Melonite from Kingash and Kuskanak, Eastern Sayans, Russia, and the extent of Bi-for-Te substitution in melonite and synthetic Ni(Te,Bi)_{2-x}

Andrei Y. Barkov^{1,*}, Gennadiy I. Shvedov², Roberta L. Flemming³, AnnaVymazalová⁴ and Robert F. Martin⁵

- ¹ Research Laboratory of Industrial and Ore Mineralogy, Cherepovets State University, 5 Lunacharsky Avenue, 162600 Cherepovets, Russia
- ² Institute of Mining, Geology and Geotechnology, Siberian Federal University, 95, Avenue Prospekt im. gazety "Krasnoyarskiy Rabochiy", 660025 Krasnoyarsk, Russia
- ³ Department of Earth Sciences, Western University, 1151 Richmond Street, London, Ontario N6A 5B7, Canada
- ⁴ Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic
- ⁵ Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Québec H3A 0E8, Canada

[Received 27 February 2016; Accepted 16 May 2016; Associate Editor: Brian O'Driscoll]

ABSTRACT

We describe occurrences of palladoan melonite in intimate intergrowths with cobaltite-gersdorffite from the Neoproterozoic dunite-wehrlite-gabbro complexes of Kingash and Kuskanak, Eastern Sayans, Russia. The observed compositional trends of melonite are consistent with the overall variations examined on the basis of numerous literature sources. The levels of Bi in NiTe₂ are normally limited to ≤ 0.25 Bi atoms per formula unit (apfu), under natural conditions. Greater levels (≤ 0.5 Bi apfu) are associated with the (Pd + Pt) enrichment in the palladoan varieties. The telluride–sulfarsenide intergrowths probably formed at Kingash and Kuskanak late in the crystallization history of the ore zones, from microdroplets of residual melt rich in semimetals (Te, Bi, As) and noble metals (Pd and Ag), below the solidus of the enclosing gabbroic rocks and within a narrow range of temperatures (500–550°C). On the basis of our observations made on specimens of melonite and synthetic Ni(Te,Bi)_{2-x} (x = 0.6), we infer that the limit of incorporation of Bi into a melonite-type phase is ≤ 0.5 Bi apfu.

Keywords: melonite, synthetic Ni Te_{2-x} , solid solutions, Neoproterozoic ultramafic-mafic complexes, Ni-Pd tellurides, Kingash, Kuskanak, Eastern Sayans, Russia.

Introduction

MELONITE, NiTe₂, named after its type locality, the Melones mine, at Carson Hill in the Mother Lode Belt, Calaveras County, California, USA (Genth, 1868; Hillebrand, 1899), is a pre-IMA or 'grandfathered' species. Among other early descriptions, Peacock and Thompson (1945) reported the

*E-mail: ore-minerals@mail.ru https://doi.org/10.1180/minmag.2016.080.119 occurrence of melonite as a minor to accessory constituent of the ore at the Robb-Montbray mine in northwestern Québec, Canada. Although melonite is a rather common species, present in various complexes and ore deposits worldwide (e.g. in ophiolites: Economou-Eliopoulos *et al.*, 2008), its patterns of solid solutions and extent of element substitutions, especially Bi-for-Te, are not well characterized. In this article, we describe occurrences of palladoan melonite at Kingash and Kuskanak, Eastern Sayans, Krasnoyarskiy kray, Russia. Our objective is to evaluate the new data in



FIG. 1. (*a*) Schematic geological map (after Tarasov and Shvedov, 2010) and the location (*b*) of the Kingash complex, Eastern Sayans, Krasnoyarskiy kray, Russia. The presently reported occurrences of melonite are shown by the red symbol.

light of overall variations gathered in the literature, compared with the presently obtained results of syntheses, and to explore the implications concerning the stoichiometry of melonite-type phases.

The intrusive bodies investigated

The Kingash intrusion (\sim 3 km × 0.7 km: Figs 1*a*, *b*) is associated with a smaller body (or block) at Kuskanak. These belong to a Neoproterozoic suite (731–710 Ma) of dunite-peridotite-pyroxenite-

gabbro (picrite) complexes (Shumikha, Golumbei, Tartai, Ognit, Zhelos, Tokty-Oi and Malyi Zadoi), associated with the Yoko–Dovyren complex in the Baikal–Patom zone. These complexes formed in a continental margin setting at the southern margin of the Siberian Craton in the East Siberian metallogenic province (Polyakov *et al.*, 2013; Tolstykh *et al.*, 2014 and references therein). The Kingash dunite-wehrlite-gabbro complex is podiform (Fig. 1*a*). It displays tectonic contacts with the country rocks and hosts zones rich in Cu-Ni, Au-Ag and platinum-group elements (PGE); MELONITE FROM EASTERN SAYANS AND Bi-FOR-Te SUBSTITUTION IN NITe2



FIG. 2. Back-scattered electron images showing grains of melonite (mel) in the Kingash (2a-c) and Kuskanak (2d-f) complexes, in association with: members of the cobaltite (cob)–gersdorffite (ger) series, michenerite [mch; Pd_{1.01}Bi_{0.87–0.89} Te_{1.10-1.11}], hessite [hs; Ag_{1.96}Te_{1.04}], submicrometric grains of coloradoite [clr; Hg_{0.94}Te_{1.06}] and molybdenite [mol; Mo_{0.93}S_{2.07}]. Also present are the main ore species: pentlandite [pn; (Fe_{4.51–4.62}Ni_{4.29–4.45}Co_{0–0.08})_{58.96–8.99}S_{8.03}], pyrrhotite [po; Fe_{0.89}S], a calcic amphibole [amp; a magnesian actinolite: (Ca_{2.00}Na_{0.11}K_{0.02})_{52.13}(Mg_{3.26}Fe_{1.67}Al_{0.09})_{55.02} (Si_{7.75}Al_{0.25})₈O₂₂(OH)₂], titanite [ttr; Ca_{1.00}(Ti_{0.94}Al_{0.08})_{51.02}(Si_{1.00}O₄)O] and a silicate mineral (sil; not analysed).

the zones located in dunite are especially important economically (Shvedov *et al.*, 1997; Glazunov, 2009; Tarasov and Shvedov, 2010; Yurichev, 2014).

Results and discussion

Associations, textures and compositions

In the Kingash complex, melonite is associated closely with zones of Cu-Ni-PGE mineralization (Fig. 1*a*), which show a great diversity in ore species and associations. The latter include base-metal

sulfides (BMS: pyrrhotite, pentlandite, chalcopyrite, cubanite, bornite, millerite), arsenides (nickeline, maucherite), native elements and alloys (copper, bismuth, awaruite, Au-Ag-Hg alloys), and various species of platinum-group minerals (PGM), and PGEbearing phases: sperrylite, moncheite, tetraferroplatinum, platarsite, irarsite, erlichmanite, iridarsenite, michenerite, merenskyite, froodite, sobolevskite, kotulskite, stibiopalladinite or mertieite-II (or both), cabriite, paolovite, unnamed Pd₂(Bi,Sb), palladoan melonite, Rh-bearing cobaltite-gersdorffite and a Pdbearing tetra-auricupride (\leq 4 wt.% Pd).

ANDREI Y. BARKOV ETAL.

No.	Locality	Pt	Pd	Fe	Ni	Te	Bi	Total
1	Kng	_	9.3	0.2	12.4	66.1	12.6	100.5
2	Kng	-	5.2	_	15.4	66.5	12.5	99.6
3	Kng	-	4.7	_	15	65.2	14	99
4	Kng	-	4.9	_	14.9	65	14.1	99
5	Kng	0.2	12.9	_	10	61.8	15	99.8
6	Kng	-	10.4	_	10.7	66.5	11.8	99.4
7	Kng	-	9.6	_	11.3	67.2	11.2	99.3
8	Ksk	_	9	0.9	12.5	72.6	4.6	99.6
9	Ksk	-	10.7	1	10.7	68.9	7.7	99
10	Ksk	-	11.9	0.7	10.1	66.2	10.4	99.3
Atoms	per formula unit	*						
No.	Pt	Pd	Fe	Ni	ΣM	Te	Bi	Te + Bi
1	_	0.3	0.01	0.72	1.03	1.77	0.21	1.97
2	_	0.16	_	0.88	1.04	1.75	0.2	1.96
3	-	0.15	_	0.87	1.02	1.75	0.23	1.98
4	_	0.16	_	0.87	1.03	1.74	0.23	1.97
5	< 0.01	0.43	_	0.6	1.03	1.71	0.25	1.97
6	-	0.34	_	0.64	0.98	1.82	0.2	2.02
7	-	0.31	_	0.67	0.98	1.83	0.19	2.02
8	_	0.28	0.05	0.71	1.04	1.89	0.07	1.96
9	_	0.34	0.06	0.62	1.03	1.85	0.13	1.97
10	-	0.39	0.04	0.6	1.03	1.8	0.17	1.97

TABLE 1. Representative compositions of melonite from the Kingash and Kuskanak complexes, Eastern Sayans, Russia.

These data obtained by wavelength-dispersion electron microprobe (EMP) analyses of melonite were acquired at the Institute of Geology and Mineralogy of the SB RAS (Novosibirsk, Russia) with a «Camebax-micro» instrument, at 20 kV and 50 nA, using synthetic Bi_2S_3 , PbTe and pure metals as standards. The $M\alpha$ line was used for Bi, $L\alpha$ for Pd, Pt, and Te and $K\alpha$ for Ni.*Values of atoms per formula unit (apfu) are based on a total of 3 apfu. – 'not detected'. Kng = Kingash; Ksk = Kuskanak.

The mineralogy and average modal abundance of the mineralized rock, estimated for the PGM-bearing samples, are: calcic amphibole (23 vol.%), clinopyroxene (diopside–hedenbergite series; 21%), sodic plagioclase (albite-oligoclase; 8%), epidote (10%), members of the chlorite group (8%), mica (biotite; 5%), feldspar, quartz and garnet (andradite and grossular): 2–3% each. These observations indicate that the melonite-bearing ore zones are associated with hydrothermally altered mafic rocks, which are hosted by the ultramafic cumulates.

Melonite occurs in intimate intergrowths with subhedral grains of members of the cobaltite– gersdorffite series (Figs 2a-f). Typically, these are present as irregular, elongate inclusions in BMS, located commonly at their boundaries with silicate minerals (e.g. Figs 2c, f). Inclusions of melonite and hessite (i.e. a rim-like phase oriented subparallel with their host: Fig. 2a) are considered to have formed from droplets of trapped melt hosted by grains of cobaltite–gersdorffite (Figs 2a, b). In addition, there are intergrowths of melonite with altaite, hosted by chalcopyrite.

The melonite solid-solution series at Kingash is notably richer in Bi than at Kuskanak (Table 1). In Figs 3a-c, we compare these ranges with the overall compositional variations of melonite (i.e. Ni-dominant members) on the basis of 123 individual data sets collected in the literature. These seem to be representative, as they reflect a wide spectrum of various parageneses settings from more than 40 localities from 21 countries. They reveal a slight negative Ni vs. Bi correlation (Fig. 3b); the coefficient of linear correlation R is -0.61 (n = 123). In contrast, the correlation found for (Pd + Pt) vs. Bi is slightly positive (R = 0.64: Fig. 3c). The majority of the points analysed are very poor in Bi, yielding levels from 'not



FIG. 3. Compositional variations of melonite in terms of plots of: (a) Te vs. Bi; (b) Ni vs. Bi; and (c) (Pd + Pt) vs. Bi (expressed in atoms per formula unit, apfu, per a total of 3 apfu) from the Kingash and Kuskanak complexes (shown by brown squares and red circles, respectively) from Eastern Sayans in Russia in comparison with the overall variations (blue diamond), which are represented by compositions of melonite from: Stanislaus mine, California, USA (Pemberton, 1983); Strathcona mine (Rucklidge, 1969), Sudbury area, Ontario, Canada (Cabri and Laflamme, 1976); Au-bearing skarns, Sinyukhinskoe deposit, the Mountain Altai, Russia (Filimonova and Vakhrushev, 1969); Middavarre copper deposit, Norway (Strand, 1975); Jaduguda uranium deposit, India (Krishna et al., 1980); Yokozuru mine, Japan (Shimada et al., 1981); Ivrea-Verbano complex, Italian Alps (Garuti and Rinaldi, 1986); Kambalda nickel deposits, Australia (Hudson, 1986); Nomgon intrusion, Mongolia (Izokh et al., 1992); Allarechka complex, Kola Peninsula, Russia (Yakovlev et al., 1991); Cu-Ni deposits at Kalatongke, Xinjiang, China (Zhan Xinzhi, 1995); Las Aguilas Ni-Cu deposit, Argentina (Gervilla et al., 1997); Nuasahi complex, India (Mondal and Baidya, 1997); Lahóca Hill Cu-Sb-As-Au epithermal mineralization, Hungary (Gellért et al., 1998); Omai gold deposit, Guiana (Voicu et al., 1999); sulfide Cu-Co ores, Pyshminsko-Kluchevskoe deposit, Middle Urals, Russia (Eremin et al., 1997; Murzin et al., 2011); Koillismaa layered complex, Finland (Kojonen and Iljina, 2001); Wellgreen Ni-Cu-PGE deposit, Yukon, Canada (Barkov et al., 2002); Keivitsansarvi Ni-Cu-PGE deposit, Finland (Gervilla and Kojonen, 2002); Shchuch'ya zone of basic intrusions, Polar Urals, Russia (Kulikova and Varlamov, 2002); Yangliuping Ni-Cu-(PGE) sulfide deposit, China (Song et al., 2004); Aguablanca Ni-Cu-PGE deposit, Iberia (Ortega et al., 2004); Cu-Ni-PGE deposits, Egypt (Helmy, 2004; 2005); Kvintum-1 Co-Ni deposit, Middle Ridge, Kamchatka, Russia (Chubarov et al., 2005); Sunrise Dam gold deposit, Australia (Sung et al., 2007); Ni-Cu sulfide prospects, Scotland (McKervey et al., 2007); Aguablanca Ni-Cu deposit, Spain (Piña et al., 2008); Zhdanovskoe deposit, Pechenga ore field, Kola Peninsula, Russia (Rychkova, 2011); Kamkor Cu-Ni deposit, Kazakhstan (Pavlova et al., 2011); Rosie nickel prospect, Australia (Godel et al., 2012); Rybozero gold deposit, Karelia, Russia (Kuleshevich, 2013); Limoeiro Ni-Cu-(PGE) sulfide deposit, Brasilia (Mota-e-Silva, 2014); Giant Mascot Ni-Cu-PGE deposit, British Columbia (Manor et al., 2014) and McCreedy East Ni-Cu-PGE deposit, Sudbury, Canada (Dare et al., 2014). Several compositions of the NiTe2-NiTe series also are included.



FIG. 4. Compositions of grains of cobaltite–gersdorffite in intergrowths with melonite (shown in Figs 2*a*–*f*) from the Neoproterozoic Kingash and Kuskanak complexes (brown squares and red circles, respectively), compared with the series of PGE-bearing cobaltite–gersdorffite from Early Proterozoic layered intrusions: Mount General'skaya and Lukkulaisvaara, Russia (blue triangles and squares, respectively) and Rio Jacaré, Brazil (red diamonds: Barkov *et al.*, 2015), and with the solvus in the system CoAsS–FeAsS–NiAsS, mol.% (Klemm, 1965).

detected' to ≤ 0.25 Bi apfu (Fig. 3*a*). It should be noted that all of the Bi-rich compositions refer to palladoan varieties rich in (Pd + Pt), as is shown by compositions reported from Ni-Cu-PGE deposits at Sudbury (Cabri and Laflamme, 1976), Las Aguilas, Argentina (Gervilla *et al.*, 1997), Keivitsansarvi, Finland (Gervilla and Kojonen, 2002), Scotland (McKervey *et al.*, 2007) and Aguablanca, Spain (Piña *et al.*, 2008). These varieties contain 0.25–0.44 Bi apfu, 0.18–0.46 Pd apfu (or 5.3–13.4 wt.% Pd), and up to 0.22 Pt apfu (0–10.8 wt.% Pt). The documented maximum values of Bi are 0.44 and 0.48 apfu, which are reported from China (Zhan, 1995) and Finland (Gervilla and Kojonen, 2002).

The compositions of cobaltite–gersdorffite intergrown with melonite are: $[(Co_{0.41-0.49}Ni_{0.34-0.42}Fe_{0.13})_{\Sigma 0.96}As_{1.03-1.04}S_{0.99-1.01}]$ at Kingash and $[(Ni_{0.46-0.47}Co_{0.36-0.37}Fe_{0.19-0.20})_{\Sigma 1.03}As_{1.00-1.02}S_{0.96-0.97}]$ at Kuskanak; the latter are notably richer in Ni and Fe. They all plot (Fig. 4) along the trend line Ni:Fe = 2 as a reflection of the ordered distribution of Ni and Fe in the structure (Béziat *et al.*, 1996), and are consistent with a crystallization trend of PGEbearing cobaltite–gersdorffite in Early Proterozoic layered complexes (Barkov *et al.*, 2015).

Content of Bi in melonite and solid solutions involving NiTe₂

The overall variations documented in natural members of the melonite series, including our

data, show that the Bi content is limited in this series, ≤ 0.5 apfu; with the majority of these data having ≤ 0.25 Bi apfu (Fig. 3*a*). High contents of Bi are invariably accompanied by the observed enrichment in Pd + Pt (Fig. 3*c*), based on compositional data in Cabri and Laflamme (1976); Zhan Xinzhi (1995); Gervilla *et al.* (1997); Gervilla and Kojonen (2002); McKervey *et al.* (2007); and Piña *et al.* (2008). In the Ivrea Verbano complex, Italy, the Bi content of melonite depends on the type of ore mineralization; thus, it could probably be used, in certain cases, as a petrogenetic indicator (Zaccarini *et al.*, 2014).

Several solid-solution series involving NiTe₂ are known. Extensive binary series are known in the system NiTe₂–PdTe₂–PtTe₂ (e.g. Cabri and Laflamme, 1976; Garuti and Rinaldi, 1986; Cabri, 2002). In addition, a series observed at Kingash extends from PdTe₂ (merenskyite) towards PdTeBi (michenerite). We expect that a limited series may also exist from NiTe₂ towards NiTeBi; that phase has been discovered at Ognit, Eastern Sayans, in Russia, and will be described separately.

A solid-solution series is developed between palladoan melonite and palladoan 'imgreite' (or hexatestibiopanickelite; Bayliss, 1990) (e.g. at Wellgreen, Yukon, Canada: Barkov *et al.*, 2002). The nickeline-type $NiTe_{1+x}$ compounds and members of the 'imgreite' (NiTe) – melonite (NiTe₂) series have been synthesized successfully (Yushko-Zakharova, 1964; Barstad *et al.*, 1966; Carbonara and Hoch, 1972). The structure of melonite $[Ni^{2+}(Te_2)^{2-}]$ and of related ditellurides is classified as being of 'polymeric CdI₂-type' (Jobic *et al.*, 1991; Bensch *et al.*, 1996).

The possible existence of a Co-rich analogue of melonite is implied by the phase $[(Ni_{0.53}Co_{0.50})_{\Sigma 1.03}]$ Te_{1.97}], a member of the series NiTe₂-CoTe₂, found in the Shanggong mine, China (Luo et al., 1999). In addition, a solid-solution series extends from melonite to kitkaite (NiTeSe), which has a melonite-type structure (Häkli et al., 1965). As noted, a potential series may extend from NiTe₂ towards NiTeBi. One more series (presumably limited) involves melonite and a Ni-rich antimonide, hypothetically defined as nisbite NiSb₂ (löllingite group); this example of solid solution $[(Ni_{0.99}Fe_{0.09} Pd_{0.08})_{\Sigma 1.2}(Te_{1.33}Sb_{0.47}Bi_{0.02})_{\Sigma 1.8}]$ was reported from the Pechenga complex, Kola Peninsula, Russia (Rychkova, 2011). It appears probable, however, that the latter phase is rather indicative of a series extending towards breithauptite (NiSb) having a nickeline-type structure, consistent with the documented series of 'imgreite' (NiTe) – melonite (NiTe₂).

Solubility limit of Bi in synthetic Ni(Te,Bi)_{2-x}

We have performed experiments in order to evaluate the limit of incorporation of Bi into the structure of melonite-type telluride, $NiTe_{2-x}$. The synthetic samples of Bi-rich telluride of Ni were prepared in evacuated and sealed silica-glass tubes, in a horizontal furnace (at the Laboratory of Experimental Mineralogy, Czech Geological Survey, Prague). In order to prevent loss of material



FIG. 5. Back-scattered electron image of synthetic Bi-rich melonite, $Ni(Te,Bi)_{2-x}$, in association with native bismuth and the phase Bi₂Te.

to the vapour phase, the free space in the tube was reduced by placing a closely fitting glass rod against the charge. A charge of ~400 mg was carefully weighed out from the pure elements. We used, as starting chemicals, a nickel powder, a tellurium ingot and bismuth beads, all supplied by the Aldrich Chem. Co. (with a 99.999% purity). The starting mixture was first melted at 1000°C for two days. The product of melting was then ground in an agate mortar under acetone and held at 200, 400 and 600°C for 75 days. The samples were quenched by dropping the capsule in cold water. The synthetic phases (e.g. Fig. 5) were analysed using wavelength-dispersive spectrometry (WDS EMP) (Table 2) and powder X-ray diffraction analysis (XRD), carried out with a Bruker D8 Advance diffractometer (CuKa radiation and a Lynx Exe XE detector).

The results obtained (WDS and XRD) indicate that the synthetic phase is an intermediate member in the NiTe-Ni(Te,Bi)2 solid-solution series (Fig. 5, Table 2). This phase has a formula of $Ni(Te,Bi)_{2}$, which may imply the existence of vacancy-type defects at the Te site. The mean composition of the Bi-rich telluride is $Ni_{1,49}(Te_{1,37}Bi_{0,63})_{\Sigma 2,0}$ or $Ni_{1,0}$ $(Te_{0.92}Bi_{0.42})_{\Sigma 1.34}$, calculated for 2 (Te + Bi) and Ni = 1 apfu, respectively; it is based on the results of seven WDS analytical points of the material synthesized at 400°C (Table 2). It is generally consistent with a homogeneity range of $Ni_{1+x}Te_2$ $(0 \le x \le 0.83)$ proposed by Lee and Nash (1990) of the CdI₂ structure type ($P\overline{3}m1$). The WDS analyses of the three synthetic samples, prepared at 200, 400, and 600°C, gave a narrow range of compositions with a slightly lower level of Bi incorporation at 200°C. On the basis on our experiments, we infer that the synthetic melonite-type phase dissolves up to 18 at.% Bi or ≤ 0.4 Bi apfu, i.e. Ni_{1.0}(Te_{0.9}Bi_{0.4})_{2-x}. This value agrees with the maximum Bi content observed in the compositions of naturally occurring specimens of melonite.

Genetic features and concluding comments

The observed intergrowths of Pd-rich tellurides with cobaltite–gersdorffite (Figs 2a-e) also are characteristic of Early Proterozoic complexes, e.g. the Mount General'skaya layered intrusion, in sub-Arctic Russia (Barkov *et al.*, 1999). They consist of late-crystallizing phases that occur interstitially in association with calcic amphibole, titanite and BMS (Fig. 2c). Commonly, they are located at grain boundaries (Figs 2e, f). Michenerite, a typical

ANDREI Y. BARKOV ETAL.

	wt.%				(Te + Bi) = 2 apfu			Ni = 1 apfu		
Sample (<i>T</i> , °C)	Ni	Te	Bi	Total	Ni	Te	Bi	Te	Bi	Te+Bi
40/3	22.96	46.78	29.41	99.16	1.54	1.45	0.55	0.94	0.36	1.30
(200)	23.15	47.15	29.09	99.39	1.55	1.45	0.55	0.94	0.35	1.29
	21.94	46.92	31.17	100.04	1.45	1.42	0.58	0.98	0.40	1.38
	21.38	45.40	32.32	99.10	1.43	1.39	0.61	0.98	0.42	1.40
	22.89	47.08	29.97	99.93	1.52	1.44	0.56	0.95	0.37	1.31
Average	22.47	46.67	30.39	99.52	1.50	1.43	0.57	0.96	0.38	1.34
40/1	22.08	44.23	33.58	99.88	1.48	1.37	0.63	0.92	0.43	1.35
(400)	22.49	44.52	33.81	100.83	1.50	1.37	0.63	0.91	0.42	1.33
	22.25	44.44	33.80	100.49	1.49	1.37	0.63	0.92	0.43	1.35
	22.21	44.66	32.93	99.79	1.49	1.38	0.62	0.93	0.42	1.34
	22.30	44.73	33.54	100.57	1.49	1.37	0.63	0.92	0.42	1.35
	22.29	44.91	33.53	100.73	1.48	1.37	0.63	0.93	0.42	1.35
	22.13	44.38	32.91	99.42	1.49	1.38	0.62	0.92	0.42	1.34
Average	22.25	44.55	33.44	100.24	1.49	1.37	0.63	0.92	0.42	1.34
40/2	22.58	43.99	33.39	99.96	1.52	1.37	0.63	0.90	0.42	1.31
(600)	22.31	43.91	33.20	99.42	1.51	1.37	0.63	0.91	0.42	1.32
· /	22.54	44.12	33.27	99.93	1.52	1.37	0.63	0.90	0.41	1.32
Average	22.48	44.01	33.29	99.77	1.52	1.37	0.63	0.90	0.42	1.32

TABLE 2. Compositions of synthetic melonite-type phase rich in Bi.

These data obtained from wavelength-dispersive analyses (in wt.%) were acquired with a CAMECA SX-100 electron microprobe, at 15 kV and 10 nA (measured on the Faraday cup), using a focused beam (1–2 μ m), pure elements as standards, and the following X-ray lines: TeL α , NiK α and BiM β .

constituent in these intergrowths, is not stable at a temperature higher than 501°C (Hoffman and MacLean, 1976). Consistently, the associated grains of cobaltite–gersdorffite appear to have equilibrated over a range of 550 to 500°C (Fig. 4). Melonite rims a core-like grain of gersdorffite (Fig. 2*d*), thus presumably indicating its crystallization at a temperature lower than 500–550°C. The shape of the interface between the coexisting phases, melonite and gersdorffite (Fig. 2*e*), implies their nearly simultaneous crystallization.

In the Neoproterozoic Kingash and Kuskanak complexes (Eastern Sayans), the intergrowths of Ni–Pd-rich ditelluride with Co–Ni-rich sulfarsenides (Figs 2a-e) have probably been formed from microdroplets of a residual melt rich in semimetals and metalloids (Te, Bi, As) and noble metals (Pd and Ag) at a temperature on the order of 500–550°C, which is clearly below the solidus of the enclosing rock. Compositional trends of melonite-related phases are consistent with the overall variations examined on the basis of numerous literature sources, and representative of various settings and localities worldwide (Figs 3a-c). These observations suggest that restrictions probably exist concerning the solubility of Bi in NiTe₂, with the common limited incorporation ≤ 0.25 Bi apfu under normal conditions. These limits could well be a reflection of complications arising as Bi replaces Te bonded in the $(Te_2)^{2-}$ pairs in the structure. Greater levels of Bi (≤ 0.5 Bi apfu) are associated closely with the palladoan varieties, consistent with the slightly positive correlation of Bi *vs*. (Pd + Pt), which contrasts with the slightly negative correlation of Bi *vs*. Ni (Figs 3*b*, *c*). The maximum Bi enrichment in natural samples probably involves the Pd–(Pt)-bearing component [(Pd,Pt)TeBi]. There is no evidence that a continuous series exists between NiTe₂ and NiTeBi under commonly attained conditions in nature.

On the basis of our experiments and observations made on specimens of melonite, including the numerous literature sources, we thus contend that the limit of the incorporation of Bi into the melonite-type phase is apparently restricted to values of ≤ 0.5 Bi apfu. Greater levels of Bi are unlikely to be present in members of the NiTe–Ni(Te,Bi)₂ series, unless special conditions of crystallization are involved, e.g. a high-pressure environment.

Acknowledgements

We thank N.S. Karmanov and L.N. Pospelova for the EMP data obtained at the Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia). We are grateful to F. Zaccarini, M. Economou-Eliopoulos and B. O'Driscoll for their reviews and constructive comments. A.Y.B. gratefully acknowledges a partial support of this investigation by the Russian Foundation for Basic Research (project # RFBR 16-05-00884).

References

- Barkov, A.Y., Thibault, Y., Laajoki, K.V.O, Melezhik, V.A. and Nilsson, L.P. (1999) Zoning and substitutions in Co–Ni–(Fe)–PGE sulfarsenides from the Mount General'skaya layered intrusion, Arctic Russia. *The Canadian Mineralogist*, **37**, 127–142.
- Barkov, A.Y., Laflamme, J.H.G., Cabri, L.J. and Martin, R.F. (2002) Platinum-group minerals from the Wellgreen Ni-Cu-PGE deposit, Yukon, Canada. *The Canadian Mineralogist*, **40**, 651–669.
- Barkov, A.Y., Fedortchouk, Y., Campbell, R.A. and Halkoaho, T.A.A. (2015) Coupled substitutions in PGE-enriched cobaltite: new evidence from the Rio Jacaré layered complex, Bahia state, Brazil. *Mineralogical Magazine*, **79**, 1185–1193.
- Barstad, J., Grønvold, F., Røst, E. and Vestersjø, E. (1966) On the tellurides of nickel. *Acta Chemica Scandinavica*, 20, 2865–2879.
- Bayliss, P. (1990) Revised unit-cell dimensions, space group, and chemical formula of some metallic minerals. *The Canadian Mineralogist*, 28, 751–755.
- Bensch, W., Heid, W., Muhler, M., Jobic, S., Brec, R. and Rouxel, J. (1996) Anionic polymeric bonds in nickel ditelluride: crystal structure, and experimental and theoretical band structure. *Journal of Solid State Chemistry*, **121**, 87–94.
- Béziat, D., Monchoux, P. and Tollon, F. (1996) Cobaltitegersdorffite solid solution as a primary magmatic phase in spessartite, Lacaune area, Montagne Noire, France. *The Canadian Mineralogist*, **34**, 503–512.
- Cabri, L.J. (2002) The Geology, Geochemistry, Mineralogy, Mineral Beneficiation of the Platinum-Group Elements. Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume 54, 852 pp.
- Cabri, L.J. and Laflamme, J.H.G. (1976) The mineralogy of the platinum-group elements from some copper–nickel deposits of the Sudbury area, Ontario. *Economic Geology*, **71**, 1159–1195.
- Carbonara, R.S. and Hoch, M. (1972) Thermodynamics and the structure of Ni_{1-x}Te. *Monatshefte für Chemie*, **103**, 695–715.

- Chubarov, V.M., Ignatyev, E.K., Moskalyova, S.V., Sidorov, E.G., Tararin, I.A. and Shapovalenko, V.M. (2005) The copper-nickel ore deposit of Kvintum-1 in cortlandites in the southern part of middle ridge of Kamchatka. *Doklady Akademii Nauk*, **403**(2) [pp. 231–236, in Russian].
- Dare, S.A.S., Barnes, S.-J., Prichard, H.M. and Fisher, P.C. (2014) Mineralogy and geochemistry of Cu-rich ores from the McCreedy East Ni-Cu-PGE deposit (Sudbury, Canada): implications for the behavior of platinum group and chalcophile elements at the end of crystallization of a sulfide liquid. *Economic Geology*, 109, 343–366.
- Economou-Eliopoulos, M., Eliopoulos, D.G. and Chryssoulis, S. (2008) A comparison of high-Au massive sulfide ores hosted in ophiolite complexes of the Balkan Peninsula with modern analogues: genetic significance. Ore Geology Reviews, 33, 81–100.
- Eremin, N., Sergeeva, N.E. and Shishakov, V.O. (1997) On finding a palladium-bearing melonite in copperrich sulphide ores of the Pyshminsko-Kluchevskoe deposit in the Urals. *Doklady Akademii Nauk*, **355**(6) [pp. 795–797, in Russian].
- Filimonova, A.A. and Vakhrushev, V.A. (1969) Melonite from the gold-bearing skarns of the Sinjukhin deposit in the Mountain Altai. *Zapiski RMO (Proceedings of the Russian Mineralogical Society)*, **98**(2) [pp. 175–182, in Russian].
- Garuti, G. and Rinaldi, R. (1986) Mineralogy of melonitegroup and other tellurides from the Ivrea-Verbano basic complex, western Italian Alps. *Economic Geology*, 81, 1213–1217.
- Gellért, B., Buzogány, P. and Weiszburg, T. (1998) Melonite (NiTe₂) in the epithermal Cu–Sb–As–Au mineralization of the Lahóca Hill, Recsk, NE Hungary. *Földtani Közlöny*, **128**, 585–606.
- Genth, F.A. (1868) Contributions to mineralogy VII. American Journal of Science, 95, 305–321.
- Gervilla, F. and Kojonen, K. (2002) The platinum-group minerals in the upper section of the Keivitsansarvi Ni–Cu–PGE deposit, northern Finland. *The Canadian Mineralogist*, **40**, 377–394.
- Gervilla F., Sanchez-Anguita, A., Acevedo, R.D., Fenoll Hach-Ali, P. and Paniagua, A. (1997) Platinum-group element sulpharsenides and Pd bismuthotellurides in the metamorphosed Ni–Cu deposit at Las Aguilas (Province of San Luis, Argentina). *Mineralogical Magazine*, 61, 861–877.
- Glazunov, O.M. (2009) Perspectives of enlargement of the mineral stock base for non-ferrous metals in the Sayan nickel–platinum province. Pp. 19–24 in: *Proceedings* of the First International Congress and Exhibition "Non-Ferrous Metals of Siberia – 2009", September 8 – 10th, 2009. Krasnoyarsk, Russia [in Russian].
- Godel, B., Gonzalez-Alvarez, I., Barnes, S.J., Barnes, S.-J., Parker, P. and Day J. (2012) Sulfides and

sulfarsenides from the Rosie nickel prospect, Duketon greenstone belt, western Australia. *Economic Geology*, **107**, 275–294.

- Häkli, T.A., Vuorelainen, Y. and Sahama, T.G. (1965) Kitkaite (NiTeSe), a new mineral from Kuusamo, northeast Finland. *The American Mineralogist*, **50**, 581–586.
- Helmy, H.M. (2004) Cu–Ni–PGE mineralization in the Genina Gharbia mafic–ultramafic intrusion, Eastern Desert, Egypt. *The Canadian Mineralogist*, 42, 351–370.
- Helmy, H.M. (2005) Melonite group minerals and other tellurides from three Cu–Ni–PGE prospects, Eastern Desert, Egypt. Ore Geology Review, 26, 305–324.
- Hillebrand, W.F. (1899) Mineralogical notes: melonite (?), coloradoite, petzite, hessite. *American Journal of Science*, **158**, 295–298.
- Hoffman, E. and Maclean, W.H. (1976) Phase relations of michenerite and merenskyite in the Pd–Bi–Te system. *Economic Geology*, **71**, 1461–1468.
- Hudson, D.R. (1986) Platinum-group minerals from the Kambalda nickel deposits, western Australia. *Economic Geology*, 81, 1218–1225.
- Izokh, A.E., Mayorova, O.N. and Lavrent'yev, Yu.G. (1992) Minerals of the platinum-group metals in the Nomgon troctolite–anorthosite–gabbro intrusion (Mongolia). *Geologiya i Geofizika*, **1** [pp. 104–110, in Russian].
- Jobic, S., Deniard, P., Brec, R., Rouxel, J., Jouanneaux, A. and Fitch, A.N. (1991) Crystal and electronic band structure of IrTe₂: evidence of anionic bonds in CdI₂like arrangement. *Zeitschrift für anorganische und allgemeine Chemie*, **598** / **599**, 199–215.
- Klemm, D.D. (1965) Synthesen and Analysen in den Dreiecks-diagrammen FeAsS–CoAsS–NiAsS und FeS₂ – CoS₂ – NiS₂. *Neues Jahrbuch für Mineralogie, Abhandlungen*, **103**, 205–255.
- Kojonen, K. and Iljina, M. (2001) Platinum-group minerals in the early Proterozoic Kuusijärvi marginal series, Koillismaa layered igneous complex, northeastern Finland. Pp. 653–656. in: *Proceedings of the sixth Biennial SGA–SEG meeting* (A. Piestrzynski *et al.*, editors). Balkema Publishers, Lisse, The Netherlands.
- Krishna, N.R, Narasimhan, D. and Rao, G.V.U. (1980) The nickel telluride mineral melonite from the Jaduguda uranium deposit, Singhbhum shear zone, Bihar, India. *Mineralogical Magazine*, 43, 775–777.
- Kuleshevich, L.V. (2013) The Rybozero gold deposit in the Yuzhno–Vygozersky greenstone belt (eastern Karelia). Pp. 89–101. in: *The Geology and Ore Deposits of Karelia*. Institute of Geology, Karelian Research Centre of the RAS, 16. Petrozavodsk, Russia [in Russian].
- Kulikova, K.V. and Varlamov, D.A. (2002) A find of telluride of the platinum-group metals in basic rocks of

the Polar Urals. *Mineralogical Museums: Proceedings* of the 4th International Symposium. St. Petersburg, June 2002 [pp. 104–105, in Russian].

- Lee, S.Y and Nash, P. (1990) Nickel-Tellurium. Pp. 2869–2872 in: *Binary Alloy Phase Diagrams 2nd ed.* (T.B. Massalski, editor). Vol. 3. ASM International, Materials Park, Ohio, USA.
- Luo, Z., Guan, K., Wang, M. and Wang, C. (1999) The features of telluride in some gold deposits, China. *Guizhou Geology* 5(3) [pp. 69–74, in Chinese].
- Manor, M.J., Scoates, J.S., Nixon, G.T. and Ames, D.E. (2014) Platinum-group mineralogy of the Giant Mascot Ni–Cu–PGE deposit, Hope, B.C. Geological fieldwork 2013, British Columbia ministry of energy and mines, British Columbia Geological Survey, Paper 2014–1, pp. 141–156.
- McKervey, J.A., Gunn, A.G. and Styles, M.T. (2007) Platinum-group elements in Ordovician magmatic Ni–Cu sulfide prospects in northeast Scotland. *The Canadian Mineralogist*, **45**, 335–353.
- Mondal, S.K. and Baidya, T.K. (1997) Platinum-group minerals from the Nuasahi ultramafic-mafic complex, Orissa, India. *Mineralogical Magazine*, 61, 902–906.
- Mota-e-Silva, J. (2014) The Limoeiro Ni–Cu–(PGE) sulfide deposit: metallogenesis, mafic magmatism and metamorphism in eastern Borborema province. PhD thesis, Geosciences Institute, University of Brasilia, Brasilia, Brazil, 304 pp.
- Murzin, VV, Varlamov, D.A. and Vikent'yev, I.V. (2011) A copper-cobalt ore in the Pyshminsko– Klyuchevskoye deposit in the Middle Urals: mineral composition of ores and metasomatites, and stages and *P*–*T* conditions of mineral formation. *Litosphera*, 6, 103–122 [in Russian].
- Ortega, L., Lunar, R., García-Palomero, F., Moreno, T., Martín-Estévez, J.R., Prichard, H.M. and Fisher, P.C. (2004) The Aguablanca Ni–Cu–PGE deposit, southwestern Iberia: magmatic ore-forming processes and retrograde evolution. *The Canadian Mineralogist*, 42, 325–350.
- Pavlova, Z.N., Omarbekova, A.E. and Levin, V.L. (2011) Minerals of nickel and cobalt in Cu–Ni ores of the Kamkor Cu–Ni deposit. *Izvestiya NAN Respubliki Kazakhstan, Series of Geology and Technical Sciences*, 4, 38–41 [in Russian].
- Peacock, M.A. and Thompson, R.M. (1945) Melonite from Quebec and the crystal structure of NiTe₂. University of Toronto Studies, Geology Series, **50**, 63–73.
- Pemberton, H.E. (1983) *Minerals of California*. Van Nostrand Reinhold Press, New York, 591 pp.
- Piña, R., Gervilla, F., Ortega, L. and Lunar, R. (2008) Mineralogy and geochemistry of platinum-group elements in the Aguablanca Ni–Cu deposit (SW Spain). *Mineralogy and Petrology*, **92**, 259–282.

- Polyakov, G.V., Tolstykh, N.D., Mekhonoshin, A.S., Izokh, A.E., Podlipskii, M.Yu., Orsoev, D.A. and Kolotilina, T.B. (2013) Ultramafic–mafic igneous complexes of the Precambrian East Siberian metallogenic province (southern frame of the Siberian craton): Age, compositions, origin, and ore potential. *Russian Geology and Geophysics*, 54(11), 1689–1704 [in Russian].
- Rucklidge, J. (1969) Electron microprobe investigations of platinum-metal minerals from Ontario. *The Canadian Mineralogist*, 9, 617–628.
- Rychkova, O.A. (2011) A noble-metal mineralization in copper-nickel ores of the Zhdanovskoe deposit of the Pechenga ore field (northwestern Kola Peninsula). Proceedings of the Second International Scientific and Applied Conference of Young Scientists and Specialists in Memory of Academician A.P. Karpinsky. St. Petersburg, 8–11 February 2011 [pp. 230–234, in Russian].
- Shimada, N., Miyahisa, M. and Hirowatari, F. (1981) Melonite and volynskite from the Yokozuru mine, Sannotake, North Kyushu, Japan. *Mineralogical Journal*, 10(6), 269–278.
- Shvedov, G.I., Tolstykh, N.D., Nekos, V.V. and Pospelova, L.N. (1997) Platinum-group minerals in Cu–Ni sulfide ores of the Kingash massif (Eastern Sayans). *Russian Geology and Geophysics*, **38**(11), 1872–1878 [in Russian].
- Song, X.-Y., Zhou, M.-F. and Cao, Z.-M. (2004) Genetic relationships between base-metal sulfides and platinum-group minerals in the Yangliuping Ni–Cu– (PGE) sulfide deposit, southwestern China. *The Canadian Mineralogist*, **42**, 469–483.
- Strand, G.S. (1975) Melonite (NiTe₂) from the Middavarre copper deposit. Contribution to the mineralogy of Norway, No. 61. Norsk Geologisk Tidsskrift, 55, 299–302.
- Sung, Y.-H., Ciobanu, C.L., Pring, A., Brugger, J., Skinner, W., Cook, N.J. and Nugus, M. (2007) Tellurides from the Sunrise Dam gold deposit, Yilgarn Craton, western Australia: a new occurrence of nagyagite. *Mineralogy and Petrology*, 91, 249–270.

- Tarasov, A.V. and Shvedov, G.I. (2010) The regularities of distribution and mineral compositions of noble metal ores in the Kingash Cu-Ni deposit (Krasnoyarskiy kray). In: Presentations of the Fourth International Mining and Geology Meeting "MinGeo Siberia 2010", the International Forum "Platinum in Geologic Formations of the World". Krasnoyarsk Research Institute of Geology and Mineral Resources, May 11-14th 2010, Krasnoyarsk, Russia [in Russian].
- Tolstykh, N.D., Polyakova, G.V., Izokh, A.E., Podlipsky, M.Yu., Mekhonoshin, A.S., Orsoev, D.A. and Kolotilina, T.B. (2014) Cu–Ni–PGE deposits of east Siberia hosted by Neoproterozoic mafic–ultramafic complexes. Abstract Volume 2014 Convention 11th International Conference on Gondwana to Asia 20–21 September, Beijing, China. *IAGR Conference Series*, No. 20, 138–140.
- Voicu, G., Bardoux, M. and Jébrak, M. (1999) Tellurides from the Paleoproterozoic Omai gold deposit, Guiana Shield. *The Canadian Mineralogist*, **37**, 559–573.
- Yakovlev, Yu.N., Mitrofanov, F.P., Razhev, S.A., Veselovsky, N.N., Distler V.V. and Grokhovskaya, T.L. (1991) Mineralogy of PGE in the mafic– ultramafic massifs of the Kola region. *Mineralogy* and Petrology, 43, 181–192.
- Yurichev, A.N. (2014) Evolution of sulfide melt in process of formation of the Kingash ultramafic massif (northwestern Eastern Sayans). Bulletin of the Tomsk Polytechnic University, Earth Sciences Section, 324(1), 56–64 [in Russian].
- Yushko-Zakharova, O.E. (1964) A new mineral nickel telluride. *Doklady Akademii Nauk SSSR*, 154, 613–614 [in Russian].
- Zaccarini, F., Garuti, G., Fiorentini, M.L., Locmelis, M., Kollegger, P. and Thalhammer, O.A.R. (2014) Mineralogical hosts of platinum group elements (PGE) and rhenium in the magmatic Ni-Fe-Cu sulfide deposits of the Ivrea Verbano Zone (Italy): an electron microprobe study. *Neues Jahrbuch für Mineralogie*, **191**, 169–187.
- Zhan Xinzhi (1995) Bismuthian palladian melonite a new variety. Acta Mineralogica Sinica, 15(2), 150–153 [in Chinese].