Geologic and mineralogical implications for element and isotope signatures in the Wiśniówka acid mine drainage waters (south-central Poland) ⊚

Zdzisław M. Migaszewski, Agnieszka Gałuszka

Jan Kochanowski University in Kielce, 15G Świętokrzyska St, 25-406 Kielce, Poland;
e-mail: zmig@ujk.edu.pl, aggie@ujk.edu.pl

Abstract

Hydrogeochemistry of Wiśniówka AMD area (south-central Poland) correlates with geology and mineralogy of Upper Cambrian (Furongian) quartzite-shale rock series. The lowermost part of this geologic section contains enormous amounts of pyrite, which is unusual in sedimentary rock mining. Moreover, this pyrite shows specific mineralogical characteristics (predominance of microscopic grains, framboids, As-banded microtextures) and negative sulfur isotope signatures. Another feature is a lack of effective-buffering minerals except for less reactive clay minerals. Additionally, the shale interbeds are commonly enriched with REE-rich aluminophosphate/phosphate minerals. Specific element and isotope signatures of rocks and waters were used to solve different geologic and environmental issues.

Keywords: pyrite, REE minerals, element signatures, stable sulfur isotopes

Introduction

Mineral and rock mining operations leave waste rock, tailings piles, settling ponds, tailings pools/seeps, acid pit ponds and lakes that may severely impact the environment. Of different active and abandoned mining areas, AMD sites are among the most hazardous ones jeopardizing different environmental compartments and human health (e.g. Plumlee 1999; Simón et al. 2001; Nordstrom 2011; Plumlee, Morman 2011; Kossoff et al. 2014; Brown et al. 2017). The main natural process of concern is the oxidation of pyrite and occasionally other Fe-bearing sulfide minerals leading to generation of sulfuric acid and various ochreous precipitates combined with a release of deleterious metal(loid)s. Pyrite is a ubiquitous mineral in massive sulfide ore and coal deposits (e.g. Plumlee 1999; Alpers et al. 2003) or mineralized rock formations (Reichenbach 1993; Migaszewski et al. 2016, 2018ab).

The element composition of AMD water bodies correlates with the local/regional geologic setting and mineral composition. However, the original element concentration patterns undergo changes as a result of geochemical processes commonly induced and catalyzed by microbial activity. The knowledge of different geologic, mineralogical and geochemical aspects provides both critical information on potential AMD hazards and proxies for reconstruction of paleoenvironmental conditions. The principal objective of this and previous studies (e.g. Migaszewski et al. 2009, 2014, 2016, 2018ab) was to elucidate variations in concentration patterns of metal(loid)s and rare earth elements (REE; La through Lu) in AMD waters and stable sulfur isotope ratios in pyrite and dissolved sulfates of the Wiśniówka mining area in the context of lithologic and mineralogical characterization of regional Upper Cambrian rock series.

Study area

The Wiśniówka AMD area is located within the western part of the Cambrian Main Range (Holy Cross Mountains), about 5 km north of the provincial capital city of Kielce (south-central Poland). The Main Range lies in the immediate proximity of the nearly parallel Holy Cross Fault (HC Thrust) that separates two tectonic units (terranes): the Łysogóry Block from the Małopolska Block (fig. 1A). The study area includes the Upper Cambrian (Furongian) section composed of alternating

quartzite/quartzitic sandstone and clayey-silty shale beds, locally with thin bentonite and tuffite layers. Tectonic setting is very complex, which is evidenced by the presence of numerous folds, slices and faults offsetting the original rock bedding (Żylińska et al. 2006 and references therein). This geologic complexity is the cause of dismembered topography of the Wiśniówka massif. In contrast to the remaining regional Cambrian formations, this site is highlighted by the occurrence of two pyrite mineralization zones of different age: the oldest (lowermost Upper Cambrian) cropping out in the Podwiśniówka quarry and the youngest (middle Upper Cambrian) exposed in the Wiśniówka Duża quarry (Migaszewski et al. 2016, 2018ab).

The principal raw material is quartzite/quartzitic sandstone that has been extracted for manufacturing of crushed aggregates. The over century lasting strip mining has left numerous tailings piles and acid water bodies of diverse geochemistry. Complex studies have been conducted in this mining area for a decade. These encompassed different aspects of mineralogy, isotope geochemistry and hydrogeochemistry in abandoned quarries and historic mine waste heaps (e.g. Migaszewski et al. 2009, 2016, 2018ab). The situation has worsened after quarrying for quartzite in the Podwiśniówka stone pit during 2013–2014. As a result of quartzite extraction a broad pyrite mineralization zone was exposed. The lowest mining bench was filled up with acid water forming a new lake (fig. 1B). In addition, to make it worse, the mine wastes were piled over a vast mining area giving rise to formation of strongly acidic seeps and pools. Another, although less dramatic threat to the environment, was posed by deeper quartzite extraction in the Wiśniówka Duża quarry. As a result of this 2017-mining operation a lake formed reaching 4 ha in area (fig. 1C). This situation gave us an opportunity to begin a new study of AMD waters and rocks employing advanced geochemical and mineralogical methods.

Methods

Fieldwork included collection of 40 rock samples from the Podwiśniówka and Wiśniówka Duża outcrops and additionally water samples from the neigboring AMD lakes. The latter were sampled in 8 series during 2016–2017. For the purpose of this study, fieldwork also included direct measurements of pH, electric conductivity (EC) and temperature (T) of water, using a manual microprocessor pH/Eh-meter SP300 and EC-meter
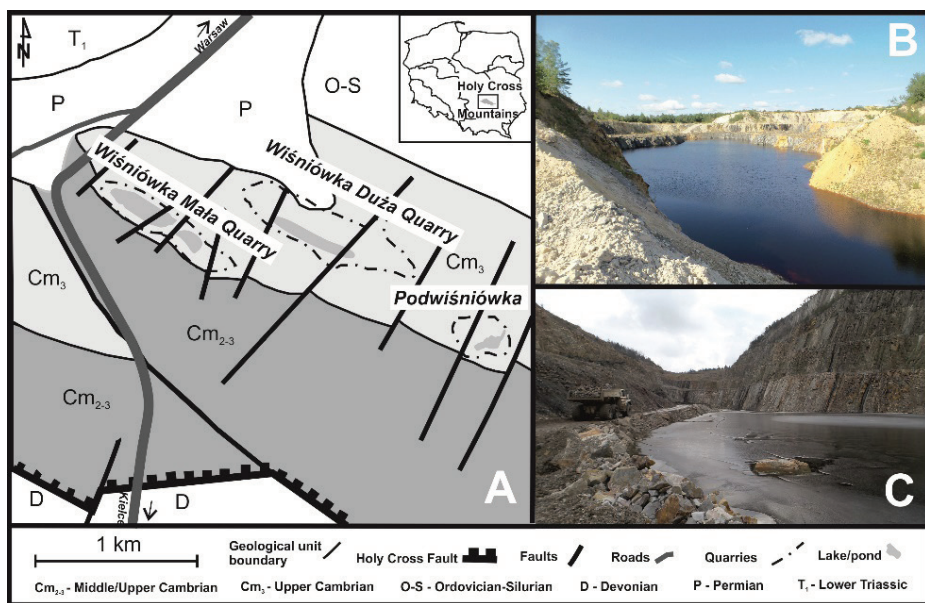

Figure 1 (A) Geologic sketch map of Wiśniówka mining area (Żylińska et al. 2006 modified by the authors) with a view of (B) Podwiśniówka and (C) Wiśniówka Duża acid pit lakes.

SC300 (both Slandi, Poland). Besides, concentrations of dissolved SO_4^{2-} and PO_4^{3-} were determined using a field spectrophotometer LF-300 (Slandi, Poland).

Trace element determinations in rocks and waters were made using an inductively coupled plasma-mass spectrometer (ICP-MS; model ELAN DRC II, Perkin Elmer). The stable S isotope determination in pyrite and dissolved sulfates was performed off-line on a dual inlet and triple collector isotope ratio modified mass spectrometer MI-1305 equipped with modified inlet and detection systems on SO_2 gas. The isotope analysis was performed at the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University in Lublin (Poland).

The principal objective of petrographic and mineralogical examinations was to find mineral phases responsible for geochemistry of nearby AMD water bodies. These included optical microscopy (Leica M205 A and Nikon LV 100 Pol), scanning electron microscopy combined with energy dispersion spectrometry (SEM-EDS; model LEO 1430, Carl Zeiss Jena) and electron microprobe (EMP; model Cameca SX-100). The SEM-EDS and EMP studies were performed at the Microanalysis Laboratory, Polish Geological Institute-National Research Institute in Warsaw.

Mineralogy and geochemistry of bedrock

Most of the Podwiśniówka beds comprise enormous amounts of pyrite which is a predominant sulfide mineral in the study area. The other sulfides (e.g. galena, sphalerite, chalcopyrite, chalcocite, tetrahedrite) are extremely scarce forming tiny endomorphs several micrometers across. Pyrite usually occurs in the form of microscopic grains and framboids averaging 0.00X–0.X mm in diameter (fig. 2A). Most of the Podwiśniówka pyrite grains show a zonal microtexture composed of alternating As-rich (up to 8.2%) and As-depleted bands (fig. 2B). Another distinctive feature of the Wiśniówka bedrock is a lack of effective acid-buffering gangue and rock-forming minerals except for low-buffering
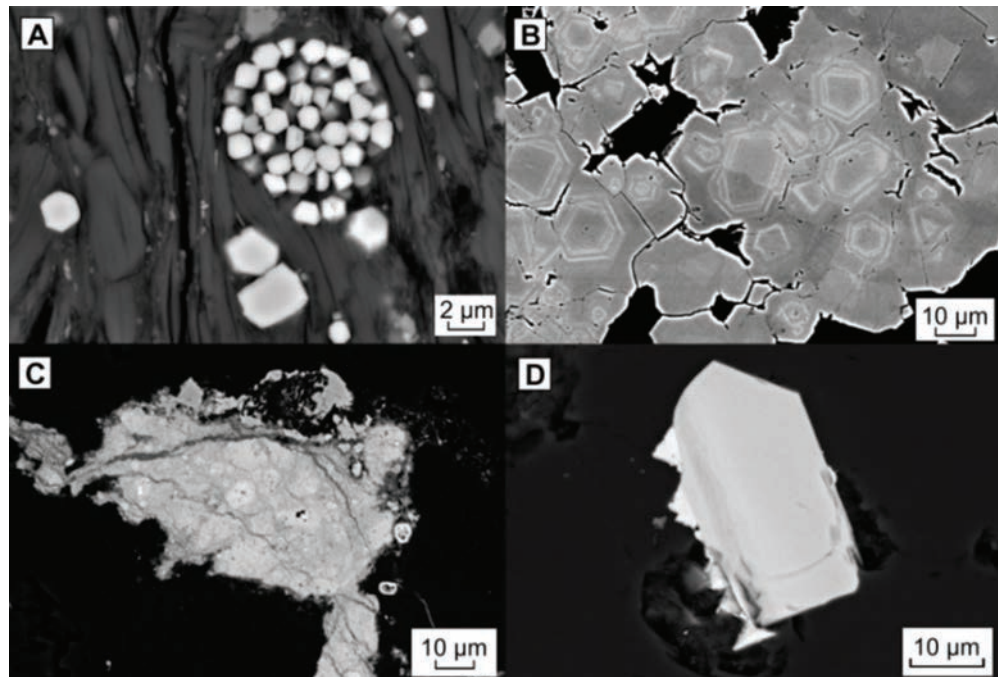

Figure 2 Back-scattered SEM images of: (A) pyrite framboid, (B) alternating bands of As-rich (light gray) and As-depleted (gray) pyrite, (C) LREE-rich goyazite crystals ($SrHAl_3[(PO_4)_2(OH)_6]$, white) within REE-depleted goyazite matrix (gray), (D) HREE-rich xenotime pyramidal crystals ($YPO4$) growing on detrital zircon ($ZrSiO_4$).

clay minerals (illite, smectite, mixed-layered illite-smectite, kaolinite/nacrite and subordinate chlorite). Nonetheless, these minerals are a source of high contents of Al in the waters examined. Both clayey-silty shales and subordinate quartzites also contain REE-rich aluminophosphate and phosphate minerals (fig. 2C, D) that undergo dissolution by pyrite oxidation products releasing different ions into acid water bodies.

As opposed to Wiśniówka Duża, the Podwiśniówka beds are highlighted by distinctly higher contents of As, Cu, Cr, Ni and Co (Table 1). In both sites arsenic predominates in quartzites/sandstones whereas the other elements, especially REE, in clayey-silty shales. It is interesting to compare North American Shale Composite (NASC)-normalized REE contents. Both quartzites and clayey-silty shales show an abundance of light REE (LREE; La through Eu) over heavy REE (HREE; Gd through Lu) which is evidenced by the LREE/HREENASC ratio of 1.44–1.45 (Wiśniówka Duża) to 1.78–1.80 (Podwiśniówka) (fig. 3A).

Metal(loid)s and REE in AMD waters

The pH of Podwiśniówka acid pit lake was stable varying from 2.4 to 2.6. The EC was in the range of 2862 to 4920 μS/cm whereas concentrations of SO_4^{2-} and PO_4^{3-} varied from 2510 to 6000 mg/L and from 2.37 to 10.0 mg/L. In contrast, the Wiśniówka Duża acid pit lake revealed the pH in the range of 3.0 to 3.7, the EC 379 to 2172 μS/cm and distinctly lower concentrations of SO_4^{2-} (135–1440 mg/L) and PO_4^{3-} (<0.01–0.455 mg/L). The highest pH and the lowest EC values and SO_4^{2-}, PO_4^{3-} and trace element concentrations were noted in March of 2017 during the large influx of melt-

Table 1. Mean values and concentration ranges of selected elements in major rock lithotypes of Podwiśniówka and Wiśniówka Duża quarries.

Localization/rocks	As	Co	Cr	Cu	Ni	ΣREE
	mg/kg (ppm)					
Podwiśniówka quarry[1])						
Clayey-silty shales	965±853	11.2±8.29	139±57.8	128±192	24.2±12.6	291±78
(n = 13)	(128–2888)	(<1–25)	(51–286)	(14–635)	(6–53)	(131–457)
Quartzites/sandstones	2135±2369	5.81±8.20	40,8±13.2	22.1±15.9	13.0±20.2	109±58.4
(n = 13)	(48–6363)	(<1–29)	(23–78)	(6–66)	(1–76)	(39.4–265)
Wiśniówka Duża quarry[2])						
Clayey-silty shales	20±9.64	1±1.21	101.7±15.9	18.8±10.5	8.89±2.70	203±38.7
(n = 9)	(7–32)	(<1–4)	(87–135)	(7–36)	(6–15)	(155–271)
Quartzites/sandstones	190±297	1.3±1.2	34.2±14.8	17.2±7.09	5.60±5.22	94.3±26.6
(n = 5)	(3–696)	(<1–3)	(22–59)	(11–29)	(1–14)	(61–126)

[1] owermost Upper Cambrian lithostratigraphic series

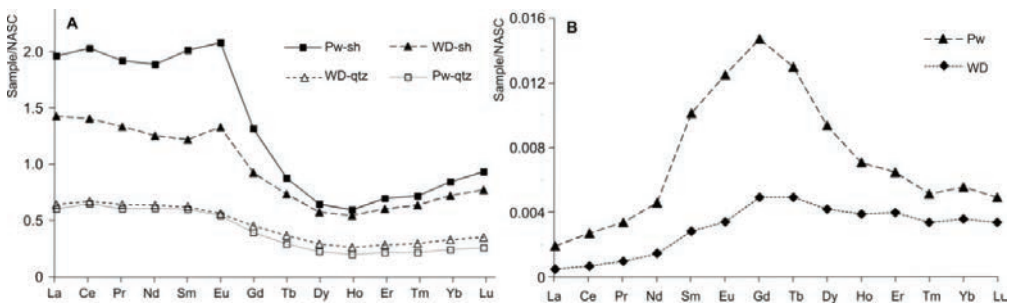[2] middle Upper Cambrian lithostratigraphic series

***Figure 3** NASC-normalized mean REE concentration patterns of: (A) Podwiśniówka and Wiśniówka Duża clayey-silty shales (Pw-sh, WD-sh) and quartzites (Pw-qtz, WD-qtz) vs. (B) Podwiśniówka (Pw) and Wiśniówka Duża (WD) acid pit lakes.*

and rainwaters into these water bodies (fig. 4).

The Podwiśniówka acid pit lake is also highlighted by the presence of REE, whose concentrations vary from 0.36 to 0.93 mg/L. These levels are higher than in the Wiśniówka Duża acid pit lake (0.04–0.35 mg/L) presumably due to larger amounts of reactive products of pyrite oxidation that come into contact with REE-rich rocks. It is interesting to note that the NASC-normalized REE concentrations patterns in these two water bodies show different shapes The Podwiśniówka shale-normalized profile is characterized by the predominance of medium REE whereas that of Wiśniówka Duża shows enrichment in heavy REE (fig. 3B).

Sulfur isotope signatures

The mean $\delta^{34}S$ values of Wiśniówka pyrite are –24.0±3.1‰ (Podwiśniówka) and –17.4±7.2‰ (Wiśniówka Duża). These differences are also reflected in the $\delta^{34}S$ of dissolved sulfates amounting to –15.3±1.0‰ (Podwiśniówka) and –10.0±1.7‰ (Wiśniówka Duża) (Migaszewski et al., 2018a). These negative sulfur isotope signatures are also unusual in sedimentary pyrites of the regional Cambri-

an lithostratigraphic section and in dissolved sulfates of local springs, streams and rivers, for instance in Holy Cross Mountains National Park located approx. 15 km east of the study area, the $\delta^{34}S$-FeS_2 values are positive with a mean of 8.7±1.0‰ and 6.2±4.6‰, respectively (Michalik, Migaszewski 2012). The same positive values have been found in most farmer's wells and unpolluted rivers of the Wiśniówka neighboring area.

Application of geochemical tracers

Different trace element and NASC-normalized REE profiles of Podwiśniówka (As>Cu>Co≈Ni>Cr and roof-shaped MREE) and Wiśniówka Duża (Cu and step-shaped HREE) were used to localize "hot spots" and provenance of exposed or unexposed deleterious mine waste material (Migaszewski et al. 2016, 2018ab). These tracers were also applied to: (i) pinpoint unexposed pyrite assemblages within faulted zones during mining operations, (ii) identify perched aquifers that recharge farmer's wells (Migaszewski et al. 2014), and (iii) determine the extent of uncontrolled acid spills into streams and rivers. In all these cases water samples were collected from
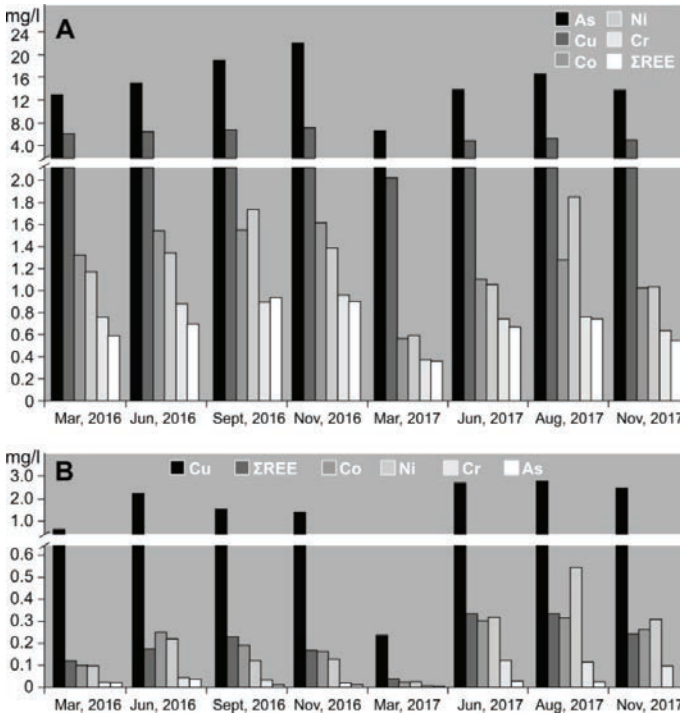

Figure 4 Concentrations of As, Cu, Co, Ni, Cr and REE in (A) Podwiśniówka and (B) Wiśniówka Duża acid pit lakes during 2016-2017.

pools, streams and wells for determining pH and trace element and REE concentrations.

The same objectives were achieved using sulfur isotope signatures despite the fact that this method is more expensive and time-consuming compared to element/REE tracers. However, some uncontrolled spills or discharges into streams and rivers give rise to an appearance of negative sulfur isotope signatures even in the absence of characteristic yellow-orange coloring (Migaszewski et al. 2018a). This is induced by different behavior of cations and anions in the environment. The former are easily adsorbed by natural colloids as opposed to anions. The negative sulfur isotope ratios will enable us to reconstruct Wiśniówka Late Cambrian euxenic-anoxic paleoenvironment. This may cast new light on the Cambrian history of the Holy Cross Mountains inlier located close to the Trans-European Suture Zone (TESZ) that separates the Precambrian East European Craton from the Paleozoic Platform of Central Europe.

Conclusions

The present and previous studies have indicated that geochemistry of Wiśniówka AMD waters reflects different mineralogy and geochemistry of two pyrite mineralization zones enhanced by geochemical interactions that occur in the rock-water-colloid systems. These and other features along with negative sulfur isotope signatures enabled us to evaluate an impact of AMD waters on the adjacent environment, establish the provenance of tailings pile material and acid tailings pools, and provide information for mining operations in a tectonically-affected area.

Acknowledgements

References

Alpers CN, Nordstrom DK, Spitzley J (2003) Extreme Acid Mine Drainage from a Pyritic Massive Sulfide Deposit: The Iron Mountain End-Member. In: Environmental Aspects of Mine Wastes. Jambor J, Blowes DL, Ritchie AIM (Eds). Mineral Assoc Canada Short Course Series 31, 407–430

Brown GE, Hochella Jr MF, Calas G (2017) Improving Mitigation of the Long-Term Legacy of Mining Activities: Nano- and Molecular-Level Concepts and Methods. Elements 13(5):325–330, doi: 10.2138/gselements.13.5.325

Kossoff D, Dubbin WE, Alfredsson M, Edwards SJ, Macklin MG, Hudson-Edwards KA (2014) Mine tailings dams: characteristics, failures, environmental impacts. Appl Geochem 51:229–245, doi: 10.1016/j.apgeochem.2014.09.010

Michalik A, Migaszewski ZM (2012) Stable sulfur and oxygen isotope ratios of the Świętokrzyski National Park spring waters generated by natural and anthropogenic factors (south-central Poland). Appl Geochem 27:1123–1132, doi:10.1016/j.apgeochem.2012.02.025

Migaszewski ZM, Gałuszka A, Dołęgowska S (2016) Rare earth and trace element signatures for assessing an impact of rock mining and processing on the environment: Wiśniówka case study. Environ Sci Pollut R 23:24943–24959, doi:10.1007/s11356-016-7713-y

Migaszewski ZM, Gałuszka A, Dołęgowska S (2018a) Stable isotope geochemistry of acid mine drainage from the Wiśniówka area (south-central Poland). Appl Geochem 95:45–56, doi.org/10.1016/j.apgeochem.2018.05.015

Migaszewski ZM, Gałuszka A, Dołęgowska S (2018b) Arsenic in the Wiśniówka acid mine drainage area (south-central Poland) – mineralogy, hydrogeochemistry, remediation. Chem Geol 493:491–503, doi.org/10.1016/j.chemgeo.2018.06.027

Migaszewski ZM, Gałuszka A, Migaszewski A (2014). The study of rare earth elements in farmer's well waters of the Podwiśniówka acid mine drainage area (south-central Poland). Environ Monit Assess 186:1609–1622, doi: 10.1007/s10661-013-3478-7

Migaszewski ZM, Gałuszka A, Hałas S, Dąbek J, Dołęgowska S, Budzyk I, Starnawska E, Michalik A (2009) Chemical and isotopic variations in the Wiśniówka Mała mine pit water, Holy Cross Mountains (South-Central Poland). Environ Geol 57:29–40, DOI 10.1007/s00254-008-1279-z

Nordstrom DK (2011) Mine Waters: Acidic to Circumneutral. Elements 7(6):393–398, doi: 1811-5209/11/0007-0393$2.50 DOI: 10.2113/gselements.7.6.393

Plumlee GS (1999) The Environmental Geology

of Mineral Deposits. In: Plumlee GS, Logsdon MJ (Eds). The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues. Soc Econ Geologists Rev in Econ Geol 6A, p 71—116

Plumlee GS, Morman S (2011) Mine Wastes and Human Health. Elements 7(6):399–404, doi: 1811-5209/11/0007-0399$2.50 DOI: 10.2113/gselements.7.6.399

Reichenbach I. (1993) Black shale as an environmental hazard; a review of black shales in Canada. Geol Surv of Canada. Open-File 2697, p 1–62

Simón M, Martin F, Ortiz I, Garcia I, Fernández J, Fernández E, Dorronsoro C, Aguilar J (2001) Soil pollution by oxidation of tailings from toxic spill of a pyrite mine. Sci Total Environ 279:63—74, doi: 10.1016/S0048-9697(01)00726-4

Żylińska A, Szczepanik Z, Salwa S (2006) Cambrian of the Holy Cross Mountains, Poland: biostratigraphy of the Wiśniówka Hill succession. Acta Geol Pol 56(4):443—461