

## TARKIANITE, (Cu,Fe)(Re,Mo)<sub>4</sub>S<sub>8</sub>, A NEW MINERAL SPECIES FROM THE HITURA MINE, NIVALA, FINLAND

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### ABSTRACT

Tarkianite, a new mineral species of ideal composition (Cu,Fe)(Re,Mo)<sub>4</sub>S<sub>8</sub>, was recently discovered in sulfide concentrate from the Hitura Ni–Cu–PGE mine, Nivala, western central Finland. It is associated with pyrrhotite, pentlandite, valleriite, chalcopyrite, cubanite, mackinawite, chromite, and the PGE minerals sperrylite, michenerite, irarsite, froodite and hollingworthite. It is black, opaque with a metallic luster, a black streak, and is brittle with an irregular fracture. VHN<sub>15</sub> is in the range 537–584, which corresponds to a Mohs hardness of 5½ to 6. Under reflected plane-polarized light, the mineral is light brown-gray and isotropic. The CIE color values (illuminant C) are: x 0.314 (air), 0.315 (oil); y 0.321 (air), 0.323 (oil) Y: 38.9 (air), 21.7 (oil); λd: 575 (air), 573 (oil); P<sub>e</sub>‰: 2.1 (air), 3.2 (oil). The measured values of reflectance in air and oil for a single grain, respectively, are 38.02, 20.91 (470 nm), 37.87, 21.76 (546 nm), 39.18, 21.84 (589 nm), 39.30, 22.12 (650 nm) and values for 400–700 nm are tabulated. Tarkianite is cubic, *F*<sub>4</sub>3*m* (by analogy with the synthetic equivalent), with unit-cell parameter refined from powder data: *a* 9.563(1) Å, *V* 874.5(1) Å<sup>3</sup>, *Z* = 4. The strongest eight lines of the X-ray powder-diffraction pattern [*d* in Å (*I*)(*hkl*)] are: 5.531(100)(111), 2.885(90)(311), 2.389(90)(400), 2.194(70)(331), 1.952(60)(422), 1.841(90)(511), 1.690(80)(440) and 1.246(50)(731). *D* (calc.) is 7.30 g/cm<sup>3</sup> (for the empirical formula and unit-cell parameter). Averaged electron-microprobe data yielded Re 53.61, Mo 12.32, Cu 5.48, Os 0.84, Fe 0.59, Ni 0.09, Co 0.08, S 26.77, total 99.78 wt.%, corresponding to (Cu<sub>0.83</sub>Fe<sub>0.10</sub>Ni<sub>0.02</sub>Co<sub>0.01</sub>)Σ<sub>0.96</sub>(Re<sub>2.79</sub>Mo<sub>1.22</sub>Os<sub>0.04</sub>)Σ<sub>4.03</sub>S<sub>8.01</sub>, based on a total of thirteen atoms. The mineral name honors Professor Mahmud Tarkian, of the University of Hamburg, Germany, for his contributions to ore mineralogy.

**Keywords:** tarkianite, new mineral species, rhenium molybdenum copper sulfide, X-ray data, electron-microprobe data, reflectance data, Hitura mine, Nivala, Finland.

### SOMMAIRE

Nous décrivons la tarkianite, nouvelle espèce minérale de composition idéale (Cu,Fe)(Re,Mo)<sub>4</sub>S<sub>8</sub>, découverte récemment dans un concentré de sulfures provenant de la mine à Ni–Cu–EGP de Hitura, près de Nivala, dans le centre-ouest de la Finlande. Lui sont associés pyrrhotite, pentlandite, valleriite, chalcopyrite, cubanite, mackinawite, chromite, et les minéraux des éléments du groupe du platine (EGP) sperrylite, michenerite, irarsite, froodite et hollingworthite. Il s'agit d'un minéral noir, opaque avec un éclat métallique, et une rayure noire. Elle est cassante avec une fracture irrégulière. La dureté mesurée (VHN<sub>15</sub>) est dans l'intervalle 537–584, ce qui correspond à 5½ ou 6 sur l'échelle de Mohs. En lumière réfléchie polarisée en plan, la tarkianite est

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brun-gris pâle et isotrope. Les paramètres CIE décrivant la couleur pour l'illuminant C sont: x 0.314 (air), 0.315 (huile); y 0.321 (air), 0.323 (huile) Y: 38.9 (air), 21.7 (huile);  $\lambda_d$ : 575 (air), 573 (huile);  $P_g\%$ : 2.1 (air), 3.2 (huile). Les valeurs de sa réflectance dans l'air et dans l'huile (%), mesurées sur un seul grain, sont 38.02, 20.91 (470 nm), 37.87, 21.76 (546 nm), 39.18, 21.84 (589 nm), 39.30, 22.12 (650 nm), respectivement, et les valeurs standards pour 400–700 nm sont présentées. La tarkianite est cubique,  $F\bar{4}3m$  (par analogie avec l'équivalent synthétique), et son paramètre réticulaire a été affiné à partir du spectre de diffraction obtenu sur poudre:  $a$  9.563(1) Å,  $V$  874.5(1) Å<sup>3</sup>,  $Z = 4$ . Les huit raies les plus intenses du spectre de diffraction [ $d$  en Å ( $hkl$ )] sont: 5.531(100)(111), 2.885(90)(311), 2.389(90)(400), 2.194(70)(331), 1.952(60)(422), 1.841(90)(511), 1.690(80)(440) et 1.246(50)(731). La densité, calculée à partir de la formule empirique et du paramètre réticulaire, est 7.30 g/cm<sup>3</sup>. Les analyses à la microsonde électronique ont donné, en moyenne, Re 53.61, Mo 12.32, Cu 5.48, Os 0.84, Fe 0.59, Ni 0.09, Co 0.08, S 26.77, pour un total de 99.78% (poids), ce qui correspond à (Cu<sub>0.83</sub>Fe<sub>0.10</sub>Ni<sub>0.02</sub>Co<sub>0.01</sub>) $\Sigma$ 0.96(Re<sub>2.79</sub>Mo<sub>1.22</sub>Os<sub>0.04</sub>) $\Sigma$ 4.03S<sub>8.01</sub>, sur une base de treize atomes. Le nom est choisi pour honorer le professeur Mahmud Tarkian, de l'Université de Hambourg, en Allemagne, et ainsi souligner des contributions aux études de la minéralogie des minerais.

(Traduit par la Rédaction)

**Mots-clés:** tarkianite, nouvelle espèce minérale, sulfure de rhénium, molybdène et cuivre, diffraction X, données de microsonde électronique, données de réflectance, mine Hitura, Nivala, Finlande.

## INTRODUCTION

The new mineral species described here, tarkianite, with a general formula (Cu,Fe,Co,Ni)(Re,Mo,Os)<sub>4</sub>S<sub>8</sub>, was recently discovered in samples of sulfide concentrate obtained from the Hitura Ni–Cu–PGE mine, Nivala, west-central Finland. The grains were found in a heavy-mineral concentrate containing pentlandite, chromite, pyrrhotite, and PGM (platinum-group minerals), consisting of sperrylite (81.1%), michenerite (6.6%), irarsite (1.9%), froodite (6.9%), hollingworthite (1.9%) and an undefined Rh–Ni–Co sulfarsenide. The average contents of the PGE (platinum-group elements, in ppb) in the sulfide concentrate are: Ir 51, Os 20, Pd 417, Pt 1125, Rh 123 and Ru 46. The average Re content is 20 ppb. The mineral is named *tarkianite* in honor of Professor Dr. Mahmud Tarkian (b. 1941), University of Hamburg, Germany, in recognition of his important contributions to ore mineralogy. Tarkian *et al.* (1991) previously described this phase from the Stillwater Complex, Sweetwater County, Montana, and resolved the crystal structure of the synthetic equivalent. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2003–004). A polished section containing tarkianite grains is preserved in the collection of the Finnish Museum of Natural History, Geological Museum, University of Helsinki, Helsinki, Finland, under sample number C4001.

## THE TYPE LOCALITY AND OTHER OCCURRENCES

### The type locality

The Hitura mine is located about 13 kilometers south of the town center of Nivala in western central Finland (lat. 63°51'N, long. 25°02'W). The Ni–Cu–PGE ore is hosted by serpentinitized ultramafic intrusions and averages Ni 0.67, Cu 0.25, Co 0.03, S 3.0 %, Pt 0.1 and Pd 0.1 ppm. The minimum U–Pb age of the Hitura com-

plex is 1877 ± 2 Ma, determined on zircon from a cross-cutting dyke of granitic pegmatite. The ore (Häkli *et al.* 1976) consists of 1) fine-grained sulfides disseminated in the serpentinite core, 2) medium-grained sulfides disseminated in the serpentinite and amphibole-dominant rock, and 3) high-grade interstitial disseminated sulfides and massive accumulations in an amphibole-dominant rock at the contact zones. In the core of the intrusive body, the main sulfides are pentlandite, mackinawite and valleriite. In the marginal zones, the main ore lodes consist of dense disseminations and net-textured primary intergrowths of pyrrhotite, pentlandite and mackinawite with secondary films of magnetite along cleavage planes of the sulfides. Chalcopyrite and graphite are common, and less common ore minerals include cobaltite, maucherite, nickeline, parkerite, native gold, Au–Ag alloy, native bismuth, pilsenite, tellurobismuthite, galena, altaite, clausthalite, ilmenite, chromite, cassiterite, monazite and uraninite. Tarkianite occurs with the primary sulfides and PGM. The concentrates were investigated for a detailed PGM study, as a follow-up to a previous study by Häkli *et al.* (1976). This earlier study showed that sperrylite is the only Pt-bearing mineral, and that the Pd-bearing minerals include michenerite, froodite, Pd-bearing irarsite and an undefined Pd-bearing Bi–Ni telluride resembling melonite. Iridarsenite, irarsite and hollingworthite were reported as Ir- and Rh-bearing minerals.

### Other occurrences

The first discovery of a phase corresponding to the formula Cu(Mo<sub>2</sub>Re<sub>2</sub>)S<sub>8</sub> was made at two localities in Sweden (Ekström & Hålenius 1982), where it is intergrown with an undefined phase of composition (Ni,Pd)<sub>5</sub>(Te,Bi)<sub>8</sub> in pyrrhotite and at the contact between siegenite and chalcopyrite. At the Coldwell complex, Ontario, a sulfide hosted by pyrrhotite and corresponding to the (approximate) formula (Re,Mo,Fe,Cu)<sub>2</sub>S<sub>3</sub> was described by Mitchell *et al.* (1989). At Stillwater, Mon-

tana, a phase with an empirical formula  $(\text{Cu}_{0.84}\text{Fe}_{0.20}\text{Ni}_{0.04})_{\Sigma 1.08}(\text{Re}_{2.72}\text{Mo}_{1.16})_{\Sigma 3.88}\text{S}_{8.00}$  is enclosed in pentlandite and pyrrhotite in a high-temperature magmatic assemblage (Volborth & Housley 1984, Volborth *et al.* 1986, Tarkian *et al.* 1991). At Lukkulaivaara, Karelia, Russia (Barkov & Lednev 1993), a phase with an empirical formula  $(\text{Cu}_{0.88}\text{Fe}_{0.21})_{\Sigma 1.09}(\text{Re}_{2.94}\text{Mo}_{1.04})_{\Sigma 3.98}\text{S}_{8.00}$  occurs in association with chalcopyrite – bornite – millerite, millerite – bornite – pentlandite and various PGM. At Ekojoki, southwestern Finland, a sulfide with a formula  $\text{Cu}_{1.02}(\text{Re}_{3.11}\text{Os}_{0.18}\text{Mo}_{1.59})_{\Sigma 4.88}\text{S}_9$  is enclosed in intercumulus pentlandite with numerous worm-like grains of mackinawite (Peltonen *et al.* 1995). At Monchegorsk, Kola Peninsula, Russia, a sulfide with similar chemical composition was found within hexagonal pyrrhotite by one of us (VVK) after the discovery of tarkianite at Hitura.

#### MATERIAL AND METHODS OF INVESTIGATION

Tarkianite was identified in a polished specimen prepared from a PGM concentrate that was obtained using a gravimetric hydroseparation method [developed by one of us (VVK) (<http://www.natires.com/>)]. The grains were located during routine back-scattered electron imaging with a Cameca SX-50 electron microprobe equipped with a PGT energy-dispersion spectrometer (EDS) as detector. The micro-indentation hardness was measured with a Leitz Durimet tester. The X-ray powder-

diffraction data were obtained with a Debye-Scherrer camera 114.6 mm in radius, employing  $\text{CuK}\alpha$  radiation. The reflectance values were measured using a computerized Zeiss MPM microphotometer and Zeiss standard WTiC (Nr 326). The measurements were made every 20 nm, both in air and using standard immersion oil. For the light source of the Zeiss microscope, we used a 100 W halogen lamp (diaphragm 0.15, measuring objective 16 $\times$ ). The area of measurement was 5  $\mu\text{m}$  in diameter.

#### GENERAL APPEARANCE AND PHYSICAL PROPERTIES

Tarkianite is black and opaque with a metallic luster. The color of the streak is black, and grains are brittle with an irregular fracture. Some grains show an idiomorphic cubic morphology (Fig. 1); the grain size is <75  $\mu\text{m}$ . Tarkianite grains are associated with pentlandite and sperrylite in the polished mounts made of the concentrates.

#### Optical properties

Under plane-polarized reflected light in air, tarkianite is light grey and isotropic. Under oil immersion, the mineral has a light brown-gray color. Reflectance measurements were made every 20 nm in both air and oil from 400 to 700 nm (Table 1, Fig. 2). The values for the standard wavelengths 470, 546, 589 and 650 nm were calculated.

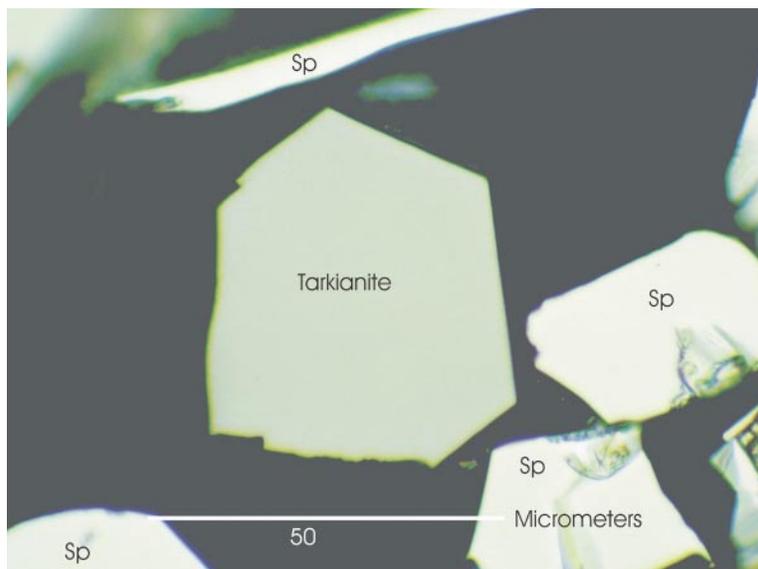


FIG. 1. A euhedral grain of tarkianite associated with sperrylite (Sp) in heavy-mineral concentrate. Plane-polarized light, oil immersion, sample 2\_72\_6. Scale bar: 50  $\mu\text{m}$ .

### Physical properties

The grains available, all less than 75  $\mu\text{m}$  in size, were mounted in epoxy. The grains are very fragile; we found it difficult to measure hardness without breaking them. Therefore, micro-indentations were made with a 15 g load, which still led to slight fracturing of the measured grains. Only two successful micro-indentation hardness measurements were made, and these gave values of VHN 537 and 584, with a mean of 561  $\text{kg}/\text{mm}^2$ . This corresponds to a Mohs hardness of 5½ to 6. The calculated density, 7.30  $\text{g}/\text{cm}^3$ , is based on the averaged empirical formula derived from the electron-microprobe analyses and the unit-cell parameter refined from the X-ray powder-diffraction data.

### X-ray crystallography

The powder-diffraction data are presented in Table 2. The mineral is cubic, space group  $F\bar{4}3m$ , and the refined unit-cell parameter,  $a$  9.563(1) Å,  $V$  874.5(1) Å<sup>3</sup>,  $Z = 4$ , is refined from 17 powder-diffraction reflections (Table 2), representing  $d$  values between 5.531 and 1.246 Å for which unambiguous indexing was possible based on an analogy with the synthetic equivalent. Comparable powder-diffraction data for the synthetic equivalents are presented in the Powder Diffraction File: 84–2349 (calculated), 80–2304 (calculated), 47–1360 (experimental), 44–149 (experimental) and 34–1384 (experimental). Tarkian *et al.* (1991) and Kohlmann & Schulz (1993) reported crystal-structure data for the synthetic equivalent. The structure is a cubic derivative of spinel of the type <sup>IV</sup>A<sub>2</sub><sup>VI</sup>B<sub>4</sub>S<sub>8</sub>, with reduced symme-

try (from  $Fd\bar{3}m$  to  $F\bar{4}3m$ ) owing to vacancies at the tetrahedrally coordinated A sites and shifts of the B and S atoms. The A-site atoms are predominantly Cu and Fe, and the B-site atoms are predominantly Re and Mo.

### Chemical composition

Quantitative electron-microprobe analyses (EPMA) of tarkianite were performed utilizing a Cameca SX–50 electron microprobe, with an operating voltage of

TABLE 1. REFLECTANCE AND COLOR VALUES FOR TARKIANITE

Wavelength	R% in air	R% in oil	Wavelength	R% in air	R% in oil
400 nm	36.55	19.65	560 nm	39.03	21.81
420	36.82	20.12	580	39.13	21.88
440	37.13	20.19	589 (COM)	39.18	21.84
460	37.80	20.80	600	39.24	21.80
470 (COM)	38.02	20.91	620	39.20	21.95
480	38.24	21.02	640	39.21	21.98
500	38.41	21.39	650 (COM)	39.30	22.12
520	38.61	21.65	660	39.30	22.26
540	38.72	21.72	680	39.42	22.39
546 (COM)	38.87	21.76	700	39.49	22.36
	CIE color values			Illuminant C	
	in air	in oil		in air	in oil
X	0.314	0.315	y	0.321	0.323
Y %	38.9	21.7	$\lambda_d$ nm	575	573
Pe %	2.1	3.2			

The index of refraction of the immersion oil is 1.5147 at 590 nm. Standard WTiC, specimen 2\_72\_6 (Fig. 1).

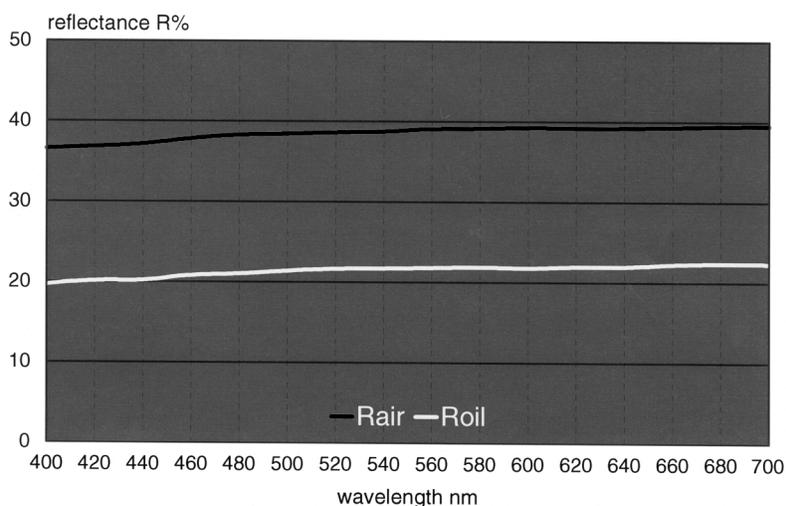


FIG. 2. Reflectance spectra of tarkianite (Table 1), sample 2\_72\_6.

25 kV, a beam current of 10 nA, and a beam-spot diameter of 1  $\mu\text{m}$ . For standards, we used pentlandite (Fe, Ni, S), chalcopyrite (Cu), cobaltite (Co) and pure metals (Re, Mo, Os). A LiF analyzing crystal was used for  $\text{ReL}\alpha$ ,  $\text{FeK}\alpha$ ,  $\text{CuK}\alpha$ ,  $\text{CoK}\alpha$ , and  $\text{NiK}\alpha$ ; a PET crystal was used for  $\text{MoL}\beta$  and  $\text{SK}\alpha$ , and a TAP crystal for  $\text{OsM}\beta$ . Peak counting time was 20 seconds for all elements. Electron-microprobe data for tarkianite are presented in Table 3.

The average of 34 analytical points yielded Re 53.61, Mo 12.32, Cu 5.48, Os 0.84, Fe 0.59, Ni 0.09, Co 0.08, S 26.77, total 99.78 wt.%, corresponding to  $(\text{Cu}_{0.83}\text{Fe}_{0.10}\text{Ni}_{0.02}\text{Co}_{0.01})_{\Sigma 0.96}(\text{Re}_{2.79}\text{Mo}_{1.22}\text{Os}_{0.04})_{\Sigma 4.03}\text{S}_{8.01}$  (Table 3), based on a total of thirteen atoms.

## DISCUSSION

Tarkianite is characterized as a new mineral species with a cubic spinel-derivative structure with general formula  $A_1\text{B}_4\text{S}_8$ , space group  $F\bar{4}3m$ , and an ideal chemical composition  $(\text{Cu,Fe,Ni,Co})(\text{Re,Mo,Os})_4\text{S}_8$ .

The tetrahedrally coordinated *A* sites are only half occupied by Cu, Fe, Ni and Co (Tarkian *et al.* 1991), and the *B*-site atoms are statistically occupied by Mo, Re and Os, and form tetrahedral clusters with metal-metal bonding distances of 2.81 Å (Perrin *et al.* 1975, 1976). The apparent valences of the elements are 1+ for Cu, 2+ for Fe, Ni, Co, 3+ for Mo and 4+ for Re and Os (Umarji *et al.* 1979), which leads to a general formula of  $[\text{Cu}_{1-x}(\text{Fe,Ni,Co})_x]_1[(\text{Re,Os})_{3-x}\text{Mo}_{1+x}]_1\text{S}_8$ .

The chemical compositions of the Re–Mo–Cu sulfides found at various localities spatially cluster in the  $(\text{Cu} + \text{Fe} + \text{Ni} + \text{Co}) - (\text{Re} + \text{Os} + \text{Mo}) - \text{S}$  triangular diagram and in the  $\text{S} - (\text{Re} + \text{Mo} + \text{Os})$  binary diagram (Figs. 3a, b), and most probably represent the same mineral phase. However, without complete optical, physical and X-ray-diffraction data, the above hypothesis cannot be tested, except in the case of the complete description of  $(\text{Cu}_{0.84}\text{Fe}_{0.20}\text{Ni}_{0.04})_{\Sigma 1.08}(\text{Re}_{2.72}\text{Mo}_{1.16})_{\Sigma 3.88}\text{S}_{8.00}$  from Stillwater and its synthesized equivalent (Tarkian *et al.* 1991).

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TABLE 2. X-RAY POWDER DATA FOR TARKIANITE

$I_{\text{est}}$	$d_{\text{meas}}$ Å	$d_{\text{calc}}$ Å	<i>hkl</i>	$I_{\text{est}}$	$d_{\text{meas}}$ Å	$d_{\text{calc}}$ Å	<i>hkl</i>
*	100	5.531	5.521 111	*	10	1.616	1.616 531
*	20	4.783	4.782 200	*	15	1.593	1.594 600
*	10	3.385	3.381 220		5	1.460	1.458 533
*	90	2.885	2.883 311		5	1.439	1.442 622
*	30	2.765	2.761 222	*	20	1.380	1.380 444
*	90	2.389	2.391 400	*	40	1.339	1.339 551
*	70	2.194	2.194 331	*	10	1.326	1.326 640
*	60	1.952	1.952 422	*	30	1.278	1.278 642
*	90	1.841	1.840 511	*	50	1.246	1.245 731
*	80	1.690	1.691 440				

Debye-Scherrer camera, Cu radiation, Ni-filter ( $\lambda$   $\text{CuK}\alpha = 1.54178$  Å). Intensities estimated visually. Not corrected for shrinkage and no internal standard. Four reflections [ $(h/d)$ Å]: (5)(2.981), (5)(2.648), (10)(2.070) and (3)(1.721)] ascribable to admixed pyrrhotite have been removed from the pattern. Indexed on 17 lines (marked with a \*).

TABLE 3. THE CHEMICAL COMPOSITION OF TARKIANITE

	average <i>n</i> = 34	range	std. dev.
Fe wt.%	0.59	0.38-1.32	0.25
Ni	0.09	0.00-0.44	0.12
Co	0.08	0.02-0.12	0.02
Cu	5.48	5.23-5.91	0.17
Mo	12.32	10.83-13.38	0.63
Re	53.61	52.81-54.93	0.48
Os	0.84	0.60-1.14	0.12
S	26.77	25.95-27.33	0.34
Total	99.78		

The analyses were done with a Cameca SX-50 electron microprobe, accelerating voltage 25 kV, beam current 10nA, beam diameter 1  $\mu\text{m}$ .

TABLE 4. COMPARISON OF THE AVERAGE CHEMICAL COMPOSITION OF TARKIANITE FROM HITURA WITH OTHER POTENTIAL OCCURRENCES

	HIT	EKO	LUK	STI	COL	SWE
Fe wt.%	0.59	3.19	1.18	1.20	4.15	1.73
Ni	0.09	1.32	n.d.	0.23	n.d.	0.55
Co	0.08	n.d.	n.d.	n.d.	n.d.	1.06
Cu	5.48	5.57	5.73	5.81	4.75	7.40
Mo	12.32	13.03	10.17	11.97	14.15	10.00
Re	53.61	49.06	55.81	54.47	48.95	53.49
Os	0.84	2.67	n.d.	n.d.	n.d.	n.d.
S	26.77	26.77	26.17	27.53	26.85	26.87
Total	99.78	101.88	99.06	101.21	98.85	101.11

n.d.: not determined; n: number of electron-microprobe analyses made. Sources: HIT: Hitura mine (*n* = 34), this study; EKO: Ekajoki (*n* = 4), Peltonen *et al.* (1995); LUK: Lukkulaivaara (*n* = 3), Barkov & Lednev (1993); STI: Stillwater Complex (*n* = 1), Tarkian *et al.* (1991); COL: Coldwell complex (*n* = 1), Mitchell *et al.* (1989); SWE: Sweden (*n* = 3), Ekström & Hälenius (1982).

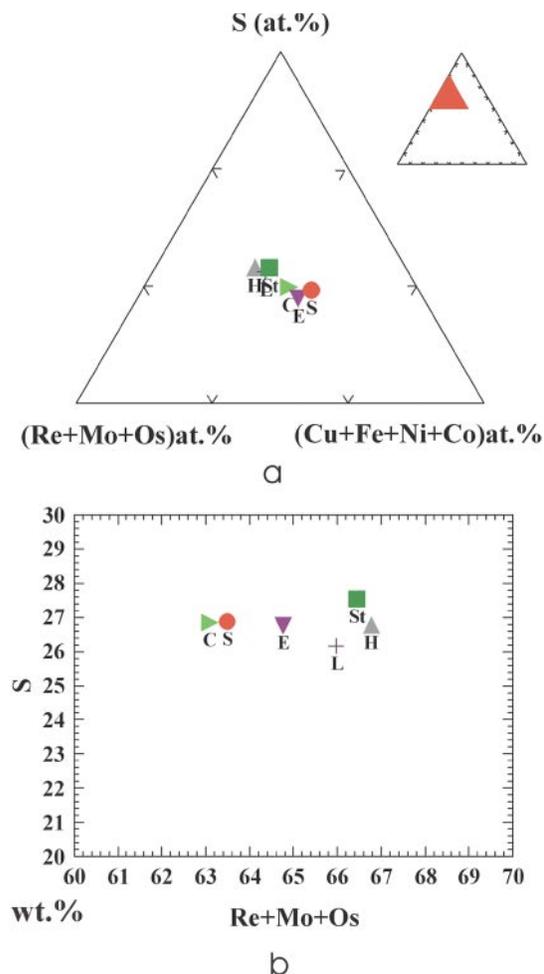


FIG. 3. Average chemical composition (Table 4) of Re-Mo-Cu sulfides plotted in terms of a) the triangular plot (Cu + Fe + Ni + Co) – (Re + Os + Mo) – S, and b) a binary plot of S versus (Re + Mo + Os). Symbols used: H: Hitura, tarkianite; L: Lukkulaisvaara, St: Stillwater, C: Coldwell, E: Ekojoki, and S: Sweden.

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