fluid and groundwater at that time.

Conditions of formation of dickite: Eh-pH diagrams

Turekian & Wedepohl (1961) quoted the average contents of V (130 ppm) and Cr (90 ppm) of ordinary (non-hydrothermal) clays. Compared with these clays, DS (see Table 1) is only slightly enriched in V and moderately (4.5 times) enriched in Cr.

As mentioned above, most V and Cr in the dickite-forming solution of DS were in a dissolved form. We assumed that the concentration of V in this solution was about 5 ppm. This assumption is based upon a content of about 5 times the V concentrations typical of natural waters, which means generally less than 1.2 ppm (Wanty & Goldhaber 1992, and references therein).

In the case of Cr, a geochemical calculation suggests that all Cr would be in dissolved form if the total concentrations of Cr in the aquatic system at 26.85 °C are lower than 7.5 ppm (Richard & Bourg 1991). Taking into account that the Cr in DS probably occurs in the form of metal hydroxides and/or oxides, Cr concentrations in dickite-forming solution of DS were probably >7.5 ppm (i.e. $>1.5 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$); for comparison, the concentrations of dissolved Cr typical of natural waters are <1 ppb (Richard & Bourg 1991).

We have constructed the stability field of VO_2^+ and Cr^{3+} assuming a total V concentration of 5 ppm in aqueous solution (Fig. 12) using the FactSage thermochemical software/Fact compound databases. For the sake of simplicity, we present only a part of the diagram. The critical boundary between the stability fields of VO_2^+ and Cr^{3+} is not significantly affected by modifying this value 10-fold in either direction.

The Eh-pH diagram in Fig. 12 is not an accurate representation of the hydrothermal solution when dickite is formed, and it is undoubtedly highly variable in its approach to the ideal. However, because it represents a quantitative estimate based on the available thermodynamic data, it should be a helpful tool, if used within its limitations.

Figure 12 only shows the domains of VO_2^+ and the solubility for crystalline VO_2 or V_2O_4 . We note that the (hydrous) $\text{V}(\text{OH})_2$ is probably more soluble than its anhydrous counterpart. It is apparent from this figure that the VO_2^+ ion is stable thermodynamically under oxidizing conditions ($E_h \geq 0.0\text{V}$) only at low pH (≤ 4). Thus, the presence of a relatively high concentration of VO_2^+ in the dickite of DS indicates that the oxalic dickite-forming solution was probably highly acidic ($\text{pH} \leq 4$).

The VO_2^+ stability field of the diagram is confined by superimposing the Eh-pH field for Cr^{3+} for the physicochemical conditions of dickite-forming solution (Fig. 12). It is apparent from this figure that for coexistence of VO_2^+ and Cr^{3+} during formation of dickite, the Eh values should be $>0.4\text{V}$ (highly oxidizing) and $\text{pH} \leq 4.0$. The VO_2^+ - Cr^{3+} domain is very close to the Eh-pH domain corresponding to modern hydrothermal waters in areas of contemporary magmatism, which are within the pH range of ca. 0–4 and Eh values of 0.4–0.8 V (Kraynov & Ryzhenko 1992).

In much of the area of interest, the dominant dissolved species is Cr^{3+} , except above pH 4, where hydroxide complex, CrOH^{2+} , is a major form. A solubility of about 7.5 ppm ($>1.5 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$) for Cr could only be attained if the solid Cr species in dickite-forming solution was amorphous $\text{Cr}(\text{OH})_3$. The anhydrous crystalline species of Cr_2O_3 is much less soluble below about 1 ppb ($10^{-8} \text{ mol} \cdot \text{l}^{-1}$). Moreover, the absence of Cr(VI) in DS implies that the Cr(III) species were only present during the formation of dickite of Nowa Ruda. Therefore, the solubility of $\text{Cr}(\text{OH})_3$ is probably more realistic for this solution.

Under the deduced oxidizing ($E_h > 0.0\text{V}$) and highly acidic ($\text{pH} \leq 4$) conditions, the bulk of the Cr in the dickite-forming solution should be present as Cr^{3+} ions, with much smaller amounts of CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$. Indeed, chemical studies indicate that the Cr^{3+} ion is prevalent only at a pH lower than 3.5 and the solubility of Cr^{3+} in an aqueous solution decreases as the solution pH rises above pH 4, with essentially complete

precipitation as $\text{Cr}(\text{OH})_3$ occurring at about pH 5.5 (Richard & Bourg 1991, and references therein). Moreover, according to reported hydrolysis constants (Rai et al. 1987), Cr^{3+} is strongly hydrolysed in aqueous solutions and the predominant species in the pH range 6.5–10.5 is $\text{Cr}(\text{OH})_3$. Thus, the dissolution of Cr(III) minerals could only occur in natural acid waters with pH < 5, giving low, equilibrium controlled, concentrations of Cr(VI) anions. For this reason, soluble Cr^{3+} is usually restricted to hydrothermal acid waters (DeLaune et al. 1998).

The V/Cr ratio has been used as a paleoenvironmental indicator of sedimentary conditions (Jones & Manning 1994, and references therein). Values of $\text{V/Cr} \geq 4$ are thought to represent suboxic/anoxic conditions. Values of $\text{V/Cr} \leq 4$ indicate slightly oxidizing (dysoxic) conditions, with the corresponding ratio values ≤ 2 suggesting oxic conditions within the deposit. The V/Cr ratio of dickite is ca. 0.4 (Table 1), indicating that this mineral formed in an oxidizing environment. Note that one of the NR dickite samples analysed by Morawiecki (1956) has a V/Cr ratio of 0.2.

The abundant association of goethite with NR dickite (Komusinski et al. 1981) is consistent with its formation occurring under oxidizing conditions as goethite occurs only in a natural aqueous milieu under oxidizing conditions with Eh above 0.15 V (Krumbein & Garrels 1952). In relation to this dickite, it should be noted that: (a) goethite is ultimately the most stable mineral phase associated with acid-sulphate waters (Bigham et al. 1996); (b) the goethite formation becomes predominant at pH > 3 (Davis et al. 1988). Pyrite trace was also detected in DS but not in the dickite samples collected by J.C. and it is probably of postdiagenetic (secondary) origin.

The findings of highly oxidizing Eh values at low pH are consistent with the physicochemical characteristics of the hydrothermal acid waters. Thus, dickite probably grew from an O_2 -enriched acid solution. Laboratory synthesis in a closed system and under hydrothermal conditions shows that the optimal pH for kaolinite formation is 3 to 3.5 (Lahodny-Sarc et al. 1993). The problem is, however, that the hydrothermal aquatic system of the Nowa Ruda Basin was probably thermodynamically open, so it might not be exactly comparable to a laboratory autoclave synthesis.

The above Eh-pH diagram is calculated for atmospheric pressure and a temperature of 26.85 °C. A thermochemical calculation indicates that no significant variations at the scale of our diagram are expected in the thermodynamic parameters up to 10 bars of atmospheric pressure. This is due to the fact that pressure only slightly affects the chemistry of both the ionic species and solids of V and Cr within the O-H geochemical system. A similar calculation also shows that in a hydrothermal solution with temperatures up to ca. 126.85 °C, the vertical line (as the boundary between the VO^{2+} solution and the solid VO_2 stability field) would be shifted from pH 3.9 to 4.5. On the other hand, the vertical line, which represents the boundary between Cr^{3+} and CrOH^{2+} , would shift from pH 4 to 3.1. Thus, a change in the temperature up to 126.85 °C would slightly shift the stability fields of VO^{2+} and Cr^{3+} in the Eh-pH diagram during formation of the NR dickite toward a pH lower than 4.

The kaolinite minerals associated with the NR veins are composed of kaolinite and dickite in variable ratios, although

dickite was the sole polymorph identified in most veins (Kowalski & Lipiarski 1973). The fact that dickite occurs only in parts of the Nowa Ruda Basin indicates that the above physicochemical conditions necessary for dickite formation were reached only locally.

Physicochemical conditions of formation of other hydrothermal kaolinites and dickites

In the following, we briefly review relevant geochemical data (ours and others) for hydrothermal kaolinites and/or dickites from Sonoma (California, USA), Cigar Lake (Saskatchewan, Canada) and Teslić (Bosnia and Hercegovina).

Hydrothermal kaolinites from Sonoma

Mosser et al. (1996) examined two V- and Cr-bearing hydrothermal kaolinites (named MILO and GEY) that formed in a hydrothermal environment at Sonoma (California, USA). The Cr and V abundances in the MILO and GEY kaolinites are presented in Table 2. These studies imply that Cr^{3+} and VO^{2+} ions are present within their structures. Low V/Cr ratios (≤ 0.1 , Table 2) for the MILO and GEY kaolinites indicate an oxygenic milieu for their formation. The fact that most of the Fe is localized in small oxide particles associated with the kaolinites (Mosser et al. 1993) strongly supports this view.

Table 2: Geochemical concentrations of V [ppm] and Cr [ppm] (on the whole-rock basis) in the Gey/Milo/Cigar Lake/Teslić samples.

Sample	V	Cr	V/Cr
Gey	320	23260	0.0
Milo	480	7530	0.1
Cigar Lake*	2475**	350	7.1
2378	190	4720	0.0
665	310	1780	0.2
664	230	3900	0.1

*This work. ** VO^{2+} concentration: 2700 ± 200 ppm.

Hydrothermal kaolinite of Cigar Lake

The U-rich hydrothermal deposit of Cigar Lake consists predominantly of kaolinite (>80 %) (Mosser et al. 1996). Table 2 lists the V and Cr concentrations of this kaolinite. Mosser et al. (1996) suggest that the Cigar Lake illite was hydrothermally transformed into kaolinite with V entering its structure.

Our ESR analyses show that most (>80 %) of the V is present as VO^{2+} ion, and Cr^{3+} is below detectable level (Table 2). Both the abundant pyrite (1.5 %) associated with this kaolinite (Mosser et al. 1996) and high V/Cr (7.1, Table 2) indicate strong reducing conditions during the formation of the Cigar Lake kaolinite.

Hydrothermal dickites and kaolinites near Teslić

Maksimović et al. (1981) investigated three samples (herein referred as 2378, 664 and 665) of V- and Cr-bearing dickite and kaolinite from a hydrothermal sulphide vein in ultramafic

rocks near Teslić (Bosnia). Samples 2378 and 665 contained predominantly dickite and kaolinite, respectively, while the third (664) contained equal proportions of both minerals. All three samples exhibited relatively high Cr and V (Table 2). Maksimović et al. (1981) suggested that the acidity of the hydrothermal solutions in which the dickite and kaolinite are formed was between pH 4.1 to 5.3 for a long period of time. Low V/Cr ratios (≤ 0.2) (Table 2) and the absence of sulphide minerals (e.g. pyrite) associated with the Teslić dickite and kaolinite imply an oxygenated hydrothermal milieu.

Conclusion

From the results and considerations given in this paper the following conclusions can be drawn:

1. High concentrations of V (190 ppm) and Cr (435 ppm) were found in the dickite of Nowa Ruda;
2. High contents of VO^{2+} and Cr^{3+} were detected in the dickite of Nowa Ruda by ESR;
3. The V (and VO^{2+}) and Cr (Cr^{3+}) enrichments of the dickite of Nowa Ruda occurred during its formation by an invasive hydrothermal acid water;
4. The ultimate source of V and Cr in the dickite of Nowa Ruda was probably the surrounding gabbroic rocks of the gabbro massifs of the Nowa Ruda Basin;
5. V and Cr were leached by initial hydrothermal acid water before its mixing with a groundwater, forming a dickite-forming solution;
6. From the geochemistry of VO^{2+} and Cr^{3+} , it is deduced that the oxidation potential Eh and pH of the dickite-forming solution were >0.4 V and ≤ 4 , respectively.

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