

Kojonenite, a new palladium tin telluride mineral from the Stillwater Layered Igneous Intrusion, Montana, U.S.A.† ‡

CHRIS J. STANLEY^{1,*} AND ANNA VYMAZALOVÁ²

¹Department of Earth Sciences, Natural History Museum, Cromwell Road, London, SW7 5BD, U.K.

²Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

ABSTRACT

Kojonenite, Pd_{7-x}SnTe₂ (where 0.3 ≤ x ≤ 0.8), is a new mineral (IMA 2013-132) discovered in specimens from the Stillwater Layered Igneous Intrusion, Stillwater Valley, Montana, U.S.A. (45°23'11"N and 109°53'03"W). Synthetic kojonenite is tetragonal, space group *I4/mmm*, with *a* = 4.001(1) Å and *c* = 20.929(3) Å giving *V* = 335.0(1) Å³ with *Z* = 2. Strongest lines in the synthetic powder pattern [PDF 01-073-5652] are (*d* in Å, *l*, *hkl*) 10.465, 29, 002; 2.496, 52, 114; 2.1986, 100, 116; 2.0930, 18, 0010; 2.0025, 48, 200. Identity between natural and synthetic kojonenite is illustrated by an electron backscattered diffraction (EBSD) study.

Reflectance data for natural kojonenite for the four COM wavelengths are [*λ* (nm), *R*_o, *R*_e] 470, 55.0, 52.7; 546, 58.5, 56.5; 589, 61.0, 58.3; 650, 63.9, 60.1 and the mineral is uniaxial negative.

Electron microprobe analysis of natural kojonenite yields a simplified formula of Pd₆SnTe₂ that extends the range reported for the synthetic of Pd_{7-x}SnTe₂ (where 0.3 ≤ x ≤ 0.8).

Keywords: Kojonenite, palladium, tin, telluride, new mineral, layered intrusion, Howland Reef, Stillwater Complex

INTRODUCTION

Kojonenite, is a new mineral (IMA 2013-132) discovered recently in specimens collected underground in 1980 by the late Alan Criddle from the first crosscut of the Minneapolis Adit, Howland Reef of the Stillwater Layered Igneous Intrusion, Stillwater Valley, Montana, U.S.A. (45°23'11"N and 109°53'03"W). The Howland Reef is a platinum-group mineral deposit that occurs within the lower part of the banded zone of the Stillwater Layered Igneous Intrusion also referred to as the Stillwater Complex and that is of Archean age and of tholeiitic composition (useful reviews can be found in Czamanske and Bohlen 1990 and in McCallum 1996). The platinum-group mineral concentration is coincident with the reappearance of olivine in the crystallization sequence of the intrusion (Bow et al. 1982). Kojonenite was formed in a sulfide-rich intercumulus segregation and occurs together with kotulskite and, more rarely, irregularly intergrown with moncheite and parlarstanide as inclusions in chalcopyrite, cubanite, pentlandite, and pyrrhotite. Together with the sulfides, kojonenite and the other tellurides also occur along cleavages in some of the silicate minerals, particularly enstatite. Host rocks to the mineralization have variable proportions of cumulus olivine, enstatite (predominantly the iron-rich variety "bronzite"), plagioclase, and augite with, in some instances, pegmatoidal development. Accessory minerals "include base metal sulfides, phlogopite, hornblende, apatite, and a magnetic chrome spinel" (Bow et al. 1982). Todd et al. (1982) reported Sn in the Howland Reef

as occurring in zvyagintsevite, rustenburgite, and as a minor constituent in keithconnite.

MINERAL NAME AND TYPE MATERIAL

Both mineral and name were approved by the Commission on New Minerals Nomenclature and Classification of the International Mineralogical Association (IMA 2013-132). The mineral is named in honor of Kari K. Kojonen (b. 1949), senior research scientist in the Bedrock Geology and Resources Group of the Geological Survey of Finland, for his contributions to the mineralogy of the platinum group minerals and to ore mineralogy in general. Kojonen has also served as Vice-Chair of the Commission on Ore Mineralogy of the International Mineralogical Association. The holotype (polished thin section AC1) and a co-type (polished thin section AC2) are deposited in the collections of the Natural History Museum, London, U.K., under the registered number BM 1981,134.

APPEARANCE, OPTICAL, AND PHYSICAL PROPERTIES

There was insufficient material for many of the physical properties to be determined on the natural specimens therefore it was decided to use synthetic material that had already been prepared for an earlier paper (Vymazalová and Drábek 2010).

In reflected plane-polarized light in polished section kojonenite forms anhedral grains (<40 μm) in aggregates (up to about 100 μm) with kotulskite as inclusions in chalcopyrite and cubanite (Fig. 1). Against kotulskite (bright cream), kojonenite appears slightly pinkish off-white and exhibits weak bireflectance, visible only on differently oriented adjacent grains. No pleochroism was detected and kojonenite is distinctly anisotropic with rotation tints in shades of dark greenish-brown. Reflectance

* E-mail: C.Stanley@nhm.ac.uk

† ‡ Open access: Article available to all readers online.

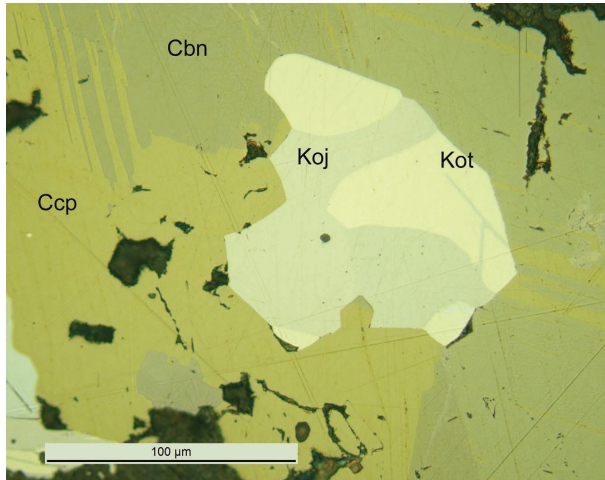


FIGURE 1. Reflected light digital image illustrating kojonenite (Koj) in association with kotulskite (Kot), cubanite (Cbn), and chalcopyrite (Ccp).

TABLE 1. Reflectance data for natural and synthetic kojonenite

λ (nm)	Natural		Synthetic	
	Ro	Re'	Ro	Re'
400	50.1	46.8	50.3	47.5
420	51.3	48.4	51.5	49.3
440	52.7	50.2	52.8	51.1
460	54.4	52.0	54.2	52.9
480	55.6	53.3	55.4	53.9
500	56.3	54.3	56.1	54.9
520	57.1	55.2	56.9	55.7
540	58.1	56.1	57.9	56.6
560	59.4	57.1	59.3	57.7
580	60.5	57.9	60.7	58.9
600	61.6	58.7	61.8	59.9
620	62.5	59.3	62.7	60.4
640	63.4	59.8	63.4	61.0
660	64.3	60.4	64.1	61.7
680	65.2	61.1	65.0	62.4
700	66.2	62.0	66.0	63.1
COM wavelengths				
470	55.0	52.7	54.8	53.4
546	58.5	56.5	58.6	56.9
589	61.0	58.3	61.2	59.4
650	63.9	60.1	63.8	61.4

measurements were made in air relative to a WTiC standard on both natural and synthetic kojonenite using a J & M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. The results are tabulated (Table 1) and illustrated in Figure 2. There is near identity of Ro for natural and synthetic kojonenite and slight differences in the magnitude of Re' can be explained by the difficulty of finding suitable grains for measurement in the synthetic material due to the small grain size. It is likely that Re' for natural kojonenite approximates Re. With $Ro > Re$, kojonenite is uniaxial negative.

CHEMICAL COMPOSITION

Compositional data for natural kojonenite, summarized in Table 2, were obtained using a CAMECA SX-100 electron probe microanalyzer operated with an accelerating voltage of 15 kV and a beam current of 10 nA on the Faraday cage; the

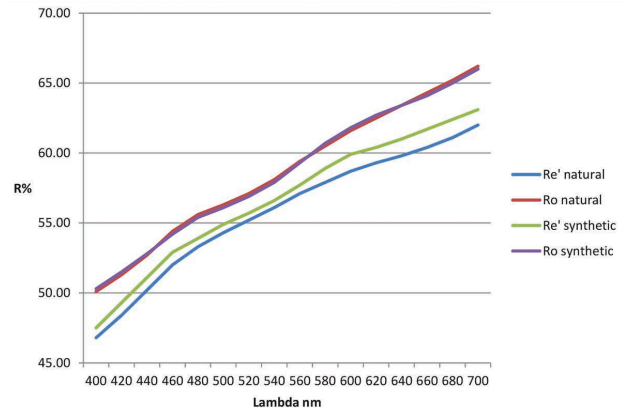


FIGURE 2. Reflectance spectra for natural and synthetic kojonenite.

TABLE 2. Electron microprobe data for kojonenite (mean of 20 analyses)

	wt%	Range	s.d.
Pd	62.48	61.83–63.12	0.33
Sn	11.74	11.29–11.91	0.14
Te	25.63	25.38–25.90	0.15
Total	99.85		

electron beam was focused to 1–2 μm . Pure elements were used as standards and concentrations were quantified on the PdL α , SnL α , and TeL α lines. All other elements were below detection limit. The empirical formula calculated from the average analysis in Table 2 is Pd_{5.96}Sn_{1.00}Te_{2.04} on the basis of 9 atoms per formula unit. The simplified formula is Pd₆SnTe₂, which requires Pd 63.1, Sn 11.7, Te 25.2 wt%. However, on the basis of the structural formula derived from work in the synthetic system, the simplified formula is Pd_{7-x}SnTe₂ that requires, for $x = 0.8$, Pd 63.8, Sn 11.5, Te 24.7 wt%, or, for $x = 0.3$, Pd 65.6, Sn 10.9, Te 23.5 wt%. As the natural material is outside the limits of this simplified formula it may imply a greater range of compositional accommodation.

CRYSTALLOGRAPHY

The crystal structure of synthetic Pd_{7-x}SnTe₂ was solved using single-crystal work by Savilov et al. (2005) and also confirmed by experimental study and X-ray powder diffraction data by Vymazalová and Drábek (2010). Complete X-ray data are listed in the PDF database (PDF 01-073-5652 and PDF 01-073-9276 cards). According to Savilov et al. (2005) the average structure of the phase Pd_{7-x}SnTe₂ (tetragonal, space group *I4/mmm*, $a = 4.001 \text{ \AA}$, $c = 20.929 \text{ \AA}$, $Z = 2$) is isotypic to nickel analogs Ni_{7-x}SnQ₂ (Q = S, Se, Te) (Baranov et al. 2003, 2004) and consists of Cu₃Au-like Sn/Pd blocks and NaCl-like Pd/Te slabs.

The structural identity of the natural kojonenite with the model proposed by Savilov et al. (2005) for the synthetic phase was confirmed by electron backscattering diffraction EBSD measurements on the natural sample.

A TESCAN Vega scanning electron microscope combined with an EBSD system (HKL NordlysNano, Oxford Instruments) was used for the measurements. The natural sample was prepared for investigation by etching the mechanically polished surface with colloidal silica (OP-U) for 5 min to reduce

surface damage. EBSD patterns were collected and processed using a proprietary computer program AZtec a Channel 5. The center of six Kikuchi bands was automatically detected using the Hough transform routine with a resolution of 50 (internal Hough resolution parameter in the HKL software). The solid angles calculated from the patterns were compared with a synthetic $\text{Pd}_{7-x}\text{SnTe}_2$ match containing 70 reflectors to index the patterns. The EBSD patterns (also known as Kikuchi patterns) obtained from the natural material (six measurements on different spots on natural kojonenite) were found to match the patterns generated from the structural model described by Savilov et al. (2005). The values of the mean angular deviation (MAD, i.e., goodness of fit of the solution) between the calculated and measured Kikuchi bands range between 0.53° and 0.36° . These values reveal a very good match; as long as values of mean angular deviation are less than 1° , they are considered as indicators of an acceptable fit (see Fig. 3)

The crystal structure of kojonenite has no exact structural analog in mineralogical classification systems. According to the chemical composition the mineral should belong to 02.BC group (tellurides with Pd) of the Nickel & Strunz classification.

IMPLICATIONS

- The stoichiometric analyses of the natural kojonenite with a formula of Pd_6SnTe_2 suggest that results in the synthetic system ($\text{Pd}_{6.2}\text{SnTe}_2$ to $\text{Pd}_{6.7}\text{SnTe}_2$, Savilov et al. 2005) may not replicate conditions in the Stillwater Complex where equilibration and solid-state diffusion could have taken place over eons.

- Synthetic kojonenite is stable up to 596°C (Vymazalová and Drábek 2010), therefore the presence of kojonenite in the natural mineral assemblage may indicate its formation below this temperature.

- According to the experimental study of the system Pd-Sn-Te (Vymazalová and Drábek 2010) kojonenite cannot only coexist with platinum group minerals like kotulskite, telluropalladinite, and paolovite but also with phases like Pd_3Te_2 , $\text{Pd}_{20}\text{Te}_7$, and the ternary phase $\text{Pd}_{72}\text{Sn}_{16}\text{Te}_{12}$, which have yet to be described as minerals but that might occur in association with kojonenite in nature.

- Kojonenite can be expected to occur in other Cu-Ni-PGE mineral deposits related to mafic and ultramafic rocks, particularly those enriched in Pd and Sn (e.g., Noril'sk, Russian Federation).

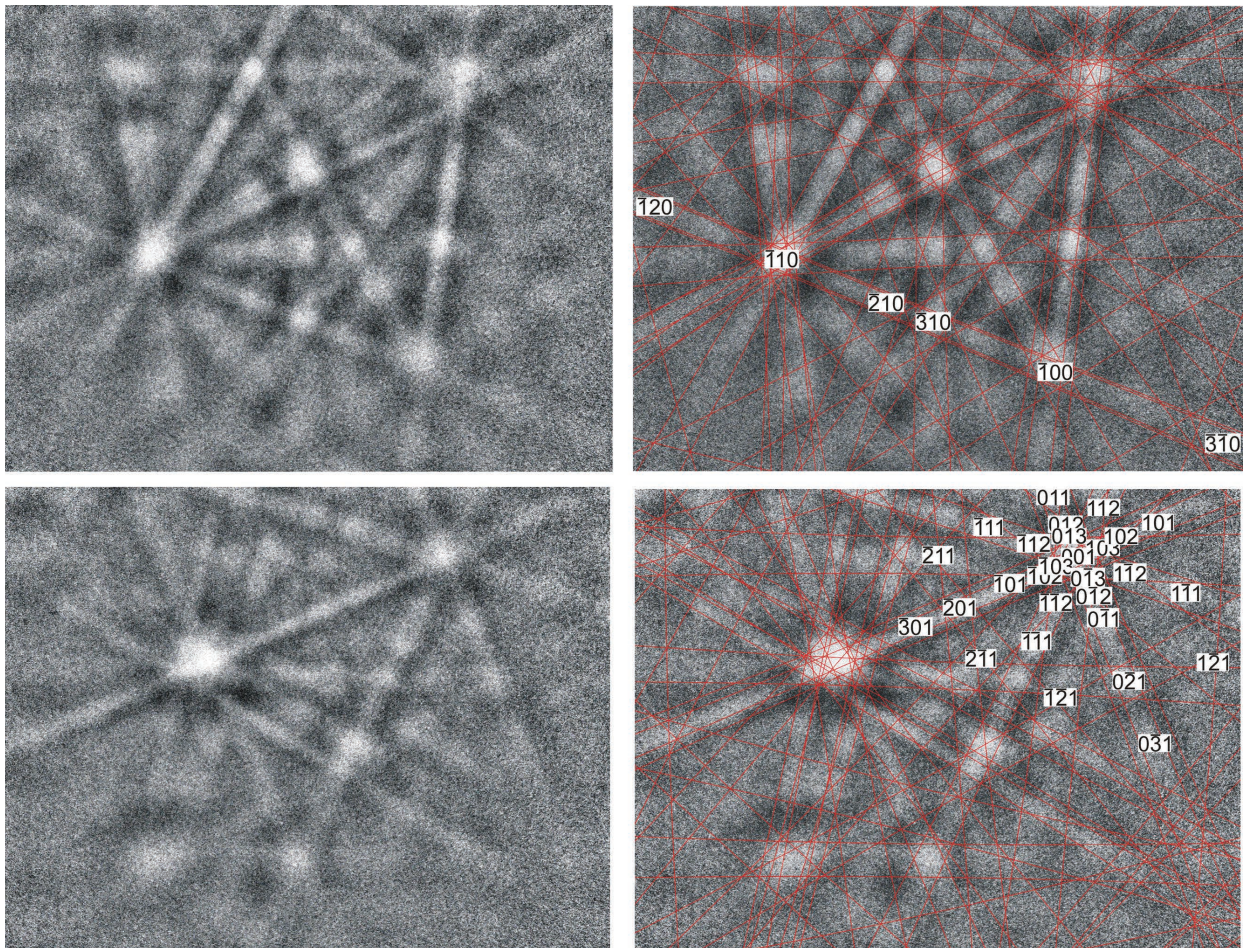


FIGURE 3. EBSD image of natural kojonenite. In the right panes, the Kikuchi bands are indexed. Upper and lower pairs were made on different grains of the kojonenite shown in Figure 1.

ACKNOWLEDGMENTS

Anaconda Copper Company (forerunner of the Stillwater Mining Company) are thanked for providing access to the late Alan Criddle who collected the suite of specimens in which kojonenite was found. The authors are grateful to Martin Racek (Faculty of Science, Charles University) for carrying out the EBSD measurements. Financial support through grant no. P210/11/P744 from the Grant Agency of the Czech Republic is acknowledged. This is a contribution to U.K. Natural Environment Research Council Security of Supply Initiative for Se and Te.

REFERENCES CITED

- Baranov, A.I., Isaeva, A.A., Kloo, L., and Popovkin, B.A. (2003) New metal-rich sulfides Ni_6SnS_2 and $Ni_6Sn_2S_2$ with a 2D metal framework: Synthesis, crystal structure, and bonding. *Inorganic Chemistry*, 42, 6667–6672.
- Baranov, A.I., Isaeva, A.A., Kloo, L., Kulbachinskii, V.A., Lunin, R.A., Nikiforov, V.N., and Popovkin, B.A. (2004) 2D metal slabs in new nickel-tin chalcogenides $Ni_{7-8}SnQ_2$ (Q=Se, Te): Average crystal and electronic structures, chemical bonding and physical properties. *Journal of Solid State Chemistry*, 177, 3616–3625.
- Bow, C., Wolfgram, G., Turner, A., Barnes, S., Evans, S., Zdepski, M., and Boudreau, A. (1982) Investigations of the Howland Reef of the Stillwater Complex, Minneapolis Adit Area: stratigraphy, structure and mineralization. *Economic Geology*, 77, 1481–1492.
- Czamanske, G.K., and Bohlen, S.R. (1990) The Stillwater Complex and its orthosites: An accident of magmatic underplating? *American Mineralogist*, 75, 37–45.
- McCallum, I.S. (1996) The Stillwater Complex. In R.G. Cawthorn, Ed., *Layered Intrusions, Developments in Petrology*, vol. 15, p. 441–483. Elsevier, Amsterdam.
- Savilov, S.V., Kuznetsov, A.N., Popovkin, B.A., Khrustalev, V.N., Simon, P., Getzschmann, J., Doert, T., and Ruck, M. (2005) Synthesis, crystal structure and electronic structure of modulated $Pd_{7-8}SnTe_2$. *Zeitschrift für Anorganische und Allgemeine Chemie*, 631, 293–301.
- Todd, S.G., Keith, D.W., Le Roy, L.W., Schissel, D.J., Mann, E.L., and Irvine, T.N. (1982) The J-M Platinum-Palladium Reef of the Stillwater Complex, Montana. I. Stratigraphy and Petrology. *Economic Geology*, 77, 1454–1480.
- Vymazalová, A., and Drábek, M. (2010) The system Pd-Sn-Te at 400°C and mineralogical implications. II The ternary phases. *Canadian Mineralogist*, 48, 1051–1058.

MANUSCRIPT RECEIVED MAY 19, 2014

MANUSCRIPT ACCEPTED SEPTEMBER 20, 2014

MANUSCRIPT HANDLED BY FERNANDO COLOMBO