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NIELSENITE, $PdCu_3$, A NEW PLATINUM-GROUP INTERMETALLIC MINERAL SPECIES FROM THE SKAERGAARD INTRUSION, GREENLAND

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Abstract

Nielsenite, $PdCu_3$, a new mineral species discovered in the Skaergaard intrusion, Kangerdlugssuaq area, East Greenland, occurs in a tholeiitic gabbro associated with plagioclase, clinopyroxene, orthopyroxene, ilmenite, titanian magnetite, fayalite and accessory chlorite-group minerals, ferrosaponite, a member of the annite–phlogopite series, hornblende, actinolite, epidote-group minerals, calcite, ankerite, apatite and baddeleyite. The mineral is found in composite microglobules principally composed of bornite–chalcocite, chalcocite, along with rare digenite, chalcopyrite, cobaltpentlandite, Co-rich pentlandite, and sphalerite. Associated platinum-group minerals include skaergaardite, keithconnite, vasilite, zvyagintsevite, (Cu,Pd,Au), (Pd,Cu,Sn) and (Pt,Fe,Cu,Pd) alloys and unnamed Au_3Cu and PdAuCu. Nielsenite occurs as discrete grains or in sulfide-bearing, droplet-shaped to irregular grains that are 5–50 μm (ave: 16 μm) in size. The mineral is steel-grey in color with a metallic luster, a black streak and a sectile tenacity. No discernible forms or faces were observed. Neither cleavage nor fracture was observed, and no micro-indentation measurements were made. The mineral is non-pleochroic and exhibits neither discernible internal reflections nor evidence for twinning. It appears bright creamy white under reflected light. Reflectance values (in %) in air (in oil) are: 57.6 (47.5) at 470 nm, 60.85 (50.8) at 546 nm, 62.8 (53.0) at 589 nm and 66.7 (57.5) at 650 nm. The average result of 11 analyses is (in wt.%): Pd 29.86, Pt 3.08, Au 3.70, Cu 61.96, Fe 0.59, Pb 0.17, total 99.36%. The empirical formula (normalized to 4 *apfu*) is: $(Pd_{0.862}Au_{0.058}Pt_{0.049}Fe_{0.028}Pb_{0.003})(Cu_{2.996}Fe_{0.004})_{\Sigma 3}$ or, ideally, $PdCu_3$. The mineral is tetragonal, space group $P4mm$, with a 3.7125(8), c 25.62(1) Å, V 353.2(1) Å^3 for $Z = 4$. The strongest six lines on the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 2.137(100)(117), 1.8596(70)(200), 1.8337(40)($00\underline{14}$), 1.3126(60)(220), 1.1188(55)(317), and 1.0663 (30)($22\underline{14}$). Nielsenite is considered to be isostructural with synthetic tetragonal $PdCu_3$ ($P4mm$). The mineral is commonly associated with skaergaardite (PdCu), which is considered to form at ~600°C under conditions of fairly high $f(S_2)$ (>7 log units). Synthetic $PdCu_3$ forms at or below 508°C and is characterized by a relatively high degree of Pd–Cu disorder, consistent with observations made for nielsenite. The name honors Troels F.D. Nielsen, geologist with the Geological Survey of Denmark and Greenland.

Keywords: nielsenite, Pd–Cu intermetallic, new mineral species, platinum-group elements, Skaergaard intrusion, Greenland.

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SOMMAIRE

La nielsenite, $PdCu_3$, nouvelle espèce minérale découverte dans le complexe intrusif de Skaergaard, dans la région de Kangerdlugssuaq, Groënland oriental, fait partie d'une association typique d'un gabbro tholéiitique, avec plagioclase, clinopyroxène, orthopyroxène, ilménite, magnétite titanifère, fayalite et, comme accessoires, des minéraux du groupe de la chlorite, ferrosaponite, un membre de la série annite–phlogopite, hornblende, actinolite, membres du groupe de l'épidote, calcite, ankérite, apatite et baddeleyite. On trouve la nielsenite en microglobules composites contenant surtout bornite–chalcocite, chalcocite et, plus rarement, digénite, chalcopyrite, cobaltpentlandite, pentlandite riche en Co, et sphalérite. Les minéraux du groupe du platine associés incluent skaergaardite, keithconnite, vasilite, zvyagintsevite, les alliages (Cu,Pd,Au), (Pd,Cu,Sn) et (Pt,Fe,Cu,Pd) et les phases sans nom Au_3Cu et PdAuCu. La nielsenite se présente en grains distincts ou bien en forme de goutelette ou irréguliers, avec sulfures piégés, entre 5 et 50 μm de diamètre (en moyenne, 16 μm). Il s'agit d'un minéral gris acier avec un éclat métallique, une rayure noire et une tenacité sécable. Nous n'avons pas vu de faces ou de formes sur les grains. Aucun clivage ou fracture n'est évident; nous n'avons pas effectué de mesures par micro-indentation. Le minéral est non-pléochroïque et ne montre aucune réflexion interne et aucune macle. Les grains sont blanc crémeux brillant en lumière réfléchie. Les valeurs de réflectance (%) dans l'air (dans l'huile) sont: 57.6 (47.5) à 470 nm, 60.85 (50.8) à 546 nm, 62.8 (53.0) à 589 nm et 66.7 (57.5) à 650 nm. Onze analyses ont donné, en moyenne (en %, poids) sont: Pd 29.86, Pt 3.08, Au 3.70, Cu 61.96, Fe 0.59, Pb 0.17, pour un total de 99.36%. La formule empirique, normalisée à quatre atomes par unité formulaire, serait: $(Pd_{0.862}Au_{0.058}Pt_{0.049}Fe_{0.028}Pb_{0.003})(Cu_{2.996}Fe_{0.004})_{\Sigma 3}$ ou, idéalement, $PdCu_3$. Le minéral est tétragonal, groupe spatial *P4mm*, avec *a* 3.7125(8), *c* 25.62(1) Å, *V* 353.2(1) Å^3 pour $Z = 4$. Les six raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont: 2.137(100)(117), 1.8596(70)(200), 1.8337(40)(00$\underline{14}$), 1.3126(60)(220), 1.1188(55)(317), et 1.0663 (30)(22$\underline{14}$). Nous considérons la nielsenite isostructurale avec l'analogue synthétique tétragonal $PdCu_3$ (*P4mm*). La nielsenite est généralement associée à la skaergaardite (PdCu), qui se serait formée à environ 600°C dans un milieu à fugacité de soufre assez élevée (au delà de sept sur l'échelle logarithmique). Le $PdCu_3$ synthétique cristallise à une température maximale de 508°C et possède un degré de désordre Pd–Cu relativement élevé, tout comme la nielsenite. Le nom choisi honore Troels F.D. Nielsen, géologue avec la Commission géologique du Dannemark et du Groënland.

(Traduit par la Rédaction)

Mots-clés: nielsenite, Pd–Cu intermétallique, nouvelle espèce minérale, éléments du groupe du platine, complexe intrusif de Skaergaard, Groënland.

INTRODUCTION

Nielsenite, ideally $PdCu_3$, is a new mineral species discovered in drill core taken from the Skaergaard intrusion (N68°09'55'', W31°41'02''), Kangerdlugssuaq area, East Greenland. The mineral was discovered from drill-core taken from the Pd5 level at a depth of between 1057 and 1058 m. It was also found in a bulk sample obtained by blasting at the toe of Forbindelsesgletscher (Skaergaard Minerals Corp.). The mineral was initially recovered from non-magnetic, heavy-mineral separates from sample 90–24 1057 (initial mass: 0.78 kg) produced using a HS–01 Hydroseparator (Cabri *et al.* 2005). The process produced 12 discrete particles of nielsenite along with seven grains of skaergaardite (PdCu; Rudashevsky *et al.* 2004), in which the nielsenite occurs as inclusions. The purpose of this communication is to provide a description of the mineral and its geological occurrence, along with comments on the potential conditions of formation.

The mineral is named after Mr. Troels F.D. Nielsen (*b.* 1950), a geologist with the Geological Survey of Denmark and Greenland, in recognition of his field work that helped to define the precious metal layers in the Skaergaard intrusion and his leadership in their subsequent mineralogical and metallurgical characterization. Both the mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (IMA 2004–046). The type material is deposited at the Geologisk Museum, Øster Volgade 5–7, DK–1350, Copenhagen K, Denmark (catalogue number 2008.1).

OCCURRENCE

The Skaergaard intrusion is an oval (~7.5 × 10 km), rhythmically layered gabbroic body that was emplaced into a basement of Archean granitic gneiss and related rocks during the Eocene (Irvine 1992). It is renowned for its rhythmic layering, extreme compositional differentiation and igneous structures (Irvine 2001). Portions of it have been prospected for precious metals (*e.g.*, the Triple Group, which contains a notable enrichment in both Au and Pd; Andersen *et al.* 1998).

Nielsenite occurs in a well-preserved, oxide-rich tholeiitic gabbro within what is now referred to as the Platinova Reef (Nielsen *et al.* 2003). This gabbro specifically occurs in the Triple Group, which itself constitutes the upper 100 m of the Middle zone in the Layered series of the intrusion. The associated platinum-group element (PGE) and Au mineralization is stratiform in nature. The average concentration of Pd over the interval in which nielsenite was found (1057–1058 m) is 2.8 g/t, with an average combined Pt + Pd + Au concentration of 3.1 g/t (Nielsen *et al.* 2003). The gabbro hosting the mineral is composed of plagioclase ($An_{44–49}$), clinopyroxene (*Mg#* 0.60–0.63), orthopyroxene (*Mg#* 0.49–0.53), ilmenite, titanian magnetite, fayalite (*Mg#* 0.40–0.50), which constitute the rock-forming minerals, along with accessory chlorite-group minerals, ferrosaponite, a member of the annite–phlogopite series, hornblende, actinolite, epidote-group minerals, calcite, ankerite, apatite and baddeleyite. Sulfides (predominantly Cu–Fe-bearing) represent ~0.05 modal % of the minerals present in the zone of PGE-bearing mineralization. These typically occur at interstices between titanian magnetite and pyroxene grains, but are also occasionally intergrown with H_2O-bearing silicates. The H_2O-bearing silicates occur proximal to sulfide and titanian magnetite, and do not replace rock-forming silicates. It may also be significant that film-like exsolution-lamellae in composite pyroxene grains (orthopyroxene + clinopyroxene) are noticeably disrupted (recrystallized?) around inclusions of both sulfides and titanian magnetite.

The sulfide inclusions may be best described as Cu–Fe sulfide aggregates, consisting primarily of bornite along with either chalcocite or digenite, but in variable proportions of the two. Morphologically, the aggregates can be either irregular in shape or have a rounded to droplet-like outline. The latter are typically <0.1 mm in diameter and are most accurately described as microglobules. In most cases, these microglobules exhibit distinct exsolution textures (chalcocite from bornite). Additional sulfides observed within the microglobules include chalcopyrite (found in ~3 modal % of the particles studied), cobaltoan pentlandite, cobaltpentlandite and sphalerite.

The platinum-group mineral (PGM) assemblage with which nielsenite is associated is dominated by skaergaardite, PdCu (Rudashevsky *et al.* 2004), itself representing >90% of the total PGM observed. Other PGM and precious-metal-bearing minerals (both as discrete grains and inclusions) include: keithconnite, ($Pd_{3–x}Te$, as inclusions in skaergaardite and unnamed $PdAuCu_2$), vasilite [$(Pd,Cu)_{16}(S,Te)_7$, as inclusions in skaergaardite and $PdAuCu_2$], and zvyagintsevite. Several unidentified Cu–Pd–Au–Pt–Fe alloys also have been observed. These include: (Cu,Pd) and (Cu,Pd,Au) alloys (representing ~3 % of the total PGM observed), which occur as discrete irregular grains or as intergrowths with skaergaardite, unnamed Au_3Cu (as an inclusion in $PdAuCu_2$), unnamed $PdAuCu_2$ (possibly Pd-rich tetra-auricupride, as discrete grains and rare inclusions in skaergaardite), unnamed (Pt,Fe,Cu,Pd) alloys (tetraferroplatinum?) and unnamed $(Pt,Pd)Cu_3$ (an inclusion in skaergaardite). More information on the minerals associated with nielsenite can be found in Rudashevsky *et al.* (2004).

Nielsenite occurs as discrete grains or in sulfide-bearing, droplet-shaped to irregular grains that are from 5 to 50 μm (ave: 16 μm) in size. In drill-core samples, the mineral may be found as inclusions in skaergaardite and may contain inclusions of an unnamed Pd–Cu–Sn alloy, but otherwise, it is not observed to occur with any other PGM. In the heavy-mineral concentrates that were processed, 12 monomineralic grains were recovered; the mineral was also identified in seven skaergaardite-dominant grains (Fig. 1). Nielsenite represents ~3% (by volume) of the total PGM assemblage (skaergaardite representing 95% by volume). In the bulk sample that was analyzed, nielsenite was found in the following associations: a) bornite–chalcocite + skaergaardite + keithconnite, and b) with chalcocite alone.

PHYSICAL AND OPTICAL PROPERTIES

All discrete grains and inclusions of nielsenite appear to be anhedral, with no apparent faces or crystal forms evident. The mineral is steel-grey in color with a metallic luster, a black streak and a sectile tenacity. No measurements of micro-indentation were made. Neither cleavage nor fracture was observed. On the basis of the empirical formula and unit-cell parameters refined from the X-ray powder-diffraction data, the calculated density is 9.53 g/cm^3. Under reflected light, the mineral appears bright creamy white. No bireflectance, internal reflections or evidence for twinning were observed. The grain used for optical analyses did not exhibit any anisotropy under cross-polarized light; we presume that this grain was oriented such that it was being viewed parallel to *c* (only *R*' is quoted, therefore). Reflectance values (Fig. 2) were measured in air and oil (Zeiss oil, n_D = 1.515, DIN 58.884 at 20°C) relative to a WTiC standard (Zeiss 314), following the methodology of Stanley *et al.* (2002). The reflectance data and color values for the grain of nielsenite analyzed are given in Table 1. It should be noted that the reflectance data are close to those of zvyagintsevite, Pd_3Pb (space group *Pm*3*m*).

TABLE 1. REFLECTANCE DATA (%) AND COLOR VALUES FOR NIELSENITE

λ	*R*'	$^{im}R'$	λ	*R*'	$^{im}R'$
400	53.2	42.7	560	61.3	51.4
420	54.4	44.1	580	62.2	52.5
440	55.6	45.2	600	63.6	53.6
460	56.9	46.6	620	64.7	55.2
480	58.3	48.1	640	66.0	56.7
500	59.2	49.0	660	67.4	58.2
520	59.9	50.0	680	68.5	60.1
540	60.7	50.6	700	69.9	61.8
COM wavelengths					
470	57.6	47.5	589	62.8	53.0
546	60.85	50.8	650	66.7	57.5
Color values: A illuminant (~2856 K): air and oil					
x	0.458	0.461	λ_d	589	590
y	0.409	0.410	P_e%	8.4	10.5
Y%	62.2	52.4			
Color values : C illuminant (~6774 K): air and oil					
x	0.321	0.325	λ_d	580	580
y	0.326	0.329	P_e%	5.6	7.2
Y%	61.5	51.6			

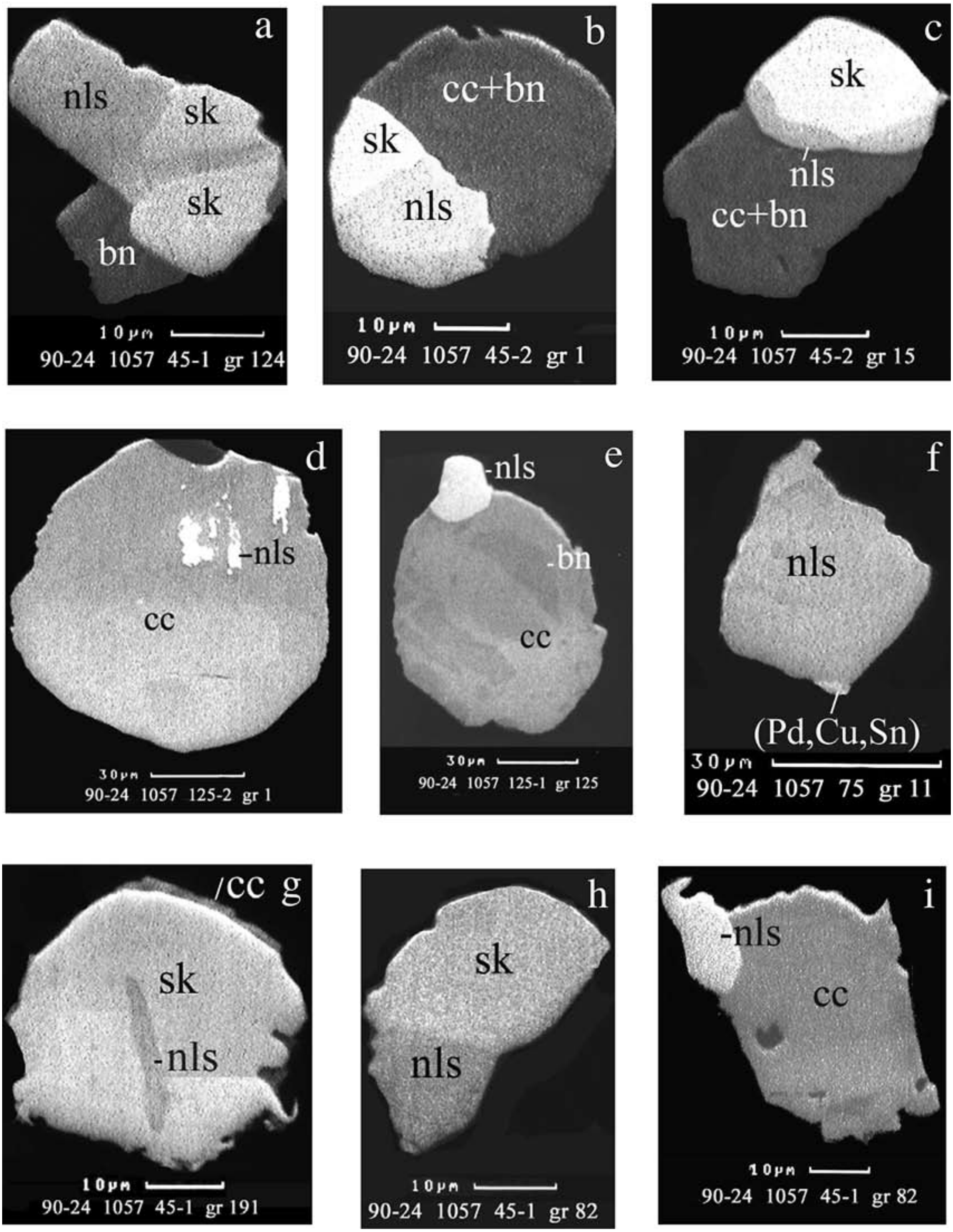

FIG. 1. BSE images of nielsenite (nls), skaergaardite (sk), chalcocite + bornite (cc + bn), bornite (bn) and chalcocite (cc). (a) An angular crystal of nielsenite with skaergaardite and bornite; (b) a microglobule containing nielsenite; c) a subrounded intergrowth of Pd–Cu intermetallic compounds with bornite–chalcocite; (d) a large microglobule of chalcocite with anhedral inclusions of nielsenite; (e) nielsenite with bornite–chalcocite (note the exsolution features in the bornite–chalcocite);

CHEMICAL COMPOSITION

Chemical analyses were conducted using energy-dispersion spectrometry (EDS) on a Camscan Microspec-4DV scanning electron microscope equipped with a Link An–1000 detector. The operating conditions included an accelerating beam voltage of 30 kV, a beam current of 1–2 nA, a beam diameter of 1 μm and counting times of 50–100 s. The following standards and X-ray lines were used: Pd metal (Pd$L\alpha$), Pt metal (Pt$L\alpha$), Au metal (Au$L\alpha$), Cu metal (Cu$K\alpha$), Fe metal (Fe$K\alpha$) and PbTe (Pb$M\alpha$).

A total of 11 EDS analyses gave the following average results (in wt. %): Pd 29.86 (21.7 – 36.3), Pt 3.08 (n.d. – 12.1), Au 3.70 (n.d. – 18.4), Cu 61.96 (54.3 – 68.4), Fe 0.59 (n.d. – 0.80), Pb 0.17 (n.d. – 1.9), total 99.36%. These results indicate only a small amount of substitution of other metals (notably Au and Pt) for Pd, similar to that observed in the related phase skaergaardite. The empirical formula for nielsenite, calculated from the arithmetic mean of the above data (normalized to 4 *apfu*), is: $(Pd_{0.862}Au_{0.058}Pt_{0.049}Fe_{0.028}Pb_{0.003})(Cu_{2.996}Fe_{0.004})_{\Sigma 3}$. The empirical formula for the grain from which the optical and X-ray powder-diffraction data were obtained is: $(Pd_{0.841}Cu_{0.133}Fe_{0.126})Cu_3$. The simplified formula for nielsenite is $PdCu_3$, which requires: Pd 35.82, Cu 64.18, total 100 wt. %. No other tests (etching, solution) were conducted on the mineral.

X-RAY CRYSTALLOGRAPHY AND RELATED STRUCTURES

X-ray powder-diffraction data (Table 2) were collected with a Debye–Scherrer camera 114.6 mm in diameter employing Ni-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å). Interplanar spacing and intensity data were determined using image-plate technology.

Two attempts were made to study nielsenite using single-crystal, four-circle diffractometry methods. In both cases, the observed reflections for the mineral were found to be weak and diffuse, presumably due to Pd–Cu disorder, as is commonly encountered in other PGM and, notably, in synthetic phases belonging to the system Pd–Cu (Subramanian & Laughlin 1991). As the degree of Pd–Cu order has important ramifications with respect to use of Pd–Cu alloys in high-temperature applications, there has been significant interest in its characterization and quantification (Mogck 2004). All phases observed in the system Pd–Cu are disordered, although there appears to be both a temperature and compositional control on the degree of disorder (Mogck 2004). The important implication here is that the inferred Pd–Cu disorder in nielsenite is normally observed in synthetic $PdCu_3$, and that this may serve as an impediment to future studies, for example a crystal-structure determination.

Three synthetic forms of $PdCu_3$ have been reported in the literature, one cubic and two tetragonal. The cubic form of $PdCu_3$ (a = 3.7220 Å; space group *Pm*3*m*; Jones & Sykes 1939) is considered to be isostructural with cubic $AuCu_3$ (Subramanian & Laughlin 1991); although no observed X-ray powder-diffraction data exist, a crystal structure has been proposed (no *R* value given; Jones & Owen 1954). Using these data, an X-ray powder-diffraction pattern was calculated and is compared with that observed for nielsenite in Table 2. Close examination reveals an overall similarity between the two, except for the doubling of several diffraction lines in nielsenite relative to those in cubic $PdCu_3$ (*e.g.*, $d \approx$ 1.86, 1.30 and 1.10 Å). This observation (*i.e.*, the degeneration of single diffraction peaks into doublets) suggests that the overall symmetry for nielsenite is lower than cubic and thus, it is unlikely that the mineral crystallizes in the space group *Pm*3*m*. Schubert *et al.* (1955) reported on the crystal structure of a tetragonal form of $PdCu_3$ (*P*4*mm*; no atomic coordinates or *R* value given), providing an observed X-ray powder-diffraction pattern with data to d = 0.884 Å (PDF card 07–138). Whereas there is broad similarity between the pattern reported by these investigators and that of nielsenite (Table 2), discrepancies relating to intensity and the presence or absence of several strong reflections (both those indexable on the proposed cell and those attributed to a superlattice) make it difficult to conclude that

(f) a subrounded grain of nielsenite with a small unnamed (Pd,Cu,Sn) intermetallic compound; (g) a grain of skaergaardite with a possible inclusion (?) of nielsenite, along with chalcocite; (h) a composite skaergaardite–nielsenite grain (note sharp contact between the phases), and (h) an angular grain of nielsenite with chalcocite.

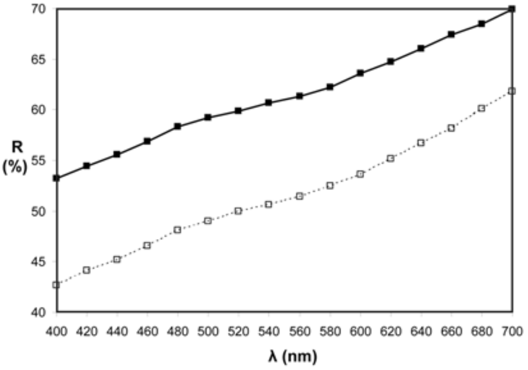

FIG. 2. Reflectance spectra for nielsenite measured in air (filled squares) and in oil (open squares).

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR NIELSENITE AND RELATED SYNTHETIC PHASES

Nielsenite				Synthetic $PdCu_3$[1]			Synthetic $PdCu_3$[2]			Synthetic $PdCu_3$[3]		
I meas[4]	*d* meas (Å)	*d* calc (Å)	*hkl*	*I* calc	*d* calc (Å)	*hkl*	*I* meas	*d* meas (Å)	*hkl*	*I* calc	*d* calc (Å)	*hkl*
				4	3.6718	101	60	3.69	101	7	3.7220	100
10	3.657	3.661	007	4	3.6650	007						
							50	2.765*				
							40	2.625	110	5	2.6319	110
							50	2.468*				
100	**2.137**	**2.133**	**117**	100	2.1332	117	100	2.134	117	100	2.1489	111
5	1.9320	1.9300	119	1	1.9303	119						
70	**1.8596**	**1.8562**	**200**	33	1.8550	200	90	1.857	200	44	1.8610	200
40	**1.8337**	**1.8303**	**0014**	13	1.8325	0014	80	1.833	0014			
							30	1.724*				
5	1.6534	1.6556	207	1	1.6551	207	50	1.654	207	2	1.6645	210
							20	1.572*				
							50	1.541*		1	1.5195	211
							50	1.502	1114			
							30	1.481*				
10	1.3126	1.3126	220	9	1.3117	220	90	1.309	1117	19	1.3159	220
60	**1.3042**	**1.3033**	**2014**	13	1.3037	2014	90	1.302	2014			
							30	1.261*		1	1.2407	300
							50	1.233	227			
							10	1.222	0021			
							50b	1.199*				
							20	1.183*		1	1.1770	310
							40	1.171	2017			
							20	1.156	314			
55	**1.1181**	**1.1179**	**317**	17	1.1174	317	100	1.116	2117	18	1.1222	311
10	1.1064	1.1065	1121	7	1.1075	1121	90	1.107	1121			
30	**1.0663**	**1.0666**	**2214**	6	1.0666	2214	90	1.067	3110	5	1.0744	222
							20	1.042*		1	1.0323	320
							30	1.026	0025			
							30	1.020	2021			
							40b	1.007*				
							30	0.996*		1	0.9947	321
							50	0.986	0026			
							30	0.980	328			
							30	0.959*				
							70	0.925	402	2	0.9305	400
5	0.9283	0.9281	400	3	0.9275	400	60	0.916	0028			
							30	0.908*				
							50	0.897	3214			
							50	0.893	1127			
							50b	0.884*				
										9	0.8539	331
25	0.8459	0.8460	3121	6	0.8462	3121				9	0.8323	420
10	0.8276	0.8278	4014	6	0.8275	4014				1	0.8122	421
							Plus 13 additional reflections to 0.785 Å					

1. Calculated data from Okamura (1970); 2. Calculated from Schubert *et al.* (1955); 3.Calculated data from Jones & Owen (1954). 4. Visually estimated. *: Superlattice reflections.

nielsenite is isostructural with the tetragonal form of $PdCu_3$ reported by Schubert *et al.* (1955). Presnyakov *et al.* (1963) reported on a tetragonal form of $PdCu_3$ (*P*4/*mmm*, *a* 3.697, *c* 3.659 Å) and Okamura (1970) reported on two tetragonal forms of $PdCu_3$ (*P*4*mm* and *P*4/*mmm*, both with *a* 3.710, *c* 25.655 Å). Neither Presnyakov *et al.* (1963) nor Okamura (1970) provided observed X-ray powder-diffraction patterns for any of the tetragonal forms of $PdCu_3$. The calculated X-ray powder-diffraction patterns for the two *P*4/*mmm* structure-types of $PdCu_3$ are indistinguishable from one another, and both are effectively indistinguishable from that calculated for the *P*4*mm* structure-type. At the same time, an *R* value has only been given for the *P*4*mm* structure-type of $PdCu_3$ (7.6%; Okamura 1970), making it difficult to evaluate the quality of the single-crystal X-ray data given in the other two studies of the *P*4/*mmm* structure-types. Given these facts, the X-ray powder-diffraction pattern for the *P*4*mm* structure-type of $PdCu_3$ has been calculated and is compared with that of nielsenite in Table 2. Agreement between the two is very good and on this basis, nielsenite is considered to crystallize in the space group *P*4*mm*. At the same time, the possibility that the mineral crystallizes in the space group *P*4/*mmm* cannot be completely excluded.

Considering its isostructural relationship to the *P*4*mm* structure-type of $PdCu_3$, nielsenite crystallizes in the space group *P*4*mm*, the X-ray powder-diffraction data being indexed on this basis (Table 2). The unit-cell dimensions were refined on the basis of all the observed lines, giving a 3.7125(8), c 25.62(1) Å, V 353.2(1) Å^3 for $Z = 4$. The Pearson Symbol Code is *tI*16.

GENETIC IMPLICATIONS

The Cu–Fe sulfides and PGM associated with nielsenite are paragenetically synchronous, crystallizing after plagioclase, clinopyroxene, orthopyroxene, ilmenite and magnetite, possibly as an intercumulus liquid (Rudashevsky *et al.* 2004). The characteristic droplet morphology of both the PGM and the host Cu–Fe sulfides suggests that the sulfide droplets and enclosed PGM droplets represent immiscible melts: 1) a Cu–Fe sulfide melt and 2) a metal melt enriched in Pd and Cu that separated from the Cu–Fe sulfide melt.

The relationship between skaergaardite (PdCu) and nielsenite is interesting. On a modal distribution basis, skaergaardite clearly dominates, suggesting that the prevailing conditions favored skaergaardite over nielsenite. Rudashevsky *et al.* (2004) noted that skaergaardite may have crystallized at $T \approx 600°C$ (likely through the ordering of Pd and Cu) under conditions of fairly high $f(S_2)$ [$\log f(S_2) > 7$ units]. Skaergaardite and nielsenite are commonly intergrown, with a fairly sharp boundary between them. Whereas they are not related *via* a strict replacement relationship, they may be genetically linked, although the temporal nature of this relationship is not clear. In a few cases (Figs. 1a, c), it appears that nielsenite overgrows skaergaardite, although in one case (Fig.1e), the opposite of this may have occurred. It is also interesting to note that the X-ray-diffraction lines on the pattern for skaergaardite are considerably sharper than those found on the nielsenite pattern, suggesting that nielsenite shows a relatively greater degree of Pd–Cu disorder than does skaergaardite. In short, although the strict genetic relationship between skaergaardite and nielsenite is not clear, the conditions favoring crystallization of nielsenite are considered to be somewhat similar to those of skaergaardite.

Karup-Møller & Makovicky (1999) studied the system Cu–Pd–S (*via* dry synthesis methods); this system is a good geochemical fit for the natural environment in which nielsenite was discovered (*i.e.*, the Triple Group). Both the natural and synthetic systems are dominated by Cu–Fe sulfides and Pd-dominant intermetallic compounds. Karup-Møller & Makovicky (1999) found that at 900°C, the ternary system is dominated by a broad range of sulfide melt that effectively bisects the system (S *versus* Pd + Cu), with only digenite, PdS and disordered Pd–Cu alloys being present. At 725°C, the sulfide melt is divided into two fields, one Cu-rich, the other Pd-rich, with digenite, PdS, Pd_4S and a disordered Pd–Cu alloy being present. At 550°C, the sulfide melt has disappeared, leaving digenite and one or more Pd–S phases (*i.e.*, with variable Pd:S ratios). The alloys include a disordered Cu–Pd phase, a disordered Pd–Cu phase and β-PdCu (skaergaardite). At 400°C, the disordered Pd–Cu phase disappears, the stability region of β-PdCu increases slightly toward more Pd-rich compositions and, of particular note, a phase corresponding to ordered $PdCu_3$ has developed, with a compositional gap existing between it and β-PdCu. No other physical, optical or crystal-structure data are available for the $PdCu_3$ phase observed by Karup-Møller & Makovicky (1999), so it is difficult to state unequivocally that this phase is equivalent to nielsenite. Numerous authors (Subramanian & Laughlin 1991, and references therein) have demonstrated that the upper stability for $PdCu_3$ is 508°C. At this temperature, $PdCu_3$ adopts a cubic $AuCu_3$-type structure over the composition range of 10–20 at.% Pd, but a tetragonal $AuCu_3$-type structure in the range of 20–25 at.% Pd. It is also interesting to note that investigators (*e.g.*, Schubert *et al.* 1955) have found that a greater proportion of Pd than indicated by stoichiometry results in the development of anti-phase domains (APD, or long-period superlattice, LPS) presumably due to Pd–Cu disorder. The implication with respect to the formation of nielsenite is that the mineral may develop at or below ~508°C (*i.e.*, at a lower temperature than skaergaardite) and that diffuse X-ray-diffraction lines observed for the mineral are due to Pd–Cu disorder.

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REFERENCES

ANDERSEN, J.C.Ø, RASMUSSEN, H., NIELSEN, T.F.D. & RØNSBO, J.G. (1998): The Triple Group and the Platinova gold and palladium reefs in the Skaergaard intrusion: stratigraphic and petrographic relations. *Econ. Geol.* **93**, 488-509.

CABRI, L.J., BEATTIE, M., RUDASHEVSKY, N.S. & RUDASHEVSKY, V.N. (2005): Process mineralogy of Au, Pd and Pt ores from the Skaergaard Intrusion, Greenland, using new technology. *Minerals Engineering* **18**, 887-897.

IRVINE, T.N. (1992): Emplacement of the Skaergaard Intrusion. *Carnegie Inst. Wash., Yearbook* **91**, 91-96.

IRVINE, T.N., ANDERSEN, J.C.Ø. & BROOKS, C.K. (2001): Excursion guide to the Skaergaard intrusion, Kangerdlugssuaq area, east Greenland. *Int. Geol. Correlation Project* **427**.

JONES, D.M. & OWEN, E.A. (1954): Experimental study of the variation of the degree of order with temperature in a Cu–Pd alloy. *Proc. Phys. Soc. London* **67**, 297-303.

JONES, F.W. & SYKES, C. (1939): The transformations in the copper–palladium alloys. *J. Inst. Metall.* **65**, 419-433.

KARUP-MØLLER, S. & MAKOVICKY, E. (1999): The phase system Cu–Pd–S at 900°, 725°, 550°, and 400°C. *Neues Jahrb. Mineral., Monatsh.*, 551-567.

MOGCK, S. (2004): *Transmission Electron Microscopy Studies of Interfaces in Multi-Component Systems*. Ph.D. thesis, Rijksuniversiteit Groningen, The Netherlands.

NIELSEN, T.F.D., RASMUSSEN, H., RUDASHEVSKY, N.S., KRETSER, YU.L. & RUDASHEVSKY, V.N. (2003): PGE and sulphide phases of the precious metal mineralisation of the Skaergaard intrusion. 2. Sample 90–24, 1057. *Geol. Surv. Denmark & Greenland* , *Rep.* **2003/48**.

OKAMURA, K. (1970): Lattice modulation in the long period ordered alloys studied by X-ray diffraction. *J. Phys. Soc. Japan*, 1005-1014.

PRESNYAKOV, A.A., DAUTOVA, L.I. & DZHANBUSINOV, E.A. (1963): The structural forms of the Cu–Pd solid solution of approximate composition Cu_3Pd. *Fiz. Metal. Metall.* **16**(1), 52-55.

RUDASHEVSKY, N.S., MCDONALD, A.M., CABRI, L.J., NIELSEN, T.D.F., STANLEY, C.J., KRETSER, YU.L. & RUDASHEVSKY, V.N. (2004): Skaergaardite, PdCu, a new platinum-group intermetallic mineral from the Skaergaard intrusion, Greenland. *Mineral. Mag.* **68**, 615-632.

SCHUBERT, K., KIEFER, B., WILKENS, M. & HAUFLER, R. (1955): Über einige metallische Ordnungsphasen mit grosser Periode. *Z. Metallkd.* **46**, 692-715.

STANLEY, C.J., CRIDDLE, A.J., FÖRSTER, H.-J. & ROBERTS, A.C. (2002): Tischendorfite, $Pd_8Hg_3Se_9$, a new mineral species from Tilkerode, Harz Mountains, Germany. *Can. Mineral.* **40**, 739-745.

SUBRAMANIAN, P.R. & LAUGHLIN, D.E. (1991): Cu–Pd (copper–palladium). *J. Phase Equilibria* **2**, 231-243.

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