

**ARISITE-(Ce), A NEW RARE-EARTH FLUORCARBONATE  
 FROM THE ARIS PHONOLITE, NAMIBIA, MONT SAINT-HILAIRE  
 AND THE SAINT-AMABLE SILL, QUEBEC, CANADA**

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ABSTRACT

Arisite-(Ce), ideally  $\text{NaCe}_2(\text{CO}_3)_2[(\text{CO}_3)_{1-x}\text{F}_{2x}]\text{F}$ , is a new layered, rare-earth fluorocarbonate mineral from the Aris phonolite (Namibia), Mont Saint-Hilaire (Quebec), and the Saint-Amable sill (Quebec). At the Aris phonolite, arisite-(Ce) occurs as vitreous, transparent, beige, beige-yellow, light lemon yellow to pinkish, tabular, hexagonal plates and prisms up to 1.5 mm in miarolitic cavities. At Mont Saint-Hilaire, arisite-(Ce) occurs in alkaline pegmatite veins, sodalite syenite and sodalite syenite xenoliths as pale pink, silvery or very pale brown, micaceous plates with a rough hexagonal outline, as thin fibers (5  $\mu\text{m}$  thick), as isolated crystals, as irregular clusters, rosettes or spherical aggregates 0.1 to 2 mm in diameter. In the Saint-Amable phonolite sill, arisite-(Ce) occurs as thin, flexible, pearly to silvery white, rounded to irregular micaceous plates (0.3 to 0.5 mm) in spherical aggregates or rosettes. Arisite-(Ce) is brittle, has a conchoidal fracture, poor cleavage perpendicular to (001), and a Mohs hardness of approximately 3–3½; it is non-fluorescent under either long- or short-wave UV radiation, dissolves slowly in room-temperature dilute HCl, and sinks in methylene iodide. Its density  $D_{\text{calc}}$  is 4.126 g/cm<sup>3</sup> for Z = 1 (Aris). Arisite-(Ce) is uniaxial negative, has a sharp extinction, with both  $\omega$  and  $\epsilon$  exhibiting a range of values within each grain:  $1.696 < \omega < 1.717(4)$  and  $1.594 < \epsilon < 1.611(3)$ , a result of chemical zoning attributed to both Ce-for-La and Na-for-Ca substitutions. The average empirical formula for arisite-(Ce) from the Aris phonolite is  $(\text{Na}_{0.97}\text{Ca}_{0.03})_{\Sigma 1.00}(\text{Ce}_{0.92}\text{La}_{0.80}\text{Nd}_{0.11}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{Ca}_{0.09})_{\Sigma 1.97}(\text{CO}_3)_2[(\text{CO}_3)_{0.71}\text{F}_{0.59}]$

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F. The mineral is hexagonal,  $P\bar{6}m2$ ,  $a$  5.1109(2),  $c$  8.6713(4) Å,  $V$  196.16(6) Å<sup>3</sup>. The strongest 11 lines of the powder X-ray-diffraction patterns [ $d_{hkl}^{NAM}/d_{hkl}^{MSH}$  in Å( $I_{obs}^{NAM}/I_{obs}^{MSH}, hkl$ )] are: 4.439/4.428(100/100,100), 4.352/4.317(52/60,002), 3.103/3.097(87/80,102), 2.561/2.558(38/50,110), 2.424/2.415(21/40,103), 2.171/2.162(12/30,004), 1.9748/1.969(42/60,202), 1.9501/1.941(16/30,104), 1.9169/1.910(12/20,113), 1.6547/1.650(11/30,114) and 1.5640/1.560(13/20,212). Arisite-(Ce) is a late-stage, postmagmatic to hydrothermal mineral at all three localities. It is a member of the flat-lying layered REE fluorcarbonate group that includes lukechangite-(Ce), cordylite-(Ce), huanghoite-(Ce), cebaite-(Ce), kukharenkoite-(Ce) and kukharenkoite-(La). All these fluorcarbonates have crystal structures characterized by separate layers of carbonate, F, REE and alkali or alkaline-earth elements. The mineral's name recalls the type locality, the Aris phonolite, Namibia.

**Keywords:** arisite-(Ce), phonolite, rare-earth elements, fluorcarbonate, new species, Mont Saint-Hilaire, Saint-Amable, Quebec, Aris, Namibia.

## SOMMAIRE

Nous décrivons l'arisite-(Ce), idéalement  $\text{NaCe}_2(\text{CO}_3)_2[(\text{CO}_3)_{1-x}\text{F}_{2x}]$ F, nouvelle espèce minérale fluorcarbonatée de terres rares en couches, découvert dans la phonolite d'Aris, en Namibie, au mont Saint-Hilaire et dans le filon-couche de Saint-Amable, au Québec. Au premier endroit, l'arisite-(Ce) se présente en plaquettes hexagonales et prismes transparents, à l'éclat vitreux, de couleur beige, beige-jaune, jaune-citron pâle à rosâtre, atteignant 1.5 mm dans des cavités miarolitiques. Au mont Saint-Hilaire, on trouve l'arisite-(Ce) dans des veines de pegmatite alcaline, dans la syénite à sodalite et des xénolites de syénite à sodalite, en plaquettes micacées rose pâle, argentées ou brun très pâle, avec une allure quasi-hexagonale, en fines fibres d'une épaisseur de 5 µm, en cristaux isolés, en groupes irréguliers, en rosettes ou en agrégats sphériques de 0.1 à 2 mm de diamètre. Au filon-couche de phonolite à Saint-Amable, l'arisite-(Ce) se présente en minces plaquettes micacées flexibles, nacrées à blanc argenté, arrondies ou irrégulières allant de 0.3 à 0.5 mm en amas sphériques ou en rosettes. L'arisite-(Ce) est cassante, possède une fracture conchoïdale, un piètre clivage perpendiculaire à (001), et une dureté de Mohs d'environ 3–3½; elle est non fluorescente en lumière ultraviolette en longueur d'onde courte ou longue. Elle se dissout lentement à température ambiante dans HCl dilué, et est plus dense que l'iode de méthylène. Sa densité calculée est 4.126 g/cm<sup>3</sup> pour  $Z = 1$  (Aris). L'arisite-(Ce) est uniaxe négative, possède une extinction nette, et les deux indices  $\omega$  et  $\epsilon$  montrent une variabilité dans chaque grain,  $1.696 < \omega < 1.717(4)$  et  $1.594 < \epsilon < 1.611(3)$ , résultat d'une zonation chimique attribuable aux substitutions Ce-pour-La et Na-pour-Ca. La formule empirique moyenne de l'arisite-(Ce) de Aris est  $(\text{Na}_{0.97}\text{Ca}_{0.03})_{\Sigma 1.00}(\text{Ce}_{0.92}\text{La}_{0.80}\text{Nd}_{0.11}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{Ca}_{0.09})_{\Sigma 1.97}(\text{CO}_3)_2[(\text{CO}_3)_{0.71}\text{F}_{0.59}]$ F. Le minéral est hexagonal,  $P\bar{6}m2$ ,  $a$  5.1109(2),  $c$  8.6713(4) Å,  $V$  196.16(6) Å<sup>3</sup>. Les onze raies les plus intenses du spectre de diffraction X, méthode des poudres [ $d_{hkl}^{NAM}/d_{hkl}^{MSH}$  en Å( $I_{obs}^{NAM}/I_{obs}^{MSH}, hkl$ )] sont: 4.439/4.428(100/100,100), 4.352/4.317(52/60,002), 3.103/3.097(87/80,102), 2.561/2.558(38/50,110), 2.424/2.415(21/40,103), 2.171/2.162(12/30,004), 1.9748/1.969(42/60,202), 1.9501/1.941(16/30,104), 1.9169/1.910(12/20,113), 1.6547/1.650(11/30,114) et 1.5640/1.560(13/20,212). L'arisite-(Ce) est un minéral tardif, postmagmatique et hydrothermal aux trois localités. C'est un membre du groupe des fluorcarbonates de terres rares en couches, qui inclut lukechangite-(Ce), cordylite-(Ce), huanghoite-(Ce), cebaite-(Ce), kukharenkoite-(Ce) et kukharenkoite-(La). Tous ces fluorcarbonates possèdent une structure cristalline à couches distinctes de carbonate, F, terres rares et éléments alcalins ou alcalino-terreux. Le nom rappelle la localité-type, la phonolite d'Aris, en Namibie.

(Traduit par la Rédaction)

**Mots-clés:** arisite-(Ce), phonolite, terres rares, fluorcarbonate, nouvelle espèce, Mont Saint-Hilaire, Saint-Amable, Québec, Aris, Namibie.

## INTRODUCTION

Arisite-(Ce) is a new rare-earth fluorcarbonate mineral recently discovered in miarolitic cavities in the Aris phonolite quarry, central Namibia (NAM), and in alkaline pegmatites and sodalite syenite xenoliths at Mont Saint-Hilaire (MSH), Quebec, Canada. In addition, arisite-(Ce) has been discovered in miarolitic cavities in the Saint-Amable phonolite sill, Varennes quarry, Verchères County, Quebec (STA), which shares a very similar mineralogy and petrology to that of the Aris phonolite. The species now known as arisite-(Ce) was first confirmed as an unknown mineral from the Aris phonolite by one of the authors (U.K.) in 2000, on the basis of material he had received independently from several German mineral collectors who suspected a new

species on the basis of analytical results obtained from a commercial laboratory. The NAM samples used in this description were provided by two micromineral collectors, another of the coauthors (W.L.) and R. Tibbit, who purchased the material from yet another coauthor (A.G.P.). The MSH and STA samples have been known for some time as UK60 (Chao *et al.* 1990) and VUK11 (Horváth *et al.* 1998); their powder X-ray-diffraction (XRD) patterns are identical. The MSH material was originally collected by László and Elsa Horváth in 1984, and then several times since that date. The STA material was originally collected by the same two collectors in 1995. A fortuitous comparison of powder XRD film patterns revealed the two unknowns from NAM and MSH to be one and the same mineral. As such, these two localities are treated as cotype localities (material

from STA was added only after the IMA CNMNC proposal was accepted). However, only the NAM material provided crystals suitable for detailed single-crystal X-ray analysis of the structure.

The mineral and name have been approved by the IMA CNMNC (IMA no. 2009-013). The name recalls the type locality, the Aris phonolite, Namibia. Cotype material has been deposited at the Canadian Museum of Nature [arisite-(Ce) from Aris: CMNMC 86067, arisite-(Ce) from MSH: CMNMC 86068].

#### BACKGROUND INFORMATION

The Aris phonolite in Namibia (Figs. 1, 2) is part of the late Tertiary ( $33 \pm 1$  Ma, Fitch & Miller 1984) Auas alkaline volcanic province, which extends 65 km from Windhoek in the north to Rehoboth in the south. This volcanic province represents the most recent occurrence of alkaline magmatism along the western margins of southern Africa, and is similar to the Klinghardt Mountain alkaline volcanic province further to the south (37 Ma: Kröner 1973, Marsh 1987). The Auas alkaline volcanic suite intrudes metasedimentary rocks (quartz-feldspar gneiss, mica schist and amphibolite)

of the Paleoproterozoic Hohewarte complex. Gevers (1934) identified over 100 occurrences of both intrusive and extrusive alkaline rocks including trachyte, phonolite, shonkinite, alkali peridotite, and also a variety of tuffs, agglomerates and breccias. The phonolite and trachyte rocks occur as dikes and plugs exposed as eroded outcrops and caps on elevated hills and buttes. The Aris phonolite dike occurs in the southern part of the province as a fine- to medium-grained, aphyric rock consisting predominantly of sanidine, nepheline and aegirine, with accessory haiüyne, leucite, monazite and zircon (von Knorring & Franke 1987). Phonolite is being recovered for road and building material in the Ariskop and Railroad quarries. The phonolite contains numerous miarolitic cavities that range from 0.1 mm to 10 cm in diameter, many of which are “wet”, containing residual hydrothermal formational fluids that are released when the cavities are broken open. Preliminary X-ray-computed tomography at the University of Texas (Austin) indicates that 15–20% of the phonolite is comprised of two-phase fluid + vapor-filled cavities. The miarolitic cavities host a range of apgaitic mineral species, including abundant villiaumite, aegirine, labuntsovite-group minerals, tapersuatsiaite, natrolite,

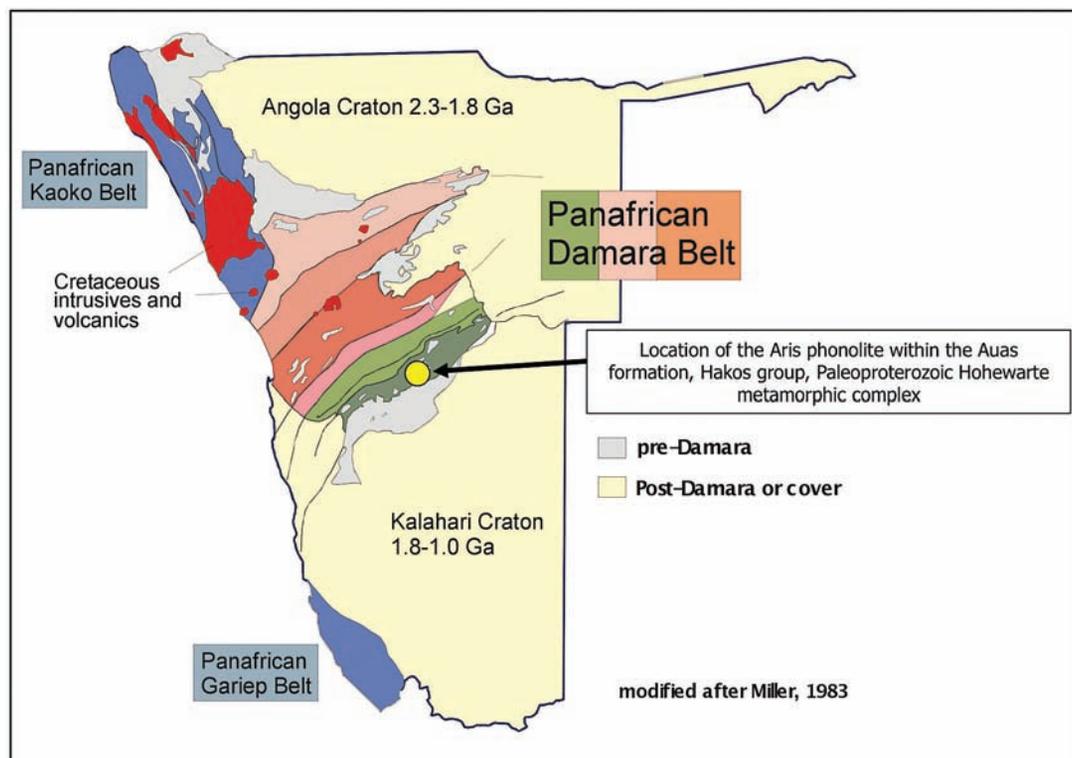


FIG. 1. Regional geology of Namibia showing the location of the Aris phonolite within the Auas Formation, Hakos Group, Paleoproterozoic Hohewarte metamorphic complex. This figure is reproduced from Fitch & Miller (1984).

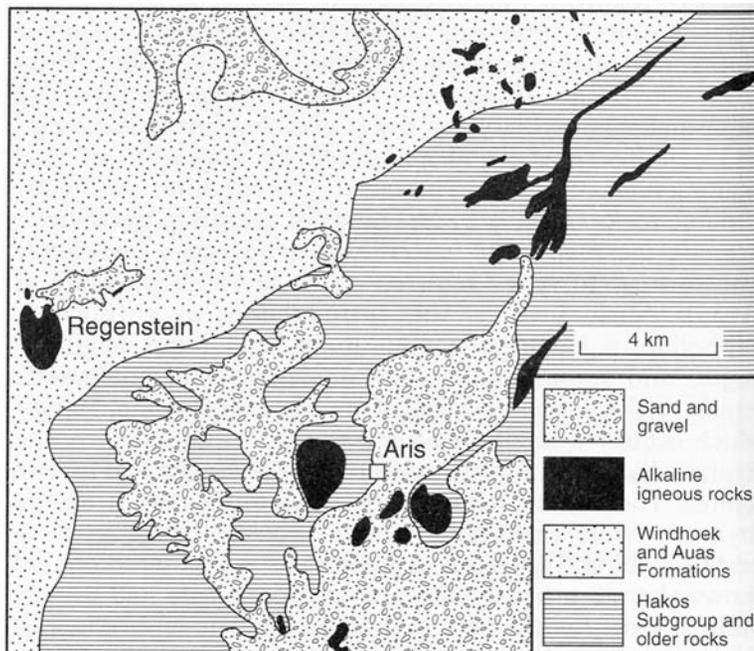


FIG. 2. Regional geology map showing location of Aris phonolite, Namibia. This figure is reproduced from Fitch & Miller (1984).

analcmite, manganoneptunite, apophyllite-(KF), fluorite, and makatite. An extensive list of the known minerals within the Aris quarries has been given by Sturla *et al.* (2005). A detailed study of the mineralogy and paragenesis of these miarolitic cavities by the senior author is still on-going.

Mont Saint-Hilaire is a well-known Cretaceous alkaline intrusive complex located 40 km east of Montreal, Quebec, and is part of the Monteregian Hills petrographic province. The nepheline and sodalite syenites, with associated alkaline pegmatite dikes, xenoliths and igneous breccias, are well exposed by quarrying operations on the east side of the mountain. The petrology of the complex was discussed by Currie *et al.* (1986), and the mineralogy, by Horváth & Gault (1990). Mont Saint-Hilaire is a mineralogically prolific locality with over 400 species known, many of which are REE-bearing carbonates.

The Saint-Amable phonolite sill (Fig. 3) shares striking mineralogical and petrological similarities with the Aris phonolite. The sill is located between the towns of Varennes and Saint-Amable in Verchères County, Quebec, approximately 20 km east-northeast of Montreal, and 7 km east of the St. Lawrence River (latitude: 45°39' N, longitude: 73°17' W). The sill is genetically related to the Cretaceous alkaline Monteregian Hills petrographic province, which forms an east-west-trending belt from Mont Mégantic (190 km east

of Montreal) to Oka (35 km west of Montreal). Along with the Saint-Amable sill, a number of other major sills have been exposed around the Montreal area by quarrying and building excavations. The Saint-Amable sill is the most extensive and thickest (0.6 to 1.2 m) yet exposed. It is likely coeval with the two closest Monteregian Hills, Mont Saint-Bruno and Mont Saint-Hilaire, dated at 90 and 135 ± 10 Ma, respectively (Gold 1979, Eby 1984, Horváth *et al.* 1998). The sill is a result of multiple injections of phonolitic magma. The phonolite is fine-grained (average grain-size 40 µm), dark grey in color, comprised predominantly of phenocrysts of nepheline in a trachytic matrix of sanidine, aegirine and natrolite. As with the Aris phonolite, the Saint-Amable phonolite contains numerous mineralized cavities and seams that are the source of rare and well-formed postmagmatic and hydrothermal minerals. Arisite-(Ce), or VUK11 as it was formally known, was found in 1995 in the southeastern corner of the quarry in one of these miarolitic cavities. A full description of the mineralogy of the Saint Amable sill can be found in Horváth *et al.* (1998).

#### PHYSICAL AND OPTICAL PROPERTIES

Arisite-(Ce) is brittle, has a conchoidal fracture, a poor cleavage parallel to (001), a Mohs hardness of approximately 3–3½, is non-fluorescent under either

long- or short-wave UV radiation, and dissolves slowly with effervescence in room temperature, dilute HCl. Arisite-(Ce) sinks in methylene iodide (*i.e.*, density  $> 3.3 \text{ g/cm}^3$ ) and has a calculated density of  $4.126 \text{ g/cm}^3$  (NAM),  $Z = 1$ . Arisite-(Ce) is uniaxial negative, has a sharp extinction, with both  $\omega$  and  $\varepsilon$  exhibiting a range of values within each grain: 1.696–1.717(4) and 1.594–1.611(3), respectively, a result of chemical zoning attributed to both Ce-for-La and 2Na-for-Ca substitutions (see below).

*The Ariskop and Railroad quarries,  
Aris phonolite, Namibia*

Arisite-(Ce) from the Aris phonolite (NAM) occurs as euhedral, hexagonal plates up to 1.5 mm (average:  $0.2 \times 1.0 \text{ mm}$ ) and rare tabular, hexagonal prisms, in miarolitic cavities (Fig. 4a). The crystals are vitreous, transparent, and range in color from beige, beige-yellow, light lemon yellow to pinkish. There is commonly a heavily included zone between the core and rim that imparts a clouded appearance to the

crystals. Observed forms include a dominant  $\{001\}$  pinacoid, with minor  $\{100\}$  prism. Re-entrant angles have been noted on thicker crystals, but the twin law is not known. Associated minerals include aegirine, analcime, apatite, fluorite, manganoneptunite, microcline, natrolite, sphalerite, taperssuatsiaite and the unnamed Fe-analogue of zackharovite. Arisite-(Ce) is a late-stage mineral in miarolitic cavities in the phonolite, a result of crystallization from residual magmatic or hydrothermal fluids. It may be replaced by fine-grained, yellowish bastnäsite-(Ce), resulting in opaque, dull crystals.

*Mont Saint-Hilaire, Quebec*

Arisite-(Ce) has been discovered in small alkaline pegmatite veins and in lenticular patches within sodalite syenite and sodalite syenite xenoliths at Mont Saint-Hilaire (MSH). It occurs as pale pink to silvery to very pale brown, micaceous plates with a rough hexagonal outline, or as thin, narrow strips that grade to thin fibers (Fig. 4b). It also develops as isolated crystals, in rosettes, irregular clusters, and in spherical aggregates

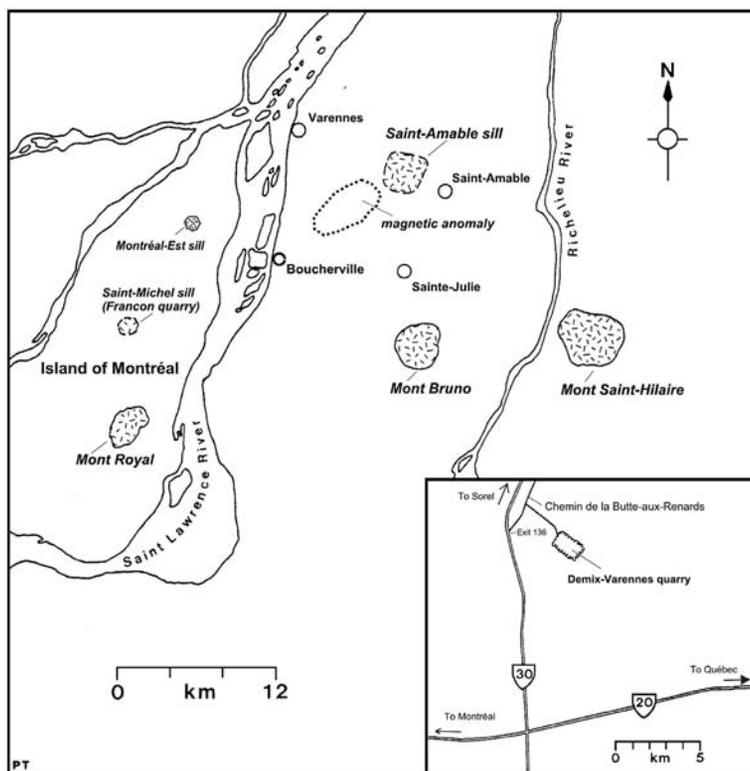


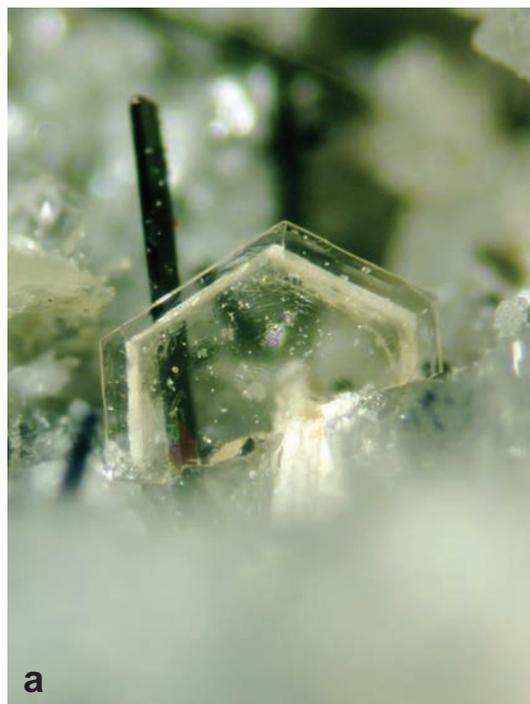
FIG. 3. Locality map showing the Saint-Amable sill and other intrusions of the Monteregian alkaline province, including Mont Saint-Hilaire. Inset: location of the Demix-Varennes quarry and the Saint-Amable sill.

0.1 to 2 mm in diameter. Individual {001} plates are exceedingly thin, no more than 5  $\mu\text{m}$  in thickness, and all crystals have a distinctive pearly luster. Forms include the {001} pinacoid (dominant), and the {100} prism (very minor). Within the alkaline pegmatites, it is associated with aegirine, albite, a clinoamphibole, a

eudialyte-group mineral, microcline, mosandrite, natrolite, gonnardite, and fluorapatite. Within the sodalite syenite xenoliths, it is associated with aegirine, "tetranatrolite", polyolithionite, fluorite, sodalite, serandite, microcline, catapleite, pyrite, pyrochlore, pyrrhotite, goethite, an alkali feldspar, and an astrophyllite-group mineral. Arisite-(Ce) is a rare, late-stage accessory mineral found predominantly in cavities (5–15 mm across) in alkaline pegmatite veins in the nepheline syenite, and, more rarely, in sodalite syenite xenoliths. It is noteworthy that arisite-(Ce) in the sodalite syenite xenoliths is the only phase not covered by a brown to pale brown film (probably a hydrocarbon), indicating that it is paragenetically one of the last minerals to crystallize.

*Saint-Amable sill, Varennes quarry,  
Verchères county, Quebec*

Arisite-(Ce) in the Saint-Amable sill (STA) occurs as thin, flexible, pearly, silvery white, rounded to irregular micaceous plates 0.3 to 0.5 mm in diameter. The plates form spherical or rosette-like aggregates. It is associated with natrolite, aegirine, albite, manganoneptunite, rhodochrosite, sphalerite, astrophyllite, and a beige to brown unidentified mineral.



**a**

FIG. 4. a. Arisite-(Ce) from the Aris phonolite, Namibia. Field of view: 2 mm. Photo taken by W. Lechner. b. Arisite-(Ce) from Mont Saint-Hilaire, Quebec. Field of view: 2 mm. Photo taken by M.E. Back, of the Royal Ontario Museum.



**b**

## CHEMICAL COMPOSITION

*Fourier-transform infrared spectroscopy*

Single crystals of arisite-(Ce) from Mont Saint-Hilaire and Namibia were analyzed by Fourier-transform infrared spectroscopy (FTIR). The crystal was positioned in a Spectra-Tech low-pressure diamond-anvil cell and pressed into a thin film. An analysis was undertaken using a Bomem Michelson MB120 spectrometer interfaced to a Spectra-Tech IR-Plan research microscope, equipped with a 0.25 mm diameter, narrow-band MCT (mercury cadmium telluride) detector. The sample was masked with fixed 100  $\mu\text{m}$  circular apertures. Spectra were acquired in the 4000 to 660  $\text{cm}^{-1}$  range at a resolution of 4  $\text{cm}^{-1}$ , by coadding 200 interferograms (Table 1). A digital version of the spectra is available from the Depository of Unpublished Data [document Arisite-(Ce) CM48\_661]. The presence of bands within the 3450–3200  $\text{cm}^{-1}$  region attributed to OH-stretching vibrations are considered to be due to the presence of minor  $\text{OH}^-$  substituting for  $\text{F}^-$  in the structure. Figure 5 shows the FTIR spectrum of arisite-(Ce) from Namibia.

*Raman spectroscopy*

A grain of arisite-(Ce) from Mon Saint-Hilaire was analyzed using a Horiba Jobin Yvon XPLOA Raman spectrometer interfaced with an Olympus BX41 microscope. A series of spectra were collected over the range 50 to 4000  $\text{cm}^{-1}$ . Each was based on an average of three 5 s acquisition cycles. The wavelength of

the excitation radiation was 532 nm; we used a 1200 grating, 100 $\times$  magnification, and a beam diameter of 2  $\mu\text{m}$ . A digital version of the spectra is available from the Depository of Unpublished Data [document Arisite-(Ce) CM48\_661]. The Raman data support the interpretations made on the basis of the FTIR data (Table 2, Fig. 6).

TABLE 1. FTIR DATA FOR ARISITE-(Ce) FROM NAMIBIA (NAM) AND MONT SAINT-HILAIRE (MSH)

NAM ( $\text{cm}^{-1}$ )	MSH ( $\text{cm}^{-1}$ )	Peak breadth	Transmittance	Designation
3427	3437	broad	strong	O-H stretching
3251	3244	broad	strong	O-H stretching
1790	1791	sharp	very weak	C-O stretching
1485	1473	relatively broad	very strong	asymmetric stretching mode of $[\text{CO}_3]$
1413		relatively broad	very strong	asymmetric stretching mode of $[\text{CO}_3]$
1075	1076	sharp	weak	symmetric stretching of $[\text{CO}_3]$
884	885	sharp	strong	out-of-plane bending of $[\text{CO}_3]$
856	857	sharp	strong	out-of-plane bending of $[\text{CO}_3]$
802		relatively sharp	strong	out-of-plane bending of $[\text{CO}_3]$
716	718	sharp	strong	in-plane bending of $[\text{CO}_3]$

Note: H–O–H bending mode at approximately 1600  $\text{cm}^{-1}$  is obscured by the relatively broad band centered at 1485  $\text{cm}^{-1}$ .

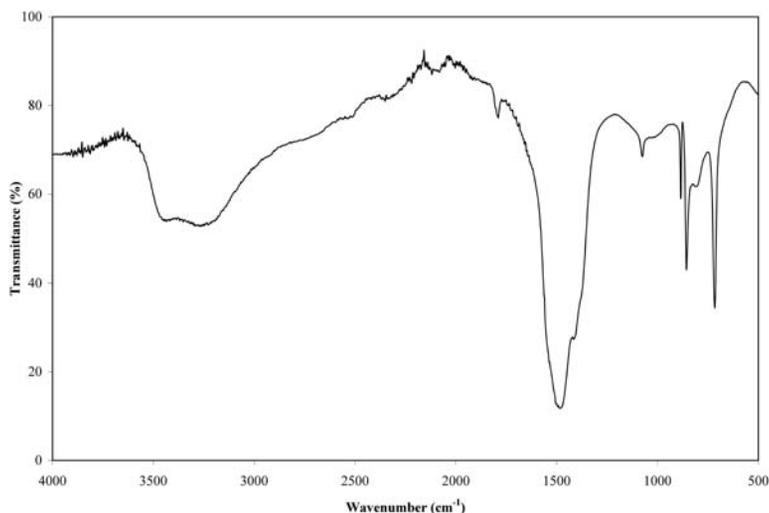


FIG. 5. FTIR spectrum of arisite-(Ce) from Aris, Namibia.

## TGA-DTA

Arisite-(Ce) from Mont Saint-Hilaire was heated from 25 to 1000°C in air using a heating rate of 5°C/minute, with a sample weight of 9.41 mg. Only two stages of weight loss were noted: (1) 205.8°C, corresponding to a 1% drop in weight, and (2) 382.0°C, corresponding to a 16.5% drop in weight. Both steps

seem to include two (or more) separable processes; both are considered to be due to CO<sub>2</sub> loss on heating. The low CO<sub>2</sub> obtained by TGA-DTA, compared to the amount calculated from EMPA results, is attributed to the variable ratio to CO<sub>3</sub><sup>2-</sup> to F<sup>-</sup> between samples from Namibia and Mont Saint-Hilaire.

## Laser-ablation ICP-MS

Two grains of arisite-(Ce) from Namibia were analyzed for <sup>13</sup>C (at.%) using a beam size of 80 μm, 60% power, 20.8 J/cm<sup>2</sup> fluence and a 5 Hz laser pulse. A standard of natural bastnäsite-(Ce) (Madagascar) was employed. The average number of counts (*n* = 5) obtained from the NAM crystals was 3895/s, and for the bastnäsite-(Ce) (*n* = 2), 4417/s. The total concentration of C in the NAM grains is less than that in bastnäsite-(Ce) (ideal concentration: 5.48 at.% C). Using the average number of counts given by the bastnäsite-(Ce) and the ideal concentration of C in bastnäsite-(Ce), the concentration of C in the NAM material was calculated to be 4.83 at.%. It should be noted that the estimated error is ±1 at.%. The LA-ICP-MS approach was also employed to check for the presence of B; values range from 8 to 11 ppm.

## Electron-microprobe analyses

Chemical analyses of arisite-(Ce) from Namibia and Saint-Amable were done with a JEOL 733 electron microprobe operating in wavelength-dispersive mode, using the Geller Microanalytical System and programs. The operating conditions were as follows: beam diameter of 20 μm, operating voltage 15 kV, and

TABLE 2. RAMAN DATA FOR ARISITE-(Ce) FROM MONT SAINT-HILAIRE (MSH)

Band (cm <sup>-1</sup> )	Peak breadth	Transmittance	Designation
152	relatively sharp	strong	lattice modes
187	relatively sharp	strong	lattice modes
396	relatively broad	weak	lattice modes
704	sharp	strong	in-plane bend of [CO <sub>3</sub> ]
1072	very sharp	very strong	symmetric stretching of [CO <sub>3</sub> ]
1455	relatively sharp	weak	asymmetric stretching of [CO <sub>3</sub> ]
1596	relatively broad	weak	H-O-H bend
1799	broad	weak	C-O stretching
2068	broad	weak	unassigned
2458	relatively sharp	strong	O-H stretch (as in bicarbonates)
2642	broad	weak	unassigned
3255	broad	strong	O-H stretching
3449	broad	strong	O-H stretching

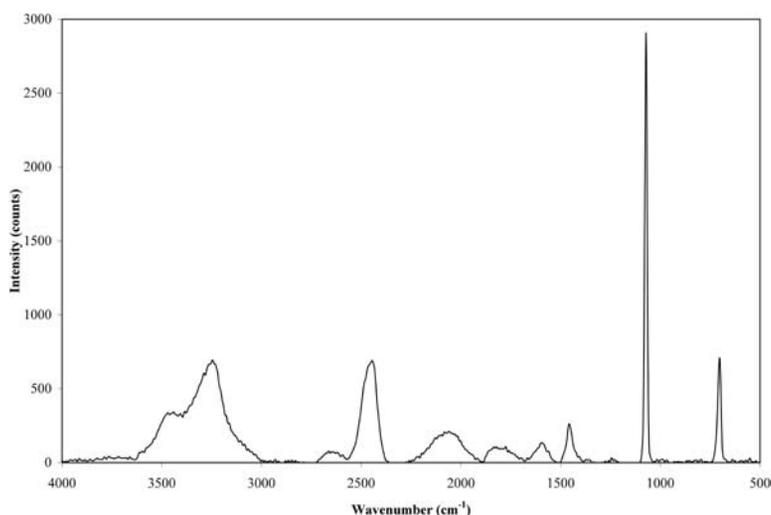


FIG. 6. Raman spectrum of arisite-(Ce) from Aris, Namibia.

a beam current of 10 nA (Na, Ca and F) and 20 nA (all other elements). Data reduction was performed using a PAP routine in XMAQNT (C. Davidson, CSIRO, pers. commun.). A total of 14 elements were sought, and the following standards were employed: Na ( $K\alpha$ , albite), Ca ( $K\alpha$ , calcite), Sr ( $L\alpha$ , celestine), La ( $L\alpha$ , synthetic  $LaPO_4$ ), Ce ( $L\alpha$ , synthetic  $CePO_4$ ), Pr ( $L\beta$ , synthetic  $PrPO_4$ ), Nd ( $L\alpha$ , synthetic  $NdPO_4$ ), Sm ( $L\alpha$ , synthetic  $SmPO_4$ ), Eu ( $L\alpha$ , synthetic  $EuPO_4$ ), Gd ( $L\alpha$ , synthetic  $GdPO_4$ ), Tb ( $L\alpha$ , synthetic  $TbPO_4$ ), Dy ( $L\beta$ , synthetic  $DyPO_4$ ), Ho ( $L\beta$ , synthetic  $HoPO_4$ ), and F ( $K\alpha$ ,  $CaF_2$ ). Given the difficulties in analyzing the samples for F by EMPA methods, and the importance of F in the structure, fluorine concentrations were measured using a TAP crystal and a fluorite standard ( $K\alpha$ ). The shape of the F  $K\alpha$  peak was compared using slow WDS scans in standard and sample to ensure the suitability of the fluorite standard. Count times for all elements were 25 seconds or 0.5% precision, with 25 second count times for the background. Samples from Namibia are

commonly zoned, with La-dominant sectors, identified as arisite-(La) (Piiilonen *et al.* 2010).

Chemical analyses of arisite-(Ce) from Mont Saint-Hilaire were done with a Camebax MBX electron microprobe operating in wavelength-dispersion mode, with the following operating conditions: beam diameter of 20  $\mu m$ , operating voltage 15 kV, and beam current 20 nA. A total of 11 elements were sought, and the following standards were employed: Na ( $K\alpha$ , albite), Ca ( $K\alpha$ , gehlenite), Sr ( $L\alpha$ , celestine), La ( $L\alpha$ , monazite), Ce ( $L\alpha$ , monazite), Pr ( $L\beta$ , synthetic REE glass), Nd ( $L\alpha$ , monazite), Sm ( $L\alpha$ , synthetic REE glass), Eu ( $L\alpha$ , synthetic REE glass), Gd ( $L\alpha$ , synthetic REE glass), and F ( $K\alpha$ , apatite). Count times for all elements were 25 seconds.

Table 3 contains individual and average values for arisite-(Ce) samples NAM and MSH. The analytical totals for the STA material were extremely low as a result of the minute size and thickness of the samples, and are not presented here. However, results indicate

TABLE 3. RESULTS OF ELECTRON-MICROPROBE (WDS) ANALYSES FOR ARISITE-(Ce) FROM NAMIBIA (NAM) AND MONT SAINT-HILAIRE (MSH)

	NAM-1	NAM-2	NAM-3	NAM-4	NAM-5	NAM-6	NAM Ave.	MSH-1	MSH-2	MSH-3	MSH Ave.
Na <sub>2</sub> O wt.%	5.82	5.86	5.96	5.64	5.96	6.08	5.89	4.51	4.44	4.52	4.49
CaO	1.03	1.43	1.43	3.03	1.00	1.15	1.51	5.29	5.42	5.47	5.39
SrO	0.02	0.00	0.01	0.32	0.19	0.11	0.11	2.80	2.67	2.86	2.78
La <sub>2</sub> O <sub>3</sub>	23.81	24.66	25.95	22.91	27.68	27.79	25.47	15.42	15.55	15.72	15.56
Ce <sub>2</sub> O <sub>3</sub>	31.11	30.72	29.08	31.01	28.59	28.26	29.80	30.84	30.98	30.32	30.71
Pr <sub>2</sub> O <sub>3</sub>	1.98	1.40	1.64	1.56	1.00	1.01	1.43	3.11	2.90	3.15	3.05
Nd <sub>2</sub> O <sub>3</sub>	4.64	4.10	3.27	3.37	2.73	3.11	3.54	8.03	8.10	8.22	8.12
Sm <sub>2</sub> O <sub>3</sub>	0.49	0.61	0.53	0.40	0.50	0.30	0.47	0.75	0.67	0.65	0.69
Eu <sub>2</sub> O <sub>3</sub>	0.00	0.14	0.00	0.03	0.15	0.06	0.06	0.02	0.10	0.08	0.07
Gd <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.06	0.00	0.00	0.00	0.01	0.34	0.77	0.52	0.54
Tb <sub>2</sub> O <sub>3</sub>	0.18	0.00	0.04	0.00	0.13	0.16	0.09	n.d.	n.d.	n.d.	n.d.
Dy <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.05	0.00	0.00	0.01	n.d.	n.d.	n.d.	n.d.
Ho <sub>2</sub> O <sub>3</sub>	0.00	0.04	0.00	0.00	0.23	0.06	0.06	n.d.	n.d.	n.d.	n.d.
CO <sub>2</sub> *	23.82	23.77	22.93	23.21	23.44	23.21	23.40	20.60	21.10	21.07	20.92
F	5.40	5.65	6.24	6.61	5.65	6.04	5.93	9.80	9.46	9.60	9.62
Sum	98.30	98.38	97.14	98.14	97.25	97.34	97.76	101.51	102.16	102.18	101.95
O=F	-2.27	-2.38	-2.63	-2.78	-2.38	-2.54	-2.50	-4.13	-3.98	-4.04	-4.05
Total	96.03	96.00	94.51	95.36	94.87	94.80	95.26	97.38	98.18	98.14	97.90
Na <i>apfu</i>	0.96	0.96	0.98	0.91	0.99	1.00	0.97	0.70	0.69	0.70	0.70
Ca	0.09	0.13	0.13	0.27	0.09	0.11	0.14	0.46	0.46	0.47	0.46
Sr	0.00	0.00	0.00	0.02	0.01	0.01	0.01	0.13	0.12	0.13	0.13
La	0.75	0.77	0.81	0.70	0.87	0.87	0.80	0.46	0.46	0.46	0.46
Ce	0.97	0.95	0.91	0.94	0.90	0.88	0.92	0.91	0.91	0.88	0.90
Pr	0.06	0.04	0.05	0.05	0.03	0.03	0.04	0.09	0.09	0.09	0.09
Nd	0.14	0.12	0.10	0.10	0.08	0.09	0.11	0.23	0.23	0.23	0.23
Sm	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02	0.02
Eu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.01
Tb	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ho	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
F	1.46	1.51	1.68	1.74	1.53	1.62	1.59	2.49	2.39	2.42	2.43
CO <sub>3</sub> *	2.77	2.74	2.66	2.63	2.74	2.69	2.71	2.26	2.30	2.29	2.28

\* calculated value; n.d.: not detected.

the arisite-(Ce) from Saint-Amable to be very similar in composition to that observed in Namibia. Empirical formulae were calculated on the basis of seven negative charges, taking into consideration a  $\text{CO}_3^{2-} \rightleftharpoons 2\text{F}^-$  substitution, as determined from the single-crystal X-ray determination of the structure. The average formulae are: 1) arisite-(Ce) from Aris, Namibia (NAM):  $(\text{Na}_{0.97}\text{Ca}_{0.03})_{\Sigma 1.00}(\text{Ce}_{0.92}\text{La}_{0.80}\text{Nd}_{0.11}\text{Pr}_{0.04}\text{Sm}_{0.01}\text{Ca}_{0.09})_{\Sigma 1.97}(\text{CO}_3)_2[(\text{CO}_3)_{0.71}\text{F}_{0.59}]\text{F}$ ; 2) arisite-(Ce) from Mont Saint-Hilaire, Quebec (MSH):  $(\text{Na}_{0.70}\text{Ca}_{0.30})_{\Sigma 1.00}(\text{Ce}_{0.90}\text{La}_{0.49}\text{Nd}_{0.23}\text{Pr}_{0.09}\text{Sm}_{0.02}\text{Gd}_{0.01}\text{Ca}_{0.16}\text{Sr}_{0.13})_{\Sigma 2.03}(\text{CO}_3)_2[\text{F}_{1.43}(\text{CO}_3)_{0.28}]\text{F}$ . The simplified formula for arisite-(Ce) from Namibia is  $\text{NaCe}_2(\text{CO}_3)_2[(\text{CO}_3)_{1-x}\text{F}_{2x}]\text{F}$ , and for arisite-(Ce) from MSH (and STA),  $\text{NaCe}_2(\text{CO}_3)_2[\text{F}_{2x}(\text{CO}_3)_{1-x}]\text{F}$ . The formulae and chemical composition suggest a solid-solution series *via* a coupled substitution,  $\text{CO}_3^{2-} \rightarrow 2\text{F}^-$ , with the end-

members  $\text{NaCe}_2(\text{CO}_3)_2(\text{CO}_3)\text{F}$  and  $\text{NaCe}_2(\text{CO}_3)_2\text{F}_2\text{F}$ , and a general formula of  $\text{NaCe}(\text{CO}_3)_2[(\text{CO}_3)_{1-x}\text{F}_{2x}]\text{F}$ . A further substitution of  $2\text{Na}^+ \leftrightarrow \text{Ca}^{2+} + \square$  is likely, resulting in a possible Ca-dominant analogue. The details of this anionic substitution are discussed by Piilonen *et al.* (2010), with supporting evidence from the structure determination.

#### POWDER X-RAY DIFFRACTION

The powder X-ray-diffraction data for arisite-(Ce) from Namibia and Saint-Amable were collected with a Bruker AXS D8 Discover microdiffractometer using a Hi-Star area detector operated with a GADDS system,  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 40 mA, with a sample-to-detector distance of 12 cm. The instrument was calibrated with synthetic corundum (PDF 00–10–0173) following a statistical procedure of calibration (Rowe 2009). Unit-cell refinement of the measured powder pattern was obtained by indexing the diffraction maxima using intensities from a powder pattern calculated using atom coordinates determined from the successful crystal-structure analysis. The refined unit-cell parameters are  $a$  5.1189(6),  $c$  8.680(1)  $\text{\AA}$ ,  $V$  196.98(4)  $\text{\AA}^3$ ,  $Z = 1$ , and reflect a mixture of both arisite-(Ce) and arisite-(La) as powder separates of the two species were not possible. Whether or not an  $hkl$  plane contributed to a reflection was determined from the powder pattern calculated using the atom parameters determined in the crystal-structure analysis and the program POWDERCELL (Nolze & Kraus 1998).

Powder X-ray-diffraction data for arisite-(Ce) from Mont Saint-Hilaire were collected with a Debye-Scherrer camera (114.6 mm diameter) employing Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Interplanar spacing and intensity data were determined using a scanned X-ray film. Whether or not an  $hkl$  plane contributed to a reflection was determined from a precession single-crystal study of two micaceous plates that, unfortunately, were not suitable for crystal-structure analysis. The powder X-ray diffraction patterns for all samples are given in Table 4.

Arisite-(Ce) is hexagonal, space group  $P\bar{6}m2$ , with unit-cell parameters taken from the single-crystal X-ray refinement of the structure (NAM):  $a$  5.1109(2),  $c$  8.6713(4)  $\text{\AA}$ ,  $V$  196.16(6)  $\text{\AA}^3$  (NAM data),  $Z = 1$ . It is related to other layered REE fluorcarbonates that have flat-lying  $\text{CO}_3^{2-}$  groups. This group, which includes lukechangite-(Ce), cordylite-(Ce), huanghoite-(Ce), cebaitte-(Ce), kukharenkoite-(Ce) and kukharenkoite-(La), all have structures characterized by separate layers of carbonate, F, REE and alkali or alkaline-earth elements (Grice *et al.* 2007). The details of the single-crystal X-ray determination of the structure of arisite-(Ce), and its relationship to other REE fluorcarbonates, are discussed by Piilonen *et al.* (2010).

TABLE 4. POWDER X-RAY-DIFFRACTION DATA FOR ARISITE-(Ce)

	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>I</i> **	<i>d</i> **	<i>hkl</i>
meas.	meas.	meas.	meas.	meas.	meas.	meas.	calc.	calc.	
NAM-	NAM-	MSH-	MSH-	STA-	STA-				
(Ce)	(Ce)	(Ce)*	(Ce)	(Ce)	(Ce)				
100	4.439	100	4.428	100	4.42	100	4.4281	100	
52	4.352	60	4.317			37	4.3380	002	
10	3.950	10	3.938	7	3.927	6	3.9441	101	
87	3.103	80	3.097	39	3.094	77	3.0988	102	
38	2.561	50	2.558	58	2.553	44	2.5586	110	
21	2.424	40	2.415	10	2.412	24	2.4213	103	
43	2.212	50b	2.206	39	2.209	33	2.2140	200	
						26	2.2025	112	
12	2.171	30	2.162	6	2.160	12	2.1689	004	
42	1.9748	60	1.969	34	1.9706	52	1.9720	202	
16	1.9501	30	1.941	5	1.9415	19	1.9478	104	
12	1.9169	20	1.910	12	1.9100	11	1.9154	113	
3	1.7597	5	1.753	1	1.7548	3	1.7580	203	
10	1.6764	20	1.672	14	1.6711	15	1.6737	210	
11	1.6547	30	1.650	4	1.6492	16	1.6539	114	
7	1.6171	30	1.610	4	1.6104	10	1.6156	105	
13	1.5640	30	1.560	10	1.5601	20	1.5615	212	
7	1.5515	15	1.545	10	1.5474	7	1.5494	204	
3	1.4776	15	1.474	7	1.4747	7	1.4760	300	
3	1.4500	10	1.447	2	1.4463	7	1.4486	213	
		5	1.432	4	1.4357	4	1.4357	115	
4	1.3985	15	1.396	3	1.3942	6	1.3974	302	
3	1.3753	10	1.370			4	1.3746	106	
1	1.3659					1	1.3657	205	
5	1.3260	25	1.323	3	1.3207	12	1.3250	214	
		3	1.312			3	1.3147	303	
3	1.2792	15	1.278	7	1.2769	10	1.2783	220	
		5	1.255			2	1.2586	116	
4	1.2287	10	1.227	5	1.2254	7	1.2281	310	
						6	1.2262	222	
		5	1.218			7	1.2203	304	
2	1.2058	10	1.202	2	1.2026	10	1.2046	215	
2	1.1941	10	1.190			7	1.1935	107	
4	1.1830	10	1.181	4	1.1808	12	1.1817	312	
1	1.1159					7	1.1153	117	
2	1.0709					10	1.0726	402	
						10	1.0687	314	

\* Intensities were visually estimated. No internal standard was used, and the film was not corrected for shrinkage. \*\* As calculated from the refined crystal structure. The values of *d* are quoted in  $\text{\AA}$ .

## ACKNOWLEDGEMENTS

The authors thank all the mineral collectors who provided arisite-bearing material: László & Elsa Horváth, Robin Tibbit, Modris Baum, Markus Ecker, Stephan Wolfsried and Hans Vidar Ellingsen. Elizabeth Moffat at the Canadian Conservation Institute, Ottawa, Ontario, collected the FTIR spectrum. The comments and suggestions by Robert F. Martin, Igor Pekov, and an anonymous referee are appreciated. Research funding is provided by a RAC grant from the Canadian Museum of Nature (PCP), and NSERC (AMM).

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Received August 7, 2009, revised manuscript accepted June 6, 2010.