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Retzian-(Nd), a new mineral from Sterling Hill, New Jersey and a redefinition of retzian

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Abstract

Retzian-(Nd) is a new mineral from the Sterling Hill Mine in Ogdensburg, New Jersey. It is orthorhombic, *Pban*, with $a = 5.690$, $b = 12.12$, and $c = 4.874$Å. The dominant rare earth is Nd and the ideal formula is $Mn_2Nd[(OH)_4AsO_4]$. Retzian-(Nd) occurs as euhedral crystals with forms {001}, {010}, {150}, {130}, {110}, {201}, and {021}, and is elongate parallel to [100]. Optically, retzian-(Nd) is biaxial (+) with refractive indices $\alpha = 1.774$, $\beta = 1.782$, and $\gamma = 1.798$ (all ± 0.002); $2V_z = 69(1)°$ measured, 71° calculated; dispersion is weak $r < v$. Retzian-(Nd) is found with rhodochrosite, willemite, sonolite, calcite, barite and chlorophoenicite in three separate parageneses at Sterling Hill.

Retzian is re-examined and redefined as $Mn_2Ce[(OH)_4AsO_4]$ with Ce > Nd > La, based on microprobe analysis of type material. The data presented here confirm the proposed crystal structure.

Introduction

Retzian was originally described by Sjögren (1894) as a new manganese calcium arsenate from the Moss mine, Nordmark, Varmland, Sweden. The chemical analysis by Mauzelius *in* Sjögren (1894) was performed on only 0.0795 g of material, owing to the extreme paucity of samples. The analysis was admittedly incomplete with 0.0082 g of unidentified residue, part of which Sjögren (1897) later ascribed to the presence of rare earths.

Retzian was subsequently re-examined by Moore (1968) who presented crystallographic data and proposed the tentative formula $Mn_2Y(AsO_4)(OH)_4$, assigning the rare-earth content to yttrium on the basis of Gladstone–Dale calculations. Moore (1967) also described the crystal structure of retzian, carefully pointing out that "the structure analysis of retzian is largely a study of a compound with an unknown composition."

The recent discovery of a second occurrence of "retzian" at the Sterling Hill Mine, Ogdensburg, New Jersey, prompted an analytical investigation of retzian to ascertain its composition and to simultaneously describe the Sterling Hill material. A fragment of the type retzian from the collection of Hjalmar Sjögren was obtained through the courtesy of Dr. Bengt Lindqvist of the Naturhistoriska Riksmuseet in Stockholm. This fragment is now recatalogued under NMNH #145882.

The present study determined that the type material is Ce-rich and the new material from Sterling is Nd-rich. This necessitates a redefinition of retzian as $Mn_2Ce(AsO_4)(OH)_4$ and the naming of the Stering Hill material as retzian-(Nd), in accordance with Levinson's rules for the naming of rare-earth analogs of known species (Levinson, 1966). The nomenclature outlined above was submitted to the IMA Commission on New Minerals and Mineral Names. It was the judgment of the Vice-Chairman that this redefinition of retzian and the designation of the name retzian-(Nd) for the Nd-analog required no vote, being a simple application of Levinson's rules already accepted by the Commission. The holotype retzian-(Nd) is deposited in the Smithsonian Institution under catalog #143762. Small por-

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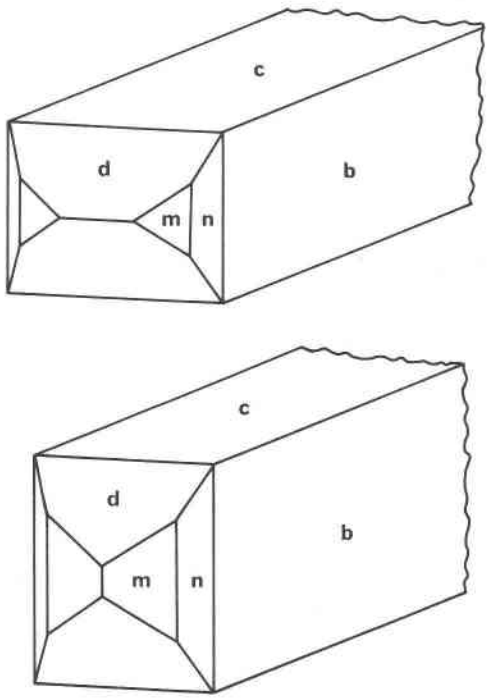

Fig. 1. Crystal drawings of typical retzian-(Nd) crystals from Sterling Hill, New Jersey.

tions of the holotype (loose crystals) have been deposited in the Royal Ontario Museum, The American Museum of Natural History in New York, The Mineralogical Museum at Harvard University, The Geological Survey of Canada, and the British Museum (N.H.).

Retzian-(Nd)

Six crystals of retzian-(Nd) from Sterling Hill were studied on the optical goniometer and two were oriented with the precession camera. Crystal drawings of typical crystals are presented as Figure 1, and the angle table is given in Table 1. Because the signals observed on the goniometer were very poor, the accuracy of these measurements is only ±1–2°. The predominant forms on retzian-(Nd) are the same as those noted by Sjögren (1897) on retzian from the Moss Mine. However, the crystal habit is markedly different inasmuch as retzian-(Nd) is elongate parallel to [100], and retzian is elongate parallel to [001]. In addition to the forms shown in Figure 1, very thin faces of {021} and {150} were observed on only one crystal.

Table 1. Angle table for retzian-(Nd) from Sterling Hill

Orthorhombic: a = 5.690, b = 12.12, c = 4.874 Å

	Measured		Calculated	
Form	φ	ρ	φ	ρ
c {001}	0°	0°	—	0°00'
b {010}	0°	90°	0°00'	90°00'
t {150}	24°	90°	23°04'	90°00'
n {130}	35°	90°	35°22'	90°00'
m {110}	65°	90°	64°51'	90°00'
d {201}	90°	59°	90°00'	59°43'
e {021}	0°	38'	0°00'	38°48'

The unit cell parameters were provided by Moore (1967) and the unit cell parameters and space group extinctions determined in our study of the Sterling Hill retzian-(Nd) are in excellent agreement with Moore's data. We used 0-level precession photographs to orient the crystals subsequently studied with the goniometer and spindle stage. The unit cell parameters for retzian-(Nd) were refined with data from a 114.6 mm diameter Gandolfi camera powder photograph obtained using NBS silicon as an internal standard. The refined parameters are given in Table 2 and the X-ray powder diffraction data are given in Table 3.

Physical and optical properties

Retzian-(Nd) occurs as pinkish-brown to reddish-brown crystals and aggregates of crystals. Where color zoning is evident, the interior of the crystals has the darker color, but it was not possible to analyze these few zoned crystals to establish compositional correlations. The streak is very light brown. The luster is vitreous to dull on crystal faces and vitreous on fracture surfaces. There is no discernible cleavage, but the crystals tend to break along parallel planes due to parallel growth. The hardness is approximately 3–4 on Mohs' scale. The fracture is uneven. The density, measured using heavy liquid techniques, is greater than 4.2 g/cm^3, but could not be more reliably estimated due to extreme paucity of material and the fact that some crystals contain cavities. The density calculated using the chemical analysis and cell parameters (Table 2) is 4.45 g/cm^3, suggesting that the 4.15 g/cm^3 of Sjögren (1894) was low. This low value could have been due to the cavities in the crystals noted above, or to interstitial spaces between crystal aggregates.

Optically, retzian-(Nd) is biaxial (+). The optical data are presented in Table 2. Determinations were

Table 2. Crystallographic and optical data for retzian-(Nd) and retzian

		Retzian - (Nd) Sterling Hill	Retzian Sweden
Ideal formula:		$Mn_2Nd[(OH)_4AsO_4]$	$Mn_2Ce[(OH)_4AsO_4]$
Unit cell parameters:	a	5.690(5) Å	5.670(3) Å *
	b	12.12(1)	12.03(1)
	c	4.874(3)	4.863(4)
Space group:		Pban	Pban
Refractive indices:	α	1.774(2)	1.777(5) **
	β	1.782(2)	1.788(5)
	γ	1.798(2)	1.800(5)
Optic axial angle:	(meas.)	$2V_z = 69(1)^o$	large, positive
	(calc.)	$2V_z = 71^o$	$2V_z = 88^o$
Dispersion:		r < v, weak	r < v, weak
Orientation and pleochroism		c || X, yellow	c || X, colorless to yellow
		b || Y, reddish-brown	b || Y, yellow to brown
		a || Z, brown	a || Z, red-brown to crimson
Absorption:		Z > Y >> X	Z > Y > X

* --Crystallographic data for retzian from Moore (1967).
**--Optical data from Larsen and Berman (1934) and Sjögren (1897).

made with the spindle stage on crystals previously oriented with the precession camera. Principal refractive indices were measured in Na light by the immersion method and oils were immediately checked using an Abbe refractometer. The optical data are in excellent agreement with those previously obtained for retzian from Sweden (Table 2).

Chemistry

Analytical techniques

Crystals of retzian-(Nd) from Sterling Hill and retzian from the Moss Mine, Sweden, were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.15 μA. The standards used were manganite for Mn; synthetic olivenite for As; synthetic ZnO for Zn; and hornblende for Fe, Mg and Ca. The rare-earth synthetic glass standards of Drake and Weill (1972) were utilized as standards for the rare earth elements. Lα lines were used in the analyses and special attention was given to possible interferences and background effects. The complete data were corrected using a modified version of the MAGIC-4 computer program. Duplicate analyses for Mn and As, using other standards, confirmed the analyses for these elements. Water was determined by DTA–TGA on 3.2 mg of a non-type sample of Swedish retzian; this resulted in a loss of 8.3 percent H_2O between 230 and 570° C, in good agreement with Mauzelius' determination of 8.4 percent and the theoretical value of 7.88 percent. The resultant analyses are presented in Table 4.

Retzian

The original analysis of retzian by Mauzelius (in Sjögren, 1894) is readily available in *The System of Mineralogy* (Palache *et al.*, 1954) and is thus not reprinted here. Although it was incomplete and contained misidentified and unknown components (10.3 percent unidentified, 19.2 percent CaO, 4.3 percent insoluble residue), it was remarkably accurate for As_2O_5, H_2O and M^{2+} cations, especially considering that it was performed on only 0.0795 g

Table 3. X-ray powder diffraction data for retzian-(Nd)

I/Io	d (obs.)	d (calc)	hkl
20	6.05	6.060	020
30	4.89	4.874	001
5	3.809	3.798	021
60	3.534	3.540	111
15	3.296	3.294	130
15	3.028	3.030	040
15	2.849	2.845	200
100	2.726	2.729	131
5	2.574	2.575	220
2	2.455	2.457	201
5	2.344	2.345	141
2	2.259	2.261	022
15	2.078	2.074	240
2	2.029	2.028	151
2	2.020	2.020	060
15	1.963	1.959	132
15	1.905	1.899	042
30	1.857	1.851	202
5	1.779	1.770	222
5	1.754	1.749	311
2	1.723		
2	1.646		
20	1.625		
2	1.583		
15	1.570		
15	1.556		
20	1.463	(plus ~20 lines to 1.108)	

Cu Kα X-radiation, intensities estimated visually, indexed with the orthorhombic unit cell a = 5.690(5), b = 12.12(1), c = 4.874(3) Å, space group Pban.

Table 4. Chemical analyses of retzian-(Nd) and retzian

	RETZIAN 145882	RETZIAN theory	RETZIAN -(Nd) 143762	RETZIAN -(Nd) theory
FeO	1.1		0.4	
MgO	1.2		2.0	
CaO	0.6		0.0	
ZnO	0.8		1.8	
MnO	27.3**	31.05	25.9	30.77
As_2O_5	27.1	25.15	26.9	24.93
La_2O_3	3.0		7.6	
Ce_2O_3	14.5	35.92	7.8	
Y_2O_3	1.7		1.6	
Nd_2O_3	6.8		10.9	36.49
Pr_2O_3	2.4		4.2	
Sm_2O_3	1.6		2.4	
Gd_2O_3	1.9		1.9	
Eu_2O_3	1.0		0.9	
H_2O	8.3*	7.88	8.3*	7.81
Total	99.3	100.00	102.6	100.00

* - Water from DTA-TGA on a separate sample (NMNH R5416).
** - Mn shown to be divalent by Sjögren (1894).
Accuracy of data: ± 7 percent of the amount present for REE & Zn.
± 3 percent of the amount present for Fe, Mg, Ca, Mn.
± 8 percent of the amount present for H_2O

of material. In a subsequent paper, Sjögren (1897) discussed the fact that Mauzelius, after analyzing a rare-earth mineral (kainosite) thought it possible that the 10.3 percent unidentified component of the original retzian analysis might be rare earths. The unidentified portion had been preserved and subsequent re-analysis indicated to Mauzelius that this assumption was valid and that retzian was a manganese rare-earth arsenate.

The analysis of the present study, given in Table 4, indicates that retzian is indeed a manganese rare-earth arsenate, but with Ce as the dominant rare-earth element, and not Y as previously assumed. The Ca reported by Sjögren is essentially absent (only 0.6 percent CaO), and it is very likely that some of the rare-earths were precipitated as CaO. Although many rare-earths are present, the dominant ones are Ce, Nd and La. Calculation of a formula, on the basis of Σ REE + M^{2+} cations = 3, yields: $(Mn_{1.77}\,Mg_{0.13}\,Fe_{0.07}\,Ca_{0.05}Zn_{0.05})_{\Sigma 2.07}\,(Ce_{0.40}\,Nd_{0.19}\,La_{0.08}\,Y_{0.07}\,Pr_{0.07}\,Sm_{0.04}\,Gd_{0.05}\,Eu_{0.03})_{\Sigma 0.93}\,(AsO_4)_{1.08}\,(OH)_{3.69}$, or, ideally, $Mn_2Ce[(OH)_4AsO_4]$, with Z = 2.

Retzian-(Nd)

The chemical composition of retzian-(Nd) differs from that of retzian principally in having Nd as the dominant rare-earth element, with Ce, La and Pr as significant substituents. There appears to be little substitution for As, and only minor Mg in substitution for Mn. The calculation of a formula, based on Σ REE + M^{2+} cations = 3, yields: $(Mn_{1.63}\,Mg_{0.22}\,Fe_{0.03}\,Zn_{0.10})_{\Sigma 1.98}\,(Nd_{0.29}La_{0.21}Ce_{0.21}\,Pr_{0.11}\,Sm_{0.07}\,Y_{0.06}\,Gd_{0.05}\,Eu_{0.02})_{\Sigma 1.02}(AsO_4)_{1.04}\,(OH)_{3.90}$, or, ideally, $Mn_2Nd[(OH)_4AsO_4]$, with Z = 2.

Little is known of rare-earth distribution in the orebodies at Franklin or Sterling Hill. Allanite is known to occur in microcline at Franklin and Frondel (1964) found Ce, La and Nd as the major rare earths with Ce > La > Nd. Thortveitite has recently been found by the senior author as inclusions within a highly zincian hercynite and contains approximately 4 weight percent Y_2O_3.

Occurrence

Retzian from the Moss Mine, Nordmark, Varmland, Sweden, was described by Sjögren (1894). The crystals were developed in cavities in fine-grained braunite and dolomite, and were closely associated with jacobsite, all of which formed before retzian.

Retzian-(Nd) was discovered in 1977 by John Kolic, a miner, in the Sterling Hill mine, Ogdensburg, Sussex County, New Jersey. The occurrence was initially documented by Moore and Ito (1978) as an associated mineral with kraisslite. This occurrence consisted of clove-brown crystals coating and imbedded within light brown rhodochrosite which, in turn, encrusts a moderately rich willemite–franklinite ore. The sample was found on a fracture surface from the 1010 stope, 700 level. It was chosen as the holotype for retzian-(Nd) (NMNH 143762). Retzian-(Nd) from Sterling Hill, like the Swedish occurrence, is extremely rare and very little material was recovered. Only two crystals were visible on the holotype specimen, but others were recovered from dissolution of the overlying calcian rhodochrosite.

In addition to the holotype, two other occurrences of retzian-(Nd) were subsequently found within the Sterling Hill mine. One of these is in the Spex-Gerstmann collection (SG #1428) in Franklin, New Jersey). This retzian-(Nd) is on a vein surface on willemite–franklinite–calcite ore and is associated with secondary willemite, magnesian sonolite, calcite and sphalerite. Semi-quantitative microprobe analysis of one crystal from this occurrence indicates that the material is retzian-(Nd) with Nd $\gg$ Ce $\approx$ La. Y_2O_3 is approximately in the 4–6 weight percent range.

The third occurrence, like the first, was discovered by John Kolic. It was found in the 1220 undercut pillar, 800 level. This is a part of the mine which has produced other rare arsenates (magnussonite, manganese-hoernesite). The matrix is a massive pink manganoan calcite with a druse surface. The druse carbonate is liberally coated with secondary crystals of franklinite, zincite and willemite, together with abundant chlorophoenicite, barite and an unknown phase. Retzian-(Nd) is the least abundant mineral in the assemblage and occurs as light brown crystals usually in intergrown clusters which are randomly and sparsely distributed. Twins are rare (only three were observed) and occur as trillings or sixlings, with a distinctly spoke-like radial appearance, not unlike cerussite, another orthorhombic mineral which forms six-rayed crystals from orthorhombic units. These twins could not be removed for study; they are few and extremely small. Semi-quantitative analysis of the rare-earth content of these crystals indicates that they are grossly inhomogeneous. However, Nd is consistently dominant over Ce and La in this material and it should be called retzian-(Nd).

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