

Monika Agnieszka KUSIAK¹ & Nonna BAKUN-CZUBAROW²

Chemistry of monazites as provenance indicator – case study from the Upper Silesia Coal Basin (Poland)³

(Figs 1–7; Tabs 1–5)

Abstract. Mineral chemistry and homogeneity, as well as crystal structure and unit cell parameters of detrital monazites isolated from sandstones of the Upper Silesia Coal Basin were studied using electron microprobe analysis (EPMA) and X-ray diffractometry (XRD). Analyzed monazite grains are chemically almost homogenous, only in a very few cases, parts of the grain are enriched in thorium and depleted in yttrium content. Typical feature of monazite from the Poruba Beds is relatively high content of Y (up to 4 wt. % Y_2O_3), what could point to higher temperature of crystallization. Monazite from the Kwaczała Arkose are, on average, richer in huttonite and slightly poorer in cheralite end-members than monazite from the Poruba Beds. Monazite from Kwaczała Arkose reveals the following unit cell parameters: $a = 6.794(1) \text{ \AA}$, $b = 7.008(2) \text{ \AA}$, $c = 6.479(2) \text{ \AA}$, $\beta = 103.82(2)^\circ$, whereas for the Poruba Beds monazite these parameters, excluding b-value, are slightly higher: $a = 6.804(3) \text{ \AA}$, $b = 7.002(5) \text{ \AA}$, $c = 6.488(4) \text{ \AA}$, $\beta = 103.85(3)^\circ$.

Key words: Upper Silesia Coal Basin, monazite, REE distribution patterns, XRD patterns, unit cell parameters, provenance indicator.

INTRODUCTION

Monazite, is an anhydrous phosphate of rare earth elements (REE), mostly cerium (Ce, La, Th) PO_4 , which name comes from Greek $\mu\omicron\nu\alpha\zeta\epsilon\upsilon$ (monazeis), meaning “to be solitary” (Breithaupt, 1829 – after Overstreet, 1967). It was named in allusion to the rare occurrence of this mineral in its first known localities.

Monazite crystals in different types of rocks commonly contain different compositional domains. Generally, such domains represent new monazite grow or re-

1 Institute of Geological Sciences, Polish Academy of Sciences, Kraków Research Centre, ul. Senacka 1, 31-002 Kraków, Poland. E-mail: ndkusiak@cyf-kr.edu.pl

2 Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00-818 Warszawa, Poland. E-mail: nbakun@twarda.pan.pl

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crystallization stages during the geological history (Williams & Jercinovic, 2002; Pyle & Spear, 2003; Williams *et al.*, 2007). The presented work is an extensive elaboration on the chemical variability of monazite grains separated from sandstones of the Upper Silesia Coal Basin (USCB). For research there were selected samples from: (1) the Poruba Beds, belonging to Paralic Series, and (2) the Kwaczała Arkose. Monazite from those samples were previously dated using CHIME (Chemical Th-U-total Pb isochron method) by means of electron (Kusiak *et al.*, 2001; Kusiak *et al.*, 2006) and proton (Lekki *et al.*, 2003) microprobes.

Monazite grains were separated using unconventional separation methods (Kusiak & Paszkowski, 1998; Paszkowski *et al.*, 1999), excluding heavy liquids. Previous work on heavy minerals from the Upper Carboniferous sandstones (Turnau-Morawska & Łydka, 1952; Łydka, 1955; Siedlecka & Krysowska, 1962) do not report the occurrence of monazite in those rocks. It can be due to the fact that monazite is not always optically distinguishable from zircon, allanite, xenotime or titanite.

GEOLOGICAL SETTING

The Upper Silesia Coal Basin (USCB) constitutes a large Late Mississippian to Pennsylvanian marine to non-marine sedimentary basin located in southwestern Poland and the northeastern Czech Republic (Fig. 1). The USCB overlies the Moravo-Silesia Zone to the west and the Kraków – Myszków Zone to the north and northeast. To the south, the basin can be traced by subsurface occurrence of coal beds below Miocene deposits and in nappes in the Outer Carpathian Mountains.

The USCB is a remnant of the Carboniferous foreland of the Variscan Orogen (Gradziński, 1982). The basement consists of Precambrian crystalline rocks of the Cadomian Brno – Upper Silesia Massif, overlain by Devonian–Mississippian platform carbonates. The foredeep succession includes flysch sediments, overlain by a coal-bearing shallow-marine to non-marine molasse. The Pennsylvanian coal-bearing rocks of the USCB concordantly overlie older strata (Kotas, 1972). The stratigraphic thickness of the coal-bearing sequence is estimated at around 8000 m and decreases eastwards (Kotas, 1994). Syn- to post-Carboniferous erosion removed part of the succession in the west. Gradziński (1982) described the depocentres of each stratigraphic unit, showing an eastward gradual shift of the maximum subsidence zone, as commonly observed in flexural foredeep basins.

Based on palaeobotanical, palynological and palaeozoological data, the coal-bearing succession is divided into four, informal units that are, in ascending order of stratigraphic age: (1) the Paralic Series (PS) of the Pendleian–Arnsbergian; (2) the Upper Silesia Sandstone Series (USSS) of the Kinderscoutian–Yedonian; (3) the Mudstone Series (MS) of the Langsetian–Duckmantian; and (4) the Cracow Sandstone Series (CSS) of the Bolsovian–Westphalian D (Dembowski, 1972).

The Paralic Series is interpreted as near-shore marine, deltaic, and fluvial in origin (Doktor and Gradziński, 2002). The Štur marine band (XVI) is the lowest member of this series (Namurian A; Kotas, 1995), whereas the base of the overlying



Fig. 1. A simplified map of the Upper Silesia Coal Basin with marked places of the collected samples

USSS is defined at the bottom of coal seam number 510, which represents the onset of on-shore deposition. The PS is characterized by marine, brackish and fresh-water horizons, and is subdivided into the Petřkovice, Hrušov, Jaklovec and Poruba Beds, based on marine and tuffaceous layers (Kotas & Malczyk, 1972). Each of these units is composed of conglomerates, sandstones, siltstones, claystones and phytogenic facies. Conglomerate clasts include sedimentary rocks, phyllites, quartz-chlorite and quartz-mica schists, microgranites, gneisses and granulites (Paszkowski *et al.*, 1995). Sandstones are composed of arkoses, lithic arenites, sublitharenites and subarkoses (Świerczewska, 1995).

The coal-bearing strata are overlain by the Stephanian Kwaczała Arkose. The Kwaczała Arkose lacks of coal seams and has features of the red-bed facies and contains silicified *Dadoxylons* trunks (Rutkowski, 1972). Petrographic data indicate that the arenites are dominated by detritus derived from metamorphic and magmatic rocks (Świerczewska, 1995). Petrological study of clasts in flysch and molasses associations suggests that the crystalline clastic materials were mostly derived from gneisses, granitoids and rhyolitic bodies of the Bohemian Massif (Paszkowski *et al.*, 1995).

MONAZITE

Monazite consists mainly of 21–32% Ce_2O_3 , 28–35% $(\text{La, Nd, \dots})_2\text{O}_3$, 6–11% ThO_2 and of about 32% P_2O_5 , not being described any natural monazite with pure Ce or Nd content. In the crystal structure $[\text{PO}_4]^{3-}$ can be substituted by $[\text{SiO}_4]^{4-}$ or $[\text{SO}_4]^{2-}$ (Ni *et al.*, 1995) and Th for Ce and La (Fron del, 1958). The upper limit of substitution of thorium is not known, but it is estimated in about 30 weight percent of ThO_2 (31.5 wt.%, noticed by Overstreet, 1967), being the total content of thorium in detrital monazite taken as constant. Usually monazite, next to thorium, contains also uranium, but most often only up to 1 weight percent U_3O_8 (Fron del, 1958). Chemical formula for “typical” monazite estimated by Suzuki *et al.* (1994) is $(\text{Ce}_{0.41-0.45}\text{La}_{0.20-0.23}\text{Nd}_{0.15-0.18})[\text{PO}_4] + \text{other REE} < 6 \text{ mol \%} + \text{Y, Th, U, Ca}$. The chemical formula for monazite from USCB, calculated for average of 85 grains, is $(\text{Ce}_{0.55}\text{La}_{0.26}\text{Nd}_{0.19})\text{PO}_4$. The most significant compositional variation in monazite results from solid-solution with huttonite (ThSiO_4), by coupled $\text{Th}^{4+}\text{Si}^{4+}$ - $\text{LREE}^{3+}\text{P}^{5+}$ substitution (Ayres & Harris, 1997). The thorium content is usually fairly constant due to its entering into the monazite crystal structure through the coupled substitutions $\text{Th}^{4+} + \text{Si}^{4+} \rightarrow \text{REE}^{3+} + \text{P}^{5+}$, $\text{Th}^{4+} + \text{Ca}^{2+} \rightarrow 2\text{REE}^{3+}$, and $\text{Th}^{4+} + 2\text{Si}^{4+} \rightarrow \text{Ca}^{2+} + 2\text{P}^{5+}$ (Catlos *et al.*, 2002). Monazite from pegmatites has a significantly higher content of the actinides (U, Th) and Ca (Demartin *et al.*, 1991).

Monazite is mainly a transparent, almost colorless mineral, showing a variety of yellowish shades. Nevertheless, Overstreet (1967) reported black monazite due to carbon contamination. In the Upper Silesia Coal Basin, the black monazite occurs in the Jaklovec Beds in “Rydułtowy” coal mine. Such monazite contains elevated sulfur content (Kusiak *et al.*, 2006). Monazite has a high relief with resinous lustre and it appears with a dark rim surrounding its outline (Mange & Maurer, 1992). Its mineralogical structure is positive biaxial, having a $2V\gamma + 6^\circ - 9^\circ$ angle of optical axes. It displays strong birefringence, $\Delta = 0.045 - 0.075$ (Deer *et al.*, 1993) and its maximum extinction angle ranges between 2° and 7° . As it is common for detrital grains it does not show a complete extinction (Mange & Maurer, 1992). Monazite’s hardness fluctuates between 4.9–5.3 at the Mohs scale (Boenigh, 1983) whilst its density [for a pure monazite $(\text{Ce,La})\text{PO}_4$] is $5.15 \pm 0.05 \text{ g/cm}^3$ (Fron del, 1958). Chemical changes in composition can cause variation of density within 4.6–5.5 g/cm^3 (Gribble & Hall, 1992), whereby the density increases with increasing thorium content.

Monazite is a monoclinic mineral (prismatic crystal class 2/m) and belongs to the $\text{P2}_1/\text{n}$ space group. Crystals are mostly plate and often thick tabular on $\{100\}$ or flattened and elongated along the c-axis or the a-axis (Fron del, 1958). Monazite crystals have often rough, uneven or striated faces due to alteration, showing distinct cleavage on the $\{100\}$ face and less distinct on the $\{010\}$ one. Monazite undergoes neither chemical nor structural changes below 1000°C (Fron del, 1958).

There are nine distinct bond distances between the REE and oxygen ions in the monoclinic monazite structure. A regular variation of the REE cation-to-oxygen bond distances is typical for both, monazite and xenotime (Ni *et al.*, 1995). There

are four LaPO_4 molecules per Bravais unit-cell. In the $(\text{La}_{1-2x}\text{Ac}_x\text{Ca}_x)\text{PO}_4$ series, the filling of the Cat^{3+} cation sites by atoms of Th (respectively U) or Ca in the monoclinic structure of LaPO_4 is random (Podor, 1995).

In the monazite crystal structure, the larger trivalent cation is coordinated by nine O-atoms in a rather irregular arrangement. These polyhedra link by sharing edges to form chains that extend in the b-direction. The chains are linked in the c-direction by (PO_4) tetrahedra that share edges with polyhedra of adjacent chain to form a layer parallel to (100). These layers stack in the a-direction by sharing edges between the $(\{\text{REE}\}\text{O}_9)$ polyhedra to form rather staggered chains that extend in the {101} direction.

Due to the abundance of light rare earth elements, monazite has high magnetic susceptibility (Heaman & Parrish, 1991), having been reported that the most magnetic grains are low in La, Ce and high in Nd, Sm, Gd, Y (Overstreet, 1967).

The isomorphic group of monazite consists of cheralite (Th,Ca,Ce,La,U,Pb) $(\text{PO}_4,\text{SiO}_4)$ (Bowles *et al.*, 1980) and huttonite $\text{Th}(\text{SiO}_4)$ (Kucha, 1980; Pabst & Hutton, 1951). The natural thorium orthophosphate end-member, brabantite $\text{CaTh}(\text{PO}_4)_2$ (Rose, 1980), has been described probably only once. Natural monazite of the intermediate composition between 31.5 and 57 wt% ThO_2 has never been reported (Podor & Cuney, 1997), and brabantite has been discarded as the isomorphic end-member of monazite system (Burke & Ferraris, 2006). Less common in the monazite-group mineral are gasparite (Ce,REE) AsO_4 , As-monazite (REE,Y) $(\text{PO}_4,\text{As}_2\text{O}_5)$ (Ondrejka *et al.*, 2007) and Nd-monazite (Nd,Ce) $(\text{PO}_4,\text{SiO}_4)$ in which Nd is predominant over Ce (Graeser & Schwander, 1987). The distribution of rare earth elements in cheralite is similar to that shown by monazite, especially monazite from granitic pegmatites.

Monazite is a selective mineral for the light rare earth elements (LREE), whereas xenotime incorporates preferentially Y and the heavy rare earth elements (HREE) (Gratz & Heinrich, 1997). LREE minerals from LaPO_4 to GdPO_4 have monoclinic structure of monazite, but HREE minerals from TbPO_4 to LuPO_4 , and YPO_4 are tetragonal, being isostructural with zircon. This phenomena can explain selective differentiation between HREE and LREE. The exception is Gd, which prefers xenotime crystal structure, but pure GdPO_4 crystallizes in monazite structure (Franz *et al.*, 1996; Gratz & Heinrich, 1998). The selectivity of monazite is connected with REE fractionation and growth conditions, and can form the following decreasing order, as monazite from carbonatites contains more La+Ce+Pr than monazite from alkaline rocks and > from quartzite veins > from granitoids > from pegmatites. Monazite from pegmatites are the richest in thorium. Monazite shows relatively steep LREE distribution pattern, a negative Eu-anomaly, and a flat HREE distribution (Franz *et al.*, 1996). The complex zonation pattern in monazite is connected with La and Nd choosing preferentially particular lattice planes (Cressey *et al.*, 1999). The morphology and zonation pattern is a function of REE fractionation. Yttrium zoning may be correlated to Th (and U) zoning, Y zoning is believed to record a history of monazite growth with or without Y-bearing phases (garnet, apatite, xenotime, allanite). Sharp boundaries exist between chemically distinct zones.

This is especially valid for Th, U, and Y, despite high metamorphic grade of some samples (there is poor evidence for diffusional homogenization, possibly except for Y).

Some of monazite grains show metamictisation resulting from the absorption at high doses of ionizing radioactivity from Th and U. In non-changed grains, in UV light, monazite shows no fluorescence (what differs it from zircon) and no or very weak cathodoluminescence. Monazite is not always clearly optically distinguishable from zircon, allanite, xenotime or titanite; third order of its interference colors may resemble epidote, zircon or small titanite grains (Scherrer *et al.*, 2000).

Most often monazite occurs as single grains, in which fluid or gas inclusions are rare. On the other hand, other type of solid inclusions like minute crystals of apatite, biotite, epidote, galena, garnet, hematite, quartz, magnetite, muscovite, rutile, sillimanite are often described. It coexists with ilmenite, rutile, zircon, cassiterite, xenotime, sillimanite and thorite.

Monazite can be used in geological thermobarometry on the basis of presence of HREE in monazite, in spite of selective REE fractionation. The pressure has no significant effect on the partitioning, until it reaches a range of 2 to 5 kbar (Gratz & Heinrich, 1997). The contents of HREE in monazite and those of LREE in xenotime increase with increasing temperature. The ratio of Gd in monazite to Gd in xenotime increases with the temperature of metamorphism from 0.25 for T=500°C to 1.0 for T=1000°C (Gratz & Heinrich, 1998). Monazite retentive nature for Pb, its tendency to grow over a range of P-T, and its unusual behaviour during diagenesis is unstable and, according to the Overstreet (1967), does not reappear until albite-epidote-amphibolite-facies or staurolite-zone conditions) suggest its use as a system capable of recording thermochronological information during prograde metamorphism of a pelite (Akers *et al.*, 1993).

Monazite and xenotime are used as geothermometers, mainly due to the REE partitioning (Gratz & Heinrich, 1997). The LREE are preferentially fractionated into monazite and the HREE into xenotime. Monazite crystals formed at high temperature could contain up to 5% Y₂O₃ (Jonasson *et al.*, 1988). With the increase of temperature, minor HREE (Gd-Yb) content in monazite and LREE (Ce, Nd, Sm) content in xenotime also increase (Andrehs & Heinrich, 1998; Gratz & Heinrich, 1998). The use of monazite composition as geothermometer would be of great value, because it could allow to obtain temperature-time point values on a single mineral grain, what would have wide application in petrogenesis, thermochronology and tectonics.

Because of its ability to accept U and Th in crystal structure, monazite is one of the most radioactive minerals after uraninite, thorianite or thorite. This feature makes monazite a very useful tool for the U/Pb and Sm/Nd isotope geochronology (Parrish & Tirrul, 1989; Noble & Searle, 1995; Hawkins & Bowring, 1999; Vavra & Schaltegger, 1999; Zhu & O'Nions, 1999; Krohe & Wawrzenitz, 2000), and for chemical CHIME dating (Suzuki & Adachi, 1991, 1994; Montel *et al.*, 1996; Braun *et al.*, 1998; Finger & Helmy 1998). Lead produced by U and Th decay, has a place in the mineral structure. Therefore, there is no natural tendency for Pb to be released

from monazite, as could be in the case of zircon (Bosch *et al.*, 2002). Nevertheless, some studies of the diffusion of Pb in monazite indicate that Pb loss may be experienced by crystals during a high-temperature metamorphic event (Suzuki *et al.*, 1994). As a diffusion is a thermally activated process, the amount of Pb diffused in monazite corresponds to the intensity of the metamorphic overprint. According to Crowley and Ghent (1999), the diffusion zones were 18–22 μm thick in monazite grains metamorphosed at 620°C, while they were much thicker (48–58 μm) in grains metamorphosed at 680°C. In hydrothermal experiments, monazite releases or incorporates Pb from a fluid depending on its relative concentrations and the external conditions (Seydoux-Guillaume *et al.*, 2002).

The development of *in situ* (= in thin section) dating techniques, like for example SIMS, LA-ICP-MS or EPMA, makes possible to obtain Th-U, U-Pb or Pb-Pb ages on individual spots in a grain. This allows the age determination on individual chemical zones within a crystal. *In situ* dating of monazite makes possible dating differences between the age of monazite as inclusion in garnet and those in the rock's matrix (Foster, *et al.*, 2000; Catlos, *et al.*, 2002). The same techniques have been applied to date metamorphic events (Parrish, 1990; Dunning *et al.*, 1995; Kalt *et al.*, 2000; Pyle & Spear, 2003), as well as to describe hydrothermal activity, mineralization processes (Corfu & Muir, 1989) and for dating detrital grains (Kusiak *et al.*, 2006). It was thought that the closing temperature for U-Pb in monazite is up to about 725°C (Copeland *et al.*, 1988; Parrish, 1990; Hawkins & Bowring, 1999), being the crystallization age preserved at higher temperature than for the granulite facies (Gebauer & Grunenfelder, 1979; Copeland *et al.*, 1988; Smith & Barreiro, 1989; De Wolf *et al.*, 1993; Suzuki *et al.*, 1994; Bingen & van Breemen, 1998; Vavra *et al.*, 1998; Timmermann *et al.*, 2000). The recent experimental studies (Cherniak *et al.*, 2004) suggest the closing temperature in monazite above 900°C. According to Spear & Pyle (2002), closing temperature above 800°C (up to 850°C) characterizes monazite inclusions in garnets (Montel *et al.*, 2000).

Monazite is a typical detrital mineral because of its physical and chemical stability and is of worldwide occurrence in beach and river sands and placer deposits. Most abundantly it occurs as subhedral to rounded grains, and is often found as tiny (< microns) grains. It tends to concentrate in black sands, because of its relatively high specific gravity, and is found with magnetite, ilmenite, zircon, garnet, rutile and other heavy minerals.

Economically, the most important monazite deposits are beach placers. Monazite is the main ore for the commercial extraction of thorium, and it has also been used as a secondary source of uranium (Boatner, 2002). In crystalline rocks, the chemical and physical aspects of geologic environment affect the presence, amount, and composition of monazite, but in sedimentary rocks these relations are subject to mechanical processes in the environment.

METHODS

Electron Probe MicroAnalysis – EPMA. Monazite were analyzed on a JEOL JXA-8600 superprobe, equipped with three wavelength-dispersive type spectrometers, based in the Saskatchewan University in Saskatoon, Canada. The accelerating voltage was 20 kV, the probe current was about 100 nA, and the effective beam diameter was 2 μ m. The PET crystal was used to analyze Pb, Th, U, Ca, P and Y, TAP crystal to analyze Si, and LIF crystal to analyze the whole spectrum of REE. The X-ray line, crystal, count time and calibration standards for each element are listed in Tab. 1. Analysed X-ray lines give minimum interferences. The background was measured in half the time on each side of the peak. The chemical composition of the standards used is given in Tab. 2.

X-ray diffraction. X-ray data of two monazite samples were obtained using CGR transmission diffractometer with Bragg-Brentano optics, working in a Debye-Scherrer-Hall geometry with the capillary sample stage. The diffractometer was equipped with curved position-sensitive detector INEL CPS-120 having sample-to-detector distance of 250 mm. The Co K α_1 radiation monochromatized with focusing quartz monochromator as well as counting time of 48 hours were applied.

Table 1

Conditions of EMPA analysis for monazites

Element	X-ray line	Crystal	Count time	Calibration standard
Si	K α	TAP	20 sec	Structure Probe Inc. – quartz (SiO ₂ – 99.99)
Ca	K α	PET	20 sec	Smithsonian Durango apatite
P	K α	PET	20 sec	Smithsonian Durango apatite
La	L α	LIF	30 sec	Smithsonian synthetic LaPO ₄
Ce	L α	LIF	30 sec	Smithsonian synthetic CePO ₄
Pr	L β	LIF	50 sec	Smithsonian synthetic PrPO ₄
Nd	L β	LIF	50 sec	Smithsonian synthetic NdPO ₄
Sm	L β	LIF	50 sec	Smithsonian synthetic SmPO ₄
Eu	L β	LIF	50 sec	Smithsonian synthetic EuPO ₄
Gd	L β	LIF	50 sec	Smithsonian synthetic GdPO ₄
Dy	L β	LIF	50 sec	Smithsonian synthetic DyPO ₄
Er	L α	LIF	30 sec	Smithsonian synthetic ErPO ₄
Yb	L α	LIF	30 sec	Smithsonian synthetic YbPO ₄
Lu	L α	LIF	30 sec	Smithsonian synthetic LuPO ₄
Y	L α	PET	100 sec	Smithsonian synthetic YPO ₄
Th	M α	PET	100 sec	Structure Probe Inc. Th metal (Th – 99.99)
U	M β	PET	200 sec	Structure Probe Inc. U metal (U – 99.99)
Pb	M β	PET	200 sec	Structure Probe Inc. crocoite

Table 2

The chemical composition of used standards

Calibration standard	Chemical composition [wt.%]
Smithsonian Durango apatite	SiO ₂ - 0.34, CaO - 54.02, Na ₂ O - 0.23, P ₂ O ₅ - 40.78, REE - 1.43, SO ₃ - 0.37, F - 3.53, Cl - 0.41
Smithsonian synthetic LaPO ₄	La ₂ O ₃ - 59.39, PO ₄ - 40.61
Smithsonian synthetic CePO ₄	Ce ₂ O ₃ - 59.60, PO ₄ - 40.40
Smithsonian synthetic PrPO ₄	Pr ₂ O ₃ - 59.73, PO ₄ - 40.27
Smithsonian synthetic NdPO ₄	Nd ₂ O ₃ - 60.30, PO ₄ - 39.70
Smithsonian synthetic SmPO ₄	Sm ₂ O ₃ - 61.28, PO ₄ - 38.72
Smithsonian synthetic EuPO ₄	Eu ₂ O ₃ - 61.54, PO ₄ - 38.46
Smithsonian synthetic GdPO ₄	Gd ₂ O ₃ - 62.34, PO ₄ - 37.66
Smithsonian synthetic DyPO ₄	Dy ₂ O ₃ - 63.11, PO ₄ - 36.89
Smithsonian synthetic ErPO ₄	Er ₂ O ₃ - 63.78, PO ₄ - 36.22
Smithsonian synthetic YbPO ₄	Yb ₂ O ₃ - 64.56, PO ₄ - 35.44
Smithsonian synthetic LuPO ₄	Lu ₂ O ₃ - 64.81, PO ₄ - 35.19
Smithsonian synthetic YPO ₄	Y ₂ O ₃ - 48.35, PO ₄ - 51.65
Structure Probe Inc. crocoite	PbO - 69.06, Cr ₂ O ₃ - 30.94

Up to 5 mg of powdered monazite samples were loaded to Lindemann-glass capillaries with inner diameter of 0.3 mm, filling them up to 8 mm high. Unit-cell parameters were calculated from X-ray powder diffraction data using UCIN software and the standard diffractogram of monazite no 11-0556 from JCPDS-ICDD database.

RESULTS

Analyzed monazite grains show typical features of this mineral with characteristic yellowish shadows. Grains are dominantly well rounded, usually “egg-shaped” or spherical. In spite of being mostly rounded, there are grains with clearly distinguishable faces, what is shown on Fig. 2. Surprisingly, in the investigated sandstone beds, monazite is concentrated not only in the finest fraction (below 0.23 mm) but also is often cumulated in a coarser fraction of 0.23–0.32 mm. Some of the grains contain inclusions of other minerals: quartz, feldspar, pyrite, apatite, zircon and other monazite. Monazite, forming inclusions in other monazite grains usually contain more thorium than it is in the host-mineral.

From both samples ten separated grains were selected for EPMA analyses. Altogether there were 21 spots analysed in each of sets. All points of analyses and chemical compositions are shown on the pictures and in the tables (Fig. 3 with Tab. 3 and Fig. 4 with Tab. 4, for Poruba Beds and Kwaczała Arkose respectively).

Monazite grains from the Poruba Beds contain 2.63–8.03 wt% ThO₂, 0.22–1.06 wt% UO₂, up to 0.2 wt% PbO and 0.32–4.09 wt% Y₂O₃, 0.50–1.94 wt% CaO and

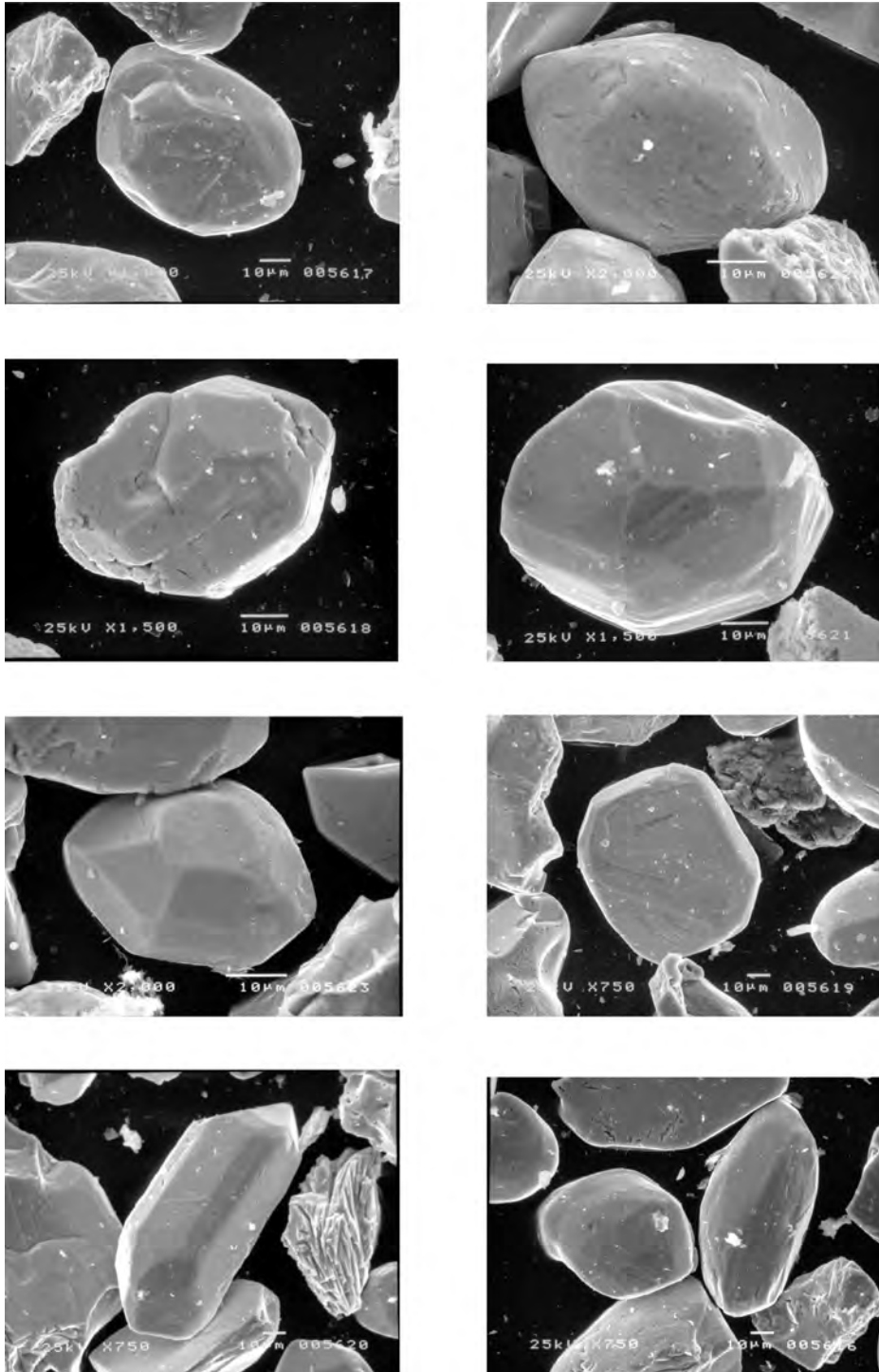


Fig. 2. SEM-EDS images of unpolished monazite grains showing their morphology

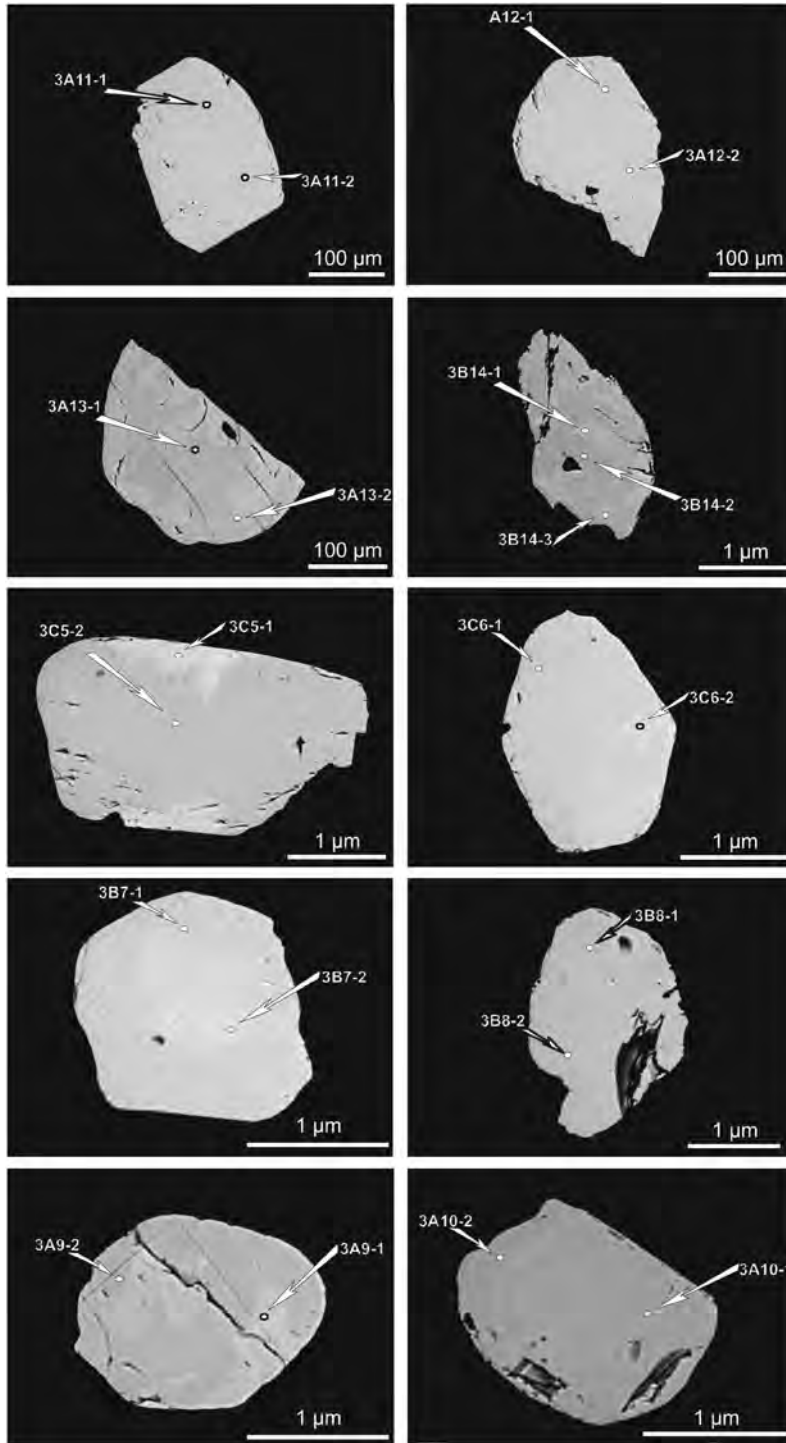


Fig. 3. BSE image of 10 monazite grains from Poruba Beds with marked points of analysis

Table 3

Chemical compositions of monazites from Poruba Beds [wt. %]

P#	SiO ₂	ThO ₂	UO ₂	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	Er ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	CaO	PbO	P ₂ O ₅	Total
3A11-1	0.26	4.19	0.81	2.64	13.13	27.64	2.90	9.21	1.73	0.04	1.37	0.65	0.00	0.00	0.00	1.09	0.00	32.75	98.43
3A11-2	0.29	4.26	0.97	2.64	14.38	27.53	2.92	8.71	1.88	0.06	1.50	0.75	0.01	0.00	0.00	1.08	0.13	33.12	100.24
3A12-1	0.39	3.70	0.54	4.09	12.89	25.68	2.76	10.30	2.04	0.25	1.86	0.71	0.01	0.00	0.00	0.87	0.05	32.16	98.29
3A12-2	0.40	3.38	0.36	2.59	14.15	27.79	2.76	9.58	1.97	0.00	1.67	0.64	0.02	0.05	0.01	0.72	0.00	32.29	98.39
3A13-1	0.85	6.25	0.10	1.83	13.41	27.55	2.90	9.70	1.64	0.13	1.01	0.31	0.08	0.02	0.05	1.94	0.00	30.46	98.23
3A13-2	1.06	6.41	0.19	2.30	12.92	26.24	2.97	9.14	1.71	0.22	0.94	0.42	0.14	0.00	0.00	1.57	0.09	31.36	97.67
3B14-1	0.90	5.81	0.68	0.77	15.26	28.90	2.80	8.90	1.66	0.00	0.72	0.15	0.00	0.00	0.00	0.93	0.07	31.70	99.25
3B14-2	0.32	4.44	0.91	2.62	12.85	27.45	2.33	9.74	2.06	0.04	1.33	0.67	0.00	0.00	0.02	1.18	0.11	31.84	97.91
3B14-3	0.55	6.25	0.41	0.74	13.18	28.39	2.69	9.88	2.14	0.03	1.30	0.21	0.00	0.00	0.05	1.11	0.20	31.69	98.82
3C5-1	0.86	5.47	0.20	0.48	17.98	30.48	3.47	7.64	0.75	0.00	0.19	0.00	0.00	0.00	0.00	0.63	0.00	31.94	100.08
3C5-2	0.94	5.30	0.19	0.32	17.07	31.36	3.21	7.70	0.94	0.00	0.28	0.00	0.00	0.00	0.00	0.50	0.10	31.09	99.00
3C6-1	0.22	2.92	0.29	2.77	13.34	27.64	3.15	9.50	1.81	0.00	1.74	0.58	0.12	0.04	0.05	0.68	0.04	32.48	97.36
3C6-2	0.27	3.91	0.35	3.48	11.93	26.61	3.10	10.08	1.88	0.08	1.97	0.82	0.00	0.01	0.00	0.82	0.15	32.81	98.29
3B7-1	0.35	4.84	0.76	3.27	12.69	25.88	2.47	9.46	1.84	0.14	1.78	0.76	0.00	0.00	0.02	1.11	0.00	32.48	97.86
3B7-2	0.38	5.24	0.77	3.13	12.48	25.81	3.37	9.30	1.93	0.02	1.60	0.83	0.01	0.00	0.00	1.18	0.10	32.48	98.63
3B8-1	0.86	8.03	0.12	0.88	12.86	28.75	2.94	9.84	1.62	0.00	0.97	0.11	0.04	0.00	0.00	1.33	0.12	31.78	100.23
3B8-2	0.78	7.87	0.16	0.73	13.39	27.60	2.82	9.66	1.53	0.16	0.84	0.00	0.00	0.00	0.00	1.26	0.10	31.54	98.44
3A9-1	0.38	5.76	0.44	2.17	14.63	27.12	3.16	9.30	1.77	0.06	0.82	0.38	0.00	0.05	0.07	1.15	0.08	32.36	99.69
3A9-2	0.26	4.47	0.39	2.83	13.71	26.92	3.17	9.26	2.17	0.09	1.56	0.63	0.01	0.02	0.01	1.00	0.07	32.60	99.17
3A10-1	0.33	2.63	0.52	2.06	13.23	28.69	2.82	9.31	2.01	0.42	1.63	0.38	0.00	0.00	0.03	0.66	0.09	32.70	97.51
3A10-2	0.24	3.24	0.72	2.34	13.27	28.16	3.33	9.60	2.30	0.38	1.16	0.65	0.00	0.00	0.00	0.85	0.15	32.85	99.22
max	1.06	8.03	0.97	4.09	17.98	31.36	3.47	10.30	2.30	0.42	1.97	0.83	0.14	0.05	0.07	1.94	0.20	33.12	
min	0.22	2.63	0.10	0.32	11.93	25.68	2.33	7.64	0.75	0.00	0.19	0.00	0.00	0.00	0.00	0.50	0.00	30.46	

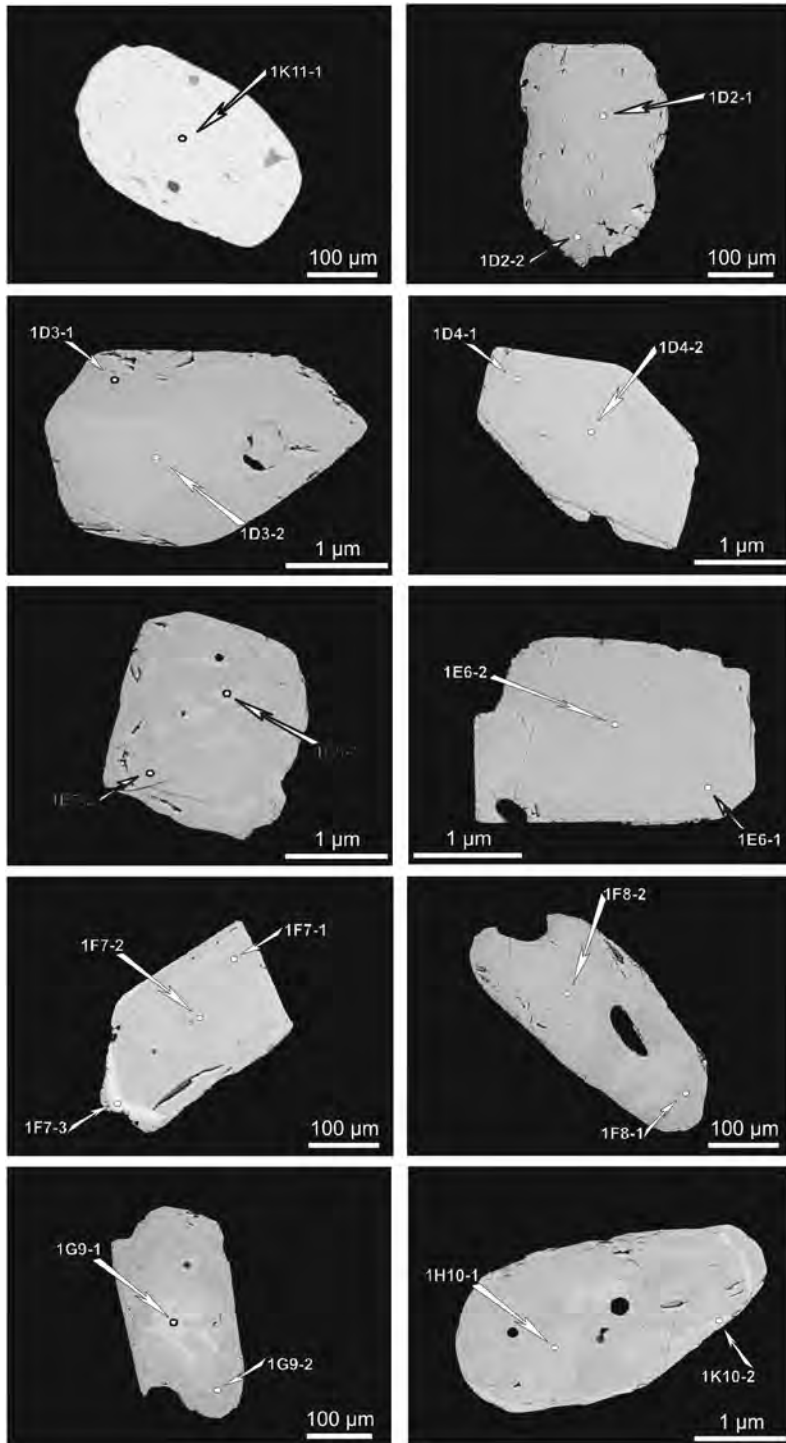


Fig. 4. BSE image of 10 monazite grains from Kwaczała Arkose with marked points of analysis

Table 4

Chemical compositions of monazites from Kwaczala Arkose [wt. %]

P#	SiO ₂	ThO ₂	UO ₂	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Eu ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	Er ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃	CaO	PbO	P ₂ O ₅	Total
IK11-1	0.20	4.31	0.86	2.82	14.33	27.66	3.05	8.64	1.49	0.00	1.33	0.58	0.14	0.01	0.06	1.04	0.09	32.68	99.29
IK11-2	0.24	4.34	0.59	3.17	13.16	27.05	2.95	9.07	1.84	0.11	1.49	0.57	0.03	0.01	0.00	0.96	0.13	32.42	98.13
ID2-1	2.55	10.31	0.17	0.91	16.22	28.85	2.68	6.68	1.01	0.13	0.33	0.00	0.00	0.03	0.03	0.61	0.16	28.65	99.32
ID2-2	1.96	8.11	0.10	1.82	15.72	27.66	2.55	7.55	1.25	0.00	0.78	0.28	0.00	0.07	0.00	0.68	0.05	30.00	98.58
ID3-1	0.87	5.83	1.09	3.28	11.46	25.60	2.63	9.17	1.67	0.23	1.73	0.71	0.00	0.00	0.03	1.03	0.17	31.82	97.32
ID3-2	0.83	6.06	1.20	3.25	12.29	25.66	2.47	9.47	1.87	0.18	1.48	0.68	0.04	0.08	0.03	1.14	0.16	32.20	99.11
IE4-1	0.29	4.29	0.40	3.16	13.44	27.15	3.19	9.23	1.91	0.00	1.23	0.56	0.13	0.00	0.00	0.97	0.11	33.06	99.13
IE4-2	0.26	4.41	0.47	3.51	12.82	26.94	3.10	8.99	1.74	0.00	1.37	0.70	0.02	0.00	0.10	0.92	0.12	32.05	97.50
IE5-1	0.33	4.39	0.49	1.41	13.91	28.15	3.07	9.54	1.70	0.16	1.30	0.31	0.00	0.00	0.02	0.95	0.08	32.59	98.39
IE5-2	0.46	5.00	0.28	0.94	14.30	28.12	2.91	10.46	1.74	0.00	1.29	0.24	0.00	0.00	0.04	1.02	0.04	33.07	99.91
IE6-1	0.25	4.61	0.90	3.13	12.44	25.08	2.74	10.18	2.25	0.11	1.63	0.78	0.00	0.00	0.00	1.19	0.13	33.07	98.48
IE6-2	0.25	4.46	0.74	3.04	13.12	26.17	3.35	10.12	2.33	0.23	1.80	0.73	0.00	0.00	0.07	1.14	0.14	32.98	100.67
IF7-1	1.86	7.38	0.62	0.51	14.52	31.04	3.55	9.21	1.39	0.02	0.59	0.00	0.00	0.05	0.06	0.55	0.07	30.21	101.64
IF7-2	1.84	7.23	0.64	0.39	15.27	29.04	2.61	8.56	0.96	0.00	0.35	0.00	0.03	0.05	0.00	0.51	0.12	29.06	96.67
IF7-3	3.38	14.35	0.42	0.67	13.51	26.90	2.84	8.39	1.31	0.00	0.41	0.00	0.00	0.00	0.00	0.46	0.11	26.72	99.47
IF8-1	0.23	4.28	0.51	3.20	13.02	26.81	3.37	9.74	2.01	0.22	1.49	0.61	0.08	0.00	0.00	1.04	0.00	32.63	99.24
IF8-2	0.39	4.77	0.52	1.30	14.11	29.03	3.18	10.23	1.58	0.07	1.29	0.27	0.00	0.00	0.03	0.97	0.07	32.11	99.94
IG9-1	0.59	6.97	0.86	1.31	14.32	26.91	2.90	7.50	1.31	0.07	0.82	0.29	0.00	0.00	0.00	1.41	0.14	32.09	97.50
IG9-2	0.24	4.63	0.34	3.64	12.11	27.20	3.46	9.28	1.80	0.00	1.82	0.79	0.00	0.03	0.07	1.11	0.14	33.62	100.28
IK10-1	1.05	2.90	0.04	0.67	17.07	33.86	3.32	8.47	0.99	0.10	0.29	0.06	0.00	0.00	0.00	0.38	0.00	31.44	100.62
IK10-2	1.90	8.65	0.13	0.66	15.68	29.81	2.42	8.05	1.01	0.00	0.34	0.00	0.00	0.00	0.00	0.56	0.13	29.88	99.21
max	3.38	14.35	1.20	3.64	17.07	33.86	3.55	10.46	2.33	0.23	1.82	0.79	0.14	0.08	0.10	1.41	0.17	33.62	
min	0.20	2.90	0.04	0.39	11.46	25.08	2.42	6.68	0.96	0.00	0.29	0.00	0.00	0.00	0.00	0.38	0.00	26.72	

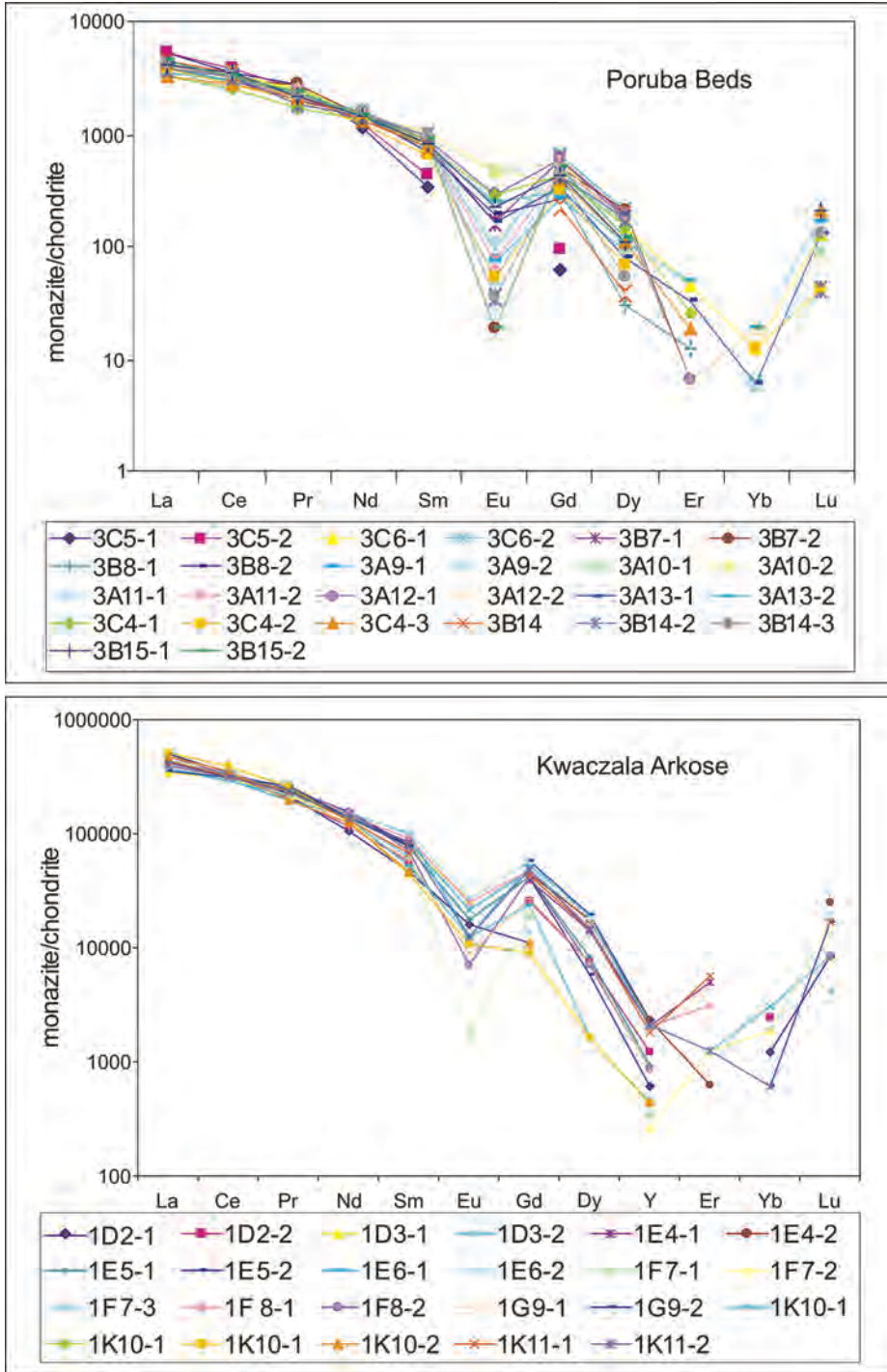


Fig. 5. Chondrite normalized REE + Y distribution of monazite in samples from Poruba Beds and Kwaczala Arkose

Table 5

X-ray data for powdered monazites and unit cell parameters

			Monazite from Kwaczała Arkose			Monazite from Poruba Beds			JC PDS-ICDD 11-0556	
h	k	l	d _{obs}	d _{cal}	I	d _{obs}	d _{cal}	I	d	I
-1	0	1	5.204	5.218	5	5.221	5.227	7	5.2	13
1	1	0	4.804	4.804	8	4.808	4.805	6	4.82	7
0	1	1	4.684	4.681	11	4.688	4.683	18	4.66	18
-1	1	1	4.183	4.185	25	4.186	4.188	21	4.17	25
1	0	1	4.076	4.091	6	4.109	4.095	10	4.08	9
0	2	0	3.500	3.504	18	3.504	6.501	20	3.51	25
2	0	0	3.298	3.299	56	3.304	3.303	55	3.30	50
1	2	0	3.092	3.095	100	3.094	3.094	100	3.09	100
2	1	0	2.930	2.985	14	2.985	2.987	14	2.99	18
-1	1	2	2.869	2.870	62	2.873	2.874	73	2.87	70
-2	0	2	2.606	2.609	14	2.608	2.613	17	2.61	18
1	1	2	2.441	2.444	16	2.445	2.446	19	2.44	18
2	2	0							2.40	5
-1	2	2							2.34	5
-3	0	1	2.250	2.250	4	2.250	2.254	2	2.25	3
0	3	1	2.189	2.190	24	2.191	2.189	29	2.19	18
-1	0	3	2.152	2.152	18				2.15	25
-1	3	1				2.127	2.131	23	2.13	25
1	3	1							2.02	3
2	1	2	1.966	1.964	29	1.968	1.965	34	1.961	25
3	0	1							1.933	7
-3	2	1	1.896	1.893	15	1.896	1.895	17	1.895	13
1	0	3	1.873	1.873	34	1.875	1.876	38	1.870	18
3	2	0	1.863	1.863	18	1.864	1.864	16	1.859	18
0	2	3	1.800	1.799	9	1.800	1.801	8	1.797	9
2	2	2	1.766	1.767	11	1.766	1.768	16	1.762	18
1	3	2	1.740	1.740	26	1.741	1.740	29	1.737	25
-3	1	3				1.692	1.691	13	1.689	13
1	2	3	1.651	1.652	5	1.653	1.653	8	1.645	7
-3	3	1							1.623	7
-3	3	0							1.600	7
2	3	2							1.535	13
2	4	1							1.463	5
-3	1	4	1.423	1.424	3				1.423	3
4	2	1	1.386	1.386	3				1.386	3
0	5	1							1.368	5
1	2	4							1.339	9
2	4	2							1.329	9
-4	0	4	1.305	1.304	4				1.307	3
-1	5	2	1.280	1.280	14				1.280	6

Table 5 continued

			Monazite from Kwaczała Arkose			Monazite from Poruba Beds			JC PDS-ICDD 11-0556	
h	k	l	d _{obs}	d _{cal}	I	dobs	dcal	I	d	I
-5	0	3							1.261	2
4	2	2	1.248	1.248	7				1.245	3
5	0	1	1.234	1.234	20	1.235	1.235	18	1.233	9
-3	5	1							1.189	3
0	6	0	1.168	1.168	12				1.168	6
2	5	2							1.153	3
-2	5	3							1.145	2
1	5	3							1.121	4
6	0	0	1.099	1.100	15				1.099	4
6	1	0							1.086	2
-6	1	3							1.074	2
1	6	2							1.064	3
0	0	6							1.046	4
0	1	6							1.034	2
-4	3	5							1.025	2
-6	3	2							1.014	2
3	6	1							0.9998	2
1	6	3							0.9899	2
4	5	2							0.9659	2
-5	3	5							0.9523	3
2	0	6							0.9343	3
-4	3	6							0.9181	3
7	0	1							0.9012	3
-6	4	4							0.8831	2
-1	6	5							0.8667	3
-7	4	1							0.8462	3
2	8	1							0.8320	2
1	7	4							0.8238	3
-1	4	7							0.8134	2
-2	1	8							0.8038	2
-1	1	8							0.7966	3
a (Å)			6.794 ± 0.001			6.804 ± 0.003			6.796	
b (Å)			7.008 ± 0.002			7.002 ± 0.005			7.006	
c (Å)			6.479 ± 0.002			6.488 ± 0.004			6.466	
β (°)			103.82 ± 0.02			103.85 ± 0.03			103.95	

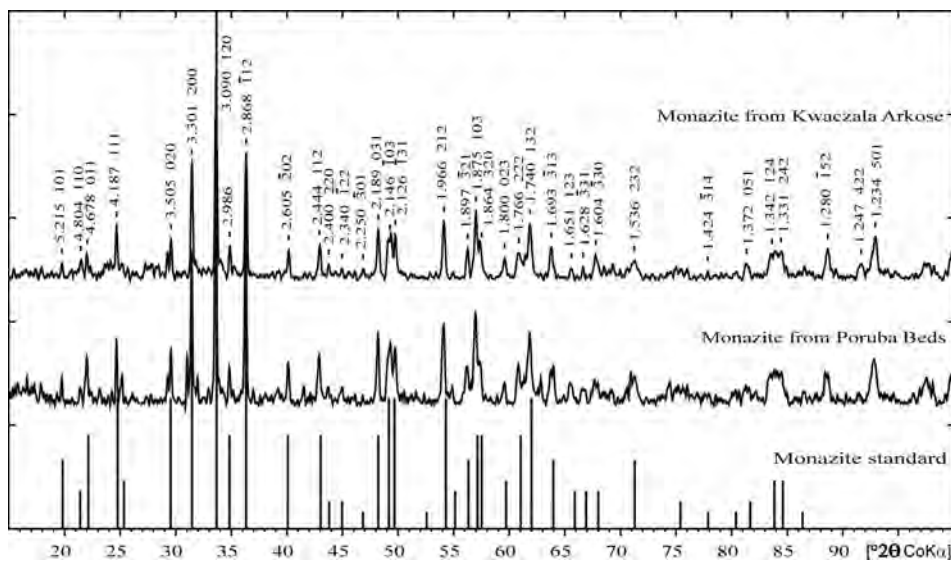


Fig. 6. X-ray diffraction patterns of the analyzed monazites

0.22–1.06 wt% SiO₂. Despite of the patchy pattern on few monazite grains, their chemical composition is quite homogeneous, showing no zoning. Brighter spots show higher Th content, but the differences are not very big between brighter and darker spots (see Fig. 3, analysis 3B14).

Chondrite normalized diagram for REE+Y data is presented on the Fig. 5-top. Yttrium is plotted between Dy and Ho on the basis of its ionic radius. The calculated chemical formula of monazite from the Poruba Beds is (Ce_{0.36–0.45}La_{0.17–0.25}Nd_{0.10–0.14})(PO₄)+other REE, with average of (Ce_{0.39}La_{0.19}Nd_{0.13})(PO₄)+other REE.

The general lack of zoning may reflect the growth of grains during a single reaction or as a result of recrystallisation of older monazite material. Recrystallisation features are visible on grain 3C5 (spot of 3C5-1, Fig. 3). Some of euhedral monazite grains from the Poruba Beds show slight evidence of abrasion, which may be an indicator of igneous source rock.

Monazite grains from the Kwaczala Arkose display slightly different chemical composition showing some depletion in light REE and enrichment in heavier ones and thorium. The chemical composition is as follows: 2.90–14.35 wt% ThO₂, 0.04–1.20 wt% UO₂, up to 0.17 wt% PbO and 0.39–3.64 wt% Y₂O₃, 0.38–1.41 wt% CaO and 0.20–3.28 wt% SiO₂. Those grains display some visible zonation, e.g., sector zoning (Fig. 4 – grain 1D3) or so-called “patchy” (Zhu & O’Nions, 1999) zonation (e.g., Fig. 4 – grain 1E5). Some monazite have margins highly enriched in Th (Fig. 4 – grain 1F7). In this sample recrystallization features on the grains are visible as well (Fig. 4 – grain 1G9). The calculated chemical formulae of monazite from the Kwaczala Arkose differs slightly from those of the Poruba Beds (Ce_{0.37–0.47}La_{0.16–0.23}Nd_{0.09–0.14})[PO₄]+other REE, with average of (Ce_{0.39}La_{0.20}Nd_{0.12})[PO₄]+other REE, being enriched in light REE.

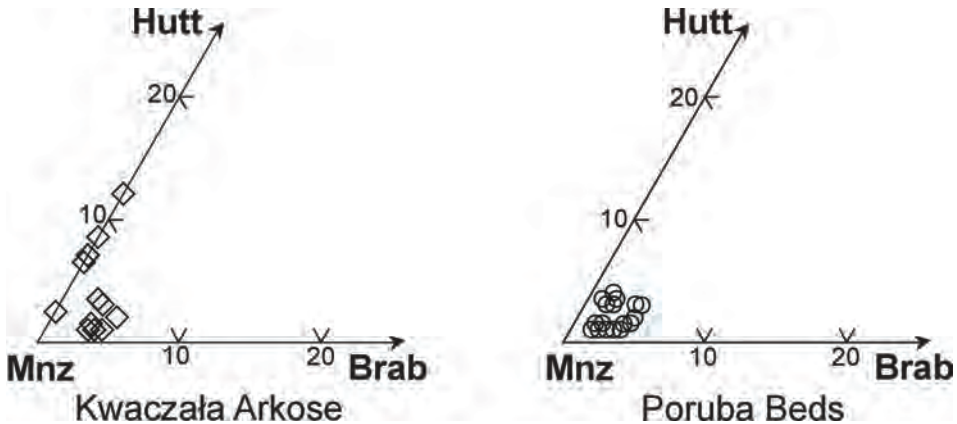


Fig. 7. Contents of huttonite (Hutt) and brabantite (Brab) end members in monazites (Mnz) from analyzed samples

The zoning observed in BSE images is reflected by chemical composition of monazite. Dark zones have lower Th (+Ca+Si) and higher Y (+HREE) contents when compared to the light ones. There is a negative correlation between Th (+Ca+Si) and Y (+HREE) and between Th and LREE, what reflects the typical coupled substitution: $\text{Th}^{4+} + \text{Ca}^{2+} = 2\text{REE}^{3+}$ and $\text{Th}^{4+} + \text{Si}^{4+} = \text{LREE}^{3+} + \text{P}^{5+}$. Yttrium, which is positively correlated with heavy REE, substitutes REE, and typically behaves similarly to the HREE. There is no systematic correlation between U and Th.

Monazite grains from the Kwaczała Arkose and Poruba Beds do not differ significantly, neither in X-ray diffraction patterns nor in the unit cell parameters, but the PB monazite's values are higher. Transmission diffraction patterns of the powdered monazite are given on Fig. 6, whereas X-ray data together with unit cell parameters are presented in Tab. 5. The Poruba Beds monazite grains show the following unit cell parameters: $a = 6.804(3) \text{ \AA}$, $b = 7.002(5) \text{ \AA}$, $c = 6.488(4) \text{ \AA}$, $\beta = 103.85(3)^\circ$, while the parameters for monazite from the Kwaczała Arkose, excluding b-value, are slightly lower: $a = 6.794(1) \text{ \AA}$, $b = 7.008(2) \text{ \AA}$, $c = 6.479(2) \text{ \AA}$, $\beta = 103.82(2)^\circ$.

CONCLUSIONS

The provenance of the rocks forming the Upper Carboniferous Coal Basin succession were discussed previously (Paszkowski *et al.*, 1995; Kusiak *et al.*, 2006). This study is the next step for supplementing our knowledge.

1. A characteristic feature of the analyzed monazites is relatively high content of yttrium, especially for grains from the Poruba Beds, which have up to 4 wt % Y_2O_3 , what could be caused by relatively high temperature of their crystallization. Apart from high-Y monazite, there also occurs a high thorium population (up to 27.9 wt % of ThO_2) among these detrital minerals from the geological units in question.

2. Monazite grains from the Kwaczała Arkose are, on an average, richer in huttonite (3.6 mol.%) than monazites from the Poruba Beds (2.1 mol.%), which, on the other hand, are slightly richer in brabantite (2.9 mol.%) than the Kwaczała Arkose monazites (2.3 mol.% – Fig. 7). One can also observe a relatively strong negative correlation between (REE + P) and (Th + Si) as well as between LREE (La+Ce+Nd) and (Th + Ca), what can be explained by the presence of monazite–huttonite and monazite–brabantite solid solutions, respectively. In the analyzed monazites from Poruba Beds, there is a positive correlation between lanthanum and actinides (Th+U), whereas for the monazite grains from the Kwaczała Arkose, this correlation is negative.

3. On the base of our observation we can assume that both units could be formed from different types of rocks. Monazites from the Poruba Beds display the feature of grains coming from high grade metamorphic rocks. On the other hand, the monazites which occur in the Kwaczała Arkose, are rather igneous like. Our conclusion is not an ultimate one. It is still possible, that the amount of analyzed detrital grains is not representative enough, or that source rocks could be mixture of different types of rocks. The strontium content in monazite, which is indicating high metamorphic facies for growing of monazite (Kusiak *et al.*, 2008), was not measured for this study. The present-day studies of monazite grains from different types of crystalline rocks, are conducted due to clear up the provenance problem.

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