Arakiite

◆

A New Zn-Bearing Hematolite-Like Mineral from Långban, Värmland, Sweden

Andrew C. Roberts
Geological Survey of Canada
601 Booth Street
Ottawa, Ontario, Canada K1A 0E8

Joel D. Grice
Mineral Sciences Division
Canadian Museum of Nature
P.O. Box 3443, Station 'D'
Ottawa, Ontario, Canada K1P 6P4

Mark A. Cooper and **Frank C. Hawthorne**
Department of Geological Sciences
University of Manitoba
Winnipeg, Manitoba, Canada R3T 2N2

Mark N. Feinglos
Box 3921
Duke University Medical Center
Durham, North Carolina 27710

ABSTRACT

Arakiite, idealized as $(Zn,Mn^{2+})(Mn^{2+},Mg)_{12}(Fe^{3+},Al)_2(As^{3+}O_3)$-$(As^{5+}O_4)_2(OH)_{23}$, is monoclinic, space group Cc, with unit-cell parameters refined from powder data: a = 14.248(8), b = 8.228(4), c = 24.23(1) Å, β = 93.62(3)°, V = 2843(2) Å^3, $a:b:c$ = 1.7316:1:2.9445, Z = 4. The strongest seven reflections in the X-ray powder-diffraction pattern are [d(Å)(I)(hkl)]: 12.07 (100) (002); 6.046 (100) (004); 4.040 (90) (006); 3.148 (30) ($\bar{4}04$, $\bar{1}17$); 3.030 (70) (224); 2.411 (40) (424, $\bar{5}15$); 1.552 (70) (640, $\bar{3}51$). The mineral was found on a museum specimen, previously labeled as dixenite, from Långban, Värmland, Sweden, and occurs on one surface as red-brown to orange-brown aggregates of micaceous plates. Associated minerals are calcite and very minor magnussonite, and the bulk of the specimen is specular hematite. Arakiite is megascopically indistinguishable from either hematolite or dixenite and possesses the following physical properties: streak is pale brown; lustre is resinous to submetallic; diaphaneity is opaque (masses) to translucent (thin edges); non-fluorescent; hardness is estimated at 3–4; cleavage is {001} perfect; tenacity is brittle; fracture is uneven, almost subconchoidal; calculated density is 3.41 g/cm^3 (for empirical formula and unit-cell parameters derived from crystal structure). Arakiite is biaxial negative, α = 1.723(4), β = 1.744(2), γ = 1.750(2); 2V (meas.) = 44(3)° (extinction), = 40(10)° (direct), 2V (calc.) = 56°; dispersion $r > v$ medium; orientation is $Y = b$ and $X \wedge c$ = +4° (in β obtuse). There is no evidence of pleochroism. The crystal structure shows that manganese occurs as Mn^{2+}, iron occurs as Fe^{3+} and arsenic occurs as both As^{3+} and As^{5+} in a 1:2 ratio. Averaged electron-microprobe analyses yielded ZnO = 4.48, MnO = 34.32, MgO = 12.76, Fe_2O_3 = 6.76, Al_2O_3 = 2.25, As_2O_3 = 6.56, As_2O_5 = 15.84, H_2O (calculated assuming stoichiometry) = [13.74], total = 96.71 weight %, corresponding to $(Zn_{0.83}Mn^{2+}_{0.17})_{\Sigma 1.00}(Mn^{2+}_{7.12}Mg_{4.77})_{\Sigma 11.89}(Fe^{3+}_{1.28}Al_{0.67})_{\Sigma 1.95}(As^{3+}O_3)_{1.00}(As^{5+}O_4)_{2.08}$-$(OH)_{22.99}$, based on 34 (O+OH) anions. (OH) was confirmed by both infrared spectroscopy and crystal-structure analysis. The mineral name is for Dr. Takaharu Araki (1929–) for his numerous crystal-structure contributions to the science of mineralogy.

INTRODUCTION

Arakiite, ideally $(Zn,Mn^{2+})(Mn^{2+},Mg)_{12}(Fe^{3+},Al)_2(As^{3+}O_3)$-$(As^{5+}O_4)_2(OH)_{23}$, is a newly recognized mineral species from Långban, Sweden. The specimen on which the new mineral occurs was acquired by one of us (M.N.F.) on exchange from the late John Fuller of The Natural History Museum, London, UK, in September 1985. It is a portion of a larger specimen (BM1921, 310) which was labeled as dixenite from Långban, Värmland, Sweden, and was initially acquired by the museum in 1921 from Mr. C. Wendler who had provided them with a number of Långban samples in the early 1920's. The misidentification is certainly legitimate; arakiite is megascopically indistinguishable from dixenite and hematolite. All three minerals occur at Långban as thin foliated reddish-colored masses on ore-bearing matrix. Routine X-ray powder-diffraction study indicated that the mineral is not identical to dixenite or hematolite. Further study using modern mineralogical techniques showed it to be a new mineral, the description of which is reported here. The crystal structure most closely resembles that of hematolite (Moore and Araki, 1978) rather than that of dixenite (Araki and Moore, 1981) and has been dealt with in a separate publication (Cooper and Hawthorne, 1999).

The mineral is named for Dr. Takaharu Araki (b. 1929), formerly of the Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois, for his numerous crystal-structure

Figure 1. **Arakiite foliated masses on specular hematite. Longest field of view is approximately 15 mm.**

contributions to the science of mineralogy. Dr. Araki, in close collaboration with Professor Paul Moore, solved the structures of many complex P-bearing and As-bearing phases, including those of hematolite and dixenite. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The specimen used for this study now resides within the Harvard Mineralogical Museum, Cambridge, Massachusetts, and has been assigned the catalog number 134608. Additional material is preserved at The Natural History Museum, London, UK, as BM1921, 310.

SPECIMEN DESCRIPTION

The single sample used for this study measures 15 x 20 x 18 mm and consists principally of massive fine-grained specular hematite. Arakiite is only found on one surface where it occurs as aggregates of micaceous plates over an area of approximately 15 x 10 mm. A color photograph of essentially the complete arakiite aggregate is presented in Figure 1. Associated minerals are colorless anhedral calcite and tiny blue-green anhedral grains of magnussonite. We have no detailed information about the site of origin within the mine.

PHYSICAL and OPTICAL PROPERTIES

Arakiite is red-brown to orange-brown with a pale-brown streak. The lustre is resinous to submetallic, and masses are opaque whereas thin edges of grains are translucent. The mineral is predominantly anhedral and mica-like with no obvious forms; it has a perfect {001} cleavage. The tenacity is brittle, fracture uneven, almost subconchoidal, and the hardness is estimated at 3 to 4, considering that it is easily scratched by a needle. There is no evidence of fluorescence under either longwave or shortwave ultraviolet radiation. Density could not be measured because of the meager quantity of pure material; the calculated density is 3.41 g/cm^3 (based on the empirical formula and unit-cell parameters determined from the crystal-structure study). Twinning was neither observed megascopically nor in the subsequent X-ray single-crystal and crystal-structure studies.

Spindle-stage optical measurements at 590 nm indicate that the mineral is biaxial negative with α = 1.723(4), β = 1.744(2), γ = 1.750(2); 2 *V* (measured by extinction method) = 44(3)°, 2 *V* (measured directly) = 40(10)°, 2 *V* (calculated) = 56°. The discrepancy between measured and calculated 2 *V* is attributable to uneven extinction related to the "curved" nature of the plates. The dispersion is *r* > *v* medium, and no pleochroism was observed. The optical orientation is Y = *b*, X ^ *c* = +4° (in β obtuse).

X-RAY DIFFRACTION

Arakiite is monoclinic, space group *Cc*, with unit-cell parameters refined from powder data: *a* = 14.248(8), *b* = 8.228(4), *c* = 24.23(1) Å, β = 93.62(3)°, *V* = 2843(2) Å^3, and *a*:*b*:*c* = 1.7316:1:2.9445. Cell parameters derived from the crystal-structure study (Cooper and Hawthorne, 1999) are: *a* = 14.236(2), *b* = 8.206(1), *c* = 24.225(4) Å, β = 93.52(1)°, *V* = 2824.0(7) Å^3, and *a*:*b*:*c* = 1.7348:1:2.9521.

A fully indexed X-ray powder-diffraction pattern is presented in Table 1. If one considers the whole pattern, the data are unique. However, strong 00*l* reflections at 12.07, 6.046, 4.040 and the strong reflection at 1.552 Å are comparable, in both intensity and spacing, to those diffraction lines published for both hematolite and dixenite and, additionally, to the unnamed Fe^{5+} analogue of hematolite (Dunn and Peacor, 1983) and to the unnamed Långban arsenate of Roberts and Dunn (1988). Studies are in progress on the latter two; suffice to say at this time that neither is crystallographically nor chemically identical to arakiite. All known members of this "family" of structures can be readily differentiated by routine X-ray powder-diffraction film methods, including 57.3 mm cameras.

CHEMISTRY

A thin cleavage plate of arakiite was analyzed with a Cameca SX-50 electron microprobe, using an operating voltage of 15 kV, a beam current of 20 nA, a beam 5 µm in diameter, and a counting time of 20 s on a peak and 10 s on background. The plate was selected from an area on the sample adjacent to that from which the cleavage plate used for the crystal-structure analysis was picked; it was fixed to the surface of a plexiglass disk and then carbon coated prior to analysis. Probe standards are as follows: cobaltite (As); gahnite (Zn); spessartine (Mn); forsterite (Mg); fayalite (Fe); kyanite (Al). An energy-dispersion scan indicated the absence of any other elements with atomic number greater than 9 except those reported here. The following elements were sought but not detected: Na, Ca, K, Ti, V, Cr, Cu, Si, P, S, F. Data were corrected using the *PAP* procedure of Pouchou and Pichoir (1984, 1985). The valence states for Mn and Fe and the number of O atoms, were determined by crystal-structure analysis prior to the final interpretation of the electron-microprobe results. The paucity of pure material prevented quantitative determination of H_2O. However, the presence of H as (OH) was confirmed both by crystal-structure analysis and powder infrared-absorption study; the formula was therefore calculated to give 23 (OH). The average of thirteen determinations and ranges and standard deviations are given in

***Table 1.* X-ray powder-diffraction data for arakiite.**

$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*	$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*
100	12.07	12.089	002	5	2.546	2.545	133
100	6.046	6.045	004	20	2.498	2.502	$\bar{4}24$
10	5.463	5.422	$\bar{1}13$	40	2.411	2.415	424
20	5.262	5.255	113			2.411	$\bar{5}15$
15	4.764	4.756	$\bar{2}04$	15	2.372	2.370	$\bar{3}31$
30	4.119	4.114	020	15	2.338	2.341	$\bar{2}28$
90	4.040	4.030	006			2.341	135
10	3.952	3.943	115	10b	2.291	2.292	515
5	3.822	3.826	312			2.288	$\bar{4}26$
10	3.648	3.664	023	5b	2.237	2.234	408
5	3.572	3.561	220			2.234	$\bar{3}34$
5	3.496	3.487	$\bar{3}14$	5b	2.157	2.161	604
20	3.404	3.415	206			2.158	$\bar{3}35$
		3.401	024			2.112	137
5	3.317	3.314	314	5	2.106	2.105	335
10	3.223	3.219	$\bar{3}15$			2.102	$\bar{6}06$
30	3.148	3.152	$\bar{4}04$	20b	2.065	2.062	517
		3.147	$\bar{1}17$	10	2.017	2.017	$\bar{6}23$
70	3.030	3.026	224	5	1.905	1.907	20$\underline{12}$
5b	2.862	2.879	026	20	1.859	1.857	429
		2.847	$\bar{2}08$	15	1.810	1.810	608
5	2.799	2.801	316			1.810	$\bar{1}3\underline{10}$
5	2.749	2.753	$\bar{4}06$	5	1.777	1.778	$\bar{2}2\underline{12}$
10	2.700	2.693	130	20	1.748	1.747	51$\underline{10}$
20	2.631	2.635	$\bar{1}32$	5	1.661	1.660	$\bar{5}1\underline{12}$
5	2.594	2.599	422	5	1.619	1.621	538
		2.597	$\bar{5}13$	20	1.573	1.574	$\bar{2}2\underline{14}$
				70	1.552	1.553	640
						1.553	$\bar{3}51$

114.6 mm Debye-Scherrer powder camera
Cu radiation, Ni filter (λ Cu$K\alpha$ = 1.54178 Å)
Intensities estimated visually; b = broad line
Not corrected for shrinkage and no internal standard
Indexed with a = 14.248, b = 8.228, c = 24.23 Å, β = 93.62°

***Table 2.* Compositional data for arakiite.**

	Weight %	*Range*	*Standard deviation*
ZnO	4.48	4.00–4.74	0.19
MnO	34.32	33.84–34.95	0.34
MgO	12.76	12.27–13.47	0.34
Fe_2O_3	6.76	6.32–7.16	0.27
Al_2O_3	2.25	2.02–2.47	0.14
As_2O_5	15.84	[23.00–24.2[1]]	0.38
As_2O_3	6.56		
H_2O[2]	[13.74][2]		
Total	96.71		

[1] Total As calculated as As_2O_5, then partitioned as $As^{5+}_2O_5$ and $As^{3+}_2O_3$ in a 2:1 ratio as determined from the crystal structure.
[2] Calculated assuming the formula derived from crystal-structure analysis.

Table 2. Arsenic was initially quantified as As_2O_5, then partitioned as $As^{5+}_2O_5$ and $As^{3+}_2O_3$, in a 2:1 ratio as observed in the structural study. With 34 anions [O + (OH)], the empirical formula for arakiite is $(Zn_{0.83}Mn^{2+}_{0.17})_{\Sigma 1.00}(Mn^{2+}_{7.12}Mg_{4.77})_{\Sigma 11.89}(Fe^{3+}_{1.28}Al_{0.67})_{\Sigma 1.95}(As^{3+}O_3)_{1.00}(As^{5+}O_4)_{2.08}(OH)_{22.99}$. The idealized formula is $(Zn,Mn^{2+})(Mn^{2+},Mg)_{12}(Fe^{3+},Al)_2(As^{3+}O_3)(As^{5+}O_4)_2(OH)_{23}$ and the end-member formula is $ZnMn^{2+}_{12}Fe^{3+}_2(As^{3+}O_3)(As^{5+}O_4)(OH)_{23}$. Zinc is the key element which differentiates arakiite from hematolite. Both minerals have structures that are based on five close-packed repeat layers. Four of the five layers are topologically identical and only differ in cation ordering. The single distinctive layer involves tetrahedrally coordinated (Zn/Mn^{2+}) in arakiite versus octahedrally coordinated (Mn^{2+}) in hematolite. Full details of the structural similarities and differences between arakiite and hematolite have been published by Cooper and Hawthorne, 1999.

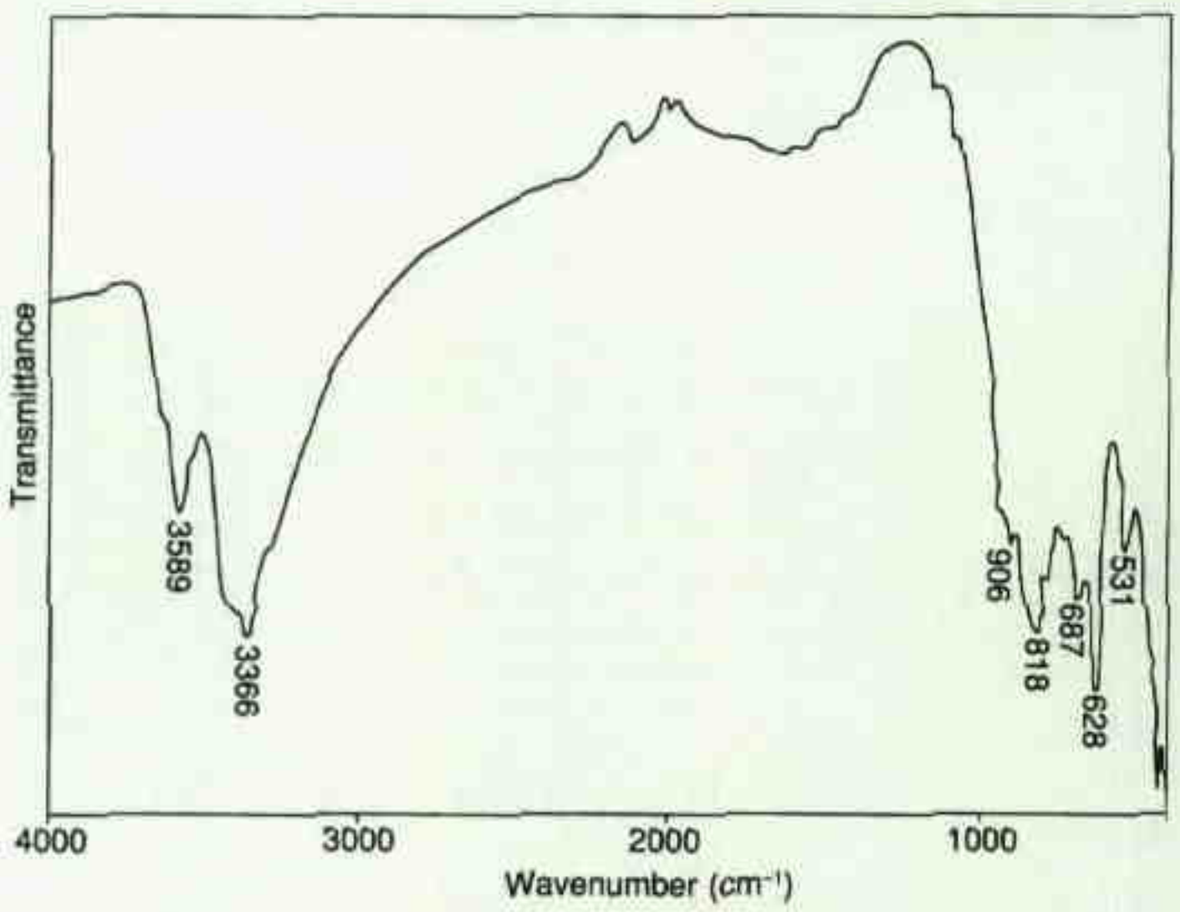

***Figure 2.* Infrared-absorption spectrum for arakiite.**

INFRARED-ABSORPTION STUDY

The equipment and procedures for acquiring the infrared-absorption spectrum for arakiite are identical to those used to obtain the spectrum of mcalpineite (Roberts *et al.*, 1994) and are not repeated here. The spectrum (Fig. 2) clearly shows absorption bands for (OH). Strong to medium-strong bands at 3366 and 3589 cm^{-1} are due to O-H stretching in the hydroxyl groups.

ACKNOWLEDGMENTS

The authors thank E. Moffatt (Canadian Conservation Institute) for the infrared spectrum of arakiite and M. Clarke (GSC) for redrafting Figure 2. FCH was supported by Research and Major Equipment grants from the National Sciences and Engineering Research Council of Canada.

REFERENCES

ARAKI, T., and MOORE, P. B. (1981) Dixenite, $Cu^{1+}Mn^{2+}_{14}Fe^{3+}(OH)_6(As^{3+}O_3)_5(Si^{4+}O_4)_2(As^{5+}O_4)$: metallic $[As_4^{3+}Cu^{1+}]$ clusters in an oxide matrix. *American Mineralogist*, **66**, 1263–1273.

COOPER, M.A., and HAWTHORNE, F. C. (1999) The effect of differences in coordination on ordering of polyvalent cations in close-packed structures: the crystal structure of arakiite and comparison with hematolite. *Canadian Mineralogist*, **37**, 1471–1482.

DUNN, P. J., and PEACOR, D. R. (1983) A ferric iron equivalent of hematolite from Sterling Hill, New Jersey and Långban, Sweden. *Mineralogical Magazine*, **47**, 381–385.

MOORE, P. B., and ARAKI, T. (1978) Hematolite: a complex dense-packed sheet structure. *American Mineralogist*, **63**, 150–159.

POUCHOU, J.-L., and PICHOIR, F. (1984) A new model for quantitative analysis. 1. Application to the analysis of homogeneous samples. *La Recherche Aérospatiale*, **3**, 13–38.

POUCHOU, J.-L., and PICHOIR, F. (1985) "PAP" (phi-rho-z) procedure for improved quantitative microanalysis. *In Microbeam Analysis* (J. T. Armstrong, ed.), San Francisco Press, San Francisco, California (104–106).

ROBERTS, A. C., and DUNN, P. J. (1988) Mineralogical data for a new, unnamed arsenate from the Långban mine, Värmland, Sweden. *Geologiska Föreningens i Stockholm Förhandlingar*, **110**, 181–182.

ROBERTS, A. C., ERCIT, T. S., CRIDDLE, A. J., JONES, G. C., WILLIAMS, R. S., CURETON, F. F. II, and JENSEN, M. C. (1994) Mcalpineite, $Cu_3TeO_6 \cdot H_2O$, a new mineral from the McAlpine mine, Tuolumne County, California, and from the Centennial Eureka mine, Juab County, Utah. *Mineralogical Magazine*, **58**, 417–424.

GeoExpositions

Gem & Mineral Shows

Las Vegas & Phoenix Shows

Wholesale & Retail Dealers

Gems, Minerals, Fossils, Lapidary
Jewelry, Beads, Meteorites

Las Vegas
June 2-4, 2000
The Las Vegas
*Mineral*Fossil*Gem*Jewelry Show*
Tropicana Resort & Casino
Grand Ballroom

Group Room Rates
$49 Sun-Thurs.
(800) 634-4000
ask for group
#SMBS500

Concurrent with GL&W, GLDA, JCK, The Bead Renaissance, and Antique Jewelry & Watch shows

FREE Admission
FREE Parking
Door Prizes

Phoenix
November 3-5, 2000
Phoenix Treasure Market of Minerals*Fossils*Gems*Jewelry
Phoenix Civic Plaza--Hall C

Door PRIZES

FREE Lapis Globe with paid admission

Dealer Discount for Multiple Shows

GeoExpositions, LLC
P.O. Box 5054, Golden, CO 80401
(303) 278-1218 (phone & fax) * GeoExpo@aol.com

Call for Group Room Rates

Handbook of
MINERALOGY
Anthony • Bideaux • Bladh • Nichols

New—Vol. IV
Arsenates, Phosphates, Vanadates
680 p., US$108+US$6.00 S&H (ISBN 0-9622097-3-2)
$5 Reward paid for each error found; for details: mineraldata.com

STILL AVAILABLE

Vol. III—Halides, Hydroxides, Oxides—628 p., 1997
US$100.00 + $6.00 S&H (ISBN 0-9622097-2-4)

Vol. II—Silica and Silicates 904 p. in 2 books, 1995
US$144.00 + $7.50 S&H (ISBN 0-9622097-1-6)

Vol. I—Elements, Sulfides, Sulfosalts—588 p., 1990
US$94.00 + $6.00 S&H (ISBN 0-9622097-0-8)

15% discount on any of vol. I, II, III if ordered with vol. IV

Prepaid Orders only VISA/ MCard accepted

Mineral Data Publishing
P.O. Box 37072
Tucson, Arizona 85740 USA
Tel: (520) 798-1513/(520) 297-4862
FAX: (520) 798-1514/(520)297-6330

TODAY'S THE DAY
Stop Smoking.
American Heart Association

Gem Crystal Treasures
Specimen and gem-quality crystals available.
Send for free list or visit our website.
Ty Lawrence
P.O. Box 14042
Portland, OR 97293
tel: (503) 731-6503 • www.gemcrystals.com

NATIONAL MINERALS
Your prime source for TOP QUALITY aesthetic ZEOLITES and Bulk Material.
By the Piece, Flat or Kilo.
Competitive Prices, Excellent Service.
FAX/Mail requirements to:
NATIONAL MINERALS, 209/1673 Motilal Nagar No. 1, Road No. 4, Goregaon (W), Mumbai-400104 INDIA.
Tel: 874-9984, 872-6874. Fax: 91-22-873-6161.