

Awaruite, iridian awaruite, and a new Ru-Os-Ir-Ni-Fe alloy from the Sakhakot-Qila complex, Malakand Agency, Pakistan

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ABSTRACT. The authors report the first occurrence of awaruite in Pakistan, in the Sakhakot-Qila ultramafites. Electron-microprobe analysis reveals a considerable variation in the compositions of awaruites from different parts of the complex. The presence of copper in awaruite, in amounts up to 5 atomic percent, is also reported for the first time. In one chromitite body, an iridian awaruite with up to 27 wt% of iridium occurs in association with 'normal' awaruite and a new Ru-Os-Ir-Ni-Fe alloy. The awaruites are discussed in relation to those from other localities.

AWARUITE is known from about twelve localities world wide, but has not been reported from Pakistan or adjacent regions. This study describes awaruite from the chromitites of the Sakhakot-Qila igneous complex, Malakand Agency, Pakistan (Ahmed, 1978). Published data on compositional variation in awaruite are scanty, and this work was undertaken to determine the variation, if any, in compositions of awaruites from a single ultramafic complex. Some of the awaruite-like alloys discovered during the exercise have been hitherto unknown in natural occurrences.

Geology and mineralogy. The Sakhakot-Qila complex is an E-W elongated body of alpine-type ultramafic rocks with two small outcrops of metagabbro towards the northern contact with the metamorphic country rocks. The ultramafites are dominantly harzburgite with some wehrlite, and minor bodies of dunite are common. Pyroxenite dykes are ubiquitous: dolerite dykes occur at three localities.

The majority of the specimens examined are chromitites, but dunite, harzburgite, and wehrlite are also represented. No structural or stratigraphical control on the occurrence of awaruite in the

body could be discerned: the mineral does, however, appear to be more abundant in chromitite than in other rock types. In most specimens awaruite is the only nickel-rich mineral, occurring as isolated grains in serpentine, chlorite, or ferrit-chromit, but in others it is associated or aggregated with pentlandite and heazlewoodite. Native copper was not found in any of the material studied. Most awaruite grains are anhedral and irregular, although some appear subhedral. They range in size from fine 10-20 μm diameter particles to rare, large crystals 4 mm across: most, however, are between 0.12 and 0.23 mm in diameter. Fig. 1 (A and B) shows two typical awaruite associations.

Resembling awaruite superficially in their mode of occurrence and metallic appearance are two new alloys found in one specimen from a low-grade chrome-ore body (GR 4078-7834) in the complex. One, an iridian awaruite, has a reflectivity similar to normal awaruite, and X-ray diffraction of a mixed sample of the two awaruites indicated that the iridian variety is also cubic. The other alloy, however, is greyish white in reflected light, compared with the yellowish-white awaruites, and this difference in reflectance may indicate a crystal symmetry other than cubic. However, the small size of grains and scarcity of material did not allow an X-ray diffraction pattern to be obtained. The reflectivity of the latter alloy in air, measured at 546 nm against a pure nickel standard, is 60.36%, and its VHN (Vickers hardness number) varies from 420 to 500 under a 20 g load and 30 s contact time. A reflected-light photomicrograph of these alloys in association is shown in fig. 1 (C).

Analytical procedure. The 'normal' awaruites were examined in polished mounts and polished thin sections, using an energy-dispersive electron microprobe: a Link Systems 860 with Kevex ED attached to a Cambridge Instruments' Geoscan. An accelerating voltage of 15 kV, a specimen current on the cobalt metal internal standard of 0.5×10^{-8} A, 100 s live-time counting time, and pure metal standards, were used.

The specimen containing the new alloys was analysed first on the energy-dispersive equipment under the above conditions, then on a wavelength-dispersive Cambridge Instruments' Microscan 9 microprobe. An accelerating voltage of 20 kV, a specimen current on the Faraday cage of 2.50×10^{-8} A, a counting time of 10 s, and pure metal standards, were used. The polished mount was repolished and the grains reanalysed on the Microscan 9 under the above conditions. All specimens were carbon-coated to a thickness of about 150 Å before analysis.

Chemistry. Averaged microprobe analyses of 'normal' awaruites are given in Table I. Ni varies over-all from 73.5 to 84.0% and iron from 12.3 to 24.9%; the Ni:Fe atomic ratios range from 2.80 to 6.39. The range of variation in individual specimens, however, is usually more limited. Cu, not previously known to substitute into the awaruite structure, is present in varying amounts in most of the grains analysed (up to 5.45 wt%) and is the third major component after Ni and Fe. Co in these awaruites is low, usually below the detection limit; its maximum is 1.2 wt%. Fig. 2. is a plot of previously reported analyses of awaruites com-

pared with over fifty analyses from this study, and shows how the field of composition for this mineral has been extended towards the nickel component.

Table II gives the compositions of the new alloys and the 'normal' awaruite associated with them. In the iridian awaruites the Ni:Fe ratio varies from 3.77 to 4.95 and is not related to the degree of substitution by Ir, or to the Ni:Fe ratio of the accompanying 'normal' awaruite (5.33 to 5.72). Similarly, in the Ru-Os-Ir-bearing alloy, although the Ni:Fe ratio varies only from 2.61 to 2.89, there appears to be no relationship between it and the amount of substitution of Ru, Os, or Ir. Scanning photomicrographs of the phases showing the distribution of these elements are given in fig. 3.

Discussion. The Ni contents of previously reported natural awaruites vary from 63 to 89 wt%, and the Co contents from zero to 4 wt%. The awaruite analyses given here not only exhibit a wider range of compositions than those previously reported for a single ultramafic complex, but are also generally more Ni-rich (fig. 2): only one published analysis (Sinton, 1969) has a higher Ni content than the most Ni-rich of the Sakhakot-Qila analyses, which contain up to 84 wt% of the element. All are awaruites as defined by Hey (1955): '4[Ni,Fe] with Ni 60% and more.' In addition, they contain up to 5.45% Cu hitherto not found in significant amounts. A bulk analysis of awaruite from the Eastern Townships, Quebec (Nickel, 1958)

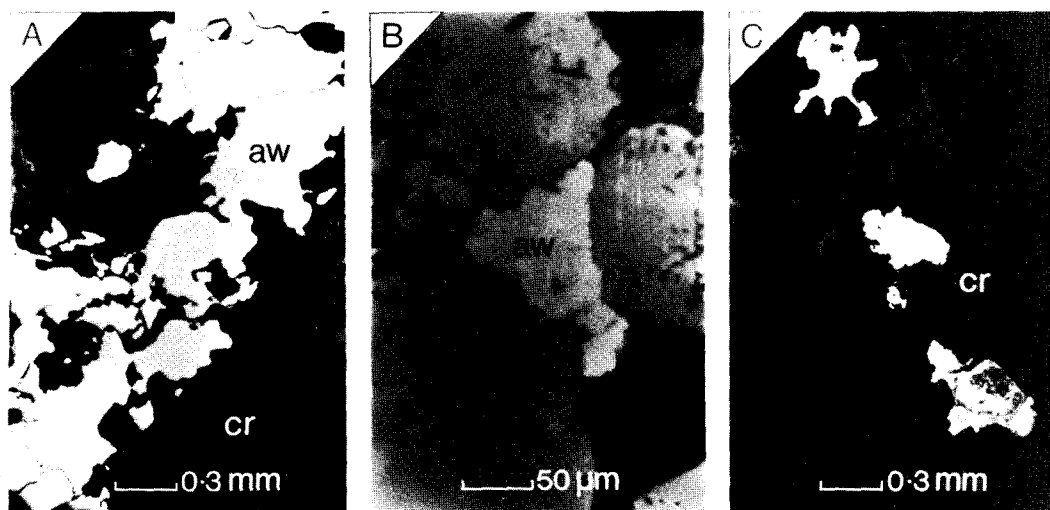


FIG. 1. Reflected-light photomicrographs showing: (A) Coarse blebs of awaruite (aw) of irregular shape in a chlorite- and serpentine-filled vein crossing chromitite, grid ref. 4200-7700. (B) A triangular anhedral awaruite (aw) interstitial to three chromite grains (cr) from chromitite from south of Heru Shah village, grid ref. 4315-8113. (C) Grains of iridian awaruite and Ru-Os-Ir-Ni-Fe alloy distributed in serpentine and chlorite around chromite grains (cr), grid ref. 4078-7834 (Table II).

TABLE I. Chemical composition of awaruites from the Sakhakot-Qila district

Spec. no.	1		2		3		4		5	
	range		range		range		range		range	
Ni	78.5	78.1-78.9	74.5	74.0-74.9	77.2	76.5-77.7	81.4	81.0-81.9	78.9	78.5-79.4
Fe	20.4	20.1-20.7	23.3	23.0-23.6	23.6	23.4-23.8	15.3	14.6-16.1	15.1	14.8-15.6
Cu	1.46	1.27-1.66	0.21	0.04-0.39	0.05	0.00-0.31	2.66	2.45-2.94	5.10	4.45-5.45
Co	0.16	0.15-0.17	0.76	0.56-1.20	0.08	0.00-0.50	0.33	0.24-0.45	b.d.	
	100.5		98.8		100.9		99.7		99.1	
Atomic per cent:										
Ni	77.4	77.4-77.4*	74.3	73.2-75.1	75.5	74.5-76.0	81.2	80.3-82.0	79.4	79.2-79.7
Fe	21.1	21.0-21.3	24.8	24.4-25.8	24.4	24.0-24.8	16.0	15.4-16.7	16.0	15.7-16.6
Cu	1.33	1.15-1.51	0.20	0.04-0.36	0.07	0.00-0.45	2.46	2.27-2.70	4.74	4.25-5.02
Co	0.16	0.15-0.17	0.75	0.56-1.19	0.05	0.00-0.30	0.33	0.24-0.44	b.d.	
Ni/Fe	3.66	3.63-3.69	3.00	2.84-3.09	3.10	3.03-3.16	5.09	4.80-5.31	4.97	4.80-5.06

Spec. no.	6		7		8		9		10	
	range		range		range		range		range	
Ni	78.3	77.8-79.1	73.8	73.5-74.1	76.0	75.6-76.2	80.8	77.1-84.0	80.6	77.5-82.6
Fe	20.5	19.4-21.1	24.9	24.9-24.9	23.3	22.3-23.8	17.3	15.0-20.9	14.4	12.3-18.6
Cu	0.68	0.51-0.79	0.46	0.34-0.59	0.94	0.55-1.14	1.35	0.83-1.84	4.00	2.45-4.97
Co	0.62	0.50-0.70	0.77	0.75-0.78	0.43	0.21-0.61	0.24	0.05-0.50	0.10	0.00-0.19
	100.1		99.9		100.7		99.7		99.1	
Atomic per cent:										
Ni	77.4	76.9-78.4	73.0	72.7-73.2	74.7	74.3-75.3	80.4	77.0-83.0	80.9	78.0-83.0
Fe	21.4	20.2-21.9	25.9	25.8-26.0	24.1	23.3-24.5	18.1	15.6-21.9	15.2	13.0-19.6
Cu	0.62	0.46-0.72	0.43	0.31-0.54	0.86	0.50-1.03	1.24	0.77-1.69	3.71	2.27-4.55
Co	0.61	0.49-0.69	0.75	0.73-0.77	0.43	0.21-0.60	0.24	0.05-0.49	0.10	0.00-0.19
Ni/Fe	3.63	3.51-3.88	2.82	2.80-2.84	3.11	3.04-3.23	4.49	3.51-5.32	5.44	3.97-6.39

Grid references to the 1:63360 topographic sheets (No. 38 N/11 and 38 N/15) issued by the Survey of Pakistan for specimens 1-10: number of analyses of each specimen given in brackets.

Specimen 1, 4122-7484 (2); specimen 2, 4060-7620 (4); specimen 3, 4200-7700 (6); specimen 4, 4188-7785 (5); specimen 5, 4460-8035 (6); specimen 6, 4167-8070 (4); specimen 7, 4120-8070 (2); specimen 8, 4460-8150 (5); specimen 9, 4441-8153 (11); specimen 10, 4492-8774 (5).

b.d. = below detection limit. *77.36-77.39.

TABLE II. Electron-microprobe analyses of Ru-Os-Ir-Ni-Fe alloy (ROI1-ROI5), and associated awaruite (A1-A3) and iridian awaruite (IR1-IR7)

	ROI1	ROI2	ROI3	ROI4	ROI5	A1	A2	A3	IR1	IR2	IR3	IR4	IR5	IR6	IR7
Ni	39.2	31.7	26.6	34.2	35.7	83.5	83.8	83.2	69.6	70.9	56.2	71.4	71.3	70.3	64.9
Fe	12.9	11.6	9.43	11.9	12.1	13.9	14.9	13.9	14.8	14.6	13.6	17.2	13.7	13.5	16.4
Cu	nd	0.10	0.27	0.29	0.27	1.42	1.43	1.21	1.18	1.19	0.95	0.99	1.41	1.25	0.88
Co	nd	0.27	0.21	0.21	0.25	0.21	0.14	0.24	0.25	0.23	0.20	0.28	0.18	0.16	0.35
Ru	25.5	30.9	32.3	27.5	26.3	0.00	0.00	0.00	0.00	0.00	0.34	0.00	0.05	0.01	0.00
Os	12.5	15.1	17.9	16.2	14.3	0.67	0.31	0.67	0.57	0.28	0.47	0.66	0.44	0.80	0.64
Ir	10.4	10.1	13.2	11.5	10.9	0.24	0.33	0.00	13.0	11.3	27.0	7.29	11.5	12.5	14.8
Pt	0.78	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.65	0.29	0.30	0.63	0.65	0.36	0.52
Total	101.3	99.8	99.9	101.8	99.8	100.0	100.9	99.2	100.0	98.8	99.1	98.5	99.2	98.9	98.5
Atomic percents:															
Ni	52.558	45.596	41.057	47.976	49.914	83.999	83.107	84.091	76.765	78.056	70.557	76.498	78.775	78.561	74.230
Fe	18.152	17.446	15.281	17.657	17.839	14.685	15.583	14.778	17.192	16.941	17.971	19.415	15.917	15.878	19.686
Cu	---	---	---	---	---	1.317	1.310	1.131	1.202	1.209	1.105	0.980	1.440	1.291	0.930
Ru	19.878	25.806	28.924	22.405	21.422	---	---	---	---	---	---	---	---	---	---
Os	5.164	6.698	8.523	7.040	6.167	---	---	---	---	---	---	---	---	---	---
Ir	4.259	4.454	6.216	4.921	4.657	---	---	---	4.373	3.794	10.367	2.387	3.869	4.269	5.154
Ni/Fe	2.90	2.61	2.69	2.72	2.80	5.72	5.33	5.69	4.47	4.61	3.93	3.94	4.95	4.95	3.77

Wavelength-dispersive electron-microprobe analyses of specimen containing new alloys (GR 4078-7834).

gave a maximum of 0.3% Cu in addition to the 4% of Co. Native Cu, although present in other awaruite-bearing rocks, has not been found in the Sakhakot-Qila complex, and it appears that the Cu has preferentially entered the Ni-Fe alloy rather than forming as a separate phase. There is a slight correlation between Cu substitution and increasing Ni content (fig. 2), and most of the awaruites described here have higher Ni contents than those previously reported.

Awaruite always occurs in serpentinized rocks, and its formation has been linked to the serpentinization process (Kanehira *et al.*, 1975). It is normally found in serpentine or secondary magnetite (Kanehira *et al.*, 1975; Chamberlain *et al.*, 1965; Hultin, 1968). The present study adds two other minerals that enclose awaruite, namely, chlorite and ferritchromite. The distribution of awaruite, therefore, is not confined, as in the Coolac serpentine belt, Australia (Golding and Bayliss, 1968), to the non-chloritic chrome ores.

Platinum group elements (PGE) are known to be more abundant in sulphide-rich ultramafic

complexes than in sulphur-poor ones, and in Alaskan-type rather than Alpine-type bodies (Crocket, 1979): the presence of PGE in the Sakhakot-Qila complex is therefore unexpected. Chromite is the most common PGE concentrator mineral, holding them either in solid solution or as inclusions of platinum group minerals (PGM) (Crocket, 1979). Olivine can also contain PGM inclusions (Page, 1971), and is capable of concentrating Ir, and less commonly, Os and Ru, from early crystallizing fractions of basic magmas (Crocket, 1979). It is possible that Ru, Os, and Ir in the Malakand occurrence became concentrated as secondary native metal alloys during the same process which led to the formation of awaruite from the Ni contained in the olivines. The mutual association and similar mode of occurrence of the iridian awaruite, the Ru-Os-Ir-Ni-Fe alloy, and the 'normal' awaruite described here support this mechanism.

Conclusions. The compositional data on awaruites from the ultramafites of the Sakhakot-Qila district show that these awaruites are more Ni-rich than

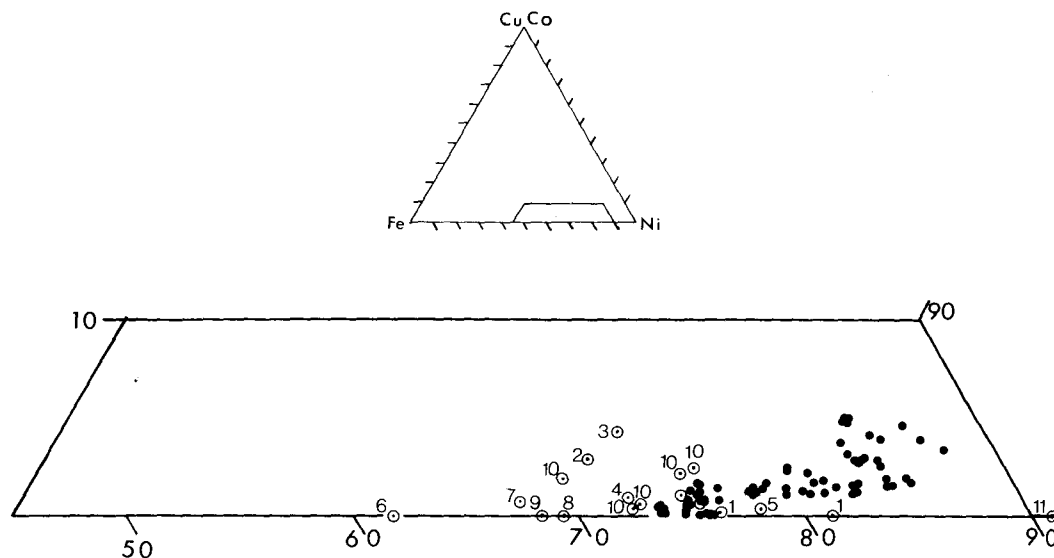


FIG. 2. Plots of chemical compositions of awaruite from different localities in the Sakhakot-Qila complex, in the Ni-Fe-Cu system (dots) and the Ni-Fe-Co system (encircled dots). Numbered analyses are from other occurrences as follows:

- | | |
|---|--|
| (1) Lord Brassey mine, Tasmania (Williams, 1960) | (8) Southern Boso Peninsula, Japan (Kanehira <i>et al.</i> , 1975) |
| (2) Heazlewood, Tasmania (Williams, 1960) | (9) 'Josephinite' locality, Oregon (Botto and Morrison, 1976) |
| (3) Eastern Townships, Quebec (Nickel, 1959) | (10) Coolac, N.S.W., Australia (Golding and Bayliss, 1968) |
| (4, 5) Feragen, Norway (Hultin, 1968) | (11) Red Mountain ultramafites, New Zealand (Sinton, 1976) |
| (6) Muskox intrusion, Canada (Chamberlain <i>et al.</i> , 1965) | |
| (7) George River, New Zealand (Skey, 1885) | |

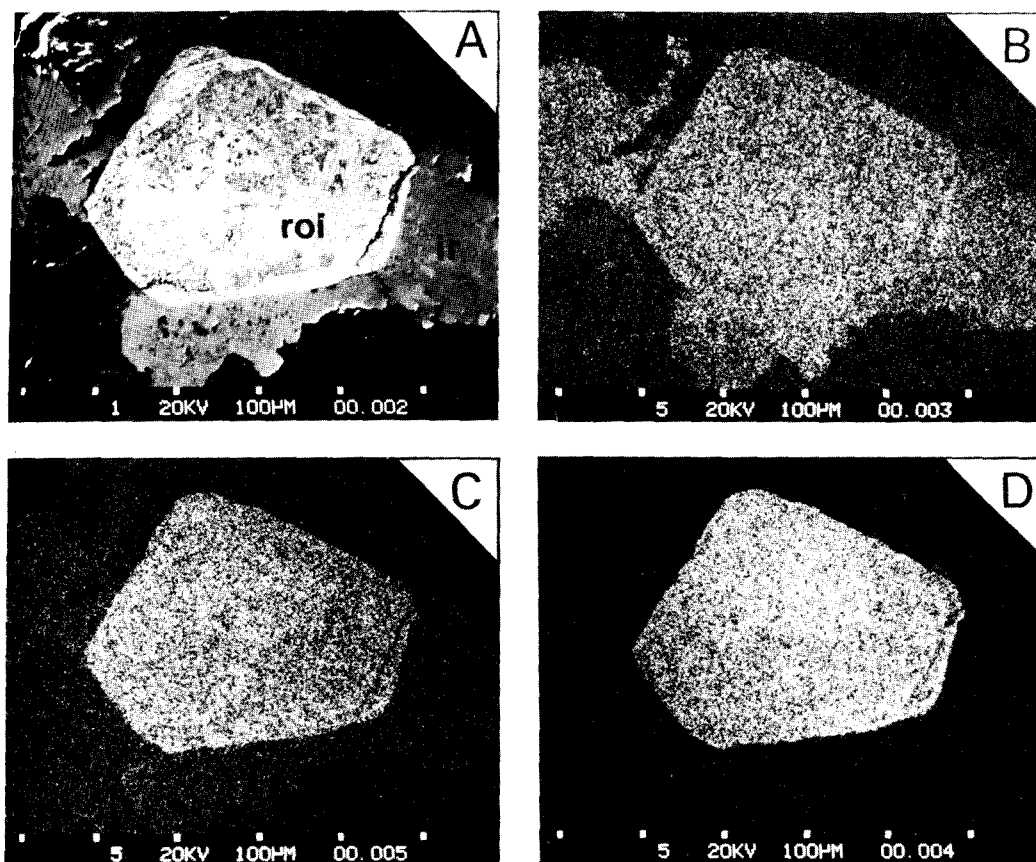


FIG. 3. Electron-probe scanning images of iridian awaruite (ir) Ru-Os-Ir-Ni-Fe alloy (roi) and enclosing chlorite from a chromitite: backscattered electron image, (A), and distribution of Ir (B), Os (C), and Ru (D). The grey material intergrown with the Ru-Os-Ir-Ni-Fe alloy is of variable composition and appears to be a mixed oxide.

most other known occurrences and exhibit a substantial compositional variation between different specimens from within the same igneous complex. Co contents rarely exceed 1%, but Cu is present in many samples and is the third major constituent after Ni and Fe: it appears to be higher in the more Ni-rich awaruites.

The awaruite occurs enclosed in serpentine, chlorite, or ferritchromit in chromitites and other ultramafites which are serpentinized to varying degrees. Other nickeliferous opaque minerals associated with awaruite and having the same mode of occurrence are heazlewoodite, pentlandite, and, in one chromitite body in the complex, an iridian awaruite and a new Ru-Os-Ir-Ni-Fe alloy. The Ru, Os, and Ir which they contain may have been derived from olivines during serpentinization in a

manner analogous to the formation of awaruite itself.

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REFERENCES

- Ahmed, Z. (1978). *Mineral. Mag.* **42**, 155-7.
 Botto, R. I., and Morrison, G. H. (1976). *Am. J. Sci.* **276**, 241-74.
 Chamberlain, J. A., McLeod, C. R., Traill, R. J., and Lachance, G. R. (1965). *Can. J. Earth Sci.* **2**, 188-215.

- Crocket, J. H. (1979). *Can. Mineral.* **17**, 391-402.
- Golding, H. G., and Bayliss, P. (1968). *Am. Mineral.* **53**, 162-83.
- Hey, M. H. (1955). *An index of mineral species and varieties*. British Museum (Nat. Hist.), London.
- Hultin, I. (1968). *Norsk Geol. Tidsskr.* **48**, 179-85.
- Kanehira, K., Banno, S., and Yui, S. (1975). *J. Japan Ass. Min. Petr. Eco. Geol.* **70**, 388-94.
- Nickel, E. H. (1958). *Geol. Soc. Am. Bull.* **69**, 1623.
- (1959). *Can. Mineral.* **6**, 307-19.
- Page, N. J. (1971). *U.S. Geol. Surv. Prof. Pap.* 694.
- Sinton, J. M. (1976). *Mineral. Mag.* **40**, 792-4.
- Skey, W. (1885). *Trans. N.Z. Inst.* **18**, 401-2.
- Williams, K. L. (1960). *Am. Mineral.* **45**, 450-3.

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