SHORT COMMUNICATIONS

Osmian hollingworthite and rhodian cobaltite-gersdorffite from the Lukkulaisvaara layered intrusion, Russian Karelia

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HOLLINGWORTHITE, ideally RhAsS, was first described by Stumpfl and Clark (1965) from the Bushveld igneous complex. Since then it has been reported from the same and other occurrences in the Bushveld (Genkin *et al.*, 1966; Stumpfl, 1972; Tarkian and Stumpfl, 1975); Werner Lake, Canada (Rucklidge, 1969); Hitura (Häkli *et al.*, 1976), Penikat (Alapieti and Lahtinen, 1986; Halkoaho *et al.*, 1990; Halkoaho, 1994), Siikakämä (Hänninen *et al.*, 1986), Finland; placers from the Urals (Begizov *et al.*, 1976), a mafic-ultramafic complex, Kola Peninsula (Distler and Laputina, 1981), Cu-Ni sulphide deposits of Noril'sk (Genkin and Evstigneeva, 1986) and alpine-type complexes, Russia (Distler *et al.*, 1986); Stillwater layered complex (Volborth *et al.*, 1986); Shetland ophiolites (Tarkian and Prichard, 1987; Prichard and Tarkian, 1988); Osthammeren, Norway (Nilsson, 1990); Two Duck Lake, Canada (Ohnenstetter *et al.*, 1991); Lukkulaisvaara, Mt. Generalskaya and Imandrovsky layered intrusions, NW Russia (Barkov and Lednev, 1993; Barkov *et al.*, 1994; 1995b), although in only a few cases are Os-rich hollingworthites recorded (Stumpfl, 1972; Distler and Laputina, 1981; Tarkian and Prichard, 1987; Ohnenstetter *et al.*, 1991).

Hollingworthite is a cubic mineral with a cobaltite-type structure, isostructural with two other platinum-group element (PGE) sulpharsenides: irarsite, ideally IrAsS (Genkin *et al.*, 1966) and platarsite, ideally PtAsS (Cabri *et al.*, 1977). Published electron microprobe data indicate that there are extensive solid solutions between hollingworthite and irarsite, and hollingworthite and platarsite. Os-rich irarsite and platarsite are also known (Begizov *et al.*, 1976; Thalhammer *et al.*, 1990; Nilsson, 1990).

This paper describes a new occurrence and chemistry of osmian hollingworthite and associated very rare rhodian cobaltite from the Lukkulaisvaara layered intrusion.

The Early Palaeoproterozoic (c. 2440 Ma; Barkov, 1992) Lukkulaisvaara intrusion belongs to the Oulanka layered complex, that is situated in northern Karelia, NW Russia. The complex represents a part of an extensive intrusion belt in the Fennoscandian shield (Alapieti *et al.*, 1990). Brief geological descriptions of the intrusion were given by Lavrov (1979) and Barkov *et al.* (1995a). The most notable feature of the intrusion is the presence of concordant to subconcordant sill-like bodies of microgabbro-norite within the gabbroic sequence. At least two of these bodies contain the PGE-rich pegmatoidal segregations, in which diverse platinum-group mineral (PGM) assemblages have been identified (e.g. Barkov and Lednev, 1993; Barkov *et al.*, 1995a;
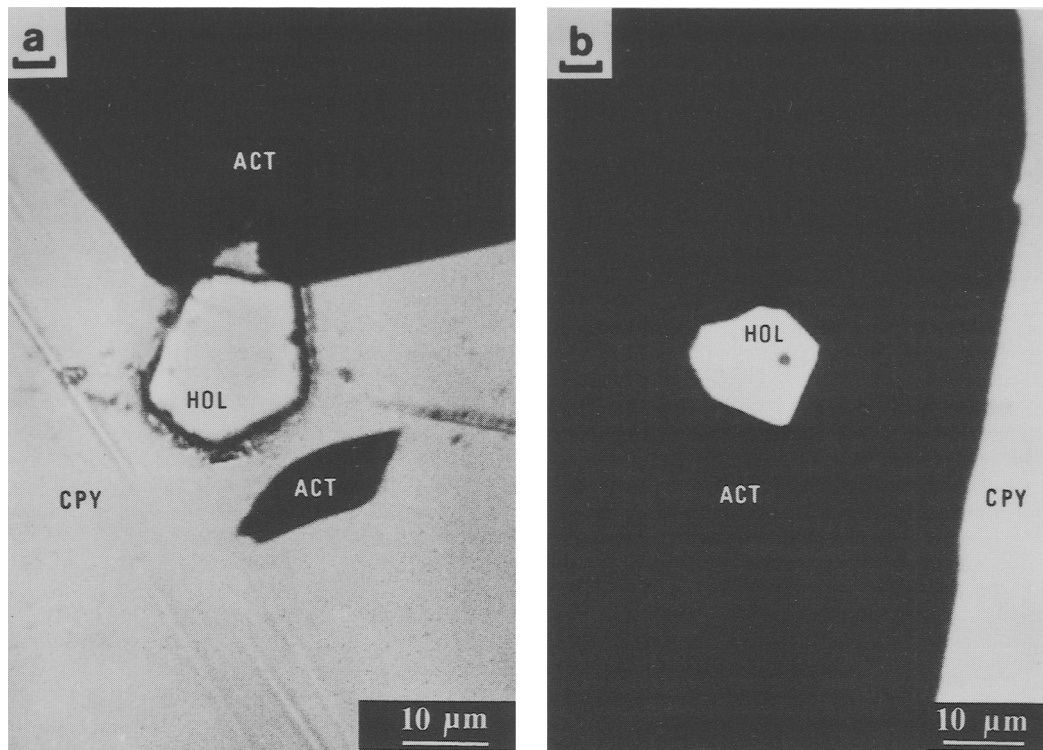
FIG. 1. Examples of typical crystals of the osmian hollingworthite from Lukkulaisvaara; (a) Euhedral hollingworthite (HOL) occurring at the boundary between actinolite (ACT) and chalcopyrite (CPY); (b) Euhedral hollingworthite (HOL) enclosed within actinolite (ACT). Reflected-light photomicrographs.

1996). The segregations occur as small (<0.5 m in thickness) irregular, podiform or stringer-like pegmatoids. There are two PGE-rich pegmatite aureoles associated with the two microgabbronorite bodies in Lukkulaisvaara, i.e. so-called *Nadezhda* and *Vostok* deposits. Both the Os-rich hollingworthite and Rh-rich cobaltite-gersdorffite are characteristic of the segregations of the last mentioned deposit only. The deposit is situated at the eastern part of the intrusion. Although the pegmatoidal rocks here are greatly altered and primary silicates are entirely replaced by Ca-amphibole and chlorite, their original pegmatoidal textures can locally be recognized. The rocks are interpreted to have been melanocratic gabbronorite before alteration. In contrast to the pegmatoidal plagioclase-bearing meta-gabbronorite from Nadezhda, where a highly unusual occurrence of staurolite and other highly aluminous metamorphic minerals has been recorded (Barkov *et al.*, in prep.), no similar assemblage in the Vostok pegmatoids was found.

The segregations of the Vostok deposit consist of up to 25–30 vol.% of base-metal sulphide mineralization principally composed of chalcopyrite and pentlandite. The PGM association includes merenskyite, members of the kotulskite-sobolevskite solid-solution series and michenerite as the most widespread PGM in the rock. Also present as relatively rare PGM are a new mineral $Pd_3Ni_2As_3$ (IMA No. 93-057; Barkov *et al.*, unpubl. data), sopcheite, stibiopalladinite or mertieite, hollingworthite, an As-bearing paolovite, and an unnamed mineral $Pd_2(Sn_{0.5}Sb_{0.5})$. Other noble-metal minerals are hessite, argentopentlandite, Ag-Au alloys, and an unnamed rhenium sulphide mineral, $(Cu,Fe)(Re,Mo)_4S_8$, that was described in a separate report (Barkov and Lednev, 1993).

The Os-bearing hollingworthite typically appears as individual subhedral to euhedral crystals (from < 5 μm in diameter to c. 30 × 20 μm) closely associated with chalcopyrite and hydrous silicates (actinolite and chlorite) (e.g. Fig. 1).

TABLE 1. Representative electron microprobe analyses of osmian hollingworthite and rhodian cobaltite–gersdorffite from the Lukkulaisvaara layered intrusion

No.	1	2	3	4	5	6	7*	8
Rh	24.53	21.67	26.98	8.96	8.22	18.3	25.78	24.89
Pt	15.12	17.63	13.91	nd	nd	20.3	–	12.47
Os	10.11	11.61	7.70	nd	nd	7.5	5.98	10.07
Ru	2.08	2.15	2.55	nd	nd	–	1.53	6.41
Ir	nd	1.23	nd	nd	nd	8.5	20.10	0.57
Pd	nd	nd	1.43	nd	nd	–	–	0.06
Co	0.59	nd	nd	14.32	13.57	–	–	–
Ni	nd	nd	nd	11.35	11.88	–	–	–
Fe	0.79	0.86	0.89	3.65	3.80	–	–	1.12
As	33.05	32.44	34.25	45.14	45.49	32.4	27.82	26.74
S	12.76	12.30	12.85	17.56	17.76	10.3	13.41	16.96
Total	99.03	99.89	100.56	100.98	100.72	97.3	97.21	99.29
Formulae (Σ atoms = 3)								
Rh	0.571	0.517	0.612	0.150	0.138	0.477	0.620	0.545
Pt	0.186	0.222	0.166	–	–	0.279	–	0.144
Os	0.127	0.150	0.094	–	–	0.106	0.078	0.119
Ru	0.049	0.052	0.059	–	–	–	0.037	0.143
Ir	–	0.016	–	–	–	0.118	0.259	0.007
Pd	–	–	0.031	–	–	–	–	0.001
Co	0.024	–	–	0.419	0.397	–	–	–
Ni	–	–	–	0.334	0.349	–	–	–
Fe	0.034	0.038	0.037	0.113	0.117	–	–	0.045
ΣM	0.991	0.995	0.999	1.016	1.001	0.980	0.994	1.004
As	1.056	1.063	1.066	1.039	1.046	1.159	0.919	0.804
S	0.953	0.942	0.935	0.945	0.954	0.861	1.035	1.192
Sb	–	–	–	–	–	–	0.053	–

Analyses 1–3: Osmian hollingworthite from Lukkulaisvaara; 4, 5: Rhodian cobaltite-gersdorffite from Lukkulaisvaara (this study); 6: Osmian hollingworthite from Bushveld (Stumpfl, 1972); 7: Shetland ophiolite complex (Tarkian and Prichard, 1987); 8: Two Duck Lake (Ohnenstetter et al., 1991). nd = not detected; * Total includes 2.59 wt.% Sb.

Interestingly, a small (c. 20 × 10 μm) subhedral grain of a Rh-rich sulpharsenide, (Co,Ni,Rh,Fe)AsS, was also found at the contact between chalcopyrite and a hydrosilicate in the same sample as Os-rich hollingworthite. The grain is optically isotropic. No X-ray data could be obtained owing to the very small size of the grain. The mineral is suggested to represent a member of the cobaltite–gersdorffite series rather than alloclasite or glaucodot. This is compatible with the fact that cobaltite–gersdorffite, but not other related polymorphic modifications, is known to contain significant concentrations of PGE (Cabri and Laflamme, 1976; Distler and Laputina, 1979; Cabri, 1992; 1994). The cobaltite structural type obviously favours incorporation of PGE into the Co-Ni sulpharsenide lattices, since a number of PGM, including the Rh-, Pt- and Ir-rich sulpharsenides, belong to the cobaltite group. However, the

PGE-rich cobaltite-gersdorffites are exceedingly rare (see Cabri, 1992).

Electron microprobe analyses of the osmian hollingworthite and rhodian cobaltite-gersdorffite were performed at the Institute of Electron Optics, University of Oulu, Finland, using a JEOL JSM-6400 scanning electron microscope equipped with a LINK eXL energy dispersive spectrometer. The analyses were carried out at 15 kV and 1.2 nA. The lines (and standards) used were Rh-L (synthetic RhSb), Pt-M (PtSn), Os-M, Ru-L, Ir-M, Pd-L, Co-K, Ni-K, Fe-K (pure elements), As-L (PtAs$_2$), and S-$K\alpha$ (pyrite). The results were processed by the ZAF-4 on-line program. They are in good agreement with the preliminary analyses carried out using a Cameca electron microprobe.

The hollingworthite compositions (Table 1) indicate significant substitution for Rh by Pt, Os

and Ru, and replacement of up to 0.5 formula units of Rh by these elements was observed. The maximum content of Os reaches as much as 11.6 wt.%. This seems to be the most Os-rich hollingworthite recorded to date. The Rh concentration of the Lukkulaisvaara cobaltite—gersdorffite (*ca.* 9 wt.%) is comparable with the highest rhodium values recorded in cobaltite from Pechenga, up to 10.5 wt.% (Distler and Laputina, 1979) and from Pipe, up to 7.2 wt.% (Cabri and Laflamme, 1981; cited in Cabri, 1992). No other PGE, except for Rh, were detected in the cobaltite from Lukkulaisvaara.

Ohnenstetter *et al.* (1991) stressed that the Ru and Os enrichments in their hollingworthite analyses were accompanied by an increase in S (e.g. Anal. No. 8, Table 1), and inferred existence of a wide range of solid solution between hollingworthite and laurite—erlichmanite. In contrast, our compositional data do not show any increase in S content coupled with enrichments in Ru and Os. It is of interest to note that other Os-rich hollingworthites (Anal. 6, 7; Table 1) also do not exhibit such a relationship between Os, Ru and S. Indeed, on the contrary, one of them is slightly sulphur-deficient due to partial substitution of S by As.

The substitutional chemistry of hollingworthite remains still not well understood. No synthetic or natural cubic OsAsS and RuAsS compounds, that are isostructural with hollingworthite, have been reported. However, monoclinic sulpharsenides OsAsS and RuAsS, osarsite and ruarsite, respectively, are known (Snetsinger, 1972; Yu and Chou, 1979). If cubic polymorphic modifications of osarsite and ruarsite do not exist, there is probably a restricted miscibility between hollingworthite and osarsite, and between hollingworthite and ruarsite. If so, an incorporation of Os and Ru into the hollingworthite structure should be constrained by crystal-chemical factors.

In summary, several types of substitution involving hollingworthite can be reasonably suggested:

(1) The most common hollingworthite—irarsite—platarsite substitution; (2) Substitution of an unnamed PdAsS for hollingworthite (e.g. Stumpfl, 1972 reported 8.9 wt.% Pd in hollingworthite from Driekop); (3) Substitution of laurite—erlichmanite for hollingworthite. It should be noted that this series proposed by Ohnenstetter *et al.* (1991) is confirmed by the existence of an As-rich erlichmanite (Begizov *et al.*, 1976). Ohnenstetter and coauthors obviously missed this composition, since they mentioned that there is little or no As—S substitution exhibited by the MeS_2 series. The composition Os 56.6, Ru 0.9, Ir 1.2, Rh 11.0, Pt 0.5, S 24.0, As 7.1, Σ 101.3 corresponds to: $(Os_{0.705}Rh_{0.253}Ru_{0.021}Ir_{0.015}$ $Pt_{0.006})_{\Sigma1.000}$ $(S_{1.774}As_{0.225})_{1.999}$ (on the basis of Σ atoms = 3). It is remarkable that the enrichment of this unusual erlichmanite in As is clearly accompanied by a strong enrichment in Rh; (4) Substitution between hollingworthite and osarsite and/or ruarsite; (5) Substitution of cobaltite—gersdorffite for hollingworthite. A composition of a highly unusual Ni-Co-rich hollingworthite from the Mt. Generalskaya layered intrusion, NW Russia (Barkov *et al.*, unpubl. data; equipment, analytical conditions and standards used are the same as those reported in this study), can be taken as a strong evidence for a continuous solid-solution series between hollingworthite and cobaltite—gersdorffite: Rh 14.36, Pd 4.75, Pt 1.29, Os 2.37, Co 7.41, Ni 7.74, Fe 3.69, As 42.74, S 15.87, Total 100.22, formula $(Rh_{0.263}Ni_{0.249}Co_{0.237}Fe_{0.125}Pd_{0.084}Os_{0.024}$ $Pt_{0.012})_{\Sigma0.994}As_{1.075}S_{0.932}$ (Σ atoms = 3). It should be particularly emphasized that the possibility of replacement of as much as *ca.* 0.7 formula units of Rh by other elements is evident from this unusual transitional member of the hollingworthite-cobaltite-gersdorffite series. Finally, the substitutions Nos. 3, 4 are probably the most restricted ones.

Microprobe analyses of actinolite and chlorite associated with hollingworthite are given in Table 2.

TABLE 2. Electron microprobe analyses of actinolite and clinochlore from Lukkulaisvaara

	Range[*]	Average[*] (n = 8)	Average[**] (n = 2)		Formulae O = 23[*]	O = 14[**]
SiO_2	54.80—56.60	55.82	27.48	Si	7.89	2.84
Al_2O_3	0.80—2.12	1.23	18.49	Al	0.20	2.25
FeO	5.83—7.05	6.55	14.25	Fe	0.77	1.23
MnO	0.15—0.26	0.21	0.17	Mn	0.02	0.01
MgO	19.12—20.96	19.98	23.60	Mg	4.21	3.63
CaO	11.87—12.77	12.47	nd	Ca	1.89	—
NiO	nd	nd	0.62	Ni	—	0.05

[*] Actinolite; [**] Clinochlore
Total Fe as FeO; n = number of analyses; nd = not detected

No compositional differences between actinolite occurring as a hydrosilicate matrix and as numerous inclusions in chalcopyrite have been found. Both actinolite and clinochlore represent the Mg-rich varieties.

The close textural association between the PGM and hydrous silicates is characteristic for the Vostok deposit in Lukkulaisvaara. However, this association is also typical for many other related deposits, including, for instance, the Penikat layered intrusion, N Finland, from the same intrusion belt (Alapieti and Lahtinen, 1986). Actinolite and clinochlore in Vostok are mostly products of a hydrothermal replacement of the primary igneous silicates. The base-metal sulphide mineralization of the segregations in both pegmatitic aureoles is thought to be of magmatic origin. Magmatic volatiles are considered to be responsible for formation of the pegmatoids as a result of a strong increase in fluid pressure in the remaining magma during the host sill crystallization (e.g. Barkov and Lednev, 1993; Barkov et al., 1995a). The textural and other criteria indicate a relatively low-temperature formation of primary PGM (e.g. $T < 600°C$ for a high-Pt braggite that is one of the most high-T primary PGM in the segregations; Barkov et al., 1995a), at a post-magmatic-hydrothermal stage, and their later metamorphic remobilization and redistribution on a local scale (Barkov, 1995a; Barkov et al., in prep.). The coexisting osmian hollingworthite, rhodian cobaltite and hydrosilicates (actinolite $\pm$ chlorite) are interpreted to have been deposited under moderately low-T hydrothermal conditions. This is in agreement with a strong evidence for a low-T crystallization and hydrothermal origin of a number of various PGE deposits (e.g. Stumpfl and Tarkian, 1976; McCallum et al., 1976; Rowell and Edgar, 1986; Watkinson and Ohnenstetter, 1992).

Acknowledgements

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Siegenite-bearing assemblages found at the Great Orme Mine, Llandudno, North Wales

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DESPITE the well known presence of siegenite and other thiospinels in the Mississippi Valley-type ores of the Southeast Missouri Lead District, U.S.A. (Hagni, 1986) and the ubiquitous presence of iron–nickel–cobalt-bearing sulphides from all of the Mississippi Valley-type deposits of Britain (Brown *et al.,* 1987; Ixer and Vaughan, 1993) no thiospinels have been recorded from British Mississippi Valley-type orefields other than a 'linnaeite' collected from the spoil heaps associated with the Great Orme Mines, Llandudno (Bevins, 1994). Siegenite is, however, reported from South Wales (Bevins and Horák, 1985) and Central Wales (Mason, 1995) but in both cases is associated with non-carbonate hosted mineralization.

The North Wales 'linnaeite' specimen (National Museum of Wales specimen NMW 83.41G. M1489) has been investigated as part of a programme to characterize the ores of the Great Orme Mine especially those that may have been exploited in the Bronze Age.

The Great Orme Mine (SH772831) lies above and to the west of Llandudno, Gwynedd. Here epigenetic copper mineralization cuts Asbian carbonates and belongs to the copper-dolomite class of deposits despite falling within the western extremity of the Northeast Wales Orefield, one of Britain's Mississippi Valley-type orefields. Indeed, this copper mineralization is the first example of the copper-dolomite association to be recorded from