

Waimirite-(Y), orthorhombic YF₃, a new mineral from the Pitinga mine, Presidente Figueiredo, Amazonas, Brazil and from Jabal Tawlah, Saudi Arabia: description and crystal structure

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ABSTRACT

Waimirite-(Y) (IMA 2013-108), orthorhombic YF₃, occurs associated with halloysite, in hydrothermal veins (up to 30 mm thick) cross-cutting the albite-enriched facies of the A-type Madeira granite (~1820 Ma), at the Pitinga mine, Presidente Figueiredo Co., Amazonas State, Brazil. Minerals in the granite are 'K-feldspar', albite, quartz, riebeckite, 'biotite', muscovite, cryolite, zircon, polyolithionite, cassiterite, pyrochlore-group minerals, 'columbite', thorite, native lead, hematite, galena, fluorite, xenotime-(Y), gagarinite-(Y), fluocerite-(Ce), genthelvite–helvite, topaz, 'illite', kaolinite and 'chlorite'. The mineral occurs as massive aggregates of platy crystals up to ~1 µm in size. Forms are not determined, but synthetic YF₃ displays pinacoids, prisms and bipyramids. Colour: pale pink. Streak: white. Lustre: non-metallic. Transparent to translucent. Density (calc.) = 5.586 g/cm³ using the empirical formula. Waimirite-(Y) is biaxial, mean $n = 1.54\text{--}1.56$. The chemical composition is (average of 24 wavelength dispersive spectroscopy mode electron microprobe analyses, O calculated for charge balance): F 29.27, Ca 0.83, Y 37.25, La 0.19, Ce 0.30, Pr 0.15, Nd 0.65, Sm 0.74, Gd 1.86, Tb 0.78, Dy 8.06, Ho 1.85, Er 6.38, Tm 1.00, Yb 5.52, Lu 0.65, O (2.05), total (97.53) wt.%. The empirical formula (based on 1 cation) is (Y_{0.69}Dy_{0.08}Er_{0.06}Yb_{0.05}Ca_{0.03}Gd_{0.02}Ho_{0.02}Nd_{0.01}Sm_{0.01}Tb_{0.01}Tm_{0.01}Lu_{0.01})_{Σ1.00}[F_{2.54}□_{0.25}O_{0.21}]_{Σ3.00}. Orthorhombic, *Pnma*, $a = 6.386(1)$, $b = 6.877(1)$, $c = 4.401(1)$ Å, $V = 193.28(7)$ Å³, $Z = 4$ (powder data). Powder X-ray diffraction (XRD) data [d in Å (hkl): 3.707 (26) (011), 3.623 (78) (101), 3.438 (99) (020), 3.205 (100) (111), 2.894 (59) (210), 1.937 (33) (131), 1.916 (24) (301), 1.862 (27) (230)]. The name

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is for the Waimiri-Atroari Indian people of Roraima and Amazonas. A second occurrence of waimirite-(Y) is described from the hydrothermally altered quartz-rich microgranite at Jabal Tawlah, Saudi Arabia. Electron microprobe analyses gave the empirical formula $(Y_{0.79}Dy_{0.08}Er_{0.05}Gd_{0.03}Ho_{0.02}Tb_{0.01}Tm_{0.01}Yb_{0.01})_{\Sigma 1.00}[F_{2.85}O_{0.08}\square_{0.07}]_{\Sigma 3.00}$. The crystal structure was determined with a single crystal from Saudi Arabia. Unit-cell parameters refined from single-crystal XRD data are $a = 6.38270(12)$, $b = 6.86727(12)$, $c = 4.39168(8)$ Å, $V = 192.495(6)$ Å³, $Z = 4$. The refinement converged to $R_1 = 0.0173$ and $wR_2 = 0.0388$ for 193 independent reflections. Waimirite-(Y) is isomorphous with synthetic SmF_3 , HoF_3 and YbF_3 . The Y atom forms a 9-coordinated YF_9 tricapped trigonal prism in the crystal structure. The substitution of Y for Dy, as well as for other lanthanoids, causes no notable deviations in the crystallographic values, such as unit-cell parameters and interatomic distances, from those of pure YF_3 .

KEYWORDS: waimirite-(Y), new mineral, hydrothermal vein, yttrium fluoride, Pitinga mine, Presidente Figueiredo Co., Amazonas State, Brazil, Jabal Tawlah, Saudi Arabia.

Introduction

THE present paper describes a new mineral species waimirite-(Y), YF_3 , from hydrothermal veins cross-cutting the albite-enriched granite facies at the Pitinga mine, Brazil. During the geological survey on the rare-earth element (REE) deposits in Saudi Arabia (Watanabe *et al.*, 2014), a second occurrence of waimirite-(Y) in an ore body was noticed. Using some anhedral-to-subhedral crystals of waimirite-(Y) from Saudi Arabia, we have determined and refined the composition and crystal structure, respectively.

The distinct crystal structures between the orthorhombic YF_3 , waimirite-(Y) and the trigonal CeF_3 , fluocerite-(Ce), (Cheetham *et al.*, 1976; Garashina *et al.*, 1980; Zalkin and Templeton, 1985; Kondratyuk *et al.*, 1988) demonstrate a difference in crystallographic feature for the fluorides of smaller and larger rare-earth ions, namely Y^{3+} and Ce^{3+} , respectively.

Synthetic YF_3 is known in two polymorphic forms: (α) trigonal, $P3m1$, stable from 1077°C to 1162°C, when it melts and (β) orthorhombic, $Pnma$, stable below 1077°C. The “cubic YF_3 ” of Nowacki (1938) is in fact the phase NaY_3F_{10} (Zalkin and Templeton, 1953). Waimirite-(Y) (IMA 2013-108) is equivalent to the β phase. Single crystals of the latter have been prepared and used for the structure determination. Fluocerite-(Ce) and fluocerite-(La) are trigonal CeF_3 and LaF_3 , respectively. As waimirite-(Y) has crystal-structure characteristics more closely related to those of high- Z $REEF_3$ phases than to those of their low- Z counterparts, a new root name was created.

The most interesting feature of the new mineral, from both the crystal-chemical and potential application aspects, is the distribution

of REE (i.e. heavy, *HREE*; and light, *LREE*). In waimirite-(Y), the (*HREE*+Y)/*LREE* ratio is ~18 and the Y/*Ln* ratio, where *Ln* means lanthanides ⁵⁷La to ⁷²Lu, is ~2.5. Clearly it is a *HREE* mineral as is also the case for xenotime-(Y), where no more than 2% *LREE* occur. In xenotime-(Y) from Pitinga *LREEs* are virtually absent. Its unit cell is smaller than that of common xenotime-(Y), due to the substitution of O by F, forming PO_3F tetrahedra (Bastos Neto *et al.*, 2013). Ideal *Ln*-free waimirite-(Y) contains 60.93 wt.% of yttrium, whereas the Y content in ideal xenotime-(Y) is 48.35 wt.%. Waimirite-(Y) could be, therefore, a spectacular ore mineral.

Rare-earth element fluoride crystalline materials are commonly studied owing to their applications in solid-state lasers and scintillators. Indeed, their good optical properties as well as their low non-radioactive emissions (mainly because of the low cut-off phonon frequencies) make these materials good host matrices for visible or infrared light emission and other optical applications. It is well known that fluoride materials can be used as active media for tunable solid-state lasers (Lage *et al.*, 2004). The orthorhombic YF_3 crystals are non-hygroscopic and colourless under normal conditions, which is essential for their use as active laser materials. Kollia *et al.* (1995) showed that YF_3 could be a laser material.

Both the description and the name of the new mineral were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA) (IMA 2013-108, Bastos Neto *et al.*, 2014b). The name waimirite is for the Waimiri-Atroari Indian people of Roraima and Amazonas. The mine is located close to the Indian Territory. The suffix “(Y)” was introduced because it is a

rare-earth mineral. The name “waimirite” was used informally for this mineral by Minuzzi *et al.* (2003). The same authors applied the name “atroarite” for a probable ralstonite.

Type material has been deposited in the collections of the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 - São Paulo, SP, Brazil, specimen number DR919 and in the Museu de Mineralogia Luiz Englert, Departamento de Mineralogia e Petrologia, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Avenida Bento Gonçalves 9500, 91501-970, Porto Alegre, RS, Brazil, specimen number 3620. Part of the cotype sample has been deposited at the University of Arizona Mineral Museum, RRUFF Project (<http://ruff.info/R130714>).

Occurrence

In the type locality, Pitinga mine (0°44'43"S 60°7'40"W), Presidente Figueiredo, Amazonas, Brazil (Bastos Neto *et al.*, 2009, 2014a), waimirite-(Y) forms hydrothermal veins (up to 30 mm thick) cross-cutting the albite-enriched facies of A-type Madeira granite (~1820 Ma). The Madeira granite is hosted by A-type volcanic rocks (Iricoumé Group, ~1880 Ma) which formed in a caldera complex. The albite-enriched granite facies corresponds to the Madeira world-class Sn-Nb-Ta (*REE*, F, Zr, Li and Th) deposit, with 130 million tons of disseminated ore. In addition, in the central portion of the albite-enriched granite facies, there is a massive cryolite deposit of 10 million tons with a grade of 31.9% Na₃AlF₆. This association of Sn with several rare metals in the same albite-enriched granite that hosts a massive cryolite deposit is unique in the world. The directly associated mineral is halloysite. Minerals in the albite-enriched granite are quartz, ‘K-feldspar’, albite, riebeckite, ‘biotite’, muscovite, cryolite, zircon, polythionite, cassiterite, pyrochlore-group minerals, ‘columbite’, thorite, lead, galena, fluorite, xenotime-(Y), gagarinite-(Y), fluocerite-(Ce), genthelvite-helvite, topaz, ‘illite’, kaolinite and ‘chlorite’. At the magmatic stage, the high F content in the melt was buffered by crystallization of cryolite. Tin, Nb and *REE* were dispersed homogeneously throughout the deposit, transported by F-bearing complexes in the melt and concentrated in the forms of cassiterite, a U-Pb-rich pyrochlore-group mineral and

xenotime-(Y), respectively. Zircon crystallization, inhibited at the early magmatic stage by high F activity, intensified at the late magmatic stage owing to a decrease in alkalinity associated with riebeckite crystallization, forming concentrations, together with xenotime and polythionite, in pegmatitic zones. Rare-earth element mineralization in the lower portion of the massive cryolite deposit is represented by gagarinite-(Y), with fluocerite-(Ce) inclusions formed by exsolution of the early gagarinite. There is no evidence for either silicate–fluoride liquid immiscibility or a continuous transition from volatile-rich silicate melt to solute-rich fluids. The abrupt magmatic–hydrothermal transition triggered three processes: (1) albitization accompanied by the crystallization of hydrothermal cryolite in the rock matrix; (2) conversion of pyrochlore to a columbite-group mineral, characterized by gradual loss of Pb and enrichment in U and Nb; and (3) formation of the massive cryolite deposit, comprised of crystals of twinned cryolite (87%) with subordinate quartz, ‘K-feldspar’ and zircon from an aqueous saline (1.7 to 22.4 wt.% equiv. NaCl) hydrothermal fluid, starting at a minimum temperature of 400°C and continuing down-temperature. The evolution of parameters (*REE*, La/Lu, *LREE/HREE*, Y) in cryolite is continuous from the magmatic stage to the low-temperature hydrothermal stage.

Waimirite-(Y) also occurs as the main *REE* mineral in hydrothermally altered quartz-rich microgranite at Jabal Tawlah (Mount Tawlah) in the Kingdom of Saudi Arabia. It is present as inclusions in an undetermined Ca-Y-F mineral. Anhedral-to-subhedral crystals of several tens to

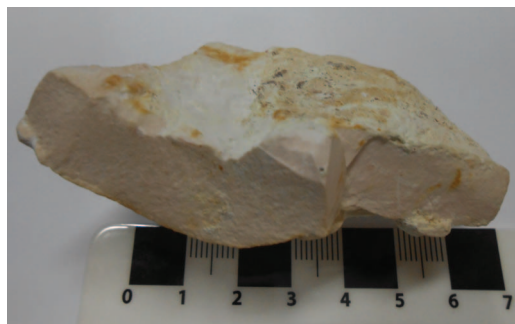


FIG. 1. Waimirite-(Y) bearing sample from the Pitinga mine, Presidente Figueiredo, Amazonas, Brazil. Cotype material (number DR919) deposited in the collections of the Museu de Geociências, USP, São Paulo, Brazil.

several hundreds of μm in size are common. Associated minerals are 'biotite', albite, muscovite, microcline, columbite-(Fe), zircon, thorite, xenotime-(Y), samarskite-(Y), ilmenite, an undetermined Ca-Y-F mineral, euxenite-(Y), fergusonite-(Y), rutile, 'illite', baryte, calcite and goethite. Waimirite-(Y) was formed from

fluorine-rich hydrothermal fluids containing large amounts of REE.

Habit and physical properties

Waimirite-(Y) from Brazil occurs as aggregates of platy crystals up to $\sim 1\ \mu\text{m}$ (Figs 1 and 2).

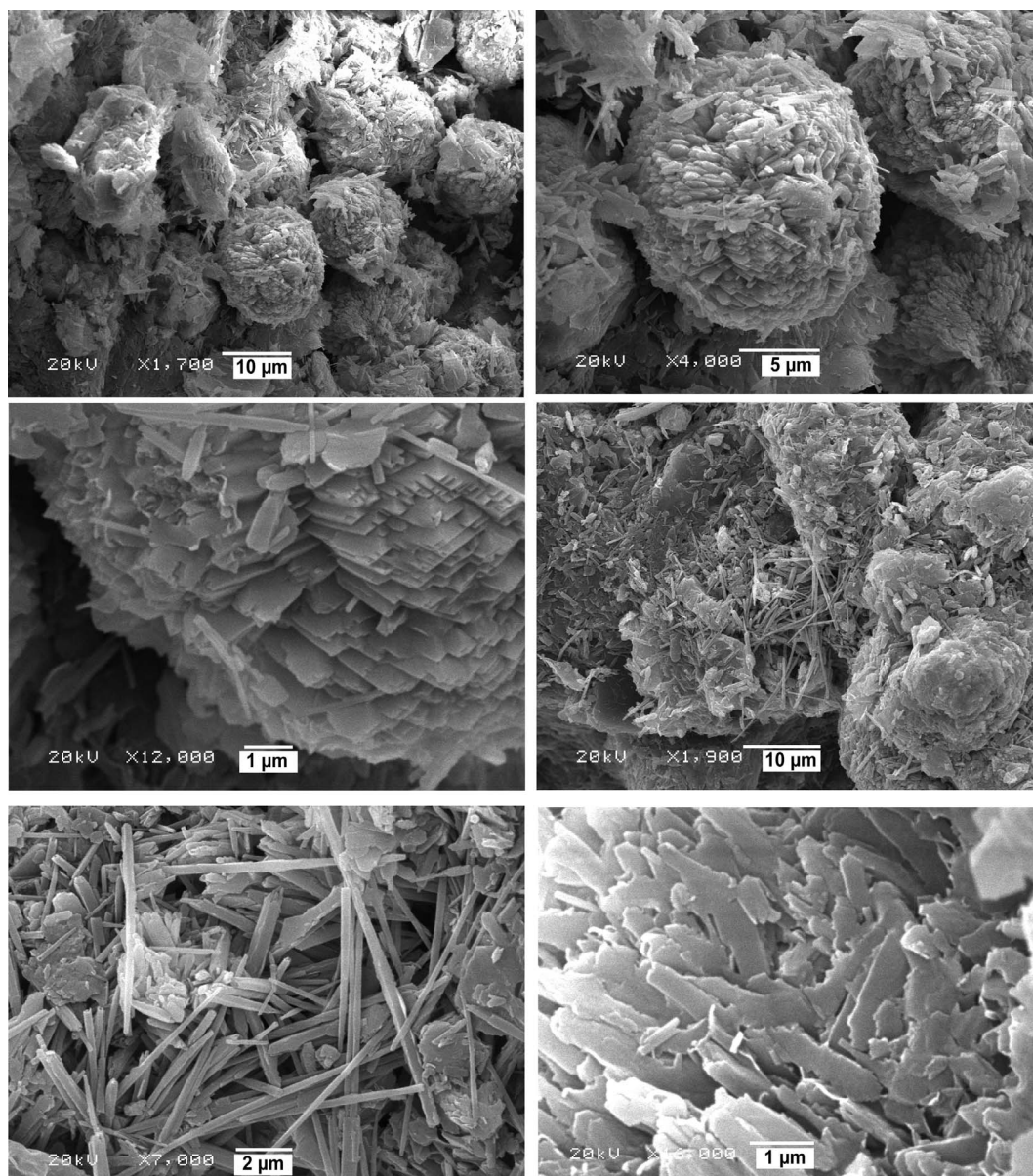


FIG. 2. Backscattered electron image of waimirite-(Y) from Brazil (spherical aggregates of plates) and halloysite (tubes).

Forms were not determined, but synthetic YF_3 displays pinacoids, prisms and bipyramids (Qian *et al.*, 2010). Cleavage was not observed, but synthetic YF_3 displays perfect cleavage on $\{010\}$ (Rotureau *et al.*, 1993). Parting was not observed. The mineral is transparent to translucent under transmitted light microscopy and displays a non-metallic lustre; it is pale pink and the streak is white. It is non-fluorescent under long wavelength (365 nm) ultraviolet radiation. The Mohs hardness was not measured due to the small crystal sizes. Fracture was not determined. Density could not be measured due to the crystal dimensions. The density calculated from the empirical formula and refined unit-cell dimensions is 5.586 g/cm^3 . Optically the mineral is biaxial; due to the crystal dimensions, only a mean $n = 1.54\text{--}1.56$ was measured.

Waimirite-(Y) from Saudi Arabia (Fig. 3) is colourless with a white streak. It is transparent and the lustre is vitreous. Cleavage is not observed and the fracture is irregular to conchoidal. The tenacity is brittle. The density could not be measured because of small grain sizes. The calculated density is 5.678 g/cm^3 on the basis of the empirical formula and refined unit-cell dimensions. The Vickers microhardness is $667\text{--}786$ (mean 700) kg/mm^2 (100 g load), corresponding to $5\frac{1}{2}\text{--}6$ on the Mohs scale. It is

optically biaxial positive with $2V = 70\text{--}80^\circ$. The mean refractive index is estimated as 1.60, because it is higher than that of albite (1.57) and lower than that of apatite (1.64) in thin section.

Mineral chemistry

Waimirite-(Y) crystals from Brazil were embedded in epoxy resin and polished. Chemical analyses (24) were completed with a CAMECA SX-100 electron microprobe (wavelength dispersive spectroscopy (WDS) mode, 15 kV, 20 nA, $\sim 5 \mu\text{m}$ beam diameter) at the University of Arizona Electron Microprobe Laboratory. A preliminary WDS scan at high current showed no peak for Eu. This indicates that it is either not present or present at $<0.01 \text{ wt.}\%$. The actual analyses were performed at a much lower current because the sample is very easily damaged under the electron beam. The three sigma detection limits under the conditions of the analyses range from ~ 0.07 to $0.13 \text{ wt.}\%$ for the Ln actually observed. The *REE* standards are synthetic glasses from the University of Edinburgh. Each glass has a single *REE*, present at a concentration of $\sim 20 \text{ wt.}\%$ oxide, in a Si-Al-Ca-O based matrix. Analytical results are represented in Table 1. Silicon ($0.12 \text{ wt.}\%$) and Al ($0.10 \text{ wt.}\%$) were subtracted because they

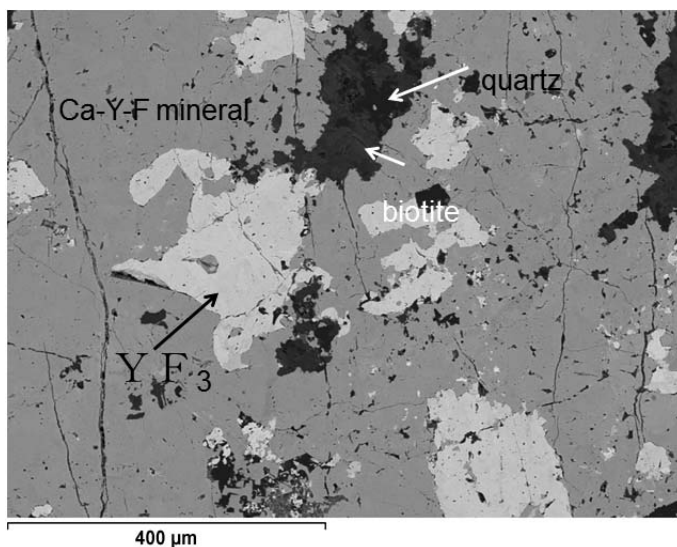


FIG. 3. Backscattered electron image of waimirite-(Y) from Saudi Arabia (light grey, subhedral crystal at the centre) associated with biotite (dark grey) and quartz (black) enclosed in the undetermined Ca-Y-F mineral (medium grey). Field of view: $\sim 0.86 \text{ mm} \times 0.65 \text{ mm}$.

TABLE 1. Analytical data for waimirite-(Y) from Brazil (mean of 24 point analyses).

Constituent	Wt.%	Range	SD	Probe standard
F	29.27	28.43–30.19	0.47	MgF ₂
Y	37.25	34.78–38.89	1.16	YAG
La	0.19	0.01–0.28	0.06	La_Ed
Ce	0.30	0.19–0.46	0.07	Ce_Ed
Pr	0.15	0.03–0.25	0.08	Pr_Ed
Nd	0.65	0.57–0.81	0.06	Nd_Ed
Sm	0.74	0.66–0.87	0.05	Sm_Ed
Gd	1.86	1.65–2.09	0.11	Gd_Ed
Tb	0.78	0.60–0.95	0.08	Tb_Ed
Dy	8.06	7.36–8.81	0.34	Dy_Ed
Ho	1.85	1.47–2.35	0.23	Ho_Ed
Er	6.38	5.80–7.24	0.36	Er_Ed
Tm	1.00	0.69–1.34	0.17	Tm_Ed
Yb	5.52	4.99–6.16	0.26	Yb_Ed
Lu	0.65	0.38–1.58	0.24	Lu_Ed
Ca	0.83	0.71–0.97	0.07	diopside
O	(2.05)			
Total	(97.53)			

belong to the associated halloysite. The percentage of F obtained from the chemical analysis of waimirite-(Y) is not sufficient to neutralize the

cations. The presence of O is required. If we consider O = 2.05 wt.%, the formula is charge-balanced. The empirical formula (based on

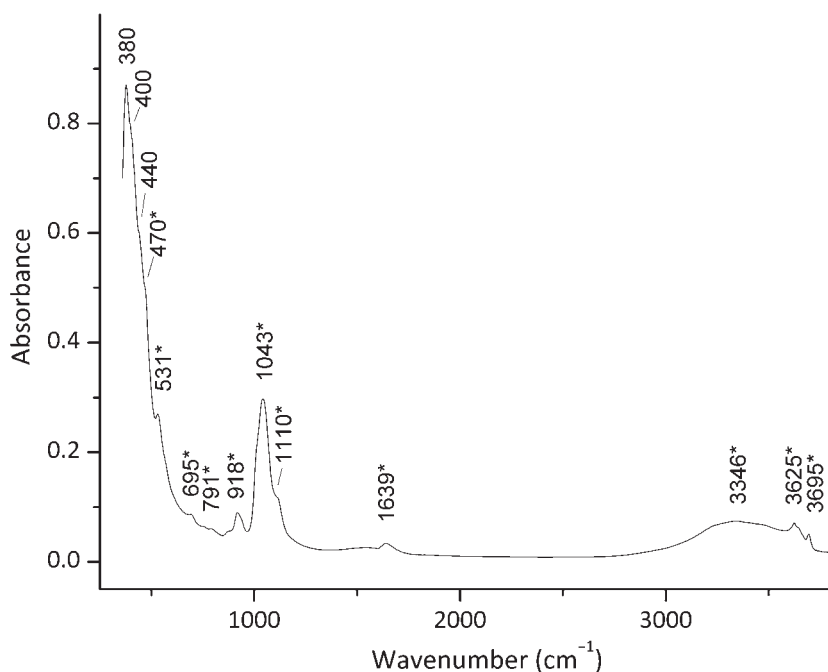


FIG. 4. Infrared spectrum of waimirite-(Y) with halloysite admixture (the bands marked with *) from Brazil.

TABLE 2. Analytical data for waimirite-(Y) from Saudi Arabia (mean of 24 point analyses).

Constituent	Wt. %	Range	SD	Probe standard
F	34.34	33.44–35.19	0.88	DyF ₃
Y	44.61	43.22–48.84	1.32	Y-Glass: SiO ₂ 54.3, Al ₂ O ₃ 12.7, CaO 20.5, Y ₂ O ₃ 11.8 wt. %
Ce	0.08	0.04–0.12	0.04	Ce-Glass: SiO ₂ 54.2, Al ₂ O ₃ 12.8, CaO 20.4, Ce ₂ O ₃ 11.9 wt. %
Nd	0.04	0.02–0.07	0.03	Nd-Glass: SiO ₂ 54.4, Al ₂ O ₃ 12.8, CaO 20.6, Nd ₂ O ₃ 11.8 wt. %
Sm	0.14	0.11–0.18	0.03	Sm-Glass: SiO ₂ 54.7, Al ₂ O ₃ 12.9, CaO 20.8, Sm ₂ O ₃ 11.2 wt. %
Gd	2.95	2.57–3.41	0.43	Gd-Glass: SiO ₂ 54.8, Al ₂ O ₃ 12.1, CaO 20.7, Gd ₂ O ₃ 12.1 wt. %
Tb	0.72	0.59–0.81	0.12	Tb-Glass: SiO ₂ 54.6, Al ₂ O ₃ 12.6, CaO 20.2, Tb ₂ O ₃ 11.9 wt. %
Dy	7.77	6.84–7.96	0.86	Dy-Glass: SiO ₂ 54.7, Al ₂ O ₃ 12.5, CaO 20.6, Dy ₂ O ₃ 12.0 wt. %
Ho	2.27	1.95–2.50	0.29	Ho-Glass: SiO ₂ 54.6, Al ₂ O ₃ 12.8, CaO 20.7, Ho ₂ O ₃ 11.9 wt. %
Er	5.39	5.05–5.68	0.32	Er-Glass: SiO ₂ 54.6, Al ₂ O ₃ 12.6, CaO 20.5, Er ₂ O ₃ 11.9 wt. %
Tm	0.69	0.61–0.75	0.07	Tm-Glass: SiO ₂ 54.8, Al ₂ O ₃ 12.4, CaO 20.3, Tm ₂ O ₃ 11.9 wt. %
Yb	1.36	1.03–1.56	0.29	Yb-Glass: SiO ₂ 54.7, Al ₂ O ₃ 12.6, CaO 20.7, Yb ₂ O ₃ 1.02 wt. %
Na	0.06	0.02–0.09	0.04	NaAlSi ₃ O ₈
Ca	0.08	0.03–0.05	0.02	CaSiO ₃
O	(0.80)			
Total	(101.30)			

one cation) is $(Y_{0.69}Dy_{0.08}Er_{0.06}Yb_{0.05}Ca_{0.03}Gd_{0.02}Ho_{0.02}Nd_{0.01}Sm_{0.01}Tb_{0.01}Tm_{0.01}Lu_{0.01})_{\Sigma 1.00}[F_{2.54}O_{0.21}\square_{0.25}]_{\Sigma 3.00}$. The low analytical total is assumed to be due to the subtraction of halloysite. Note that ionic conductivity of synthetic orthorhombic YF_3 and HoF_3 is related to vacancies in F sites (Sorokin *et al.*, 2002, Trnovcová *et al.*,

2003). Vacancy abundance in the study of synthetic HoF_3 (Sorokin *et al.*, 2002) is comparable with values inferred for waimirite-(Y). The simplified formula YF_3 requires: Y 60.93, F 39.07, total 100.00 wt.%.

Chemical analyses for waimirite-(Y) from Saudi Arabia were carried out with a JEOL

TABLE 3. Powder XRD data for waimirite-(Y).

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc.} (Å)	1 <i>d</i> _{obs.} (Å)	<i>I</i> _{obs.}	2 <i>d</i> _{obs.} (Å)	<i>I</i> _{obs.}	3 <i>d</i> _{obs.} (Å)	<i>I</i> _{obs.}
0	1	1	3.707	3.707	26	3.70	28	3.696	55
1	0	1	3.624	3.623	78	3.62	49	3.612	75
0	2	0	3.439	3.438	99	3.43	55	3.426	75
1	1	1	3.206	3.205	100	3.20	100	3.197	100
2	1	0	2.896	2.894	59	2.90	71	2.886	95
2	0	1	2.584	2.587	4			2.577	5
1	2	1	2.494	2.495	17	2.49	20	2.488	50
2	1	1	2.419	2.420	6	2.42	4	2.413	25
2	2	0	2.340	2.340	4	2.34	6	2.332	19
0	0	2	2.200	2.203	10	2.20	16	2.196	45
1	0	2	2.080					2.076	2
2	2	1	2.066	2.067	19	2.07	24	2.060	80
0	3	1	2.033					2.027	1
1	1	2	1.991	1.993	14	1.988	30	1.987	85
1	3	1	1.937	1.937	33	1.935	55	1.932	100
3	0	1	1.916	1.916	24			1.910	95
2	3	0	1.862	1.862	27	1.859	40	1.856	100
0	2	2	1.853			1.848	32	1.849	60
3	1	1	1.846	1.845	17			1.840	70
1	2	2	1.780	1.780	8	1.777	25	1.776	70
2	1	2	1.752	1.752	11	1.749	12	1.748	70
0	4	0	1.719	1.719	10	1.717	11	1.714	60
3	2	1	1.674	1.674	10	1.672	17	1.669	70
4	0	0	1.596	1.597	4	1.596	11	1.591	35
1	4	1	1.553	1.553	5	1.551	8	1.549	35
1	3	2	1.541	1.538	4	1.538	6	1.537	25
3	0	2	1.530	1.524	4			1.526	7
2	4	0	1.514					1.509	1
4	0	1	1.501					1.496	5
3	1	2	1.493	1.494	4	1.491	4	1.490	35
4	1	1	1.466	1.467	5	1.467	12	1.466	45
4	2	0	1.448	1.447	3	1.447	10	1.443	25
0	1	3	1.435	1.432	3	1.431	14	1.432	25
2	4	1	1.431					1.427	20
2	3	2	1.421	1.424	4	1.419	10	1.418	50
1	1	3	1.400			1.397	5	1.397	12
3	2	2	1.398	1.399	3			1.394	15
4	2	1	1.375					1.371	4
0	4	2	1.355	1.355	3	1.354	11	1.351	25

1. Pitinga mine, Presidente Figueiredo, Amazonas, Brazil (this paper). The strongest lines are given in bold.

2. Jabal Tawlah, Saudi Arabia (this paper).

3. Synthetic (Greis, 1976); $a = 6.3654$, $b = 6.8566$, $c = 4.3916$ Å, $V = 191.67$ Å³; PDF#32-1431.

JXA-8900 WDS electron microprobe analyser (20 kV, 20 nA, beam diameter = 2 µm). The average of five analyses and standard materials are presented in Table 2. The empirical formula is (Y_{0.79}Dy_{0.08}Er_{0.05}Gd_{0.03}Ho_{0.02}Tb_{0.01}Tm_{0.01}Yb_{0.01})Σ1.00[F_{2.85}O_{0.08}□_{0.07}]Σ3.00 on the basis of one cation.

Infrared spectrometry

The infrared (IR) absorption spectrum of waimirite-(Y) (Fig. 4) was obtained from a

powdered sample (mixed with KBr and pelletized) using a Bruker Alpha FTIR spectrometer in the range from 360 to 3800 cm⁻¹, with resolution of 4 cm⁻¹. A strong band at 380 cm⁻¹ (with shoulders at 400 and 440 cm⁻¹) corresponds to waimirite-(Y). All bands marked by an asterisk correspond to H₂O-bearing halloysite and coincide with the bands in the IR spectrum of halloysite-10 Å (Chukanov, 2014). In particular, the bands at 1639 and 3346 cm⁻¹ correspond to H₂O; the bands at 3625 and 3695 cm⁻¹ correspond to OH groups of halloysite-10 Å. No

TABLE 4. Crystal data, data-collection information and refinement details.

Space group	<i>Pnma</i> (#62)
Cell parameters	
<i>a</i> (Å)	6.38270(12)
<i>b</i> (Å)	6.86727(12)
<i>c</i> (Å)	4.39168(8)
<i>V</i> (Å ³)	192.495(6)
<i>Z</i>	4
Structural formula	(Y _{0.832} Dy _{0.168})F ₃
<i>D</i> _{calc.} (g/cm ³)	5.543
<i>μ</i> (mm ⁻¹)	74.130
Data collection	
Diffractionmeter	Rigaku R-Axis RAPID II
Radiation	CuKα (graphite-monochromatized)
Temperature	298 K
Crystal size (mm)	0.05 × 0.03 × 0.02
2θ _{max}	136.4°
Total no. oscillation images	180
Fundamental sweeps ω (°)	80.0–260.0 in 5.0 steps
χ (°)	54.0
φ (°)	0, 90, 180, 270
exposure rate (s/°)	60
Another sweep ω (°)	80.0–60.0 in 5.0 steps
χ (°)	0
φ (°)	0
exposure rate (s/°)	60
Index ranges	−7 ≤ <i>h</i> ≤ 7; −8 ≤ <i>k</i> ≤ 8; −5 ≤ <i>l</i> ≤ 5
Total no. reflections	1941
No. unique reflections	193
No. reflections, <i>I</i> > 2σ(<i>I</i>)	191
<i>R</i> _{int}	0.0360
Refinement	
No. of variable parameters	24
<i>R</i> ₁ , <i>I</i> > 2σ(<i>I</i>)	0.0163
<i>R</i> ₁ , all data	0.0173
<i>wR</i> ₂ , all data	0.0388
Goof	1.041
Δρ _{min} , Δρ _{max} (e / Å ³)	−0.596, 0.532

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}; w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]; P = [2F_c^2 + F_o^2]/3$$

other bands of OH groups are observed in the IR spectrum. Halloysite is poorly crystallized (which is typical of this mineral) and could not be detected by XRD. However, multiple distinct bands present in the IR spectrum definitely indicate its presence. The IR spectrum demonstrates the absence of carbonate and borate groups.

Crystallography

Powder XRD data for waimirite-(Y) from Brazil were obtained with a D8 Advance DaVinci diffractometer using CuK α radiation at the X-ray Diffraction Laboratory, Geosciences Institute, University of São Paulo. Data (in Å for CuK α) are given in Table 3. Unit-cell parameters refined from powder data (indexed by analogy with the synthetic equivalent) are as follows: Orthorhombic, *Pnma*, $a = 6.386(1)$, $b = 6.877(1)$, $c = 4.401(1)$ Å, $V = 193.28(7)$ Å³, $Z = 4$, $a:b:c = 0.929:1:0.640$.

The XRD investigations of waimirite-(Y) from Saudi Arabia were carried out with a single-crystal fragment of small size (0.05 mm \times 0.03 mm \times 0.02 mm) that was picked from the thin section used for the electron-microprobe analysis. The powder XRD pattern was obtained using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered CuK α radiation. The data were recorded on an imaging plate and processed with a Fuji BAS-2500 bio-image analyser using a computer program written by Nakamuta (1999). The XRD pattern (Table 3) is basically identical to those of waimirite from the type locality and of the

synthetic YF₃ (Greis, 1976). The unit-cell parameters were refined with an internal Si-standard reference material (NBS #640b) using a computer program by Toraya (1993); $a = 6.381(2)$, $b = 6.870(2)$, $c = 4.3915(12)$ Å, $V = 192.51(10)$ Å³, $Z = 4$, which are comparable to those refined from the single-crystal X-ray diffraction (SCXRD) data $a = 6.38270(12)$, $b = 6.86727(12)$, $c = 4.39168(8)$ Å, $V = 192.495(6)$ Å³, $Z = 4$.

The SCXRD data were obtained from the same fragment on a Rigaku R-AXIS RAPID curved imaging plate diffractometer using CuK α radiation monochromatized and focused by a VariMax confocal multilayer mirror. The orthorhombic space group symmetry of *Pnma* was suggested by extinctions in the SCXRD data. Experimental details of the data collection are given in Table 4. The data were corrected for absorption, empirically, Lorentz and polarization effects. The positions of Y and F atoms in the synthesized YF₃, determined by Cheetham and Norman (1974), were used as starting parameters in the present refinement of *SHELXL-97* (Sheldrick, 2008). The scattering factors for the neutral atoms and anomalous dispersion factors were taken from the *International Tables for X-ray Crystallography, Volume C* (Wilson, 1992). As Dy is the predominant lanthanide in waimirite-(Y) from Saudi Arabia, the scattering curve of Dy was employed in the calculations representing the lanthanides (*Ln*). The occupancy parameters of Y and Dy were refined at the Y site. The refinement converged into $R_1 = 0.0163$ and $wR_2 = 0.0388$ for 191 reflections with $F_o > 2\sigma(F_o)$. The final positional parameters, the equivalent isotropic

TABLE 5. Final atom positions, equivalent and anisotropic displacement parameters (Å²) for waimirite-(Y) from Saudi Arabia.

Site	x/a	y/b	z/c	U_{eq}		
Y*	0.36773(6)	0.25	0.44001(10)	0.0033(3)		
F1	0.0234(5)	0.25	0.5896(8)	0.0093(9)		
F2	0.1649(4)	0.0635(4)	0.1220(6)	0.0086(8)		
Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y*	0.0037(3)	0.0011(3)	0.0049(4)	0	−0.00086(15)	0
F1	0.0096(18)	0.0088(18)	0.0095(17)	0	0.0010(13)	0
F2	0.0093(12)	0.0061(14)	0.0103(12)	−0.0015(10)	−0.0004(10)	−0.0001(9)

* 0.832(18)Y + 0.168Dy.

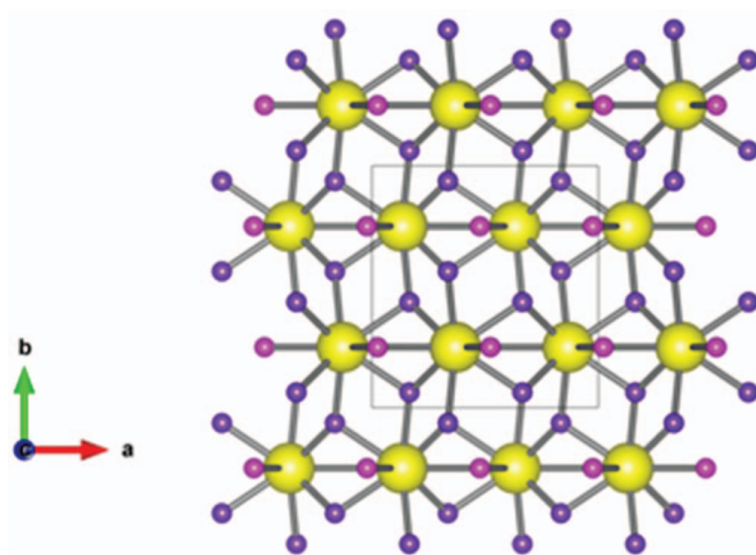


FIG. 5. A projection of the crystal structure of waimirite-(Y) onto (001) drawn using *VESTA* (Momma and Izumi, 2011). Yellow, pink and purple spheres indicate Y, F1 and F2, respectively.

displacement parameters and the anisotropic displacement parameters are given in Table 5. The crystal structure of waimirite-(Y) drawn using *VESTA* (Momma and Izumi, 2011) is shown in Fig. 5. Selected interatomic distances are summarized in Table 6. The bond valences were calculated from the interatomic distances following the procedure of Brown and Altermatt (1985), using the parameters of Brese and O'Keeffe (1991) and are listed in Table 7.

Discussion

Two polymorphs are known for YF₃, the trigonal ($P\bar{3}c1$, #165) (Uvarov *et al.*, 1984) having the fluocerite-type structure (Garashina *et al.*, 1980) and the orthorhombic ($Pnma$, #62) (Zalkin and Templeton, 1953; Cheetham and Norman, 1974). Trifluorides of rare-earth elements (*REE*: Y and lanthanoids, *Ln*, La–Lu) crystallize in the orthorhombic structure for Y, and *Ln* as small as Y, namely Sm–Lu, only, whereas trigonal *Ln*F₃ has

TABLE 6. Interatomic distances (Å) for waimirite-(Y) from Saudi Arabia and isostructural synthetic analogues.

Waimirite-(Y) (Saudi Arabia)*	YF ₃ **	SmF ₃ ***	HoF ₃ **	YbF ₃ **
Y–F1	2.292(3)	2.282(4)	2.37	2.22
–F1	2.294(3)	2.287(4)	2.39	2.25
–F2 × 2	2.295(2)	2.281(3)	2.36	2.27
–F2 × 2	2.305(2)	2.299(3)	2.37	2.27
–F2 × 2	2.306(2)	2.310(2)	2.39	2.27
–F1	2.529(3)	2.538(4)	2.49	2.61
Mean	2.325	2.321	2.39	2.30
<i>a</i> (Å)	6.38270(12)	6.3537(7)	6.676	6.218
<i>b</i> (Å)	6.86727(12)	6.8545(7)	7.062	6.785
<i>c</i> (Å)	4.39168(8)	4.3953(5)	4.411	4.431
<i>V</i> (Å ³)	192.495(6)	191.42	207.96	186.94

* Present study; ** Cheetham and Norman (1974); *** Bukvetskii and Garashina (1977).

TABLE 7. Bond-valence sums weighted on the occupancies for waimirite-(Y) from Saudi Arabia.

	— Y ($Y_{0.832}Dy_{0.168}$) —			Sum
F1	0.353	0.351	0.186	0.891
	0.351			
	0.186			
F2	0.350	0.341	0.340	1.032
	0.350	0.341	0.340	1.032
	0.341			
	0.341			
	0.340			
Sum	0.340			
	2.955			2.955

been reported for all *REE* with any size of ions. The trigonal *REEF*₃ minerals are rich in the larger *Ln* ions, i.e. *LREE*, and are known and described as dominated by Ce or La, fluocerite-(Ce) (Styles and Young, 1983) and fluocerite-(La) (Chistyakova and Kazakova, 1969), respectively. In the crystal structure of fluocerite-(Ce) and its synthetic *Ln*-equivalents, *REE* are coordinated by nine F atoms with two more distant neighbours (Zalkin and Templeton, 1985; Kondratyuk *et al.*, 1988).

On the other hand, waimirite-(Y), YF₃, is the only *REEF*₃ orthorhombic mineral species. The Y atom forms a 9-coordinated YF₉ tricapped trigonal (an YF₆ trigonal prism with an extra F atom attached to each of its three rectangular faces) in the crystal structure of orthorhombic YF₃ (Cheetham and Norman, 1974). The present crystallographic investigation confirmed that the

crystal structure of waimirite-(Y) is isostructural with the synthetic orthorhombic YF₃, as well as the *LnF*₃ (Bukvetskii and Garashina, 1977 for Sm, Ho and Yb; Garashina and Vishnyakov, 1977 for Ho).

The unit-cell volume of orthorhombic *REEF*₃ (*REE* = Y and Sm–Lu) tends to increase with increasing ionic radii of *REE*³⁺. However, as Garashina *et al.* (1980) pointed out, the increase is not isotropic. One dimension, *c*, remains mostly constant and decreases slightly with the increase in the radii of *REE*³⁺, whereas two other dimensions, *a* and *b*, increase. Garashina *et al.* (1980) explained the anisotropy in the unit cell with the anomalous *REE*–F interatomic distance. The longest distance among nine *REE*–F of the *REEO*₉ polyhedron decreases, although the other shorter eight *REE*–F distances increase, as usual, with increasing ionic radii of *REE*³⁺. Garashina *et al.* (1980) suggested a reduction in the contribution of the 9th F for the chemical bond to *REE*. Such structural features relating to the *REE*³⁺ radius were observed in waimirite-(Y) from Saudi Arabia. The *REE*–F interatomic distances and unit-cell parameters of waimirite-(Y) are close to those of synthetic YF₃ and HoF₃ (Table 6). The bond-valence calculation (Table 7) revealed the scarce contribution in chemical bond between the 9th F and (Y,Dy) [0.186] in waimirite-(Y) from Saudi Arabia.

About 80 atomic % of *REEs* are Y in waimirite-(Y) from Saudi Arabia and the remaining 20% are lanthanoids (La–Lu). Dysprosium is the dominant element among the lanthanoids. The chemistry of waimirite-(Y) from Saudi Arabia shows a lanthanoid distribution pattern rich in *HREE* (Fig. 6). The replacement of *HREE* such as Dy

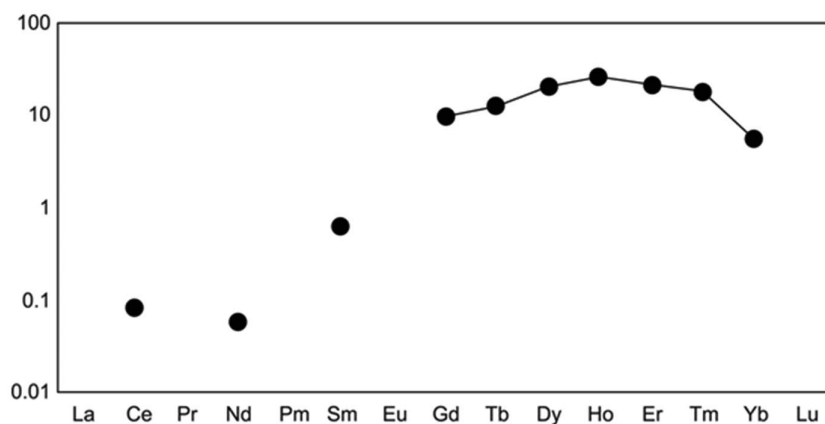


FIG. 6. Chondrite-normalized lanthanide distribution pattern of waimirite-(Y).

for Y conduce very slight variation in crystallographic values of waimirite-(Y) from Saudi Arabia in comparison to the pure YF₃. Consequently, the unit-cell parameters and interatomic distances of waimirite-(Y) from Saudi Arabia are very close to those of pure YF₃. Dysprosium has been a valued resource for recent material engineering in magnet industries. Waimirite-(Y), (Y,Dy)F₃, is the most important ore mineral in the REE deposit at Jabal Tawlah, Saudi Arabia.

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