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Opuščeni rudnik Remšnik z ramsbeckitom in namuwitom(?)

Abandoned Remšnik mine with ramsbeckite and namuwite(?)

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Key-words: ramsbeckite, namuwite, secondary minerals of copper, zinc and lead, Remšnik, Kobansko, north Slovenia

Izvleček

Polimetalno rudišče Remšnik se nahaja na Kobanskem v severni Sloveniji. Mineralizacija nastopa v narivni coni med staropaleozojskimi nizkometamorfnimi kamninami Štalenskogorske formacije, Remšniškega pokrova in retrogradno metamorfnih skrilavcev Avstroalpinske podlage. Hidrotermalno orudenje in okremenitev sledita skrilavemu klivažu v delno brečiranih lečah dolomitnih marmorjev ter podrejeno metatufitov in filitov. Najverjetneje je nastalo v povezavi z živahnim terciarnim magmatizmom, ki je ugotovljen in razkrit na območju današnjega Pohorja. Mineralno paragenezo prevladujočega Pb, Cu, Zn srebronosnega sulfidnega orudenja spremlja pestra združba sekundarnih mineralov. Med njimi se nahajata pri nas prvič opisana redka vodna sulfata bakra in cinka. Zelene, prosojne monoklinske kristale, velikosti le nekaj desetink milimetra, smo z vrstičnim elektronskim mikroskopom določili kot ramsbeckit $(Cu, Zn)_{15}(SO_4)_4(OH)_{22} \cdot 6(H_2O)$. Zelenkaste barve so tudi lističasti, po obliki heksagonalni, cvetasti kristalni zraščenci, ki najverjetneje pripadajo namuwitu $(Cu, Zn)_4(SO_4)(OH)_6 \cdot 4(H_2O)$. Zaradi submikroskopske velikosti in majhne količine njegova določitev še ni zanesljiva.

Abstract

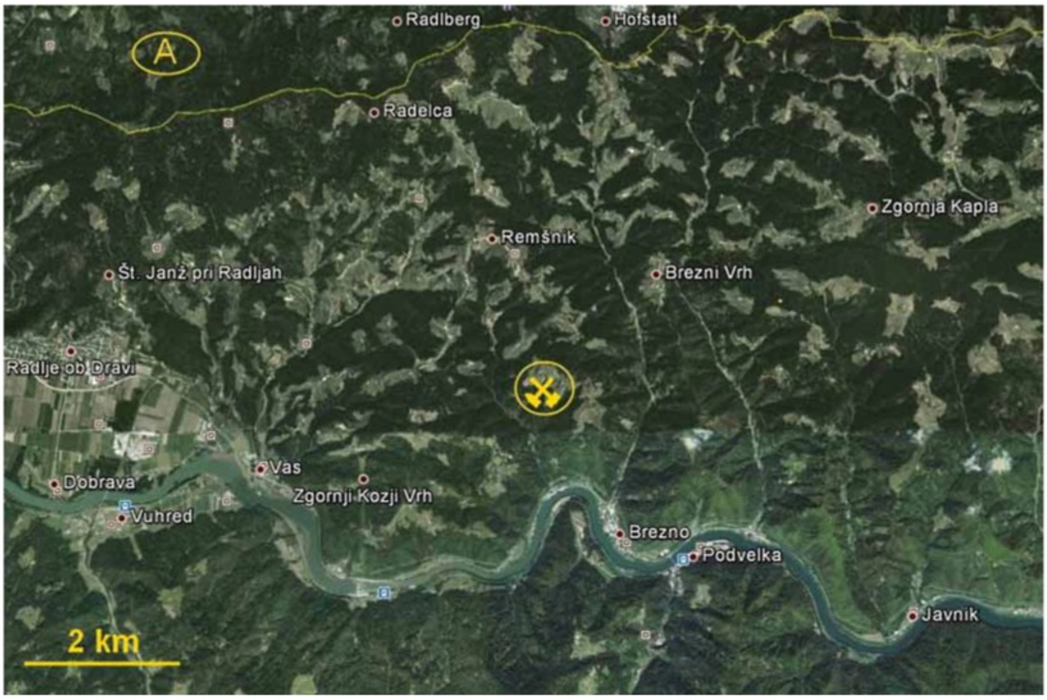
The polymetallic Remšnik ore deposit is situated at the Kobansko area in northern Slovenia. Mineralization occurs in the thrust zone of the weakly metamorphosed old Palaeozoic rocks of the Magdalensberg formation, the Remšnik nappe, onto the retrogressed schists of the Austroalpine metamorphic basement. Hydrothermal ore mineralization and silicification follow slaty cleavage in partly brecciated marmorized dolomite lenses and subordinately in metatuffites and phyllites. Its origin is most probably connected to the lively Tertiary magmatism, occurring at the Pohorje Mountains. Mineral paragenesis of the predominant Pb, Cu and Zn silver bearing sulphide ore is associated with numerous secondary minerals. Among them, two rare sulphates with H_2O of Cu and Zn occur, found for the first time in Slovenia. The green, transparent monoclinic crystals, only some tenth of millimetre in size were determined by SEM as ramsbeckite $(Cu, Zn)_{15}(SO_4)_4(OH)_{22} \cdot 6(H_2O)$. Greenish in colour are also leafy, hexagonal, flowery intergrown crystals, which most probably belong to namuwite $(Cu, Zn)_4(SO_4)(OH)_6 \cdot 4(H_2O)$. Its submicroscopic size and small quantity did not permit reliable determination, yet.

Uvod

Dosedanje raziskave Avstroalpinika pri nas so bile usmerjene predvsem na območje Pohorja, medtem ko so bili ostali deli vključeni v manjšem obsegu. Podrobno proučevanje mineralnih surovin in mineralogije je bilo pogosto postavljeno v ozadje. Zbiralski vnemi ljubiteljev mineralov se moramo zahvaliti, da se pri nas tudi na področju odkrivanja mineralov stvari premikajo naprej.

Čeprav je rudišče Remšnik znano že dolgo časa, spoznavanje njegove mineralne združbe še ni zaključeno. Za sledenje rudnih pojavov in s tem rudišč so pogosto prvi indikatorji sekundarni minerali, ki se pojavljajo v oksidacijskih conah. Navadno najdemo le neznatne količine teh mineralov, vendar nam lahko kažejo, kaj se nahaja v njihovi okolici. Najdba ramsbeckita v remšniškem rudišču je zato pomembna tako z mineraloškega vidika, kot tudi z vidika sledenja sorodnih pojavov rudne mineralizacije na drugih območjih.

Remšnik danes kot rudno nahajališče ni več zanimiv, kljub temu pa predstavlja na širšem območju za strukturne geologe edini vpogled v tretjo dimenzijo, predvsem pa »Meko« za zbiralce redkih mineralov. Le-ti se radi pošalijo, da jih je Bog kaznoval z množico modrih in zelenih mineralov. Zato ni čudno, da tudi predstavljena najdba ramsbeckita pripada zelenim kristalčkom. Vendar pa so se že makroskopsko, še posebno pa pod lupo, razlikovali od do sedaj



Sl. 1. Položaj vasi Remšnik in opuščenega Janičkovega rova. Izsek iz Google Earth.

Fig. 1. Location of the Remšnik village and the abandoned Remšnik mine (Janiček pit). Cut out from Google Earth.

znanih v remšniškem rudišču. Njihova določitev je predstavljala osnovo za pričujoče raziskave.

Ramsbeckit so do sedaj, razen v matičnem nahajališču pri Ramsbecku in še nekaterih mestih v Nemčiji, našli v kar nekaj rudnikih po svetu: npr. v Italiji, prvič v rudniku »La Venezia« v limonitizirani jalovini (Orlandi & Perchiazzi,1989), o najdišču poročajo iz rudnikov Ecton v Pennsylvaniji (Peacor et al, 1987), Penrhiw (Mason & Green, 1995) in drugih iz Velike Britanije, z Japonske (Ohnishi et al, 2004) i.t.d. Po sedaj znanih podatkih so ga našli v enajstih državah na različnih lokacijah. Na mnogih mestih verjetno še čaka naključnega najditelja, saj ga pred tem dobro varuje obilica drugih zelenkastih mineralov in mikroskopska velikost kristalov.

Geografski položaj

Vzporedno s Pohorjem poteka na severni strani Dravske doline hribovje, ki ga uvrščamo med sredogorja. Ker nima enotnega pogorja, so ga v preteklosti večkrat neuspešno poskušali poimenovati enotno. V nekaterih atlasih je vpisano ime Kobansko, v drugih Kozjak. V osrednjem delu tega območja se v povirju levih pritokov reke Drave (Brezniškega, Štimpaškega in Vaškega potoka) nahaja raztreseno naselje Remšnik. Na zahodnem pobočju jugo-jugovzhodno potekajočega remšniškega hrbta, se južno od naselja nahaja opuščen rudnik Remšnik (sl. 1).

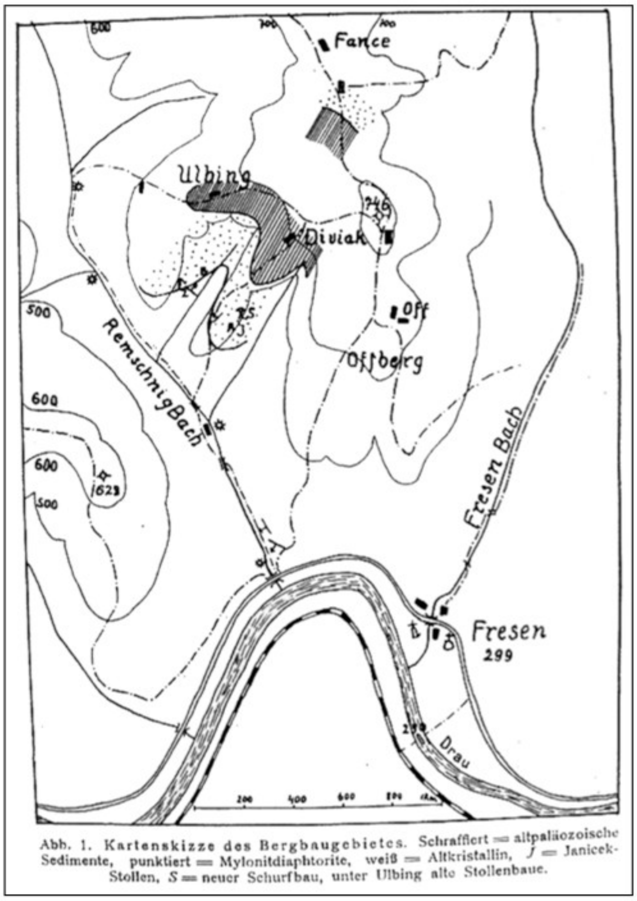
Od rudarskih objektov je najdostopnejši Janičkov rov, ki je označen na sliki 1. Območje je dokaj zaraščeno, zato ga prišlekom ni lahko najti.

Nekaj podatkov o rudišču

Rudišče Remšnik je pritegnilo pozornost raziskovalcev in rudarjev že pred več kot 250 leti. V arhivskih virih (Arhiv R Slovenije) najdemo, da je baron Michelangelo Zois leta 1763 odprl rudnik in zgradil topilnico na Breznu, kar pomeni, da je bilo rudišče gotovo odkrito že prej, čeprav pisnih virov o tem nismo zasledili. Koncesija za odprtje rudnika je bila podeljena na podlagi fevdnega pisma z dne 14. junija 1850 pod št. 1937. Glasila se je na ime »Drauwalder silberhältiger Blei, Kupfer und Zink Bergbau« (srebronosni svinčev, bakrov in cinkov rudnik Dravski gozd). Prvi lastniki rudnika so bili Jakob Krušnik, Karl Kranz in Johan Baumgartner. Izdelana sta bila dva rova, ki so ju poimenovali Marija in Franz, oz. tako imenovan Zwilling Stollen (dvojčični rov). V tem času so nakopano rudo talili v Ožbaltu ob Dravi. Po podatkih graške trgovinske zbornice so leta 1853 pridobili 74,658 kg srebra, tri leta kasneje le še okoli 50 kg. Oktobra 1887 je postal lastnik Karel Wehrkan iz Litije in ga že leta 1888 prodal Litijski rudarski družbi. Ta je prenehala z odkopavanjem rude na Remšniku 22. decembra 1891. V tem času so izkopali rov pod kmetijo Dijak in ga poimenovali Janičkov rov, rudnik pa »Fressen Bergbau«. Do druge svetovne vojne se je zamenjalo še nekaj lastnikov, dokler rudnik 1946. leta ni bil nacionaliziran. Po tem obdobju so ga obiskovali le geologi in zbiralci mineralov.

V remšniškem rudniku so namesto lesenega podporja uporabljali jalovinski material, s katerim so podzidali in podpirali rove in stene večjih odkopnih mest. Prav zato je Janičkov rov, kljub temu, da je le 3 do 5 m pod površjem, v sprednjem delu še danes dostopen, v zadnjem delu pa zarušen.

Po dosedanjih podatkih se orudenje v Remšniku nahaja v staropaleozojskih nizkometamorfnih kamninah Štalenskogorske formacije. Nastopa v obliki leč v območju metatufitov in dolomitnih marmorjev ter filitov (Drovenik et al, 1980). Najstarejši nam znani članek o rudišču predstavlja objava Tornqui-



Sl. 2. Tornquistova geološka skica z označenima rovoma Janiček in Ulbing pod narivnim stikom staropaleozojskih kamnin z retrogradno spremenjenimi in milonitiziranimi kamninami. Reproducirana slika 1 (iz: Tornquist, 1929).

Fig. 2. Tornquist geological sketch with marked Janiček and Ulbing pits under the thrust contact of old-Paleozoic rocks with retrogressed and mylonitized rocks. Reproduced Figure 1 (From: Tornquist 1929).

sta (1929), kjer omenja rudarska dela pod kmetijo Ulbing. Avtor je v svoji objavi na sliki 1 označil dva rudniška rova (Janičkov in Ulbing) pod narivnim stikom staropaleozojskih kamnin (nem. altpaläozoische Sedimente) z retrogradno spremenjenimi in milonitiziranimi kamninami (nem. Mylonitdiaphtorite), ki je prikazana na sliki 2. Na manuskriptni geološki karti odkopa pod kmetijo Dijak iz arhiva rudnika Mežica (Poročila geološke službe rudnika Mežica, 1984-1989) uvrstitev kamnin med milonite ali prave filite ni opredeljena. Znana je le uvrstitev krovnih kamnin v Štalenskogorsko formacijo, ki sta jim Mioč in Ramovš (1973) na tem območju določila spodnjedevonsko starost. Zato še vedno obstaja dvom, na katero formacijo (če je samo ena) je pravzaprav vezana mineralizacija.

O genezi rudišča so mnenja deljena. Orudenje nekateri povezujejo s pohorskim (Tornquist, 1929; Duhovnik, 1956; Berce, 1963, Grafenauer, 1965), drugi pa s paleozojskim magmatizmom (Hegemann, 1960; Drovenik et al, 1980).

Polimetalno rudišče Remšnik se ponaša z raznolikostjo mineralov, ki ji kar ni videti konca. Mineralno paragenezo sestavljajo številni rudni in jalovinski minerali, katerih skupno število že presega 55. Od rudnih mineralov so bili do sedaj določeni: galenit, sfalerit, pirit in halkopirit kot prevladujoči, podrejeno pa kuprit, tetraedrit, boulangerit, bornit, halkozin, covellin, freibergit, gersdorffit, akantit in polibazit. Drovenik (1980) in Grafenauer (1966) še nista našla polibazita in akantita, zato je Drovenik domneval, da je srebro (in bizmut) vgrajen v strukturi galenita in halkopirita. Posredno namiguje, da bi bila za visoko vsebnost srebra v galenitu lahko kriva tudi neustrezna analitska metoda.

Glavni jalovinski minerali v rudi so kremen, dolomit s povišano vsebnostjo železa in podrejeno kalcit in aragonit. Posebno pestrost pa predstavljajo sekundarni minerali, ki so nastali v oksidacijski coni remšniškega rudišča. Naj naštejemo le nekatere: kuprit, tenorit, hematit, goethit, manganovi oksidi in hidroksidi, malahit, azurit, smithsonit, cerusit, hidrocinkit, brianyoungit, rosasit, aurikalcit, barit, sadra, linarit, langit, baverit, posnjakit in karbonatni cianotrihit, aragonit, piromorfit in krizokola (chrysocolla).

Nekaj pogostejših mineralov Kobanskega (predvsem kristale kremena) so prikazali Žorž in sodelavci (2007).

Material in metode preiskav

Prikazani rezultati temeljijo tako na terenskih opazovanjih, kot tudi laboratorijskih preiskavah. Vzorci so bili odvzeti ob orudeni žili iz Janičkovega rova. Pestrost sekundarnih mineralov, ki se nahajajo v razpokah, lahko vidimo pod stereolupo, vendar so premajhni za določitev. Količina najdenih vzorcev ni bila zadostna, niti pa primerna za izdelavo petrografskih preparatov in/ali obrusov, saj bi tanke prevleke z brušenjem izgubili. Izdelana je bila rentgenska difraktometrijska analiza na koščku vzorca z mikrokristalnim oprhom. Drobnih kristalčkov, ki smo jih želeli določiti, prav tako ni bilo mogoče izolirati za kemično analizo. Tako je od palete preiskovalnih metod, zaenkrat ostala le preiskava z vrstičnim elektronskim mikroskopom. Analize so izdelane s SEM znamke JEOL JSM 6490LV pri pospeševalni energiji 20 kV, na delovni razdalji 10 mm. Uporabljen je način BSE pri nizkem vakuumu, brez naprševanja. Osnovna semikvantitativna kemična sestava je določena z Oxford INCA EDS (compo način) pri enaki pospeševalni energiji.

Rezultati in diskusija

Na Osnovni geološki karti 1:100 000, list Slovenj Gradec (Mioč & Žnidarčič, 1977) je remšniško nahajališče označeno med Remšniškim pokrovom iz štalenskogorskih kamnin in talninsko Pohorsko formacijo iz retrogradno metamorfnih skrilavcev Avstroalpinske podlage. Med njima se nahaja tanek pas filitov. Določitev filitov na tem območju in vzhodno od tod je nekoliko sporna. Zaradi večfaznih sekundarnih sprememb ni jasno, ali pripadajo pravim filitom ali pa milonitom, ki so nastali retrogradno iz dinamometamorfno spremenjenih kamnin Pohorske formacije (po Mioču, 1978 imenovane Kobanska serija). Nesporno je vanje vključenih tudi del štalenskogorskih kamnin, zajetih v narivno cono.

Tako makro-, kot tudi mikroteksture kamnin nakazujejo več faz tektonskega delovanja, vključno z dvakrat reaktiviranim subhorizontalnim strižnim premikanjem, zaradi katerega so v vse kamnine vtisnjene dinamometamorfne spremembe. Prvo se odraža kot plastične deformacije z nastankom foliacije. Pri tem so bile kamnine intenzivno milonitizirane. Pri drugem pa je nastal skrilav klivaž, ki pretežno sledi foliaciji. Nastanek teh struktur je v širšem območju vzhodnega Avstroalpinika povezan

Sl. 3. Razpoke in sekundarni klivaž nakazujejo delovanje desnega striga (rdeče puščice). Janičkov rov daje zavetje netopirjem. Opuščen rudnik Remšnik. Foto Z. Žorž.

Fig. 3. Fractures and secondary cleavage indicate dextral sense of shear (red arrows). The Janiček pit gives shelter to bats. Abandoned Remšnik mine. Photo Z. Žorž.

z zgornjekrednim krovnim narivanjem in terciarnim vzhodno usmerjenim alpskim pobegom (npr. Fodor et al. 1998, 2002, 2008). Strukturni parametri širšega območja nakazujejo, da sta bila Pohorje in Kobansko/Kozjak ob vtiskanju granodioritne magme v spodnjem miocenu še enoten blok in sta se ločila šele pozneje.

Stopnja dosedanjih raziskav ne dovoljuje enoznačne opredelitve geneze rudišča. Kljub temu pa se nakazujejo nekatere pomembne povezave, ki negirajo njegovo paleozojsko poreklo: sulfidna rudna mineralizacija in močna okremenitev, ki je prikrila teksturni značaj kamnin, sta sledili klivažu, ki je terciarnega (predvidoma miocenskega) nastanka; kobanski blok se je ločil od pohorskega verjetno v srednjem miocenu in je bil do tedaj bliže vplivnemu območju granodioritne intruzije; mineralna sestava in izotopska sestava žvepla v Remšniku in na Okoški gori na Pohorju sta sorodni (Drovenik et al. 1976, 1980). Na osnovi tega obstaja velika verjetnost, da je orudenje povezano z miocenskim pohorskim magmatizmom, kot so že domnevali Tornquist (1929), Duhovnik (1956), Berce (1963) in Grafenauer (1965). Še vedno pa ostaja vprašanje, ali je lahko povezano tudi z remobilizacijo starejše (kredne/paleozojske?) mineralizacije, saj naj bi po Droveniku in sodelavcih (1980) orudenje na Okoški gori nastalo v paleozoiku. To starost argumentirajo z blastično rastjo rudnih mineralov v času regionalne metamorfoze, kar pa ni zadosten razlog.

Prečno na foliacijo in skrilav klivaž potekajo mlajše poševne razpoke, nastale kot posledica obnovljenega strižnega premikanja. Oblikujejo sekundarne klivažne ravnine ter označujejo delovanje desnega striga (sl. 3). Te razpoke niso okremenjene in so brez primarne (sulfidne) mineralizacije. Vse

Sl. 4. Delno zarušen Janičkov rov. Vidne so subhorizontalne razpoke vzporedne starejšemu klivažu in strma prelomna površina (zgoraj). Levo spodaj je odlomljen blok brečiranega in nato še močno okremenjenega dolomita. Janičkov rov, opuščen rudnik Remšnik. Foto Z. Žorž.

Fig. 4. Partly collapsed Janiček pit. Subhorizontal fractures are parallel to the older cleavage. Steep fault surface (top of the figure) cut other structures. Fallen block of brecciated and subsequently strongly silicified dolomite can be seen at the bottom left. Abandoned Remšnik mine. Photo Z. Žorž.

Sl. 5. Modrikasti in zeleni oprhi sekundarnih mineralov na prečnih prelomnih površinah. Vzdolž klivaža po foliaciji se nahaja predvsem sulfidno svinčevo, cinkovo, bakrovo orudenje in okremenitev (sveži odlomi v sredini slike). Remšnik, Janičkov rov. Foto Z. Žorž.

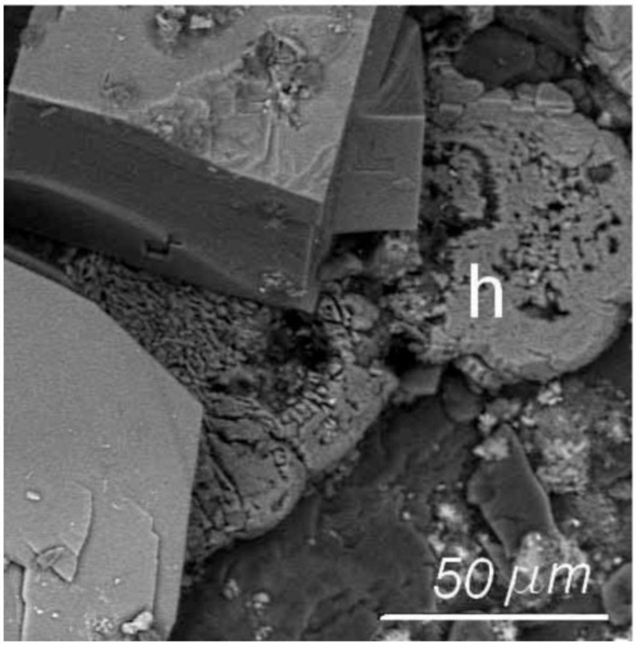
Fig. 5. Bluish and green coatings of secondary minerals on transverse fault plains. Prevailingly sulphide copper zinc and lead ore mineralization and silicification occur along the cleavage parallel to foliation (fresh surfaces in the photo centre). Janiček pit, abandoned Remšnik mine. Photo Z. Žorž.

Sl. 6. Rjavi (na levi skoraj črni) do 1 mm veliki kristali beaverita na kremenu iz Janičkovega rova. Opuščen rudnik Remšnik. Najdba in zbirka Z. Žorž. Foto: B. Moser.

Fig. 6. Brown (nearly black on the left), up to 1 mm big crystals of beaverite on quartz from the Janiček pit. Abandoned Remšnik mine. Find and collection Z. Žorž, photo B. Moser.

Sl. 7. Modri rosasit ter brezbarvni in prozorni aragonitni ježki iz Janičkovega rova. Opuščen rudnik Remšnik. Velikost motiva 15 x 12 mm. Najdba, zbirka in foto Z. Žorž.

Fig. 7. Blue rosasite and colourless transparent aragonite needles from the Janiček pit. Abandoned Remšnik mine. Size of the motif 15 x 12 mm. Find, collection and photo Z. Žorž.



strukture sekajo genetsko najmlajši subvertikalni prelomi (sl. 4) prevladujoče smeri jugozahod-severovzhod, redkeje prečno nanje.

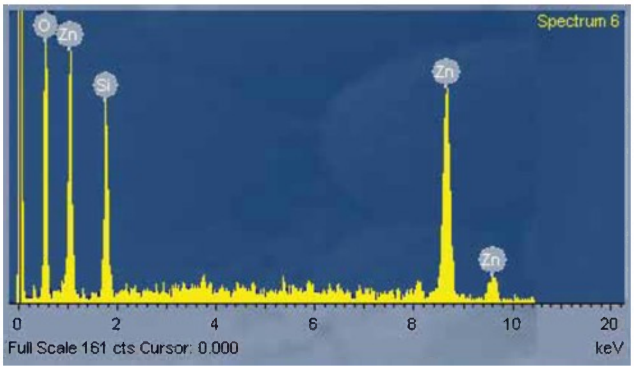
Razmere v Janičkovem rovu kažejo, da so orudene pretežno karbonatne leče ter delno širša porušena narivna cona, v kateri so zajete tako kamnine Štalenskogorske, kot tudi Pohorske formacije. Primarna rudna mineralizacija in okremenitev sta sledili razpoklinski poroznosti starejšega skrilavega klivaža, ki makroskopsko sovpada s foliacijo, medtem ko v dveh generacijah prečnih razpok in prelomov najdemo v glavnem sekundarno mineralizacijo (sl. 5). Brečirane kamnine so prepojene s kremenico, zato so na videz masivne.

Večino redkih sekundarnih mineralov je na Remšniku našel Z. Žorž in določil skupaj z Moserjem (Žorž & Moser, 2002). Med njimi je posebno zanimiv beaverit, svinčev-bakrov-železov-aluminijev sulfat. Po dosegljivih podatkih je bil ta mineral do najdbe Z. Žorža poznan le kot rumen oprh, tu pa se nahajajo milimetrski, karamelno rjavi, prozorni do prosojni kristali (sl. 6). Nastopa kot prevleke na kremenu.

Med karbonati je zelo slikovita parageneza rosasita in aragonita na nekoliko limonitizirani kremenovi podlagi (sl. 7).

V osnovi nekaterih sekundarnih mineralov smo s SEM določili hemimorfit (h) s kemično formulo $(Zn_4Si_2O_7(OH)_2 \cdot (H_2O)$. V vzorcih je tako mikrozrnat, da je tudi z vrstičnim elektronskim mikroskopom vidna le njegova skorjasta (natečna) struktura. Na SEM sliki 8 (levo) se nahaja ob kristalih ramsbeckita. EDS spekter hemimorfita (slika 8 desno) prikazuje glavne elemente kemične sestave Zn, Si in O.

Redki minerali, določeni v remšniškem rudišču, nastopajo v sledovih in so mikroskopske do submikroskopske velikosti, zato so do zadnjih nekaj let ostali neopaženi. Med njimi sta dve posebno lepi obliki sulfatov, ki pri nas do nedavna še nista bili najdeni. Gre za sekundarna minerala, ki nastajata v procesu pripovršinskega preperevanja bakro-



Sl. 8. Majhno svetlo sivo polje hemimorfita (h) ob dveh kristalih ramsbeckita. SEM posnetek (levo, izsek iz slike 13) in EDS spekter hemimorfita (zgoraj). Opuščen rudnik Remšnik.

Fig. 8. Small light grey field of hemimorphite (h) near two ramsbeckite crystals. Left - SEM (BSE) image (cut from fig. 12); top - EDS spectrum of hemimorphite. Abandoned Remšnik mine.

vo cinkovih rud, odvalov in žlinder. Prvi pripada ramsbeckitu, ki sta ga na kratko predstavila Žorž in Trajanova (2010).

Določitev drugega minerala je še vedno vprašljiva, saj nastopa v neznatni količini in v tako drobnih kristalih, da ga pod binokularno lupo nismo opazili in ga tudi s SEM analizo nismo uspeli enoznačno dokazati. Njegova semikvantitativna kemična sestava in kristalna oblika pa nakazujeta, da zelo verjetno pripada namuwitu.

Ramsbeckit

Značilne rudne žile v remšniškem rudišču so sestavljene predvsem iz halkopirita, galenita in sfalerita v osnovi iz kremena in karbonatov, od katerih je najpogostejši dolomit. V opuščenih rovih dosežejo v povprečju debelino med 3 in 5 cm. Debelejše žile so navadno sestavljene iz več slojev, ki so med seboj ločeni s trakovi kremena in dolomita. Slednji je videti kot pole razlistane osnovne kamnine in/ali pa remobiliziranega karbonata iz nje. Sekundarna mineralizacija se nahaja v odprtih razpokah in prelomih. Razpoke sekundarnega klivaža položno, vzdolžno sekajo rudne žile. V najmlajših, strmih prelomih in razpokah so se kot oprhi odlagali le sekundarni minerali, značilni za oksidacijsko cono.

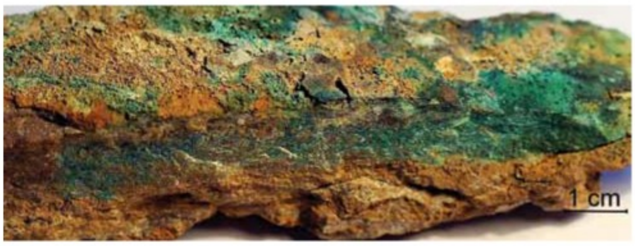
Debelejša orudena žila z ramsbeckitom se nahaja v spodnjem (drugem) obzorju, ki je okrog 7 m pod površjem. Sestavljena je predvsem iz halkopirita, galenita in sfalerita. Med posameznimi sloji v žili je kristaliziral pirit, ki ima razvite kristalne ploskve pentagonskega dodekaedra, velikosti do enega milimetra. Oprhi bakrovo cinkovih sekundarnih mineralov so se odložili v razpoki v zgornjem delu žile. Razpoka v sredini žile je vsebovala največ linarita in langita. V spodnjem delu žile so prevladovali kristali malahita in rosasita v združbi z redkima aurihalkitom in hidrocinkitom.

Kljub večanju števila najdb, ramsbeckit še vedno spada med redke sulfate. Po Nickel-Strunzovi klasifikaciji mineralov spada med vodne sulfate z dodatnimi anioni, v prostorsko skupino P 2_1/a 2/m. Matično nahajališče je rudnik Bastenberg blizu kraja Ramsbeck v Nemčiji, po katerem je dobil svoje ime. Odkrit je bil leta 1984, IMA pa ga je potrdila 1985 (Internet 1). Prvi so ga opisali Hodenberg in sodelavci leta 1985 in zanj podali stehiometrično kemijsko formulo $(Cu, Zn)_7(SO_4)_2(OH)_{10}·5(H_2O)$. Določili so mineralno paragenezo (Hodenberg et al. 1985), ki je povsem primerljiva z remšniško. Kristalno zgradbo je leta 1988 določil Effenberger. Revidiral je kemijsko formulo in jo iz prejšnje oblike popravil v $(Cu,Zn)_{15}(SO_4)_4(OH)_{22}·6(H_2O)$.

Ramsbeckit iz Janičkovega rova nastopa v pravilnih kristalih, velikih nekaj desetink mm, največ do 0,5 mm, ki so makroskopsko vidni le kot barvne prevleke (sl. 9). Pri povečani fotografiji so lokalno že prepoznavni nejasni, živo zeleni kristali (sl. 10). Pod binokularno lupo imajo zeleno barvo, vendar zaradi močne refleksije od kristalnih ploskev, fotografije niso bile uspešne. Za boljšo predstavo barve minerala je ustrezna fotografija ramsbeckita iz nahajališča Penrhiw na Walesu, prikazana na spletni strani (Internet 2 ali Internet 3), ki povsem odgovarja primerkom iz Remšnika. Kristali so prosojni in imajo nekoliko svileno steklast sijaj. Na vzorcu, ki je bil shranjen v suhem prostoru, so kristali nekoliko izgubili zeleno barvo, medtem ko je modrikasta niansa postala izrazitejša.

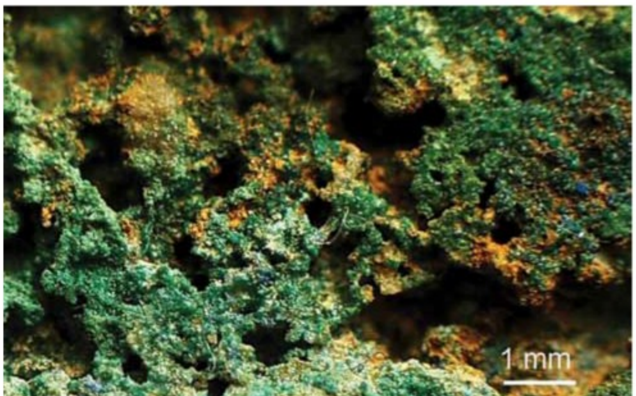
Ramsbeckit kristalizira v monoklinskem sistemu. Kristali so različnih oblik. Najizrazitejša je ploskev osnovnega pinakoida (001), po katerem je vidna nejasna razkolnost. Izraziti sta ploskvi (100) in (010). Ploskev (210) je praviloma manjša od ostalih (sl. 11), medtem ko se ploskvi (120) in (310) v večini primerov sploh nista razvili (sl. 12, v sredini). V nekaterih kristalih pa so razvite le ploskve (100), (001) in (010) (sl. 12, levo spodaj in desno zgoraj).

Skice idealiziranih oblik kristalov ramsbeckita, ki smo jih našli do sedaj, so prikazane na sliki 13. Na sliki 13 B so z indeksi označene kristalne ploskve oblik 1, 2 in 3 s slike 13 A. Kristalne ploskve, ki določajo morfologijo ramsbeckita so pinakoidi (001), (100), (010) in (210) ter prizma 3. reda (110) (slika 13, risbi 2A, 2B). Prizma (110) je lahko bolj, ali manj izrazita. Kristali ramsbeckita imajo lahko razvite samo kristalne ploskve pinakoidov (slika 13,



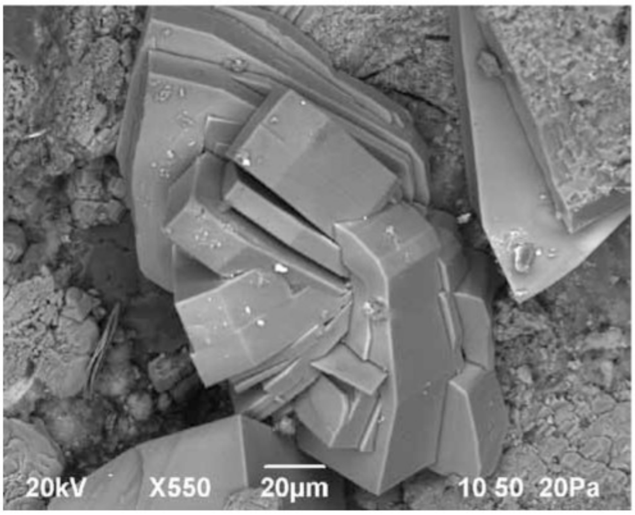
Sl. 9. Modrikasto zelene prevleke prevladujočih sulfatnih sekundarnih mineralov z ramsbeckitom iz Janičkovega rova. Opuščen rudnik Remšnik. Foto M. Trajanova.

Fig. 9. Bluish green coatings of predominant sulphate minerals with ramsbeckite from Janiček pit. Abandoned Remšnik mine. Photo M. Trajanova.



Sl. 10. Zeleni kristali ramsbeckita iz Janičkovega rova. Redka modra zrna so langit. Opuščen rudnik Remšnik. Foto M. Demšar.

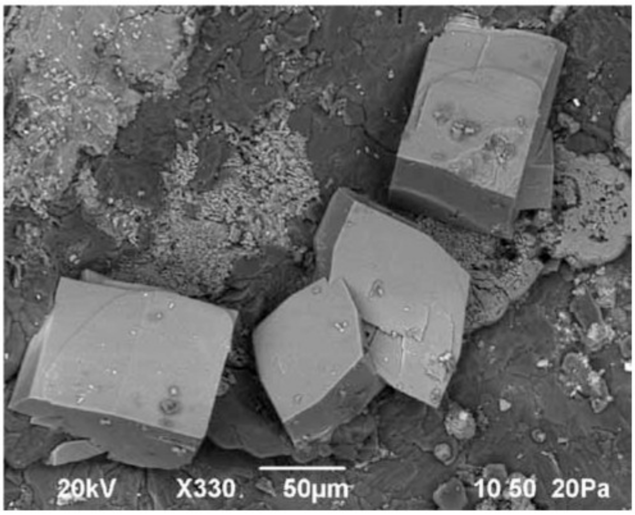
Fig. 10. Bright green crystals of ramsbeckite from Janiček pit. Blue grains belong to langite. Abandoned Remšnik mine. Photo M. Demšar.



Sl. 11. Kristalni zraščenci ramsbeckita z lepo vidnimi ploskvami osnovnega pinakoida in prizem. SEM (BSE) posnetek.

Fig. 11. Intergrown ramsbeckite crystals with expressed plains of basal pinacoid and prisms. SEM (BSE) image.

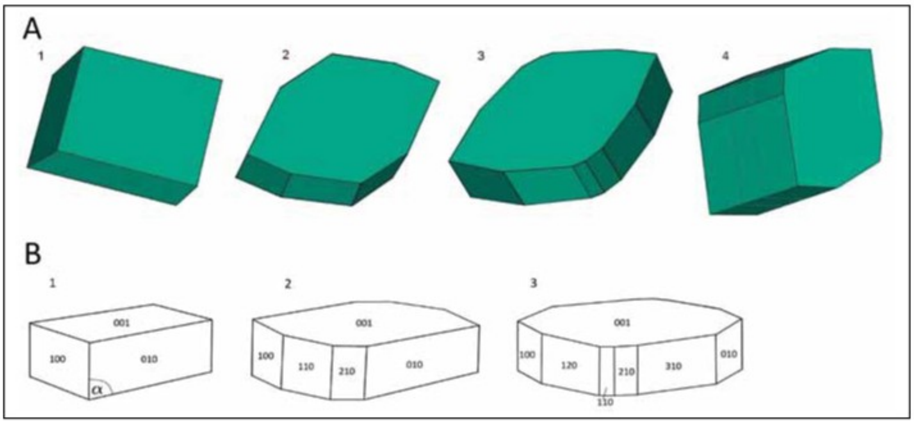
risba 1A, 1B). Najpogostejša je oblika 2, pri kateri je lahko ploskev (010) krajša, na račun podaljšane ploskve (210), kot je primer oblika 2 na sliki 13A. Najpestrejša in redkejša je oblika 3, ki ima razvitih največ kristalnih ploskev. V tem primeru je ploskev (110) lomljena, tako da se je razvila ploskev (120). Tudi ploskev (010) je lomljena in na njen račun je nastala ploskev (310) (sl. 13, oblika 3A, 3B). Primer te oblike vidimo na sliki 11 na spodnji desni polovici največjega kristala osrednjega zraščenca.



Sl. 12. Dve zrni ramsbeckita v sredini predstavljata najpogostejšo obliko s ploskvami (001), (100), (110), (010) in (210). Levo spodaj in desno zgoraj sta kristala z razvitimi pinakoidi. SEM posnetek.

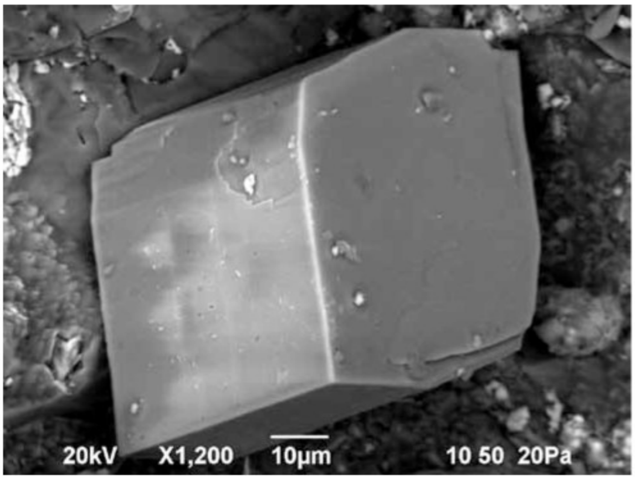
Fig. 12. Two grains in the figure centre represent the most frequent form with planes (001), (100), (110), (010) and (210). Crystals with developed pinacoids can be seen at the bottom left and top right. SEM (BSE) image.

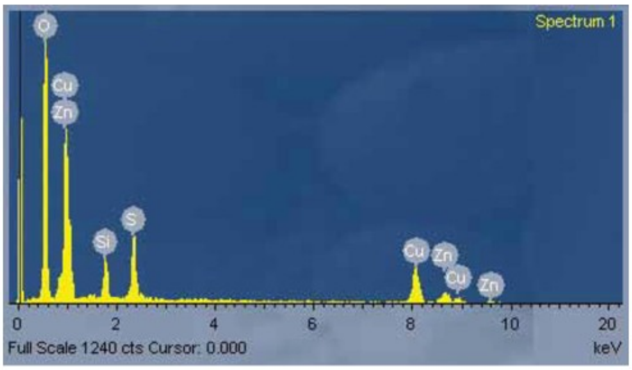
Peacor in sodelavci (1987) in Ohnishi in sodelavci (2004) omenjajo razkolnost ramsbeckita po osnovnem pinakoidu, ki je nakazana tudi v našem primeru (slika 11, na osrednjem zraščencu, zgoraj). Višji kristal 4 (sl. 13A) najverjetneje predstavlja dvojček. Kot zasledimo v Mineraloškem priročniku, verzija 1 (Bideaux & Nichols, 2004, ©



Sl. 13. Skica do sedaj najdenih kristalnih oblik ramsbeckita v opuščenem rudišču Remšnik. Glej razlago v tekstu.

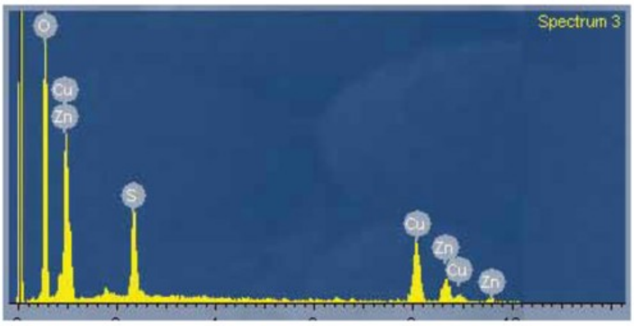
Fig. 13. Sketch of the so far found ramsbeckite crystal forms in the abandoned Remšnik mine. See explanation in the text.





Sl. 14. EDS spekter ramsbeckita (leva točka na sliki levo).

Fig. 14. EDS spectrum of ramsbeckite (left spot in the left figure).



Sl. 15. EDS spekter čiste površine zrna ramsbeckita vidnega na desni strani na sliki 12.

Fig. 15. EDS spectrum of clear ramsbeckite grain surface seen at the right side of figure 12.

2004-2013), ima ramsbeckit ponavljajoče dvojčke, ki oblikujejo cilindrične skupke. Tak primer bi lahko predstavljal kristal na SEM posnetku (sl. 14 levo). Podobnost nekaterih oblik kristalov z remšniškimi (np. oblika 1 s slike 13A, 13B) vidimo na sliki 1 Ohnishi-ja in sodelavcev (2004) iz rudnika Hirao blizu Osake na Japonskem, kjer prevladujejo na videz romboedrski kristali.

Kvalitativna kemična sestava ramsbeckita je prikazana na EDS spektru (sl. 14 desno). Zaradi drobnih zrnc na površini kristala se pojavi neznaten pik Si. Za ploščati ramsbeckit nenavadno visok kristal verjetno predstavlja dvojček, ki je enak obliki 4 na sliki 13 A.

EDS spekter čistega ramsbeckita (sl. 15) je sneman na čisti, gladki površini spodnjega kristala ob zgornjem desnem robu slike 11. V sestavi zato ni primesi silicija, kot na EDS spektru na sliki 14.

Po kemični sestavi je ramsbeckitu sorodnih kar nekaj redkih mineralov sulfatov, kot na primer: langit, posnjakit, wroewolfeit, spangolit, ktenasit, pa tudi namuwit.

Na rentgenskem difraktometru smo poskusili snemati košček vzorca z mikrokristalnim oprhom, vendar analiza ni bila uspešna.

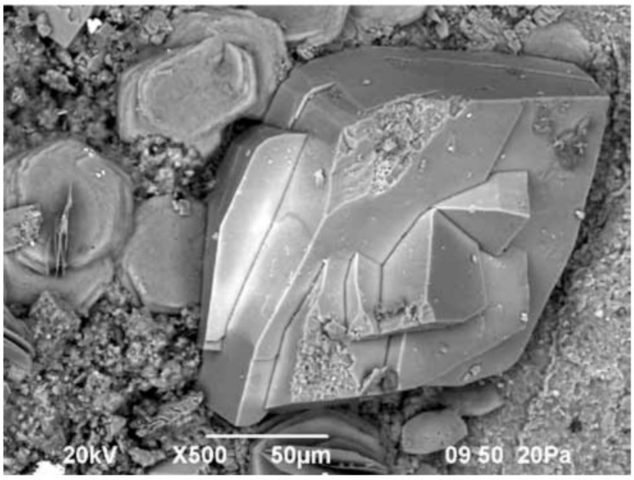
Namuwit

V sestavi modrikasto zelenih, na oko amorfnih oprhov, se v razpokah ob ramsbeckitu nahaja še en mikrokristalen sekundarni sulfatni mineral, ki smo ga zaenkrat določili kot namuwit.

Namuwit so prvič opisali Bevins in sodelavci leta 1982. Določen je bil v vzorcu iz rudišča Aberllyn, ki se nahaja v zbirki Narodnega muzeja na Walesu, po katerem je dobil ime (NAtional MUseum of Wales). Istega leta ga je potrdila IMA (Internet 4). Leta 1983 je bil na kratko prikazan tudi v reviji American mineralogists pod »New mineral names« (Fleischer & Pabst, 1983). Od tedaj dalje so ga našli na številnih mestih po svetu, tako v oksidacijskih conah bakrovo cinkovih rudišč, kot tudi na rudniških odvalih, največkrat v paragenezi z ramsbeckitom.

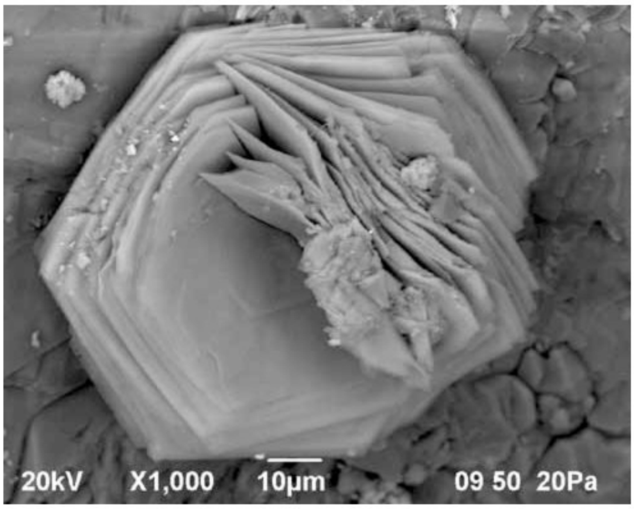
Kemijska formula namuwita je $(Cu, Zn)_4(SO_4)(OH)_6{\cdot}4(H_2O)$ (Bevins et al., 1982). Avtorji ga opisujejo kot svetlo morsko zelen mineral z bisernim sijajem. Ker je v začetnih raziskavah upoštevana le kemična sestava, določena na SEM EDS, smo ga prišteli k ramsbeckitu (Žorž & Trajanova, 2010). Zaradi oblike kristalov s šesterokotnimi preseki, podobnimi sljudam, je bila določitev dvomljiva, zato smo s SEM naredili dodatne raziskave. Skupaj z ramsbeckitom smo ga poskušali določiti tudi z rentgensko difrakcijo, vendar neuspešno. Z EDS dobljena kvalitativna kemična sestava je enaka kot za ramsbeckit. Semikavntitativna kemična sestava pa se nekoliko razlikuje, čeprav je zaradi uporabe nepoliranega vzorca in premajhnih zrnc nezanesljiva.

Po obliki rozet je namuwit zelo podoben še enemu sulfatu, posnjakitu, razlikuje pa se po barvi (posnjakit je moder, namuwit bledo zelen) in kemični sestavi, ker vsebuje poleg bakra tudi cink. Na osnovi tega in oblike kristalov sklepamo, da mineral najverjetneje pripada namuwitu. Značilni svetlo zeleni, submikroskopski cvetasti skupki namuwita (sl. 16) na skorjastih prevlekah sorodne kemične sesta-



Sl. 16. Ob zraščencu ramsbeckita se nahajajo drobni kristalni skupki namuwita (?), ki kažejo šesterokotno simetrijo. SEM (BSE) posnetek.

Fig. 16. Tiny crystal clusters of namuwite (?), showing hexagonal symmetry, are seen beside ramsbeckite. SEM (BSE) image.

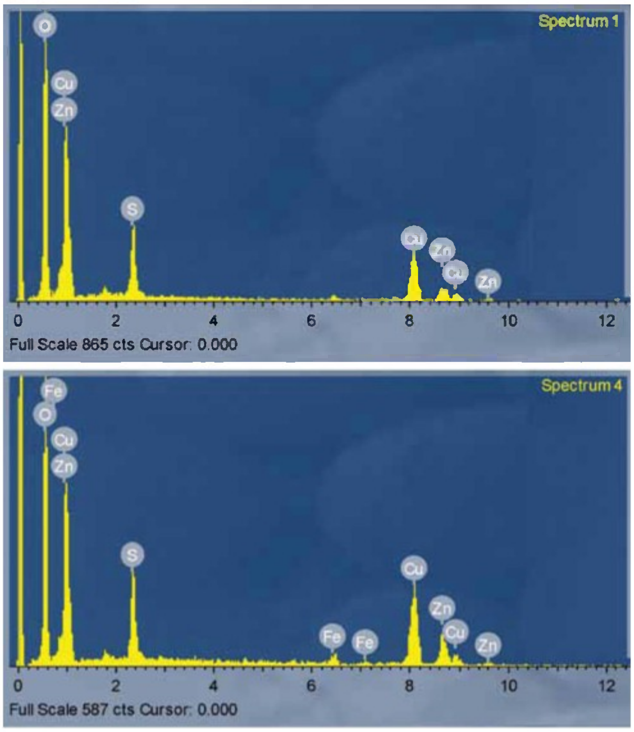


Sl. 17. Cvetasto preraščanje heksagonalnih ploščic namuwita. SEM (BSE) posnetek.

Fig. 17. Flowery intergrowing of hexagonal plates of namuwite. SEM (BSE) image.

ve ob ramsbeckitu so enaki oblikam, ki so jih opisali Bevins in sodelavci (1982) in Groat (1996). Po njihovih podatkih je namuwit izomorfen s sintetičnim cinkovim sulfatom $(Zn_4SO_4OH)_2 \cdot 4H_2O$).

Kristali rastejo iz pretežno amorfne podlage in redko presegajo velikosti 50 µm, izjemoma pa dosežejo tudi 80 µm. Imajo izrazito razkolnost po ploskvah osnovnega pinakoida (001). Pogosti so primeri prečnega preraščanja lističev, kot je vidno na slikah 16 (ob levem robu) in 17.



Sl. 18. EDS spektra namuwita s slike 17.
Fig. 18. EDS spectra of namuwite from figure 17.

Kvalitativna kemična sestava remšniškega namuwita s slike 17 je prikazan na sliki 18. Tako kot ramsbeckit, pripada bakrovemu cinkovemu vodnemu sulfatu z dodatnimi anioni. Zaradi neugodne lege kristalnih ploskev glede na lego detektorja, imajo piki spektra nesorazmerno velikost.

Kristalno strukturo namuwita je določil Groat (1996). Sestavljen je iz ponavljajočih slojev tetraeder-oktaeder-tetraeder (T-O-T), ki so z vodikovo vezjo povezani z medslojno H_2O. Isti avtor je ugotovil, da je namuwit podvržen procesom hidracije in dehidracije, odnosno prehodom iz tetrahidrata v pentahidrat in obratno, pri približno sobni temperaturi.

Zaključek

Polimetalno orudenje v Remšniku je nastalo vzdolž klivažnih razpok sovpadajočih s foliacijo, kar nakazuje njegovo terciarno starost in zelo verjetno povezanost s pohorskim magmatizmom. V procesu oksidacije in pripovršinskega preperevanja primarne sulfidne mineralizacije so v mlajših razpokah kristalizirali številni sekundarni minerali, med katerimi najdemo tudi zelo redke vrste. Pri nas sta to prvič opisana bakrovo cinkova sulfata ramsbeckit in namuwit. Določitev slednjega še ni enoznačna, zato upamo, da bo naslednja najdba količinsko bogatejša in bo omogočila uporabo analitskih tehnik, s katerimi bomo potrdili ali ovrgli sedanjo določitev.

Zahvala

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Abandoned Remšnik mine with ramsbeckite and namuwite(?)

Introduction

The investigations of the Austroalpine in Slovenia have been focused mostly on the area of Pohorje, while other areas have been included to a lesser extent. Detailed study of mineral deposits and mineralogy has usually been left aside. It is the enthusiasm of mineral collectors we have to thank that things are moving forward also in the area of mineral finds in Slovenia.

Though the Remšnik ore deposit has been known for a long time, the recognition of its mineral association is still not finished. Secondary minerals in the oxidation zones are frequently first indicators for tracing ores. Only insignificant quantities of these minerals are usually found, but they indicate what might occur in the surroundings. The find of ramsbeckite in the Remšnik ore deposit is therefore important from mineralogical point of view and also for tracing of cognate ore mineralization in other regions.

Remšnik is nowadays not of interest as an ore deposit; nevertheless, it represents the only insight into the third dimension in this region to structural geologists and particularly a "Mecca" for rare minerals collectors. The latter often like to joke that God punished them with a vast number of blue and green minerals. It is thus not surprising that also the presented ramsbeckite find belongs to green crystals. Despite the fact, they differ macroscopically and particularly under the hand lens from the so far known minerals in the Remšnik ore deposit. Their determination is the basis for the presented study.

Ramsbeckite has been already found in several mines around the world beside the parent occurrence near Ramsbeck in Germany, e.g.: in limonitic gangue in »La Venezia« mine for the first time in Italy (Orlandi & Perchiazzi, 1989), it is reported from Ecton mine in Pennsylvania (Peacor et al, 1987), from Penrhiw mine (Mason & Green, 1995) and other locations in Great Britain, from Japan (Ohnishi et al., 2004) etc. As for known data, it was found on different locations in 11 countries up to now. In other localities, it is probably still waiting for a coincidental finder, as it is well hidden among numerous other greenish minerals and by its microscopic crystal size.

Geographic setting

Parallel with the Pohorje Mountains and north of the Drava valley, a hilly area extends in northern Slovenia. As it has no continuous mountain chain, several attempts were made in the past to name the area with one name. The name Kobansko appears in some topographic maps and in the others Kozjak. In the central part of this region, drained by the Brezniški, Štimpaški and Vaški brooks, the scattered village of Remšnik is situated. On the western slopes of the south-southeast trending Remshnik ridge, abandoned Remshnik mine (Janiček pit) occurs south of the village (Fig. 1).

Janiček pit marked in Figure 1 is the most accessible mining object. Its surrounding is densely vegetated and therefore not easy to be found.

Some data about the Remšnik ore deposit

The Remšnik ore deposit first attracted attention of researchers more than 250 years ago. We can read in documents stored in the Archive of Slovenia that count Michelangelo Zois opened the mine in 1763 and constructed a smelter in Brezno by the Drava River. This shows that the deposit had been discovered much earlier, though we could find no written sources to support this theory. A concession for the mine opening has been vested on the base of feudal letter dated June 14th 1850, under No. 1937. It was worded under the name »Drauwalder silberhältiger Blei, Kupfer und Zink Bergbau« (silver bearing lead, copper and zinc mine Drava forest). The first owners of the mine were Jakob Krušnik, Karl Kranz and Johan Baumgartner. Pits were named Maria and Franz, or the Zwilling Stollen (the twin pit). At that time, the produced ore had been melted in the village of Ožbalt by the Drava River. According to the data of the then Graz Chamber of Commerce 74.66 kg of silver was extracted in 1853 and only about 50 kg three years later. In October 1887, Karel Wehrkan from Litija became the owner of the mine and as soon as in 1888 he sold it to the Litija Mining Company. They stopped with exploitation of ore in Remšnik on December 22nd, 1891. In the meantime, they excavated a pit near the Dijak farm and named it Janiček pit and the mine itself »Fressen Bergbau«. Until the Second World War, the ownership of the mine had changed several times. It was nationalized in 1946 and afterwards only geologists and mineral collectors entered the pits.

In the Remšnik mine, gangue material was used to support the pit walls instead of wooden pillars. Walls of the pits and bigger excavated spaces have been underpinned by blocks of country rock, which is why the Janiček pit is still accessible today in the front part, though only 5 to 7 m below the surface. It is collapsed in the back part.

According to the available data, ore mineralization in the Remšnik mine occurs in the old Palaeozoic low metamorphic rocks of the Magdalensberg formation. The mineralized bodies form lenses in metatuffs, dolomitic marbles and phyllites (Drovenik et al. 1980). The oldest known publication about the mine is the one by Tornquist (1929), where he mentioned mining works below the Ulbing farm. He designated two mine pits in his Figure 1 (Janiček and Ulbing) below the thrust contact of old Palaeozoic rocks (altpaläozoische Sedimente) with retrogressed and mylonitized rocks (Mylonitdiaphtorite), shown in Figure 2. The manuscript geological map of the exploitation pit below the Dijak farm, kept at the Mežica mine Archive (Reports of the geological service, 1984-1989) contains no distinction between mylonites and phyllites. Consequently, it is still not clear, which formation (if it is only one) the mineralization is connected to. Only hanging wall rocks are pertained to Magdalensberg formation to which Mioč and Ramovš (1973) determined Lower Devonian age in the Remšnik area.

There are different opinions about the Remšnik ore deposit genesis. Some researchers connect the mineralization to the Miocene Pohorje magmatism (Tornquist, 1929; Duhovnik, 1956; Berce, 1963, Grafenauer, 1965), others to the Palaeozoic magmatism (Hegemann, 1960; Drovenik et al. 1980).

The Remšnik polymetallic ore deposit prides itself on variety of minerals. The mineral paragenesis consists of numerous ore and gangue minerals, together exceeding 55 types. The following ore minerals have been determined: galenite, sphalerite, pyrite and chalcopyrite as the prevailing types, and subordinately cuprite, tetrahedrite, boulangerite, bornite, chalcosine, covelline, freibergite, gersdorffite, acanthite and polybasite. Drovenik (1980) and Grafenauer (1966) did not found polybasite and acanthite yet; therefore Drovenik supposed that silver (and bismuth) is a component of the galenite and chalcopyrite structure. Indirectly, he made a hint that inadequate analytical method could be the reason for high content of silver in galenite.

The main gangue minerals in the ore are quartz, iron dolomite and subordinately calcite and aragonite. Particularly variegated are secondary minerals, which crystalized in the oxidizing zone of the Remšnik mine. Among numerous types only some are stated: cuprite, tenorite, hematite, goethite, manganese oxides and hydroxides, malachite, azurite, smithsonite, cerussite, hydrozincite, brianyoungite, rosasite, aurichalcite, barite, gypsum, linarite, langite, baverite, posnjakite and carbonate cyanotrichite, aragonite, pyromorphite and chrysocolla.

Žorž and co-workers (2007) presented some more frequent minerals (particularly quartz crystals) of the Kobansko area.

Materials and methods of investigation

Presented results are based on field observations and laboratory investigations. Samples were taken near the vein with ore mineralization from the Janiček pit. Diversity of secondary minerals occurring in fractures can be seen under binocular lens, but they are too small for determination. The quantity of gathered samples was not suitable for making either thin sections and/or polished samples; thin coatings would be lost in preparation. A small piece of sample with microcrystallized coating was scanned by X-ray diffractometer. It was equally impossible to isolate thin crystals for chemical analysis. Finally, from the pallet of investigation methods, the only one that remained was scanning electron microscopy (SEM). The analyses were made with SEM JEOL JSM 6490LV at the acceleration energy of 20 kV and at working distance of 10 mm. The BSE mode in low vacuum was used, without coating. Basic semiquantitative chemical composition was determined by Oxford INCA EDS (compo mode) with the same acceleration energy.

Results and discussion

On the 1:100 000 scale Basic geological map of Slovenia, sheet Slovenj Gradec (Mioč & Žnidarčič, 1977) the Remšnik mine is marked between the Remšnik nappe composed of Magdalensberg formation rocks and the footwall Pohorje formation of retrograde schists of the Austroalpine basement. A thin belt of phyllites occurs between the two. Determination of phyllites in this area and further eastward is somewhat disputable. Due to multiple secondary alterations, it is not clear whether this layer belongs to real phyllite or to mylonite, originating retrogressively from dynamometamorphosed rocks of the Pohorje formation (named Kobansko series after Mioč, 1978). It is clear, however, that a part of the Magdalensberg formation rocks, trapped in the thrust zone, is comprised in the phyllite belt.

Macro- and microstructures of the rocks reveal several phases of tectonic activity, including twice reactivated subhorizontal shear movements, due to which dynamometamorphic imprint can be followed in all rocks. The first one is reflected as ductile deformations, yielding mylonitization and foliation. The second shear produced a slaty cleavage, which broadly follows foliation. The origin of these two structures is associated with upper Cretaceous nappe stacking and Tertiary Austroalpine eastward escape (e.g. Fodor et al. 1998, 2002, 2008). Structural parameters of the wider area suggest that Pohorje and Kobansko/Kozjak were still one common block at the time of the Pohorje granodiorite magma emplacement in Lower Miocene and were separated later.

The state of previous investigations does not allow strict definition of the Remšnik ore deposit genesis. Nevertheless, some important relations can be drawn, which neglect its Palaeozoic origin: sulphide mineralization and strong silicification, which obscured structural properties of the rocks, followed cleavage, which is of Tertiary (probably of Miocene) origin; the Kobansko block separated from the Pohorje block probably in middle Miocene and Kobansko was until then, closer to the impact area of the granodiorite intrusion; mineral composition and sulphur isotope composition of the Remšnik and Okoška gora (Pohorje) ore deposits are closely related (Drovenik et al. 1976, 1980). Consequently, there is a great probability that the Remšnik ore mineralization is connected to the Miocene Pohorje magmatism, as has already been proposed by Tornquist (1929), Duhovnik (1956), Berce (1963) and Grafenauer (1965). The question is, whether the mineralization could be related to remobilization of preexisting (Cretaceous/Palaeozoic?) ore minerals, as Drovenik and co-workers (1980) attribute Palaeozoic age to the Okoška gora ore deposit. They argue the age with blastic growth of ore minerals in the time of regional metamorphism, what to us is not a sufficient proof.

Younger oblique fractures, which cut foliation and slaty cleavage, developed as a consequence of renewed shearing. Secondary cleavage plains formed indicating dextral sense of shear (Fig. 3). These fractures are not silicified and contain no primary (sulphide) ore mineralization. All structures are cut by the youngest subvertical faults (Fig. 4) of prevailingly southwest-northeast trend, and subordinately transversely to this direction.

Conditions in the Janiček pit, in which the rocks of the Magdalensberg and Pohorje formations are comprised, show that mostly carbonate lenses and partly wider thrust zone contain ore mineralization. The primary ore mineralization and silicification followed fracture porosity of the older slaty cleavage, which macroscopically follows foliation, while only secondary mineralization can be found in two generations of transverse fractures and faults (Fig. 5). Silicified brecciated rocks appear massive.

Z. Žorž found most of rare secondary minerals in the Remšnik mine and determined them together with Moser (Žorž & Moser, 2002). Among them, particularly interesting is beaverite, the lead-copper-iron-aluminium sulphate. Upon attainable data, beaverite was known only as yellow coatings before the Z. Žorž find; here, caramel brown, transparent to translucent crystals up to one millimetre in size occur as coatings on quartz (Fig. 6).

Among carbonates, the rosasite and aragonite at partly limonitized quartz base (Fig. 7) are particularly beautiful.

In the base of some secondary minerals, hemimorphite has been determined by SEM. It is nearly amorphous; therefore, also under SEM, just its colloidal texture is noticed. It can be seen near the ramsbeckite crystals at the left side of Figure 8. The main chemical components of hemimorphite Zn, Si and O are shown at the EDS spectrum (Fig. 8, right).

Rare minerals, determined in the Remšnik mine, occur in traces in microscopic to submicroscopic sizes; therefore, they have remained unnoticed until recent years. Among them are two especially beautiful forms of sulphates, found in Slovenia for the first time. They belong to secondary minerals formed in the process of near-surface weathering of copper and zinc ores, dumps and slags. The first one belongs to ramsbeckite, which was shortly introduced by Žorž and Trajanova (2010). It represents grassy green to bluish green microcrystal coatings in some fractures and fissures (Fig. 5, lower half).

Determination of the second mineral is still questionable. It occurs in so insignificant a quantity and as so tiny crystals that it is invisible under binocular lens and we did not manage to actually prove its type by SEM analysis. Semiquantitative chemical composition and crystal habit indicate that it most probably belongs to namuwite.

Ramsbeckite

Characteristic Remšnik mine ore veins are composed mostly of chalcopyrite, galenite and sphalerite in the matrix of quartz and carbonates, of which the most frequent is dolomite. In the abandoned pits, the veins reach an average thickness between 3 and 5 centimetres. Thicker veins usually consist of several layers separated by bands of quartz and iron dolomite. The latter looks like split wall rock and/or remobilized carbonate from it. Secondary mineralization is found in opened fractures and faults. Fractures of secondary cleavage cut the ore veins obliquely. Only coatings of secondary minerals characteristic for oxidation zone occur in the youngest steep fractures and faults.

A thicker ore vein with ramsbeckite was found in the lower (second) level, lying about 7 m below the surface. The vein consisted mostly of chalcopyrite, galenite and sphalerite. Between separate layers of the vein, pyrite crystallized as pentagon dodecahedrons up to 1 mm in size. Coatings of the copper and zinc secondary minerals occur in the fracture in the upper part of the vein. The fracture in the middle of the vein contained mostly linarite and langite. In the lower part of the vein, malachite and rosasite prevailed in association with some aurichalcite and hydrozincite.

Ramsbeckite is still considered as a rare sulphate despite increasing number of finds. In the Nickel-Strunz classification of minerals, it belongs to the group of sulphates with additional anions, with H_2O, and to the space group P 2_1/a 2/m. It is named after Ramsbeck in Germany (Bastenberg mine), where it was found for the first time in 1984 and approved by IMA in 1985 (Internet 2). First description is of Hodenberg and co-workers (1985), who presented ramsbeckite stoichiometric chemical formula $(Cu, Zn)_7(SO_4)_2(OH)_{10}\cdot 5(H_2O)$ and determined mineral paragenesis, which is comparable with the one in Remšnik mine. Effenberger (1988) determined crystal structure of ramsbeckite. He revised chemical formula, and from previous form it was corrected to $(Cu,Zn)_{15}(SO_4)_4(OH)_{22}\cdot 6(H_2O)$.

Ramsbeckite from the Janiček pit occurs in euhedral crystals some tenth of mm in size, maximum up to 0.6 mm and is macroscopically seen only as coloured coatings (Fig. 9). At magnified photo unclear, bright green grains are seen locally (Fig. 10). They have green colour under binocular lense and strong reflection from crystal planes, which prevents us to make a successful photo. Therefore, the photo of ramsbeckite from Penrhiw mine in Wales (Internet 2 or 3) is suitable to better imagine the colour of the mineral, which is the same as the one in Remšnik. The crystals are transparent with silky glassy lustre.

The ramsbeckite crystals of the sample kept in a dry room become slightly less green and blue tint became stronger.

Ramsbeckite crystallize in the monoclinic system. The crystals have diverse habits. The most pronounced is the crystal face of basal pinacoid (001), along which indistinct cleavage can be seen. Distinctive are faces (100) and (010). The face (210) is usually smaller than the others (Fig. 11), while the faces (120) and (310) in most cases are not developed at all (Fig. 12 in the middle). In some crystals only faces (100), (001) and (010) developed (Fig. 12, bottom left and top right).

Sketch of idealized ramsbeckite crystals found so far in the Remšnik mine, is given in Fig. 13. Figure 13 B show indexed crystal faces of forms 1, 2 and 3 shown in figure 13A. Crystal faces defining ramsbeckite morphology are pinacoids (001), (100), (010) and (210) and prism of the 3rd order (110) (Fig. 13, forms 2A, 2B). The prism (110) can be more, or less pronounced. Some of the crystals developed only crystal faces of pinacoids (Fig. 13, sketch 1A, 1B). The most frequent is form 2, which can have shorter (010) face on the account of longer (210) face, as can be seen in Fig. 13A, form 2. Faces richest, but infrequent is form 3. In this case, an additional face (120) developed on the account of the face (110). Seemingly, face (310) developed on the account of the face (010) (Fig. 13, forms 3A and 3B). An example of such form can be seen in figure 11 at the bottom right half of the biggest crystal in the central intergrown crystal cluster.

Peacor et al. (1987) and Ohnishi et al. (2004) determined ramsbeckite cleavage along basal pinacoid, which can be traced also in our case (Fig. 11, crystal at the top of the central intergrown crystals). High crystal of form 4 (Fig. 13A) most probably belongs to twins. As we can find in the Handbook of Mineralogy, version 1 (Bideaux & Nichols, 2004, © 2004-2013), ramsbeckite has repeated twinning, forming cylindrical aggregates. An example of such twin can be seen in SEM image (Fig. 14 left). Similarity of some crystal forms with the ones from Remšnik (e.g. form 1 in Fig. 13A and 13 B) can be seen in figure 1 of Ohnishi and co-workers (2004) from the Hirao mine, near Osaka in Japan, where rhombohedra-like crystals prevail.

Qualitative chemical composition of ramsbeckite is shown in EDS spectrum (Fig. 14 right). Indistinct Si peak occurs due to small grains on the crystal surface. Unusually high crystal form for tabular ramsbeckite is the same as form 4 in figure 13A.

An EDS spectrum of pure ramsbeckite (Fig. 15) is scanned on the clear smooth surface of the bottom crystal at the right edge of figure 11. Therefore, no admixtures of Si appear in the spectrum in comparison to Fig. 14.

Several rare sulphate minerals are related to ramsbeckite in chemical composition as for example: langite, posnjakite, wroewolfeite, spangolite, ktenasite, and also namuwite.

An attempt was made to scan a piece of sample with microcrystalline coating with X-ray diffractometer, but the analysis was not successful.

Namuwite

Beside ramsbeckite another microcrystalline secondary sulphate is present in the composition of macroscopically amorphous bluish green coatings. With a shade of doubt, it is determined as namuwite.

Namuwite was described for the first time by Bevins and co-workers in 1982. It was determined in a sample originating from the Aberllyn mine. It is kept in the National Museum of Wales, whereupon its name originates (NA-MU-W-ite). The same year, the mineral was approved by IMA (Internet 4). It was shortly presented in the American mineralogists periodical under the »New mineral names« (Fleischer & Pabst, 1983). From then on, the mineral was found in oxidation zones of Cu, Zn ore deposits, as well as in mine gouges in several places around the world.

Namuwite chemical formula is $(Cu, Zn)_4(SO_4)(OH)_6{\cdot}4(H_2O)$ (Bevins et al., 1982). The authors described it as a sea blue mineral with emerald luster. Because only chemical composition, determined by SEM EDS, had been considered in the initial investigations, it was ascribed to ramsbeckite (Žorž & Trajanova, 2010). Due to its hexagonal form the determination was dubious; therefore we made additional SEM analyses. The x-ray diffraction analysis was made together with ramsbeckite, but was unsuccessful. EDS qualitative chemical composition of namuwite is the same as the one of ramsbeckite. It differs semiquantitatively, but because of small grains and the use of unpolished sample the results were not reliable and are not applicable.

As for the form of rosettes namuwite is similar to another sulphate mineral, posnjakite. They can be differentiated according to the colour (posnjakite is blue, namuwite pale green) and chemical composition (Zn beside Cu in namuwite). Based on the mentioned facts and on crystal form, we concluded that the mineral most probably belongs to namuwite. Typical are light green submicroscopic flowery aggregates (Fig. 16) on crusty coatings of related chemical composition, occurring together with ramsbeckite. They are the same as the forms described by Bevins and co-workers (1982) and Groat (1996). According to their data namuwite is isomorphous with the synthetic zinc sulphate $(Zn_4SO_4OH)_2{\cdot}4H_2O)$.

The namuwite crystals grow out of predominantly amorphous ground and rarely exceed 50 μm, exceptionally 80 μm in size. They have pronounced cleavage along basal pinacoid (001). Frequent transverse intergrowing of leaflets can be seen, like the ones in figures 16 (near the left edge) and 17.

Qualitative chemical composition of the Remšnik mine namuwite from figure 17 is shown in figure 18. Like ramsbeckite, it belongs to copper, zinc sulphate with additional anions and H_2O. The spectra peaks have disproportional heights due to the unfavourable orientation of the crystal surface according to the detector position.

Groat (1996) determined crystal structure of namuwite. It consists of repeated tetrahedral-octahedral-tetrahedral (T – O – T) layers held together by hydrogen bonds to interstitial H_2O molecules. The author found out that namuwite is subjected to hydration, dehydration processes, and to transitions from tetrahydrate to pentahydrate at about room temperature.

Conclusion

Polymetallic ore mineralization of the Remšnik mine developed along cleavage fractures coinciding with foliation, which indicates its Tertiary age and most probable connection with the Pohorje magmatism. Numerous secondary minerals crystallized in younger fractures in the process of oxidation and near-surface weathering. Among them some very rare types can be found, such as copper zinc sulphates ramsbeckite and namuwite (?) described for the first time in Slovenia. The namuwite determination is still not univocal; therefore, we hope that the next find will be of bigger quantity enabling thus the use of analytical techniques which will confirm or reject the present determination.

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Literatura - References

Arhiv RS, 1950: Rudarska knjiga A za okrožje Celje. Ljubljana: 185-204.

Arhiv RS, 1850a: Fevdna in koncesijska knjiga: Drauwalder Gesmbh Lehensbrief.

Berce, B. 1963: The formation of the ore-deposits in Slovenia. Rendiconti della Società Mineralogica Italiana, 19: 1-16.

Bevins, R.E., Turgoose, S. & Williams, P.A. 1982: Namuwite, $(Zn, Cu)_4SO_4(OH)_6 \cdot 4H_2O$, a new mineral from Wales. Mineralogical Magazine, 46: 51-54.

Bideaux, A. & Nichols, B. 2004: Handbook of mineralogy. Mineralogical Soc. of America. Mineral Data Publishing, version 1/ V: © 2004-2013, 791 p.

Drovenik, M., Duhovnik, J., & Pezdič, J. 1976: Izotopska sestava žvepla v sulfidnih rudnih nahajališčih v Sloveniji. Rud. met. zbornik, 2-3: 193-246.

Drovenik, M., Pleničar, M. & Drovenik, F. 1980: Nastanek rudišč v SR Sloveniji. Geologija, 23/1: 1-157.

Duhovnik, J. 1956: Über die metallogenetischen Epochen und Provinzen Jugoslawiens. Berg- und Hüttenmännische Monatshefte 101. Jahrgang 2: 30-32.

Effenberger, H. 1988: Ramsbeckite, $(Cu, Zn)_{15}(OH)_{22}(SO4)_4 \cdot 6H_2O$: revision of the chemical formula based on a structure determination. Neues Jahrbuch für Mineralogie, Monatshefte, 38–48.

Fleischer, M. & Pabst, A. 1983: New mineral names. American Mineralogist 68: 280-283.

Fodor, L., Gerdes, A., Dunkl, I., Koroknai, B., Pécskay, Z., Trajanova, M., Horváth, P., Vrabec, M., Jelen, B., Balogh, K. & Frisch, W. 2008: Miocene emplacement and rapid cooling of the Pohorje pluton at the Alpine-Pannonian-Dinaridic junction, Slovenia. Swiss J. Geosci., Birkhäuser Verlag, 255-271.

Fodor, L., Jelen, B., Márton, E., Rifelj, H., Kraljić, M., Kevrić, R., Márton, P., Koroknai, B. & Báldi-Beke, M. 2002: Miocene to Quaternary deformation, stratigraphy and paleogeography in Northeastern Slovenia and Southwestern Hungary. Geologija, 45/1: 103–114, Ljubljana; doi:10.5474/geologija.2002.009.

Fodor, L., Jelen, B., Márton, E., Skaberne, D., Čar, J. & Vrabec, M. 1998: Miocene - Pliocene tectonic evolution of the Slovenian Periadriatic fault: implications for Alpine - Carpathian extrusion models. Tectonics, 17: 690-709.

Geološka služba rudnika Mežica I. 1984-1989: Metalogenetska problematika kovinskih nahajališč v metamorfnih kameninah na Kobanskem in Pohorju, ECM Inštitut za gospodarski in socialni razvoj Ravne na Kor. Arhivska poročila o delu od 1984 do 1989.

Groat, L.A. 1996: The crystal structure of namuwite, a mineral with Zn in tetrahedral and octahedral coordination, and its relationship to the synthetic basic zinc sulfates. American mineralogist, 81/1-2: 238-243.

Grafenauer, S. 1965: Genetska razčlenitev svinčevih in cinkovih nahajališč v Sloveniji. Rud. Met. Zbornik, 2: 165-171.

Grafenauer, S. 1966: Metalogenija i mineraloške karakteristike bakrovih pojava u Sloveniji. Referati VI. savetovanja geologa SFRJ II, Ohrid, 377-396.

Hegemann, F. 1960: Über extrusiv-sedimentäre Erzlagerstätten der Ostalpen. II. Teil. Zeitschrift für Erzbergbau und Metallhüttenwesen, B.-A. XII: 122-127.

Hodenberg, R.V. Krause, W., Schnorrer-Köhler, G. & Täuber, H. 1985: Ramsbeckite, $(Cu, Zn)_7(SO4)_2(OH)_{10} \cdot 5H_2O$, a new mineral. Neues Jahrbuch für Mineralogie, Monatshefte: 550–556.

Mason, J.S. & Green, D. I. 1995: Supergene minerals including exceptional ramsbeckite from Penhriw mine, Ystumtuen, Dyfed. UK Journal of Mines and Minerals, 15: 21-27.

Mioč, P.& Ramovš A. 1973: Erster Nachweis des Unterdevons im Kozjak Gebirge (Posruck), westlich von Maribor (Zentralalpen). Bull. Sci. Cons., Acad. Sci. Yugosl. (A), 18/7-9: 135-136.

Mioč, P. 1978: Osnovna geološka karta SFRJ 1 : 100.000. Tolmač za list Slovenj Gradec. Zvezni geološki zavod, Beograd: 74 p.

Mioč, P. & Žnidarčič, M. 1977: Osnovna geološka karta SFRJ 1 : 100.000, list Slovenj Gradec. Zv. geol. zavod, Beograd.

Ohnishi, M., Kobayashi, S., Kusachi, I., Yamakawa, J. & Shirakami, M. 2004: Ramsbeckite from the Hirao mine at Minoo, Osaka, Japan. Journal of Mineral. and Petrol. Sci., 99: 19-24.

Orlandi, P. & Perchiazzi, N. 1989: Ramsbeckite, $(Cu, Zn)_{15}(OH)_{22}(SO4)_4 \cdot 6H_2O$, a first occurrence for Italy from "La Veneziana" mine, Valle dei Mercanti, Vicenza. Eur. Journ. Mineral., 1: 147–149.

Peacor, D.R., Dunn, P.J. & Sturman, B.D. 1987: Ramsbeckite: an American occurrence at the Ecton mine, Pennsylvania. Mineralog. Record, 18: 131–132.

Štrucl, I. 1984-1989: Metalogenetska problematika kovinskih nahajališč v metamorfnih kameninah na Kobanskem in Pohorju, ECM Inštitut za gospodarski in socialni razvoj Ravne na Kor. Arhivska poročila o delu od 1984 do 1989.

Tornquist, A. 1929: Die perimagmatische Blei-Kupfer-Silber-Zinkerzlagerstätte von Offberg im Remschnigg. Akad. Wissenschaften, mat.-naturw. Kl. Abt. I, 138 /1-2: 47-68.

Žorž, Z. & Moser , B. 2002: Remšnik, zgodovina-geologija-minerali. Založba Voranc, Ravne na Koroškem.

Žorž, Z., Golob, F., Rečnik, A. & Hinterlechner-Ravnik, A. 2007: Mineralizirane alpske razpoke na Kobanskem in na severnem Pohorju. V: Rečnik, A. (ur.): Nahajališča mineralov v Sloveniji. Institut Jožef Stefan, Odsek za nanostrukt. materiale: 269-272.

Internetni viri dostopni / Internet resources available to 20.5.2013

Internet 1: http://www.mindat.org/min-3358.html

Internet 2: http://www.museumwales.ac.uk/en/800/?mineral=120

Internet 3: http://webmineral.com/specimens/picshow.php?id=966&target=Ramsbeckite

Internet 4: http://www.mindat.org/min-2837.html