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HARRISONITE, A NEW CALCIUM IRON SILICATE–PHOSPHATE FROM ARCEDECKNE ISLAND, DISTRICT OF FRANKLIN, ARCTIC CANADA[1]

ANDREW C. ROBERTS AND JOHN A.R. STIRLING

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

JOEL D. GRICE

Mineral Sciences Section, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

THOMAS FRISCH AND RICHARD K. HERD

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

JOHN L. JAMBOR

CANMET, 555 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

Harrisonite, ideally $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, is a minor but relatively widespread constituent of an iron silicate – quartz – apatite layered body found in granulite-facies gneisses on Arcedeckne Island, off northern Boothia Peninsula, District of Franklin, Arctic Canada (Lat. 71°54′N, Long. 95°23′W). Harrisonite occurs as both individual discrete equidimensional grains and as a rim around fluorapatite; associated minerals are quartz, almandine, ferrosilite, fayalite, biotite, ilmenite, zircon and monazite-(Ce). Individual grains are anhedral, are varicolored from yellow-brown to orange-brown, average between 0.2 and 0.5 mm in size, and have a distinctive conchoidal fracture. The streak is pale yellow; tenacity brittle; luster glassy to vitreous; translucent to transparent; cleavage very poor; *D*(meas.) 4.02(3), *D*(calc.) 4.01 g/cm^3 for the empirical formula; nonfluorescent in ultraviolet light; hardness less than 5. Harrisonite is uniaxial negative ω 1.770(5), ε 1.759(3), weakly pleochroic in pale yellow tints. The symmetry is hexagonal (rhombohedral), space group $R\bar{3}m$, with *a* 6.240(2), *c* 26.784(5) Å, *V* 903.2(4) Å^3, *c/a* 4.2923, and *Z* = 3. The strongest nine lines of the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 5.00(60)(012), 4.46(50)(006), 3.119(100)(107), 2.976(50)(009), 2.689(80)(021), 2.558(100)(116), 2.505(80)(024), 1.903(60)(125,02$\underline{10}$) and 1.560(80)(12$\underline{11}$,220). Electron-microprobe analyses gave CaO 7.65, FeO 52.27, MgO 3.89, MnO 0.11, SiO_2 15.99, P_2O_5 19.18, total 99.09 wt.%, which yield the empirical formula $Ca_{1.01}(Fe^{2+}{}_{5.36}Mg_{0.71}Mn_{0.01})_{\Sigma 6.08}(Si_{0.98}O_4)_2(P_{0.99}O_4)_2$ on the basis of O = 16. The valence state for iron and the number of oxygen atoms were confirmed by crystal-structure analysis. The mineral name honors the late Dr. James M. Harrison, former Director of the Geological Survey of Canada, for his many outstanding contributions to Canadian geoscience.

Keywords: harrisonite, new mineral species, calcium iron silicate-phosphate, X-ray data, chemical composition, Arcedeckne Island, Boothia Peninsula, District of Franklin, Arctic Canada.

SOMMAIRE

La harrisonite, de composition idéale $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, est un accessoire relativement répandu dans une masse de roche litée riche en silicates de fer, quartz et apatite, découvert dans des gneiss équilibrés dans le facies granulite, sur l'île d'Arcedeckne, au nord de la péninsule de Boothia, district de Franklin, dans l'Arctique canadien (lat. 71°54′N, long. 95°23′W). Cette nouvelle espèce minérale forme des grains équidimensionnels distincts ou bien un liseré autour de la fluorapatite. Lui sont associés quartz, almandine, ferrosilite, fayalite, biotite, ilménite, zircon et monazite-(Ce). Les grains individuels sont xénomorphes, varient d'un jaune brunâtre à orange brunâtre, sont entre 0.2 et 0.5 mm de large, et possèdent une fracture conchoïdale distinctive. Sa rayure est jaune pâle, sa tenacité, cassante, et son éclat, vitreux; elle est translucide à transparente. Le clivage est de piètre qualité. La densité est 4.02(3) (mesurée), et 4.01 (calculée à partir de la formule empirique). Elle est non

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fluorescente dans la lumière ultraviolette. Sa dureté est inférieure à 5. Elle est uniaxe négative, ω 1.770(5), ε 1.759(3), et faiblement pléochroïque dans des teintes jaune pâle. Sa symétrie est hexagonale (rhomboédrique), groupe spatial $R\bar{3}m$, avec a 6.240(2), c 26.784(5) Å, V 903.2(4) Å^3, c/a 4.2923, et Z = 3. Les neuf raies les plus intenses en diffraction X (méthode des poudres) [d en Å(I)(hkl)] sont: 5.00(60)(012), 4.46(50)(006), 3.119(100)(107), 2.976(50)(009), 2.689(80)(021), 2.558(100)(116), 2.505(80)(024), 1.903(60)(125, 02$\underline{10}$) et 1.560(80)(12$\underline{11}$,220). Les analyses à la microsonde électronique ont donné CaO 7.65, FeO 52.27, MgO 3.89, MnO 0.11, SiO_2 15.99, P_2O_5 19.18, total 99.09% en poids, ce qui se traduit par la formule empirique $Ca_{1.01}(Fe^{2+}_{5.36}Mg_{0.71}Mn_{0.01})_{\Sigma 6.08}(Si_{0.98}O_4)_2(P_{0.99}O_4)_2$ sur une base de seize atomes d'oxygène. La valence du fer et le nombre d'atomes d'oxygène ont été confirmés par affinement de la structure cristalline. Le nom honore James M. Harrison, décédé, anciennement directeur de la Commision géologique du Canada, pour ses nombreuses contributions remarquables aux connaissances géoscientifiques au Canada.

(Traduit par la Rédaction)

Mots-clés: harrisonite, nouvelle espèce minérale, silicate–phosphate de calcium et de fer, données de diffraction X, composition chimique, île d'Arcedeckne, péninsule de Boothia, district de Franklin, Arctique canadien.

INTRODUCTION

Harrisonite, ideally $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, is a newly recognized mineral species from the District of Franklin, Arctic Canada. It was noted in 1990 by one of the authors (JARS) in a program of quantitative electron-microprobe analyses of polished thin sections prepared from rocks collected in 1986 on Arcedeckne Island, off northern Boothia Peninsula. These rocks were collected during regional reconnaissance studies of the Precambrian Shield of the Boothia Uplift (Frisch *et al.* 1987, Frisch & Sandeman 1991). The mineral, initially misidentified as either fayalite or ferrosilite during preliminary petrographic study, consistently shows peaks for P as well as Si on energy-dispersion spectra. The occurrence of a silicate–phosphate in a granulite-facies mineral assemblage is highly unusual and warranted further study. Subsequent analysis by X-ray powder diffraction of Si- and P-rich grains extracted from a polished thin section failed to produce a match with any inorganic compound listed in the ICDD Powder Diffraction File. A full mineralogical investigation was initiated, and the resultant data are reported herein.

The new mineral is named in honor of Dr. James Merritt Harrison (1915–1990), former Director of the Geological Survey of Canada and internationally recognized geoscientist, for his many outstanding contributions to Canadian geoscience. Dr. Harrison "guided the GSC through the important transition from an era of travel by canoe and packhorse, into the modern era in which the use of aeroplanes and helicopters, aerial photography, geophysical surveys and radioactive dating of rocks, have made possible major scientific advances and the rapid exploration of Canada's remote frontier area, including the Arctic Islands and the Polar Continental Shelf" (Price 1990). The new mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Holotype material, consisting of seventeen rock fragments of various sizes, eight vials of crushed rock, four polished thin sections, and five thin sections are housed in the Systematic Reference Series of the National Mineral Collection of Canada (NMCC) at the Geological Survey of Canada, Ottawa, Ontario under catalogue number 66402. Additional cotype material, consisting of the crystals of harrisonite used for a study of its optical properties and the crystal-structure analysis, as well as four polished thin sections of the harrisonite-bearing rock, are housed in the Display Series of the National Mineral Collection of Canada at the Canadian Museum of Nature, Ottawa, Ontario under catalogue number 59685.

OCCURRENCE AND ASSOCIATED MINERALS

Harrisonite is found on Arcedeckne Island, 1.2 km long by 0.7 km wide, which lies in Peel Sound, off northern Boothia Peninsula, in the District of Franklin, Arctic Canada, at latitude 71°54′N and longitude 95°23′W (Fig. 1). The island and the neighboring part of Boothia Peninsula are underlain by Archean to early Proterozoic, high-grade metamorphic and igneous rocks of the Boothia Uplift, a north-trending salient of the Churchill Structural Province of the Canadian Shield (Frisch *et al.* 1987).

Harrisonite is a minor but relatively widespread constituent of a layered quartz – Fe silicate – apatite body, approximately 700 m long by 300 m wide, which forms the western promontory of Arcedeckne Island and is concordantly bordered on the east by garnet – cordierite – sillimanite gneiss and subordinate garnet – orthopyroxene tonalite gneiss. This body consists of alternating 0.2- to 0.7-m-thick layers of apatite-rich and garnet-rich Fe silicate – quartz rock. The grain size is medium to coarse and uniform; smooth, curved grain-boundaries between all minerals suggest equilibrium crystallization at a temperature and pressure compatible with granulite-facies conditions. Lithology, mineralogy, layering and structural concordance with aluminous metasedimentary rocks suggest that the harrisonite-bearing quartz – Fe silicate – apatite body represents a highly metamorphosed, bedded, shaly and phosphatic iron formation.

Harrisonite has been petrographically identified in two distinct modes of occurrence: (1) a thin rim

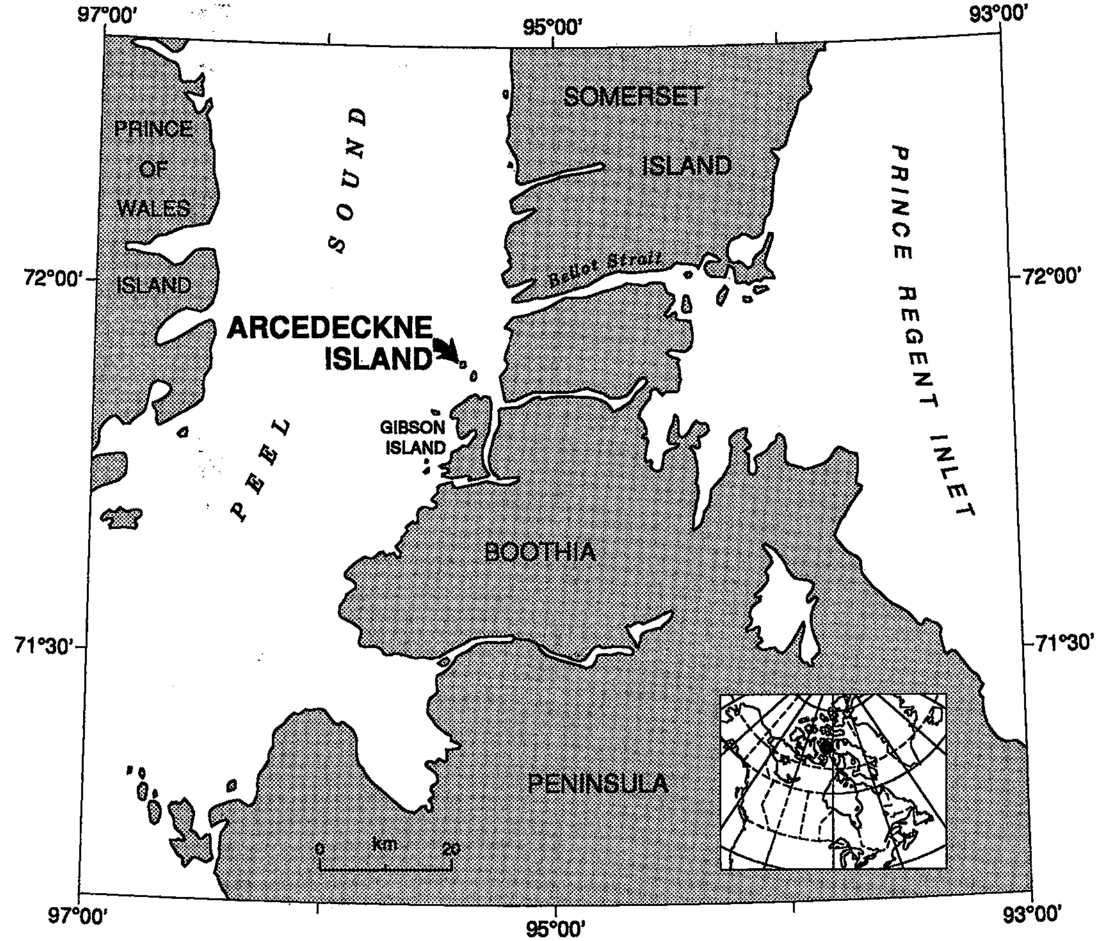

FIG. 1. Geographical map of northern Boothia Peninsula, District of Franklin, Arctic Canada, showing the location of Arcedeckne Island.

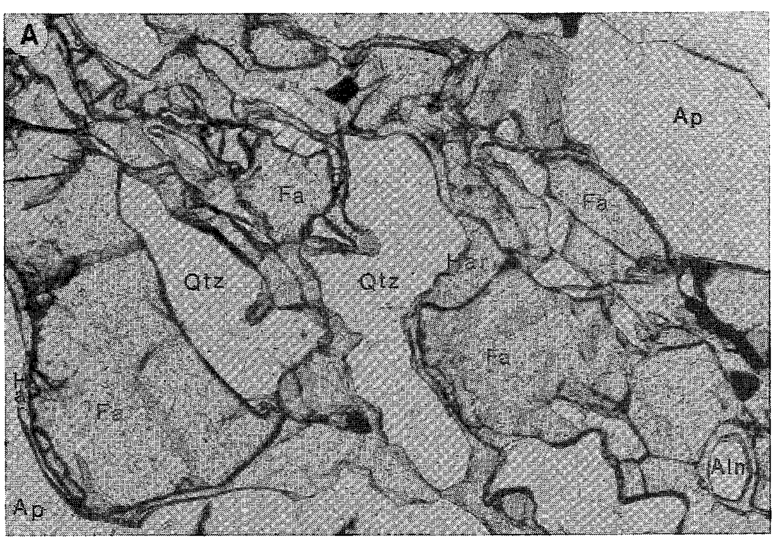

FIG. 2A. Photomicrograph showing the occurrence of harrisonite (Har) as a thin rim around fluorapatite (Ap), associated with quartz (Qtz), fayalite (Fa) and almandine (Alm). Field of view is 1 mm.

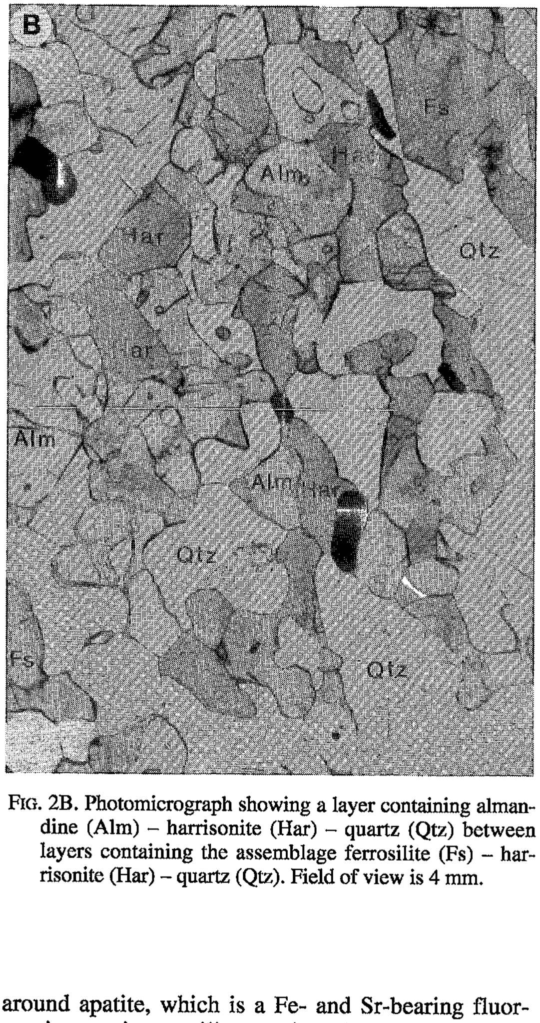

FIG. 2B. Photomicrograph showing a layer containing almandine (Alm) – harrisonite (Har) – quartz (Qtz) between layers containing the assemblage ferrosilite (Fs) – harrisonite (Har) – quartz (Qtz). Field of view is 4 mm.

around apatite, which is a Fe- and Sr-bearing fluorapatite, against a silicate mineral, such as fayalite ($Fa_{93}Fo_7$), quartz or almandine ($Alm_{89-91}And_{2-4}Prp_5$) (Fig. 2A); (2) discrete granular grains associated with quartz, almandine and ferrosilite (Fs_{75-78}) (Fig. 2B). The other constituents of the rock, all very minor, include ilmenite, Fe-rich biotite, zircon and monazite-(Ce). Fayalite and ferrosilite have not been found to coexist, but almandine is abundant throughout the body.

Physical Properties

Harrisonite occurs both as discrete anhedral equidimensional grains and as a thin rim around fluorapatite. It has also been observed as an inclusion in ferrosilite and, in turn, as the host for small inclusions of quartz. Anhedral grains up to 2 mm in diameter have been megascopically observed in a magnetic fraction made from a portion of the type specimen. Most grains, however, average between 0.2 and 0.5 mm in size. No

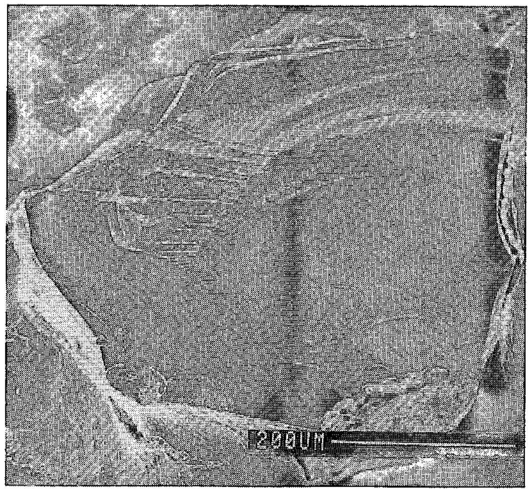

FIG. 3. SEM photomicrograph of an anhedral grain of harrisonite showing the distinctive conchoidal fracture. Scale bar: 200 μm.

crystal forms were observed. The color varies from yellow-brown to orange-brown, inclining to a darker brown in masses. Thin edges of grains are a distinct yellow-brown. Two diagnostic properties distinguish it from the associated minerals: a glassy to vitreous luster combined with a distinctive conchoidal fracture. Harrisonite could be visually misidentified as obsidian except for the color differences. A SEM photomicrograph of an anhedral grain of harrisonite showing the conchoidal fracture is presented in Figure 3. The streak is pale yellow, and the opacity varies from translucent in masses to transparent on thin edges. The mineral is brittle, is nonfluorescent under both long- and short-wave ultraviolet light, and has a very poor cleavage. The hardness is less than 5 since the grains can be scratched with a needle. The measured specific gravity, determined in Clerici solution, was found to be 4.02(3). Twinning was neither observed megascopically nor microscopically, nor found during the course of the X-ray single-crystal investigation.

Optical Properties

The two crystals previously used for the single-crystal study were subsequently used to determine the optical properties. Spindle-stage mounts observed in Na gel-filtered light (λ 589.9 nm) show that harrisonite is uniaxial negative, ω 1.770(5), ε 1.759(3), and very slightly pleochroic in pale yellow tints. The estimated standard deviations of the indices of refraction are somewhat higher than expected owing to the shape and orientation of the grains used for optical study. In polished thin section, the mineral is pale yellow and very similar in appearance to both the associated fayalite and ferrosilite. The harrisonite commonly displays an optic axis figure with a small $2V$ (~5°); this is most likely due to strain in the mineral, which causes a slight divergence in the uniaxial isogyres.

CHEMISTRY

Grains of harrisonite in a polished thin section were chemically analyzed with a Cameca SX-50 electron microprobe utilizing an operating voltage of 15 kV and both 10 and 30 nA beam currents. The following standards were employed: wollastonite (Ca), magnetite (Fe), synthetic MgO (Mg), rhodonite (Mn), quartz (Si) and apatite (P). An energy-dispersion spectrum indicated the absence of elements with atomic number greater than 9 other than those reported here; Ti, Al, Cr, Na, K, Cl and F were specifically sought, but not found. The average of four analyses gave CaO 7.65(5), FeO 52.27(66), MgO 3.89(12), MnO 0.11(7), SiO_2 15.99(20), P_2O_5 19.18(30), total 99.09 wt.%. With O=16, the empirical formula is $Ca_{1.01}(Fe^{2+}_{5.36}Mg_{0.71}Mn_{0.01})_{\Sigma 6.08}(Si_{0.98}O_4)_2(P_{0.99}O_4)_2$. The simplified formula, $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$ and a Fe:Mg ratio of 7.57:1, requires CaO 7.71, FeO 52.37, MgO 3.88, SiO_2 16.52, P_2O_5 19.52, total 100.00 wt.%. The type material is magnesian harrisonite. The valence state for iron and the number of oxygen atoms were determined by crystal-structure analysis (Grice & Roberts 1993) prior to the final interpretation of the electron-microprobe results.

Calculations using the Gladstone–Dale relationship yield a K_P of 0.1911 and a K_C of 0.1925 for the empirical formula using constants reported by Mandarino (1981); hence $1-(K_P/K_C)$ is 0.0073, indicating superior compatibility (Mandarino 1981) between the physical and chemical data.

X-RAY CRYSTALLOGRAPHY

Precession single-crystal studies of two anhedral fragments, employing Zr-filtered Mo radiation, show that harrisonite is hexagonal rhombohedral, with measured unit-cell parameters a 6.213 and c 26.67 Å. One crystal was mounted such that 110* is parallel to the dial axis, and the other crystal was mounted such that c^* is parallel to the dial axis. The following levels were photographed: 110* Λ c^*, $hk0 \rightarrow hk4$, $h0l$ and hll. A 300-hour exposure of the $h0l$ zone did not indicate multiplicity of either cell parameter. The diffraction symmetry is $\bar{3}m$, and the permissible space-groups are $R\bar{3}m$ (166), $R3m$ (160) and $R32$ (155) (diffraction aspect R**).The correct space-group is $R\bar{3}m$ on the basis of the crystal-structure determination (Grice & Roberts 1993). The X-ray powder-diffraction data are presented in Table 1. The refined unit-cell parameters, a 6.240(2), c 26.784(5) Å, V 903.2(4) Å^3 and c/a 4.2923, are based on 19 X-ray powder lines between 3.119 and 1.362 Å for which unambiguous indexing was possible. All indexed reflections were checked on single-crystal precession films. The powder data are unique and bear no resemblance to any other inorganic phase listed in the Powder Diffraction File. With $Z = 3$, the calculated density for the simplified formula $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$ and a Fe:Mg ratio of 7.57:1 is 4.01 g/cm^3, close to the measured specific gravity of 4.02(3).

TABLE 1. X-RAY POWDER DATA FOR HARRISONITE

*I*est	*I*calc	*d*Åmeas	*d*Åcalc	*hkl*	*I*est	*I*calc	*d*Åmeas	*d*Åcalc	*hkl*
10	8	5.29	5.30	101	5	5	1.785	1.786	0015
60	28	5.00	5.01	012	10	8	1.765	1.766	033*
50	32	4.46	4.46	006	30	13	1.670	1.671	036
100	64	3.119	3.123	107*		12		1.671	306*
50	47	2.976	2.976	009*	10	6	1.635	1.638	0213*
15	15	2.947	2.945	113*	10	7	1.624	1.624	2110*
80	77	2.689	2.688	021*	20	15	1.599	1.599	1016*
100	100	2.558	2.557	116*	80	10	1.560	1.565	1211
80	80	2.505	2.506	024*		77		1.560	220*
20	21	2.410	2.412	205*	20	20	1.550	1.550	1115*
10	15	2.217	2.220	0111*		1		1.496	131
40	39	2.206	2.207	027*	3	2	1.490	1.490	312
15	7	2.103	2.103	208*		1		1.488	0018
3	5	1.952	1.954	214	5	8	1.473	1.473	226
60	15	1.903	1.908	125	3	3	1.444	1.443	315
	54		1.902	0210	3	4	1.426	1.423	0216
30b	22	1.806	1.809	2011	20	22	1.382	1.382	229*
	10		1.802	217	20	16	1.362	1.361	2017*

- 114.6 mm Gandolfi camera employing Fe-filtered Co radiation (λCoKα 1.79021 Å)
- run at CANMET by Mr. Paul Carrière
- intensities visually estimated; b = broad line
- corrected for film shrinkage; no internal standard
- indices marked with an asterisk were used for unit-cell refinement
- indexed with a 6.240,c 26.784 Å
- *I*calc derived from crystal-structure analysis (Grice & Roberts 1993)

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