

# LAFOSSAITE

## A NEW MINERAL FROM THE LA FOSSA CRATER VULCANO, ITALY

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### ABSTRACT

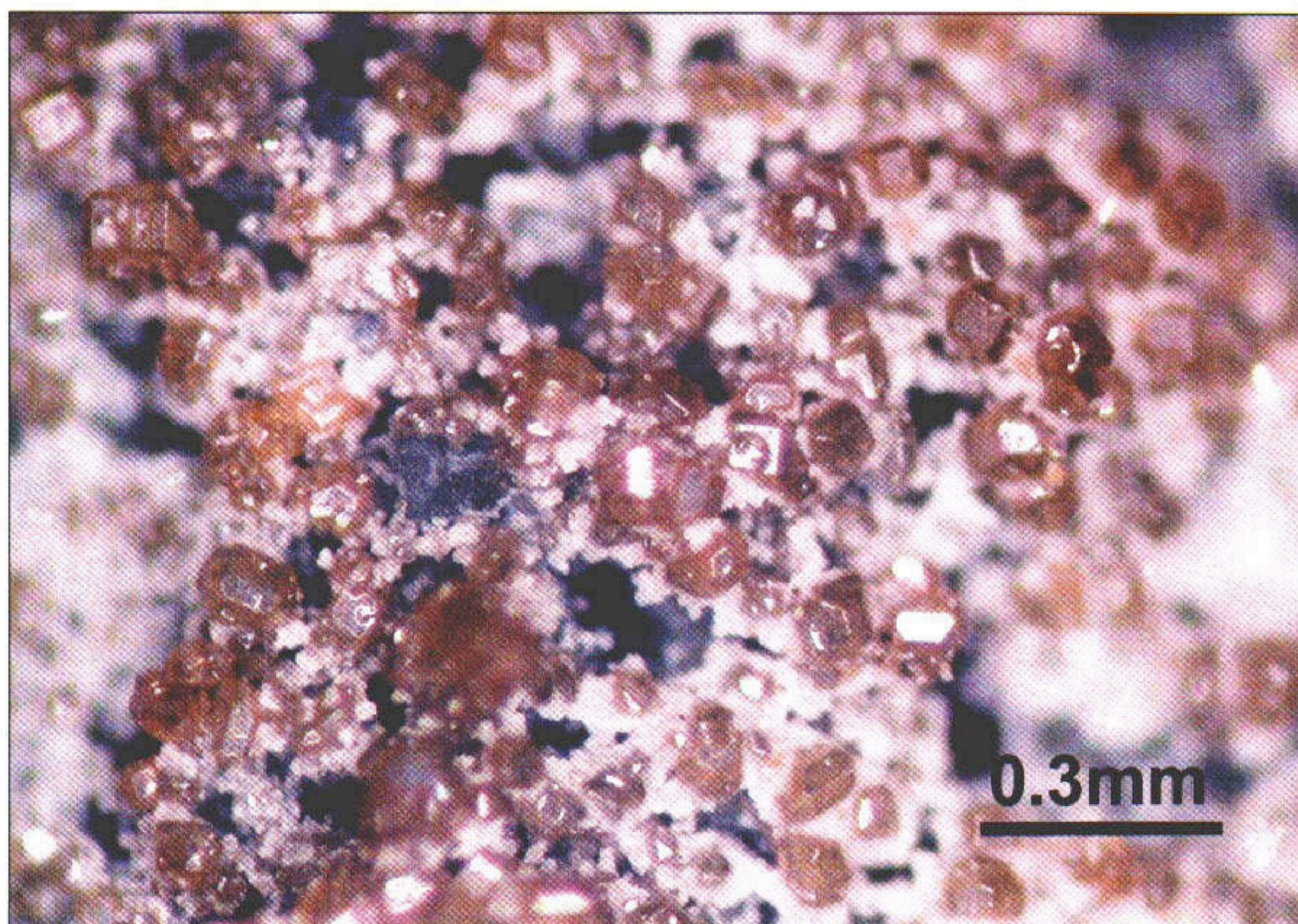
Lafossaite, idealized formula  $\text{TiCl}$ , is cubic, space group  $P\text{-}m\bar{3}m$  (by analogy with the synthetic inorganic equivalent) with unit-cell parameter refined from powder data:  $a = 3.8756(3) \text{ \AA}$ ,  $V = 58.213(8) \text{ \AA}^3$ ,  $Z = 1$ . The strongest six reflections in the X-ray powder-diffraction pattern are [ $d(\text{\AA})(I)(hkl)$ ]: 3.887(80)(100); 2.745(100)(110); 2.237(55)(111); 1.937(50)(200); 1.733(45)(210); 1.583(70)(211). The mineral occurs on a single specimen ( $6 \times 7 \times 9 \text{ cm}$ ) collected from one of the active  $400^\circ\text{C}$  fumaroles on the rim of the La Fossa crater, island of Vulcano, Aeolian archipelago, Sicily, Italy, as a drusy coating on one surface. The mineral formed as a sublimate directly from fumarolic gas and is associated with a number of other sublimate minerals including cannizzarite, galenobismutite, pyrite and an undefined Fe-K-Si-bearing phase. Crystals do not exceed 0.2 mm in size and are euhedral to subhedral (predominant) cubes and octahedra which are tightly intergrown in some areas. Forms are {100} (smooth and lustrous) major, {111} (rough and non-lustrous) minor, and {110} (rough and non-lustrous) very minor. Lafossaite possesses the following physical properties: color is gray-brown (R.H.S. 199D); streak is off-white to cream (and resinous looking); luster is resinous to greasy; diaphaneity is translucent; non-fluorescent; Mohs hardness is estimated at 3–4; tenacity is malleable; fracture is subconchoidal; cleavage and parting are not evident; calculated density is  $7.212 \text{ g/cm}^3$  (for empirical formula and unit-cell parameter refined from powder data). The mineral is yellow-brown in plane-polarized transmitted light, isotropic with no pleochroism, and  $n \gg 1.8$ . In plane-polarized reflected light, it is grayish-white, with white internal reflections and no evidence of anisotropy, bireflectance or

pleochroism. The calculated index of refraction (589 nm) is 2.264. Reflectance values, in air and in oil, are tabulated. Averaged electron-microprobe analyses:  $\text{Ti} = 81.74$ ,  $\text{Cl} = 10.79$ ,  $\text{Br} = 5.99$ , total = 98.52 weight %, corresponding to  $\text{Ti}_{1.03}(\text{Cl}_{0.78}\text{Br}_{0.19})_{20.97}$ , based on 2 total atoms. The mineral is soluble in dilute HCl. The mineral name is for the locality.

### INTRODUCTION

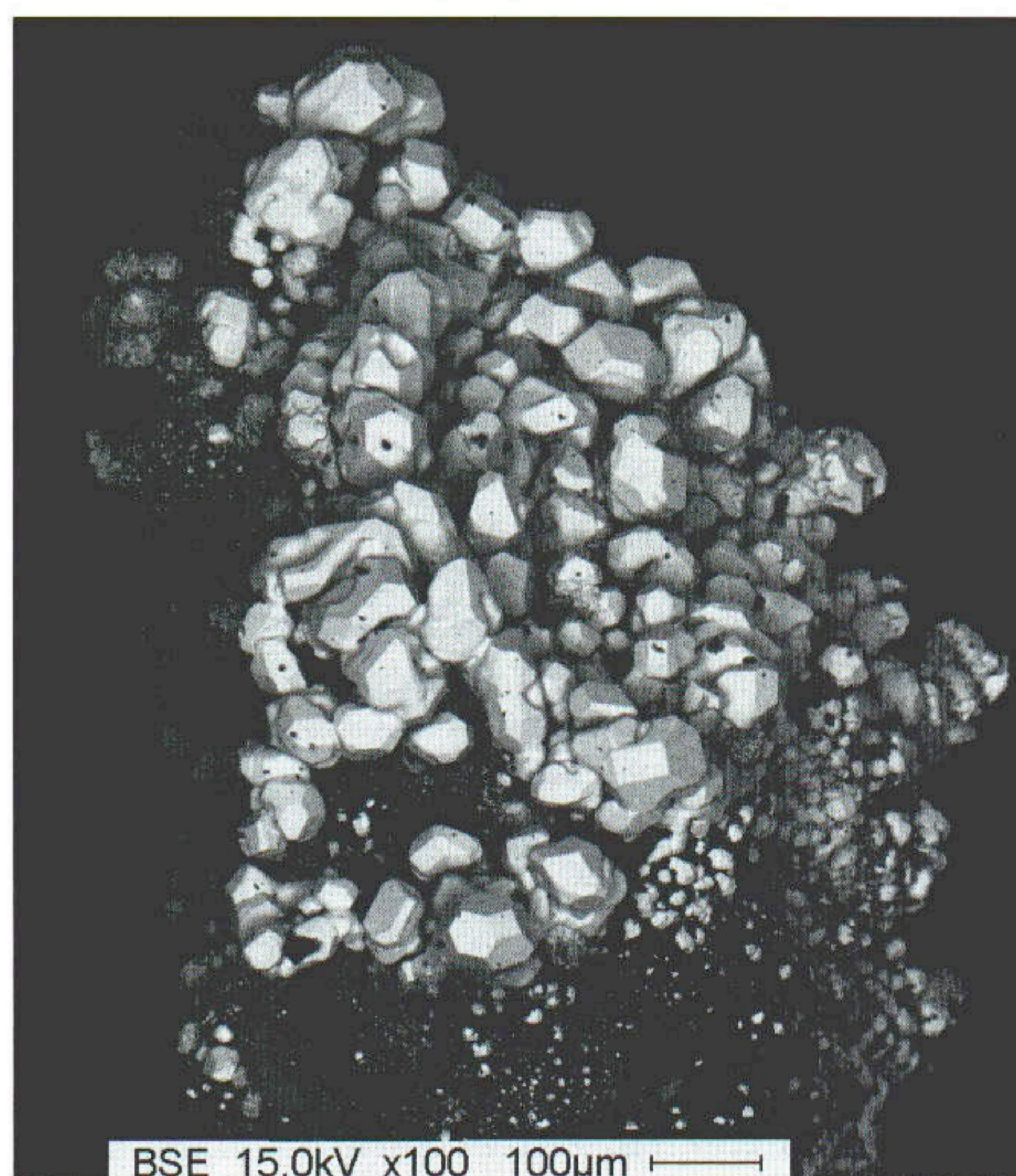
Lafossaite, ideally  $\text{TiCl}$ , is a newly recognized mineral species that was collected from an active fumarole in the La Fossa crater on the island of Vulcano, Italy. Preliminary energy-dispersion spectra (EDS) acquired with a scanning-electron microscope (SEM) strongly suggested that the mineral was new to science. Further study using modern mineralogical techniques has confirmed this supposition and the results are reported herein.

The mineral is named lafossaite after the locality, which is the current active volcanic crater on Vulcano. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. (2003-32). The holotype specimen is housed in the research collection of one of us (T.M.S.) at the Institut für Mineralogie und Petrographie (ETH Zürich), a portion ( $4 \times 5 \times 6 \text{ mm}$ ) of which has been deposited in the Systematic Reference Series of the National Mineral Collection of Canada, Geological Survey of Canada, Ottawa, under catalog number 68098. The polished section used for quantitative electron-microprobe analyses and reflectance studies is housed in the mineral collections at The Natural History Museum, London, UK, as BM2004,55.



**Figure 1.** Aggregates of subhedral to euhedral lafossaite crystals. Scale bar: 0.3 mm.

**Figure 2.** Euhedral lafossaite crystal aggregates. Scale bar: 100  $\mu$ m.



## OCCURRENCE

Lafossaite occurs as a drusy coating of tiny crystals sporadically distributed over the irregular surface of a single sample ( $6 \times 7 \times 9$  cm) comprised of fragments of partly altered (by fumarolic gases) ash and lapilli cemented together by other sublimate minerals (*i.e.*, silica, hieratite, sal ammoniac and other unidentified phases). It was collected by one of us (T.M.S.) in September 2001 from a  $400^\circ\text{C}$  fumarole on the rim of the La Fossa crater on the island of Vulcano, Aeolian archipelago, Sicily, Italy (latitude  $38^\circ 23'$  N, longitude  $14^\circ 58'$  E).

Associated sublimate phases are fine-grained pyrite and euhedral cannizzarite and galenobismutite crystals, many of which are coated by small lafossaite crystals. In addition, it is associated with a very fine-grained white opaque crust which is an intimate mixture of lafossaite and an undefined phase which shows (by SEM-EDS) variable Fe, K and Si. Typically, isolated lafossaite grains and aggregates are surrounded by this white mixture. Only one specimen has been found, despite an extensive search for further material. The mineral must be considered very rare.

The lafossaite sublimed at about  $400^\circ\text{C}$  from fumarolic gas containing appreciable concentrations of the halogen acids HF, HCl and HBr (Wahrenberger *et al.*, 2004). The gases discharging from the crater rim fumaroles contain up to 2.25 mg/kg of thallium and the dominant transport mechanism is considered to be the volatile molecular complex  $\text{TlCl}$  (Wahrenberger *et al.*, 2004). Cannizzarite and bismuthinite crystals from the crater rim fumaroles contain up to 200 and 2500 mg/kg of thallium, respectively. Bebić *et al.* (1998) have shown that the aquated  $\text{Tl}^+$  ion and  $\text{TlCl}(\text{aq})$  may also play an important role in the transport of thallium in hydrothermal systems.

## PHYSICAL PROPERTIES

Lafossaite single grains and aggregates occur as a crust ( $6 \times 2.5$  mm) on one surface of the type (NMCC) specimen (Fig. 1). Individual crystals form subhedral (predominant) to euhedral cubes and octahedra (which may be tightly intergrown in some areas) that do not exceed 0.2 mm in size and tend to average a little less in most cases (Fig. 2). Forms observed include  $\{100\}$  major (face is smooth and lustrous and brightly reflecting under binocular light),  $\{111\}$  minor and  $\{110\}$  very minor (both of these forms have rougher non-lustrous faces which do not reflect under binocular

light). The mineral is gray-brown (close to R.H.S. 199D) and the streak is off-white to cream (and resinous looking). It should be mentioned that grains do not “powder” in the conventional sense of the word; they flatten out or “squish” into a very thin sheet when pressed between two frosted glass slides. This characteristic makes X-ray powder-mount sample preparation rather difficult (but not impossible). The luster is resinous to greasy and the crystals are translucent. Lafossaite is malleable with a subconchoidal fracture, no observable cleavage or parting, and is non-fluorescent under both longwave and shortwave ultraviolet light. The hardness (Mohs’) is estimated to be 3–4. The density could not be measured because of the small size of available crystals and dearth of material. The calculated density, on the basis of the empirical formula and unit-cell parameter refined from powder data, is  $7.212 \text{ g/cm}^3$ .

## X-RAY STUDIES

A crystal of lafossaite, mounted with  $a^*$  parallel to the dial axis was examined by single-crystal precession methods with Zr-filtered Mo X-radiation. The following levels were photographed:  $hk0$ ,  $hkl$  and  $a^* \wedge 011^*$ . The mineral is cubic,  $a = 3.901 \text{ \AA}$ , with no systematic space-group extinctions and  $m3m$  diffraction symmetry. The space group is assumed to be  $P-m3m$  (221) by analogy with the synthetic inorganic equivalent compound (see below). The refined unit-cell parameter from powder data:  $a = 3.8756(3) \text{ \AA}$ ,  $V = 58.212(8) \text{ \AA}^3$ ,  $Z = 1$ , is based on all 11 reflections with  $d$  values between 3.887 and 1.119  $\text{\AA}$  for which unambiguous indexing was possible, based on visual inspection of single-crystal precession films. A fully indexed powder pattern is presented in Table 1. These data are virtually identical to PDF 78-625 which is the calculated powder pattern for  $\text{Tl}(\text{Cl}_{0.78}\text{Br}_{0.22})$  (Popova *et al.*, 1966) and, somewhat surprisingly, to sal ammoniac,  $\text{NH}_4\text{Cl}$  (PDF 7-7), which is isostructural with lafossaite. Both minerals are products of fumarolic activity and sal ammoniac has also been identified on Vulcano. Thus, while routine X-ray powder-diffraction studies will not reliably differentiate between the two mineral species, it will narrow down the choices to one or the other, and allow qualitative chemistry (routine EDS on a SEM) to differentiate between the two. The experimental powder data for end-member synthetic  $\text{TlCl}$  is given in PDF 6-486; this data should be added to the Mineral File of the PDF and named "lafossaite, syn."

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

	$I_{est.}$	$d_{meas.}^{\text{\AA}}$	$d_{calc.}^{\text{\AA}}$	$hkl$
*	80	3.887	3.876	100
*	100	2.745	2.740	110
*	55	2.237	2.238	111
*	50	1.937	1.938	200
*	45	1.733	1.733	210
*	70	1.583	1.582	211
*	25	1.370	1.370	220
*	20	1.291	1.292	300
*			1.292	221
*	25	1.226	1.226	310
*	10	1.169	1.169	311
*	15	1.119	1.119	222

- 114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni-filter ( $\lambda_{\text{CuK}\alpha} = 1.54178 \text{ \AA}$ ).
- Intensities estimated visually; \* = lines used for unit-cell refinement.
- Corrected for shrinkage and no internal standard.
- Indexed on  $a = 3.8756 \text{ \AA}$ .

## CRYSTAL STRUCTURE

The crystal structure of the synthetic inorganic equivalent of lafossaite is very well known and was first successfully solved over eighty years ago by Davey and Wick (1921). Since then, the  $\text{TlCl}$  structure has been studied by a number of researchers (Swanson *et al.*, 1955 and references therein), most recently by Smakula and Kalnajs (1955) (PDF calculated pattern 89-4255) and by Popova *et al.* (1966) (PDF calculated patterns 78-623 to 78-627). The structure belongs to the CsCl-type and consists of a framework of face-sharing hexahedra with Tl at 0, 0, 0 and Cl(Br) at  $1/2, 1/2, 1/2$ . The Pearson Symbol Code (PSC) is  $cP2$ . Popova *et al.* (1966) also studied the crystallographic effects of Br substitution for Cl within the structure.

## CHEMISTRY

Several lafossaite crystals were analyzed with a Cameca SX-50 electron microprobe utilizing an operating voltage of 10 kV, a beam current of 10 nA, and a beam diameter of 5  $\mu\text{m}$ . Data were ZAF corrected and count times were 10s on peak and 5s on background. Synthetic  $\text{Tl}(\text{Br},\text{I})$  (for Tl and Br) and synthetic  $\text{KCl}$  (for Cl) were used as appropriate standards. A 100s energy-dispersion scan showed no elements other than those reported. I, K and Na were sought but not detected. The average of fourteen determinations are given in Table 2 and the empirical formula (based on total atoms = 2) for lafossaite is  $\text{Tl}_{1.03}(\text{Cl}_{0.78}\text{Br}_{0.19})_{20.97}$ . The idealized formula,  $\text{TlCl}$ , requires Tl = 85.22, Cl = 14.78, total = 100.00 weight % and the formula  $\text{Tl}(\text{Cl}_{0.8}\text{Br}_{0.2})_{\Sigma 1.0}$ , requires Tl = 82.17, Cl = 11.40, Br = 6.42, total = 100.00 weight %. The mineral is insoluble in cold  $\text{H}_2\text{O}$  and somewhat soluble in dilute  $\text{HCl}$ . Lafossaite is the first naturally occurring Tl-bearing halide and is the second member of the sal ammoniac group (Strunz classification 3.AA.25). It has been previously reported (as unnamed  $\text{TlCl}$ ) by Gorshkov *et al.* (1998) as 1-12  $\mu\text{m}$ -sized equant particles within diamondiferous kimberlite rock at the Udachnaya pipe, Yakutia, Russia.

**Table 2. Compositional data for lafossaite.**

	Atomic Weight %	Range	Standard Deviation
Tl	81.74	79.95 - 84.00	1.49
Cl	10.79	9.77 - 11.63	0.57
Br	5.99	5.49 - 6.34	0.28
Total	98.52		1.75

## OPTICAL PROPERTIES

A grain mount, with a Na-gel filtered light (590 nm), shows that lafossaite is yellow-brown in plane-polarized transmitted light, isotropic, and displays no pleochroism. The index of refraction is  $\geq 1.80$  and could not be accurately measured with the available immersion oils.

In plane-polarized reflected light ( $\sim 3200^\circ \text{K}$ ), lafossaite is grayish-white with distinct white internal reflections. There is no evidence of anisotropy, birefractance, nor pleochroism. Reflectance measurements were made in the visible region (400-700 nm) at intervals of 20  $\mu\text{m}$  using a Leitz MPV-SP microscope-spectrophotometer. A  $\text{WTiC}$  reflectance standard (Zeiss 314) was used as a reference for air and oil (Leica  $N_D = 1.518$ ) measurements. These were done with 20 X objectives, the numerical apertures of which were confined to 0.40, and the diameter of the measured disks was 9  $\mu\text{m}$ . The reflectance curve ( $R$ ) descends continuously from short

**Table 3. Reflectance data for lafossaite.**

$\lambda_{nm}$	$R$	$^{im}R$	$\lambda_{nm}$	$R$	$^{im}R$
400	17.7	5.4	560	15.1	3.9
420	16.8	5.0	580	15.0	3.9
440	16.5	4.7	589 (COM)	15.0	4.0
460	16.2	4.5	600	14.9	3.9
470 (COM)	16.0	4.4	620	14.8	3.9
480	15.8	4.4	640	14.8	3.8
500	15.6	4.2	650 (COM)	14.7	3.8
520	15.4	4.1	660	14.7	3.8
540	15.2	4.1	680	14.6	3.8
546 (COM)	15.2	4.0	700	14.6	3.8

to long wavelength. In Table 3, we summarize the data collected from the only grain available in polished section. The values may be slightly low because the grain surface is scratched and not well polished. For 589 nm, the calculated index of refraction is 2.264.

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