

Parascandolaite, KMgF_3 , a new perovskite-type fluoride from Vesuvius

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Received: 13 February 2014 / Accepted: 21 March 2014 / Published online: 8 April 2014
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Abstract The new mineral parascandolaite, isotypic to cubic perovskites, space group $Pm\bar{3}m$ (no. 221) is the natural analog of the synthetic fluoride KMgF_3 and is related to neighborite, NaMgF_3 . It was found as a volcanic sublimate at Vesuvius volcano on 1944 eruption lava scoria, associated with opal, cerussite, mimetite, phoenicochroite and coussellite. It occurs as transparent colorless to white cubic crystals up to 0.5 mm in length with vitreous luster. The density measured by flotation in a diiodomethane–toluene mixture is $3.11(1) \text{ g/cm}^3$; that calculated from the empirical formula and single-crystal X-ray data is 3.123 g/cm^3 . The mineral is isotropic with $n = 1.395(5)$ (580 nm). The six strongest reflections in the X-ray powder diffraction pattern are: [d_{obs} in $\text{Å}(I)(h k l)$] 2.001(100)(2 0 0), 2.831(83)(1 1 0), 2.311(78)(1 1 1), 1.415(56)(2 2 0), 1.633(35)(2 1 1) and 1.206(22)(3 1 1). The unit-cell parameter is $a = 4.0032(9) \text{ Å}$. The structure was refined to a final $R(F) = 0.0149$ for 35 independent observed reflections [$I > 2\sigma(I)$]. The mineral is named after the Italian mineralogist Antonio Parascandola (1902–1977).

Keywords Parascandolaite · New mineral species · Fumarole sublimate · Crystal structure · Potassium magnesium trifluoride · Vesuvius

Introduction

Vesuvius is one of the most studied volcanos in the world and one of the most dangerous for the more than 800,000 inhabitants living on its slopes. For this reason, studies conducted in various fields of geology and geophysics monitor 24 h a day everything that happens in this area. The Somma–Vesuvio volcanic complex consists of an older volcano dissected by a summit caldera, Mt. Somma and a recent cone, Vesuvio, that grew within the caldera after the AD 79 eruption. A detailed description of the complex geological situation arising from a long series of eruptions is reported for instance by Santacroce et al. (2008) and Fulignati et al. (1998, 2000). However, little is known about the solid phases deposited or continuously forming from active fumaroles, subsequent to the last eruption in 1944. Unfortunately in 1944, perhaps in part because of the war, only one scientist, Antonio Parascandola (1902–1977) was undertaking studies of the mineralogy of these fumaroles. In the course of our systematic studies of fumarole minerals, in May 2013, we found the analog of synthetic KMgF_3 , a cubic perovskite-type fluoride (DeVries and Roy 1952; Muradyan et al. 1984; Burns et al. 1996; Chakhmouradian et al. 2001, Mitchell et al. 2006). This was approved as a new mineral species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2013-092), and named parascandolaite to honor Antonio Parascandola. He graduated in Chemistry and Pharmacy from the University of Napoli (Italy). From 1932 to 1972, he taught mineralogy, geology and later volcanology and physical geography at the Pozzuoli Aeronautical Academy, at the Istituto di Mineralogia della Facoltà di Scienze of Napoli and at the Istituto di Mineralogia e Geologia della Facoltà di Agraria of Portici (Napoli). His remarkably accurate studies appeared in “Notizie Vesuviane” between 1947 and 1961 and in

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“Bollettino della Società Geologica Italiana,” accompanied by countless observations about the conditions of formation of the minerals in the fumaroles (for instance, Parascandola 1950, 1951).

This paper deals with the description of the new mineral parascandolaite, together with its crystal structure refinement.

Occurrence, morphology, physical properties and composition

Only one sample of parascandolaite (type material deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, Italy, specimen number 2013–2014) was found as a volcanic sublimate on 1944 scoria in an active fumarole (fumarole B5, temperature about 80 °C). A picture of the Vesuvius crater with the fumarole area is shown in Fig. 1. The mineral is associated with opal, cerussite (PbCO_3), mimetite [$\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$], phenicochroite [$\text{Pb}_2(\text{CrO}_4)\text{O}$] and coulsellite [$\text{CaNa}_3\text{AlMg}_3\text{F}_{14}$]. It forms transparent colorless to white cubic crystals up to 0.5 mm in length (Fig. 2), with a vitreous luster. No twinning was observed. Cleavage is perfect on $\{100\}$. No fluorescence was observed under either short- or long-wave ultraviolet radiation. The density measured by flotation in a diiodomethane–toluene mixture is $3.11(1) \text{ g/cm}^3$; that calculated from the empirical formula and single-crystal X-ray data is 3.123 g/cm^3 . The mineral is isotropic with $n = 1.395(5)$ (580 nm) determined by immersion in an ethyl/amyl alcohol solution. The refractive index determined on the synthetic material by DeVries and Roy (1952) is $1.404(2)$.

Quantitative analysis was undertaken in energy dispersive spectrometry mode using a JEOL JSM 5500 LV



Fig. 1 A view toward the east rim of the Vesuvius crater, with the fumarolic area highlighted yellow

scanning electron microscope equipped with an IXRF Sirius SD-10128-LE microprobe (20 kV excitation voltage, 10 pA beam current, $2 \mu\text{m}$ beam diameter). Element concentrations were measured using the K_α lines for K, Mg and

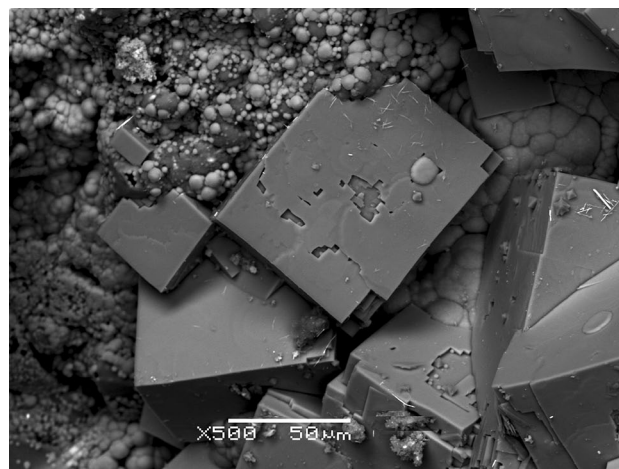


Fig. 2 Scanning electron microscope backscattered electron image of crystals of parascandolaite associated with colloform opal

Table 1 Chemical composition of parascandolaite (average of 8 analyses)

Constituent	wt%	Range	SD	Analytical standards
K	32.65	32.54–32.76	0.10	Synthetic KMgF_3
Mg	20.24	20.10–20.40	0.12	Synthetic KMgF_3
F	46.71	46.46–47.25	0.37	Synthetic KMgF_3
Total	99.60			

Table 2 X-ray powder diffraction data for parascandolaite

<i>h k l</i>	Parascandolaite			Synthetic KMgF_3 PDF2 entry 00-018-1033	
	I_{rel}	$d_{\text{obs}} (\text{Å})$	$d_{\text{calc}} (\text{Å})^a$	I_{rel}	$d_{\text{obs}} (\text{Å})$
1 0 0	1	3.997	3.995	2	3.988
1 1 0	83	2.831	2.825	94	2.819
1 1 1	78	2.311	2.307	83	2.302
2 0 0	100	2.001	1.998	100	1.994
2 1 0	1	1.782	1.787	1	1.784
2 1 1	35	1.633	1.631	24	1.628
2 2 0	56	1.415	1.413	36	1.410
2 2 1, 3 0 0	2	1.322	1.332	<1	1.330
3 1 0	16	1.267	1.263	6	1.261
3 1 1	22	1.206	1.205	8	1.203

^a Calculated with $a = 3.9950(2) \text{ Å}$, obtained from least-squares refinement of the above data using the program UNITCELL (Holland and Redfern 1997)

F. No significant amounts of other elements were detected. The mean composition is reported in Table 1. The empirical formula obtained from these data and on the basis of 5 atoms per formula unit is $K_{1.01}Mg_{1.01}F_{2.98}$, whereas the formula calculated on the basis of three F atoms is $K_{1.02}Mg_{1.02}F_3$. The idealized formula is $KMgF_3$ which requires: K 32.47, Mg 20.19, F 47.34, total 100.00 wt%.

X-ray data

X-ray powder diffraction (XRPD) data (Table 2) were obtained using a Rigaku DMAX II diffractometer, with graphite monochromated $CuK\alpha$ radiation. The unit-cell parameter refined from the powder data using the program UNITCELL (Holland and Redfern 1997) is: $a = 3.9950(2)$ Å. This value is slightly higher, but comparable to the previously reported values of 3.9897(1) Å obtained from XRPD data by Chakhmouradian et al. (2001) using full-profile refinement, 3.9859(8) Å and 3.9892(4) Å reported by Burns et al. (1996) and Muradyan et al. (1984), respectively, from single-crystal data. Mitchell et al. (2006) gave a value of 3.9924(2) Å at 293 K, obtained by Rietveld refinement of powder neutron diffraction data. The unit-cell parameter calculated using 490 single-crystal reflections with $I > 5\sigma(I)$ and $10.18^\circ < 2\theta < 52.35^\circ$ is significantly larger: 4.003(1) Å. These differences are not due to variation in chemical composition with respect to the ideal formula $KMgF_3$, as confirmed by the chemical analysis, but they may be due to the different procedures of data refinement leading also to underestimation of the e.s.d.'s.

A total of 663 intensities corresponding to a complete scan of the reciprocal lattice up to $2\theta = 62.34^\circ$ were collected from a single crystal ($0.02 \times 0.02 \times 0.02$ mm) using a Bruker Apex II diffractometer equipped with a 2 K CCD detector and $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). Details of the data collection procedure and structure refinement are reported in Table 3. A 1-min frame time and a 0.5° frame width were used. The intensity data were reduced using the program SAINT (Bruker 2001) and corrected for Lorentz-polarization and background effects. An absorption correction ($\mu = 2.135$ mm $^{-1}$, $T_{min} = 0.861$) was applied using the SADABS program (Sheldrick 2000). After averaging the symmetry-related reflections ($R_{int} = 0.0102$), 37 independent data were obtained. The structure (Fig. 3) was refined from the known atomic coordinates (Muradyan et al. 1984) using the SHELXL97 program (Sheldrick 2008) implemented in the WinGX suite (Farrugia 1999). The final R is 0.0149 for 35 observed reflections [$I > 2\sigma(I)$]. The coordinates and displacement parameters of the atoms are reported in Table 4. Observed and calculated structure-factor tables may be obtained from the authors.

Table 3 Single-crystal diffraction data and refinement parameters for parascandolaite

Crystal system	Cubic
Space group	$Pm\bar{3}m$
a (Å)	4.003(1)
V (Å 3)	64.14(1)
Z	1
Radiation	$MoK\alpha$ ($\lambda = 0.71073$ Å)
μ (mm $^{-1}$)	2.135
D_{calc} (g/cm 3)	3.117
Measured reflections	663
Independent reflections, R_{int}	37, 0.0102
Observed reflections [$I > 2\sigma(I)$]	35
Parameters refined	5
Final R [$I > 2\sigma(I)$] and $wR2$ (all data)	0.0149, 0.0342
S	1.416

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR2 = \left\{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \right\}^{1/2};$$

$$w = 1 / [\sigma^2(F_o^2) + (0.0133q)^2 + 0.0247q] \text{ where}$$

$$q = [\max(0, F_o^2) + 2F_c^2] / 3; S = \{ \Sigma [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$$

where n is the number of reflections and p is the number of refined parameters

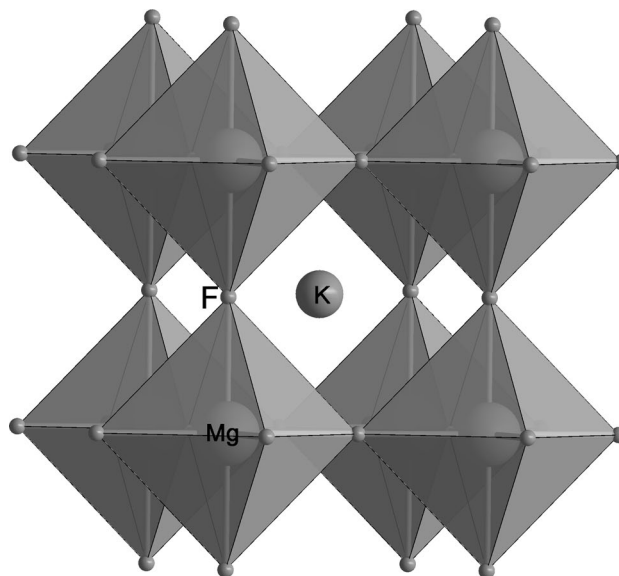


Fig. 3 Perspective view of the structure of parascandolaite

Discussion

The synthetic compound $KMgF_3$, isotypic to cubic perovskites, was widely studied for its technological applications, due to luminescent properties of its doped varieties. It was originally made by melting mixtures of KF

Table 4 Atomic coordinates and displacement parameters [U_{ij} , Å²] for parascandolaite

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	1/2	1/2	1/2	0.0149(3)	0.0149(3)	0.0149(3)	0	0	0
Mg	0	0	0	0.0089(4)	0.0089(4)	0.0089(4)	0	0	0
F	0	0	1/2	0.0181(6)	0.0181(6)	0.0134(9)	0	0	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + \dots + 2U_{12}hka^*b^* + \dots)$; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

and MgF_2 (DeVries and Roy 1952) or by adding HF to a slurry of K_2CO_3 and MgCO_3 and evaporating the mixture to dryness (Swanson et al. 1968). Parascandolaite is its natural analog and is related to orthorhombic neighborite NaMgF_3 . Potassium-rich neighborites, $(\text{Na}_{1-x}\text{K}_x)\text{MgF}_3$, have been extensively investigated by Zhao (1998) and Chakhmouradian et al. (2001), using X-ray and neutron diffraction techniques, who showed a transition from an orthorhombic ($Pbnm$) symmetry in NaMgF_3 to the cubic ($Pm\bar{3}m$) structure of KMgF_3 , via an intermediate tetragonal structure, with increasing K content. The large K^+ cations fill the dodecahedral cavity in the cubic perovskite phase and their replacement by smaller Na^+ cations induces a collapse to the distorted lower-symmetry structures, with rotation of the MgF_6 octahedra and displacement of Na and K from the “ideal” position. The relationships between the orthorhombic cell of neighborite and the cubic one of KMgF_3 are: $a_o \approx \sqrt{2}a_c$, $b_o \approx \sqrt{2}a_c$, $c_o \approx 2a_c$.

The natural occurrence of KMgF_3 is not unprecedented, even if it was not recognized as a valid mineral species before. Parascandolaite probably corresponds to unnamed mineral UM1960-02-F:KMg (Smith and Nickel 2007). A paper by Hermann et al. (1960) cited by Hey (1963) reports the occurrence of a potassium magnesium fluoride with probable composition KMgF_3 from the Nyiragongo volcano, Democratic Republic of Congo, and a phase with the same composition but without diffraction data was reported by Povarennykh (1972) with the name “kamaflagite.” Other occurrences of minerals compositionally intermediate between KMgF_3 and NaMgF_3 include altered carbonatites at the Oldoinyo Lengai volcano, Tanzania (Mitchell 1997; Zaitsev et al. 2008) and at the Khannenshin carbonatite complex, Afghanistan (Tucker et al. 2011).

In spite of the current low temperature of the B5 fumarole (about 80 °C) and of the almost complete absence of hydrofluoric acid, this fumarole reached a maximum temperature of 800 °C in March 1954. Parascandolaite formed by reaction of the fumarolic gases containing hydrofluoric acid with the K-rich host rock, when the temperature of the fumarole was definitely higher than that currently observed.

Structure refinement of parascandolaite was the first carried out on a pure single natural crystal of KMgF_3 . The resulting K–F distances are 2.8305(4) Å and 2.0015(3) Å, respectively. For comparison, the K–F distance measured

by Mitchell et al. (2006) in the synthetic KMgF_3 is 2.823 Å and that in the isostructural KNiF_3 is 2.8366(4) Å (Kijima et al. 1983). The Mg–F bond length reported by Mitchell et al. (2006) is 1.996 Å and that observed in RbMgF_3 is 2.005 Å (Wu and Hoppe 1984). The MgF_6 and KF_{12} polyhedra volumes are 10.690 and 53.450 Å³, respectively; those determined by Mitchell et al. (2006) are 10.606 and 53.030 Å³, respectively.

Conclusions

The discovery of parascandolaite suggests that the study of the sublimates formed in the fumaroles at Vesuvius, in spite of their low activity, is far from being complete. Further recognition of interesting or new minerals and their paragenetic associations is still possible as already shown by the recent discovery of d’ansite-(Mn), $\text{Na}_{21}\text{Mn}^{2+}(\text{SO}_4)_{10}\text{Cl}_3$, (Demartin et al. 2012) and of the second occurrence of the exceedingly rare fluoride coussellite, in this environment.

Acknowledgments The authors are grateful to the Guest Editor A.R. Chakhmouradian, to Roger Mitchell and to an anonymous referee for helpful suggestions and comments.

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