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D'ansite-(Mn), $Na_{21}Mn^{2+}(SO_4)_{10}Cl_3$ and d'ansite-(Fe), $Na_{21}Fe^{2+}(SO_4)_{10}Cl_3$, two new minerals from volcanic fumaroles

F. Demartin[1,*], I. Campostrini[1], C. Castellano[1], C. M. Gramaccioli[1] and M. Russo[2]

[1] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy
[2] Istituto Nazionale di Geofisica e Vulcanologia, Sez. Napoli – Osservatorio Vesuviano, via Diocleziano 328, 80124 Napoli, Italy

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ABSTRACT

The new minerals d'ansite (Mn), $Na_{21}Mn^{2+}(SO_4)_{10}Cl_3$, and d'ansite (Fe), $Na_{21}Fe^{2+}(SO_4)_{10}Cl_3$, occur as encrustations in fumaroles at Vesuvius, Naples, Italy and La Fossa crater, Vulcano, Aeolian Islands, Italy, respectively. Both minerals are cubic and crystallize in space group $I\bar{4}3d$. D'ansite (Mn) forms colourless translucent tristetrahedral crystals up to 0.2 mm on edge; d'ansite (Fe) forms aggregates of colourless to white complex isometric crystals of about the same size. Chemical analyses obtained by energy dispersive spectrometry on an electron microprobe gave the following mean compositions: d'ansite (Mn), Na_2O 39.37, MnO 3.46, MgO 0.13, SO_3 49.99, Cl 6.36, O Cl −1.44, total 97.87 wt.%, corresponding to an empirical formula, on the basis of 43 anions, of $Na_{20.61}(Mn^{2+}_{0.79}Mg_{0.05})_{\Sigma 0.84}S_{10.13}O_{40.09}Cl_{2.91}$; and d'ansite (Fe), Na_2O 39.12, FeO 4.18, MgO 0.12, SO_3 49.91, Cl 6.81, O Cl −1.54, total 98.60 wt.%, corresponding to an empirical formula of $Na_{20.42}(Fe^{2+}_{0.94}Mg_{0.05})_{\Sigma 0.99}S_{10.08}O_{39.89}Cl_{3.11}$. The six strongest reflections in the X ray powder diffraction pattern of d'ansite (Fe) [listed as d_{obs}(Å) (I) (hkl)] are as follows: 2.807(100)(044), 2.570(37)(235), 1.714(29)(129), 3.384(27)(233), 3.113(26)(134), 2.108(15)(237). The unit cell parameters obtained from single crystal data are 15.9291(9) and 15.882(3) Å for d'ansite (Mn) and d'ansite (Fe), respectively. The structure of both minerals was refined, using single crystal diffraction data, to final R parameters of 0.0309 and 0.0336 on reflections with $I > 2\sigma(I)$. The structure contains three independent Na sites, one of which is partially occupied by Mn^{2+} or Fe^{2+}, two independent sulfate anions and one chlorine site.

Keywords: d'ansite (Mn), d'ansite (Fe), new mineral species, crystal structure, sublimates, fumaroles, Vulcano Island, Vesuvius, Italy.

Introduction

D'ansite, $Na_{21}Mg(SO_4)_{10}Cl_3$, was first described in 1909 by R. Görgey from evaporite deposits near Innsbruck in the Tyrol region, Austria, but it was not named or studied mineralogically until Autenrieth and Braune (1958) produced crystals in their studies of the system $Na^+-Mg^{2+}-SO_4^{2-}-Cl^--H_2O$. Strunz (1958) determined the structure of synthetic material produced by these authors and reported that the mineral crystallized in space group $I\bar{4}3m$. Burzlaff and Hellner (1961) synthesized several analogous phases containing a number of different cations in place of Mg^{2+}, including Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+} and Zn^{2+}, and determined the structure of 'Zn d'ansite', also in space group $I\bar{4}3d$.

In 1972, d'ansite was found to be widely distributed in a Palaeogene salt deposit in Central China (Yihua *et al.*, 1975). The structure was

* E mail: francesco.demartin@unimi.it
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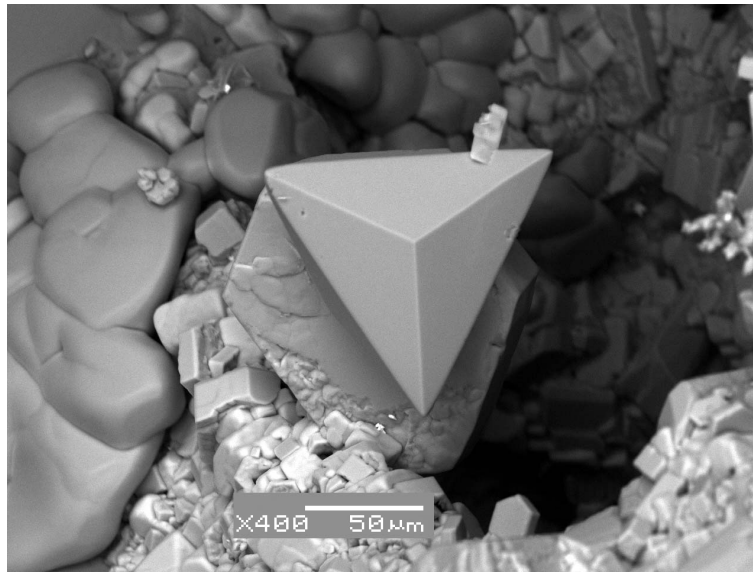

FIG. 1. A backscattered electron image of a tristetrahedral crystal of d'ansite (Mn) with aphthitalite from Vesuvius, Naples, Italy.

solved in space group $I\bar{4}32$, but the agreement index, *R*, of ~15% was poor. The structure of 'Zn d'ansite' was reconsidered by Burzlaff and Grube (1980) who noted that the crystals of this synthetic phase were invariably twinned and proposed a lower symmetry. On the basis of the optical properties and the anomalous displacement parameters for the atoms on the threefold axis, *R*3*c* or *Cc* were reported as possible space groups. Fifteen years later, Lange and Burzlaff (1995) applied the Laue diffractometer technique to a crystal of 'Zn d'ansite', and refined its structure in space group $I\bar{4}3d$.

In the course of our studies of fumarole minerals, which have already resulted in the discovery of several new species (Demartin *et al*., 2010*a*,*b*, 2011; Campostrini *et al*., 2011), two new minerals related to d'ansite, containing Fe^{2+} and Mn^{2+} in place of Mg^{2+}, have been characterized and named d'ansite (Fe) and d'ansite (Mn), respectively. The first of these minerals was collected in 2008 in an intracrater fumarole with a temperature of about 300ºC at La Fossa Crater, Vulcano Island [fumarole FA in Borodaev *et al*. (2000) and Pinto *et al*. (2006)]; this mineral was described in Campostrini *et al*. (2011) as unknown species UKI fo29. The second of these minerals was collected in May 1927 by A. Malladra in a 1926 eruption fumarole with a temperature of about 350ºC at Vesuvius, Naples. Both minerals and their names have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2011 065 and 2011 064). Holotype d'ansite (Mn) has been deposited in the mineral collections of the Osservatorio Vesuviano, Naples (under catalogue number OV128). The crystal fragment used for the structure determination is housed in the reference collection of the Dipartimento di

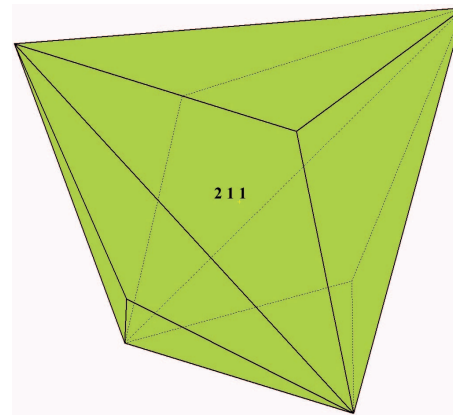

FIG. 2. Crystal drawing of d'ansite (Mn).

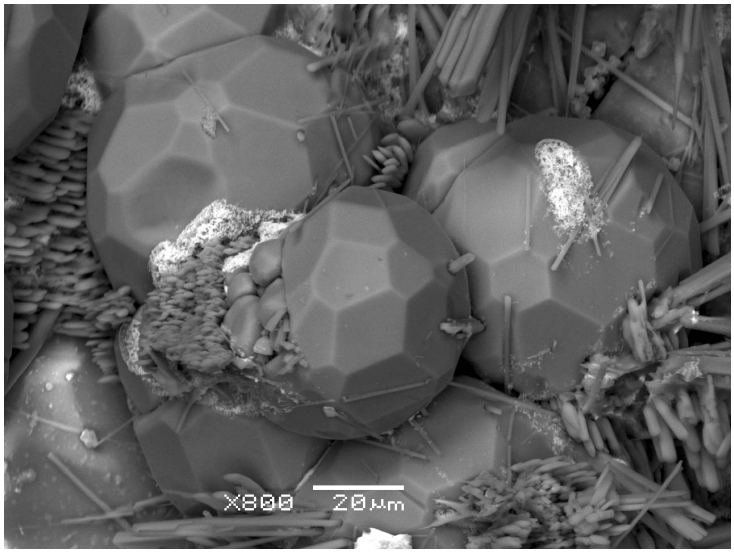

FIG. 3. Backscattered electron images of d'ansite (Fe) with adranosite from La Fossa Crater, Vulcano, Aeolian Islands, Italy.

Chimica at the Università degli Studi di Milano (catalogue no. 2011 03) together with the type specimen of d'ansite (Fe) (catalogue no. 2011 02). A description of the two new species is reported in the following text.

Occurrence, physical properties and chemical data

D'ansite (Mn) forms colourless translucent triste trahedral crystals up to 0.2 mm on edge (Figs 1 and 2) associated with halite and aphthitalite. Its

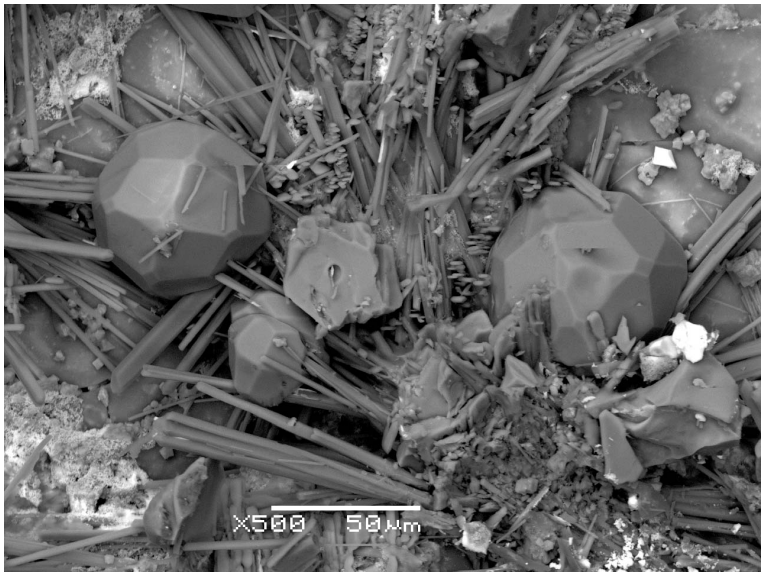

FIG. 4. Backscattered electron images of d'ansite (Fe) with adranosite from La Fossa Crater, Vulcano, Aeolian Islands, Italy.

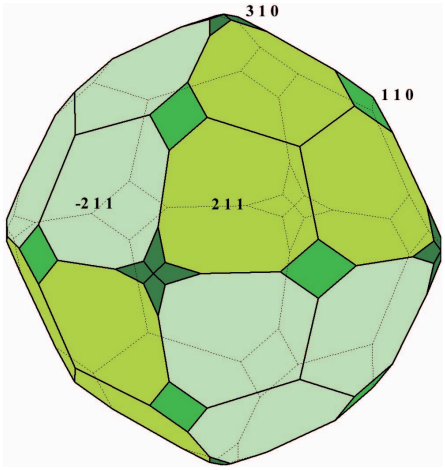

FIG. 5. Crystal drawing of d'ansite (Fe) (see the crystal in Fig. 4, upper left, for comparison).

calculated density is 2.610 g cm^{-3} (from single crystal X ray data and chemical composition). It is optically isotropic with n 1.50(1) (at a wavelength of 589 nm, determined by immersion in benzene–monochlorobenzene). The compat ibility index, $[1 - (K_p/K_c)]$, is 0.001, which is superior according to Mandarino (1981).

D'ansite (Fe) occurs as aggregates of colour less to white complex isometric crystals up to 0.2 mm in size (Figs 3–5) on a pyroclastic breccia, associated with sassolite, adranosite and as yet uncharacterized sulfate chlorides, which are currently under investigation. Its measured density is 2.62(1) g cm^{-3} (determined by flotation in tribromomethane–trichloromethane); and its calculated density is 2.644 g cm^{-3} (on the basis of single crystal X ray data and chemical composi tion). It is optically isotropic with n 1.51(1) (at a wavelength of 589 nm, determined by immersion in benzene–monochlorobenzene). The compat ibility index, $[1 - (K_p/K_c)]$, is −0.005, which is superior according to Mandarino (1981).

Both minerals have a white streak and a vitreous lustre, and neither is fluorescent when exposed to either LW or SW ultraviolet radiation. Their hardness was not determined, their tenacity is brittle and no cleavage is evident.

Chemical analyses of both minerals were carried out on a JEOL JSM 5500LV electron microscope equipped with an energy dispersive spectrometer operating at 20 kV, 10 pA with a

TABLE 1. Analytical data for d'ansite (Mn) and d'ansite (Fe).

Constituent	Mean (wt.%)	Range	SD	Probe standard
D'ansite (Mn)*				
Na_2O	39.37	38.47–40.20	0.52	Albite
MnO	3.46	3.38–3.62	0.22	Almandine spessartine
MgO	0.13	0.06–0.18	0.16	Almandine spessartine
SO_3	49.99	49.22–50.68	0.35	Adranosite
Cl	6.36	6.20–6.63	0.24	Adranosite
O=Cl	−1.44			
Total	97.87			
D'ansite (Fe)**				
Na_2O	39.12	38.49–41.05	0.53	Albite
FeO	4.18	3.91–4.35	0.25	Almandine garnet
MgO	0.12	0.07–0.18	0.13	Almandine garnet
SO_3	49.91	49.56–51.68	0.36	Adranosite
Cl	6.81	6.28–7.42	0.24	Adranosite
O=Cl	−1.54			
Total	98.60			

* The mean values based on 6 analyses. The empirical formula derived from chemical analysis on the basis of 43 anions p.f.u. is $Na_{20.61}(Mn^{2+}_{0.79}Mg_{0.05})_{\Sigma 0.84}S_{10.13}O_{40.09}Cl_{2.91}$. The simplified formula is $Na_{21}Mn^{2+}(SO_4)_{10}Cl_3$.
** The mean values based on 8 analyses. The empirical formula derived from chemical analysis on the basis of 43 anions p.f.u. is $Na_{20.42}(Fe^{2+}_{0.94}Mg_{0.05})_{\Sigma 0.99}S_{10.08}O_{39.89}Cl_{3.11}$. The simplified formula is $Na_{21}Fe^{2+}(SO_4)_{10}Cl_3$.

2 μm beam diameter. The analytical results are reported in Table 1. The elemental concentrations were determined using the $K\alpha$ lines of Na, Mg, Mn, Fe, Cl and S. The empirical formula (on the basis of 43 anions) derived from the chemical analysis of d'ansite (Mn) is $Na_{20.61}(Mn^{2+}_{0.79}Mg_{0.05})_{\Sigma 0.84}S_{10.13}O_{40.09}Cl_{2.91}$; that of d'ansite (Fe) is $Na_{20.42}(Fe^{2+}_{0.94}Mg_{0.05})_{\Sigma 0.99}S_{10.08}O_{39.89}Cl_{3.11}$. The corresponding simplified formulae are $Na_{21}Mn^{2+}(SO_4)_{10}Cl_3$ and $Na_{21}Fe^{2+}(SO_4)_{10}Cl_3$, respectively.

X-ray data

The X ray powder diffraction data for d'ansite (Fe) were collected using a Rigaku D MAXII diffractometer with Cu$K\alpha$ radiation (Table 2). The unit cell parameter a 15.8842(7) Å was obtained from a least squares refinement using the program *UNITCELL* (Holland and Redfern, 1997). The powder pattern of d'ansite (Mn) could not be measured due to the extreme scarcity of material and the pattern calculated from single crystal X ray data is reported in Table 2 instead.

TABLE 2. X ray powder diffraction data for d'ansite (Mn) and d'ansite (Fe).

	D'ansite (Mn)		D'ansite (Fe)			
$h\ k\ l$	$(I/I_o)_{calc}$*	d_{calc} (Å)*	$(I/I_o)_{obs}$	$(I/I_o)_{calc}$*	d_{obs} (Å)	d_{calc} (Å)**
1 1 2	10	6.503	7	10	6.499	6.485
0 2 2	1	5.632	1	1	5.586	5.616
0 1 3	3	5.037	3	3	5.055	5.023
1 2 3	30	4.257	6	31	4.239	4.245
0 0 4	35	3.982	4	35	3.969	3.971
0 2 4	12	3.562	2	12	3.545	3.552
2 3 3	95	3.396	27	96	3.384	3.387
2 2 4	3	3.252	8	2	3.216	3.243
1 3 4	45	3.124	26	43	3.113	3.116
1 2 5	15	2.908	14	16	2.900	2.900
0 4 4	100	2.816	100	100	2.807	2.808
0 3 5	3	2.732		3		
2 3 5	38	2.584	37	36	2.570	2.577
0 2 6	25	2.519	12	25	2.514	2.512
1 4 5	8	2.458	5	11	2.451	2.451
1 3 6	5	2.349	3	5	2.337	2.342
4 4 4	8	2.299	1	6	2.298	2.293
3 4 5	10	2.253	4	9	2.246	2.246
1 2 7	18	2.168	15	16	2.161	2.162
2 4 6	2	2.129	2	2	2.133	2.123
0 3 7	1	2.092	2	2	2.083	2.086
2 3 7	16	2.023	15	14	2.018	2.017
0 0 8	3	1.991		6		
0 2 8	2	1.932	2	2	1.927	1.926
3 5 6	17	1.904	14	15	1.899	1.899
2 2 8	2	1.877	9	2	1.875	1.872
1 3 8	9	1.852		7		
2 5 7	2	1.804		2		
0 1 9	3	1.759		3		
1 2 9	25	1.718	29	25	1.714	1.713
4 6 6	4	1.698		4		
1 5 8	2	1.679	2	2	1.676	1.674
3 6 7	6	1.643	4	5	1.632	1.638
4 4 8	4	1.626	3	4	1.623	1.621
1 1 10	3	1.577	3	2	1.574	1.573

* Calculated from the refined structure.
** Calculated from a = 15.8842(7) Å, obtained from least squares refinement of the observed data using the program *UNITCELL* (Holland and Redfern, 1997).

TABLE 3. Crystal data and structure refinement details for d'ansite (Mn) and d'ansite (Fe).

	D'ansite (Mn)	D'ansite (Fe)
Formula	$Na_{21.49}Mn_{0.51}(SO_4)_{10}Cl_3$	$Na_{21.48}Fe_{0.52}(SO_4)_{10}Cl_3$
Crystal system	cubic	cubic
Space group	*I*43*d*	*I*43*d*
a (Å)	15.9291(9)	15.882(3)
V (Å^3)	4041.8(4)	4006(1)
Z	4	4
D_{calc} (g cm^{-3})	2.611	2.644
Wavelength (Å)	0.71073	0.71073
μ (mm^{-1})	1.256	1.287
Min/max transmission factors	0.920, 1.000	0.883, 1.000
Crystal size (mm)	0.07 × 0.07 × 0.07	0.03 × 0.03 × 0.03
θ range for data collection (°)	0.99−34.05	1.00−24.21
Index ranges	$-24 \leqslant h \leqslant 24$, $-24 \leqslant k \leqslant 24$, $-24 \leqslant l \leqslant 24$	$-18 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 18$
Measured reflections	23,904	11,394
Unique reflections, R_{int}	1366, 0.035	540, 0.16
Observed reflections [$I > 2\sigma(I)$]	1287	407
Refinement methods	Full matrix least squares on F^2	Full matrix least squares on F^2
R [observed reflections]	0.0309	0.0336
wR_2 [all data]	0.0822	0.0548
S (goodness of fit on F^2)	1.061	0.925
Weighting scheme	$w = 1/[\sigma^2(Fo^2) + (0.0469q)^2 + 5.803q]$	$w = 1/[\sigma^2(Fo^2) + (0.0201q)^2]$
Min and max electron density residual (e Å^{-3})	−3.86, 4.80	−0.27, 0.32

Refinement parameters are: $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = \{S[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$; $q = [\max(0, Fo^2) + 2Fc^2]/3$; $S = \{\Sigma[w(Fo^2 - Fc^2)]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

The unit cell parameters obtained for both minerals from single crystal reflections with $I > 2\sigma(I)$ are reported in Table 3, together with other details concerning data collection and refinement. The diffraction intensities were collected using a Bruker Apex II diffractometer equipped with a 2K CCD detector and Mo*K*α radiation (λ 0.71073 Å); a one minute frame time and 0.5° frame width were used. Intensity data were reduced using the program *SAINT* (Bruker, 2001), and corrected for Lorentz, polarization and background effects. An absorption correction was applied using the *SADABS* program (Sheldrick, 2000). Taking the debate on the space group of d'ansite, outlined in the foregoing text, into account, and having checked that no violations of the extinction rules for the $I\bar{4}3d$ space group were present, such a symmetry was considered to be the most plausible and the structure was solved *ab initio* by direct methods and refined using the *SHELXL97* program (Sheldrick, 2008) implemented in the *WinGX* suite of software (Farrugia, 1999). In agreement with the indications of the chemical analysis and of the anisotropic displacement parameters, during the refinement a partial replacement of Na by Mn or Fe in Wyckoff site 16*c* was allowed and the corresponding occupancies refined (Tables 4 and 5).

The chemical formula obtained from the refinement of d'ansite (Mn), $Na_{21.49}Mn_{0.51}(SO_4)_{10}Cl_3$, is in good agreement with the formula calculated from the chemical analyses and has 22.51 positive charges for the cation sum, compared to 23 negative charges for the anions. Due to the similarity in the scattering factors of Mg and Na, a structural model with the small amount of Mg that was detected in the chemical analysis was not refined, although such a model might have improved the charge balance.

TABLE 4. Atom coordinates and displacement parameters [U_{ij}/U_{eq}] (Å^2) for d'ansite-(Mn).

Atom	Wyckoff site	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na1	48*e*	0 88363(6)	0 37538(6)	0 84843(6)	0 0216(4)	0 0241(4)	0 0247(4)	0 0044(3)	0 0034(3)	0 0049(4)	0 0235(2)
Na2	24*d*	0 0000	0 2500	0 0442(1)	0 176(3)	0 048(1)	0 0154(7)	0	0	−0 045(2)	0 080(1)
Na3/Mn	16*c*	0 07623(7)	0 57623(7)	0 92377(7)	0 0356(6)	0 0356(6)	0 356(6)	−0 0039(4)	−0 0039(4)	0 0039(4)	0 0356(6)
S1	24*d*	0 01843(4)	0 5000	0 7500	0 0114(2)	0 0172(3)	0 0125(2)	0 0007(2)	0	0	0 0137(1)
S2	16*c*	0 96021(3)	0 46021(3)	0 03979(3)	0 0150(1)	0 0150(1)	0 0150(1)	−0 0011(1)	−0 0011(1)	0 0011(1)	0 0150(1)
O1	48*e*	−0 0337(1)	0 4269(1)	0 7295(1)	0 0238(7)	0 0248(8)	0 0326(9)	−0 0044(6)	−0 0035(6)	−0 0077(6)	0 0270(4)
O2	48*e*	0 0727(1)	0 5211(1)	0 6784(1)	0 0340(9)	0 0305(9)	0 0320(9)	0 0066(7)	0 0210(7)	0 0011(7)	0 0322(4)
O3	48*e*	0 9134(2)	0 4767(2)	−0 0372(1)	0 068(2)	0 045(1)	0 031(1)	−0 0081(9)	−0 025(1)	0 023(1)	0 0479(6)
O4	16*c*	0 9078(2)	0 4078(2)	0 0923(2)	0 085(2)	0 085(2)	0 085(2)	0 030(2)	0 030(2)	−0 030(2)	0 085(2)
Cl	12*b*	0 0000	0 2500	0 8750	0 0191(2)	0 0191(2)	0 0170(3)	0	0	0	0 0184(2)

Refined occupancies for the Na3 site are Na = 0 873(1), Mn = 0 127(1) The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + \quad + 2U_{12}hka^*b^* + \quad)$ The value of $U_{eq} = ⅓(U_{11} + U_{22} + U_{33})$

TABLE 5. Atom coordinates and displacement parameters [U_{ij}/U_{eq}] (Å^2) for d'ansite-(Fe).

Atom	Wyckoff site	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na1	48*e*	0 88098(4)	0 37440(4)	0 84834(3)	0 0236(3)	0 0239(3)	0 0252(3)	0 0024(3)	0 0017(3)	0 0014(3)	0 0243(2)
Na2	24*d*	0 0000	0 2500	0 04293(5)	0 152(1)	0 0371(6)	0 0180(5)	0	0	−0 0320(7)	0 0689(4)
Na3/Fe	16*c*	0 08027(4)	0 58027(4)	0 91973(4)	0 0454(3)	0 0454(3)	0 0454(3)	−0 0027(3)	−0 0027(3)	0 0027(3)	0 0454(3)
S1	24*d*	0 01852(3)	0 5000	0 7500	0 0102(2)	0 0240(3)	0 0172(3)	0 0034(3)	0	0	0 0171(1)
S2	16*c*	0 96103(3)	0 46103(3)	0 03897(3)	0 0164(1)	0 0164(1)	0 0164(1)	−0 0018(2)	−0 0018(2)	0 0018(2)	0 0164(1)
O1	48*e*	−0 03390(6)	0 42636(6)	0 73325(6)	0 0194(5)	0 0323(6)	0 0305(6)	0 0005(5)	0 0027(5)	−0 0101(6)	0 0274(3)
O2	48*e*	0 07233(6)	0 51656(6)	0 67692(7)	0 0355(6)	0 0312(7)	0 0449(7)	0 0132(6)	0 0243(6)	0 0076(6)	0 0372(4)
O3	48*e*	0 91376(8)	0 47536(7)	−0 03641(7)	0 0887(9)	0 0642(8)	0 0259(6)	−0 0094(6)	−0 0257(7)	0 0365(7)	0 0596(4)
O4	16*c*	0 90884(8)	0 40884(8)	0 09116(8)	0 1002(9)	0 1002(9)	0 1002(9)	0 0308(8)	0 0308(8)	−0 0308(8)	0 1002(9)
Cl	12*b*	0 0000	0 2500	0 8750	0 0244(2)	0 0244(2)	0 0136(4)	0	0	0	0 0208(2)

Refined occupancies for the Na3 site are Na = 0 870(1), Fe = 0 130(1) The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + \quad + 2U_{12}hka^*b^* + \quad)$ The value of $U_{eq} = ⅓(U_{11} + U_{22} + U_{33})$

TABLE 6. Relevant interatomic distances (Å), angles (º) and bond valences (vu).

	D'ansite (Mn)		D'ansite (Fe)	
Na1–O1	2.334(2)	0.20	2.349(1)	0.20
Na1–O1	2.449(2)	0.16	2.419(1)	0.17
Na1–O2	2.354(2)	0.19	2.355(1)	0.19
Na1–O3	2.479(2)	0.15	2.489(1)	0.15
Na1–O3	2.509(2)	0.14	2.504(1)	0.14
Na1–Cl	2.758(1)	0.17	2.767(1)	0.17
		Σ = 1.01		Σ = 1.02
<Na1–O>	**2.425**		**2.423**	
Na2–O1 ×2	2.893(2)	0.06 ×2	2.882(1)	0.07 ×2
Na2–O2 ×2	2.432(3)	0.16 ×2	2.449(1)	0.16 ×2
Na2–O3 ×2	2.689(3)	0.10 ×2	2.680(1)	0.10 ×2
Na2–O4 ×2	3.010(1)	0.05 ×2	3.008(1)	0.05 ×2
Na2–Cl	2.696(2)	0.19	2.667(1)	0.20
		Σ = 0.93		Σ = 0.96
<Na2–O>	**2.756**		**2.755**	
Na3–O1 ×3	3.005(2)	0.05 ×3	3.034(1)	0.05 ×3
Na3–O2 ×3	2.248(2)	0.24 ×3	2.177(1)	0.28 ×3
Na3–O3 ×3	3.104(3)	0.04 ×3	3.202(1)	0.03 ×3
Na3–O4	2.249(3)	0.24	2.161(1)	0.29
		Σ = 1.23		Σ = 1.37
<Na3–O>	**2.732**		**2.740**	
S1–O1 ×2	1.467(2)	1.53 ×2	1.460(1)	1.56 ×2
S1–O2 ×2	1.470(2)	1.52 ×2	1.465(1)	1.54 ×2
		Σ = 6.10		Σ = 6.20
<S1–O>	**1.469**		**1.463**	
O1–S1–O1	111.1(2)		110.5(1)	
O1–S1–O2 ×2	109.9(1)		109.5(1)	
O1–S1–O2 ×2	108.9(1)		109.4(1)	
O2–S1–O2	108.0(2)		108.6(1)	
<O–S1–O>	**109.5**		**109.5**	
S2–O3 ×3	1.460(3)	1.56 ×3	1.431(1)	1.68 ×3
S2–O4	1.447(3)	1.61	1.436(2)	1.66
		Σ = 6.29		Σ = 6.70
<S2–O>	**1.457**		**1.432**	
O3–S2–O3 ×3	111.8(1)		112.9(1)	
O3–S2–O4 ×3	107.1(1)		105.8(1)	
<O–S2–O>	**109.5**		**109.4**	

The chemical formula obtained from the refinement for d'ansite (Fe), $Na_{21.48}Fe_{0.52}(SO_4)_{10}Cl_3$, is in good agreement with the formula calculated from the chemical analyses and has 22.52 positive charges for the cation sum, compared to 23 negative charges of the anions. This result can be considered to be satisfactory, especially in view of the weak scattering power of the crystal as a result of its small size (~0.03 × 0.03 × 0.03 mm) and low quality. Final atom coordinates and displacement parameters are listed in Tables 4 and 5. Relevant interatomic distances are listed in Table 6.

Results and discussion

Our structure refinements of d'ansite (Mn) and d'ansite (Fe) confirm that the correct space group

for the d'ansite mineral series is $I\bar{4}3d$. A view of the structure of d'ansite (Mn) is shown in Fig. 6. The asymmetric unit contains a site in a general position (Na1), and another site on a twofold axis (Na2), both exclusively occupied by Na^+; a third site [Na3/Mn or Na3/Fe] on a threefold axis is statistically occupied by Na^+ and Mn^{2+} (or Fe^{2+}); two sulfate anions are located about a twofold axis ($S1O_4^{2-}$) and a threefold axis ($S2O_4^{2-}$), respectively and a chloride anion is located on a $\bar{4}$ position. The coordination geometry of each sodium site is different. Taking into account some interatomic distances that are significantly greater than the sum of the ionic radii of sodium and oxygen (of ~2.6 Å up to 3.1 Å), the Na1 site can be considered to have a distorted octahedral coordination with a mean Na1–O distance of 2.423 and 2.425 Å for the two minerals, respectively, and a chloride ion in an apical position at ~2.76 Å from the Na^+ ion. The Na2 site has a distorted ninefold coordination with a mean Na2–O distance of 2.755 and 2.756 Å and a Na2–Cl distance of ~2.68 Å. Partial substitution of Na for Mn or Fe occurs at the Na3 site, which has a coordination number of 10, and a mean Na3–O distance of 2.732 and 2.740 Å (Fig. 7). The chloride ion is octahedrally coordinated in a $[ClNa_6]^{5+}$ moiety, with an average Na–Cl distance of 2.736 Å, which is slightly but significantly shorter than the corresponding distance in sodium chloride (2.820 Å). A bond valence analysis carried out using the parameters of Brown (2009) (Table 6) is in agreement with the exclusive occupation of the Na1 and Na2 sites by sodium, and with partial replacement of sodium by a divalent cation at the Na3 site.

The sulfate anions have an average S–O distance which is comparable to the grand mean value found in sulfate minerals (1.473 Å; Hawthorne *et al.*, 2000), with a significant difference in the case of d'ansite (Fe) probably due to the lower accuracy of the diffraction data resulting from the poorer quality of the crystal. This difference reflects also in an overestimation of the valency of S2 calculated using the bond valence parameters reported in Brown and Altermatt (1985) in comparison to the theoretical value of 6.

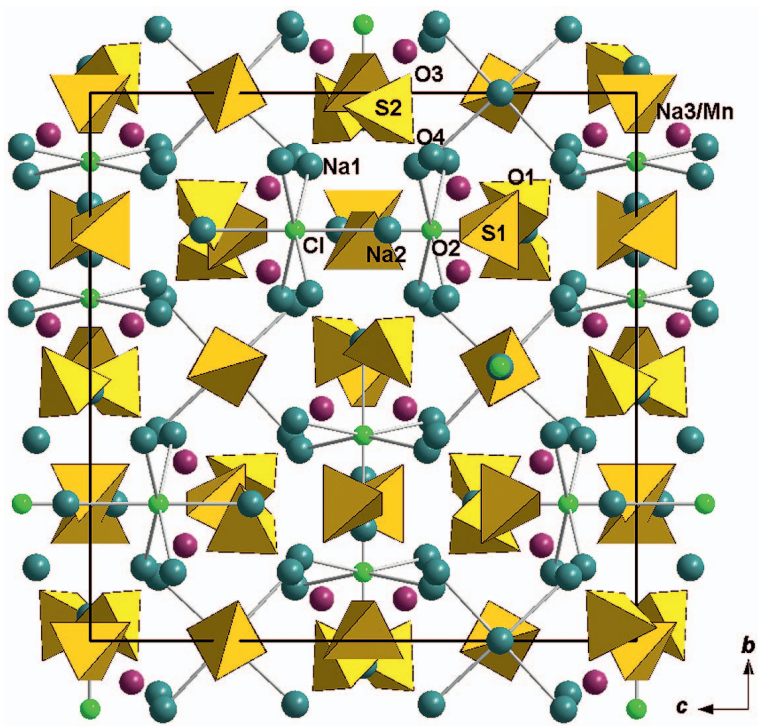

FIG. 6. A projection along [100] of the crystal structure of d'ansite (Mn), which is made up of $[ClNa_6]^{5+}$, Na^+/Mn^{2+} cations and SO_4^{2-} tetrahedra.

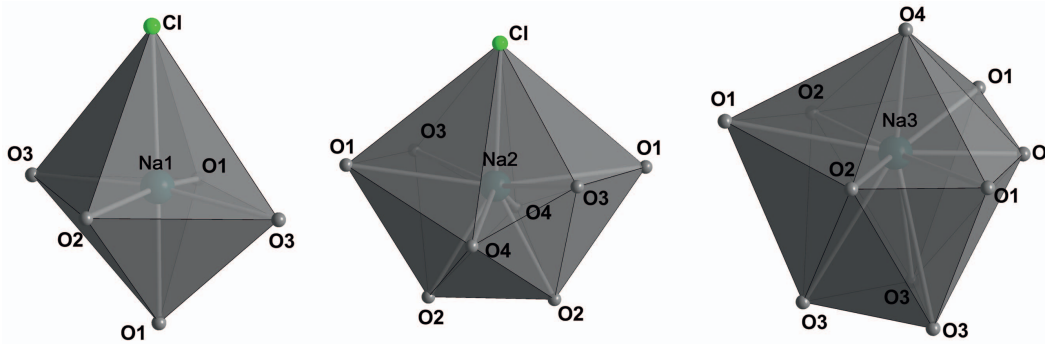

FIG. 7. The coordination polyhedra of the Na sites.

This report of d'ansite (Mn) and d'ansite (Fe) from Vesuvius and Vulcano is the first record of d'ansite series minerals from fumaroles, an environment which differs substantially from the evaporites from which the magnesium analogue, d'ansite, was first described. We have recently been informed that d'ansite (Fe) has also been found as a secondary mineral at Mežica (Slovenija), where it is associated with d'ansite and metasideronatrite 2*M* (M. Ciriotti, pers. comm.).

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