

SODALITE-GROUP MINERALS FROM THE SOMMA-VESUVIUS VOLCANO (NAPLES, ITALY): A COMBINED EPMA, SIMS, AND FTIR CRYSTAL-CHEMICAL STUDY

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ABSTRACT

This work is focused on the crystal-chemical characterization of the cationic and anionic components of sodalite-group minerals (SGM) occurring in various igneous-to-metamorphic rocks and ejecta from the alkaline-potassic Somma-Vesuvius volcano (southern Italy). A combination of different analytical techniques, *i.e.*, XRD, SEM, EPMA, SIMS, FTIR, and μ -FTIR-FPA imaging, were used. Minor and trace volatile elements (H, C, and F) have been quantified for the first time (to the authors' knowledge) by SIMS, and *in situ* ion probe data were integrated with information derived from FTIR spectroscopy.

The studied samples correspond to sodalite *sensu stricto*, nosean, and haüyne. SIMS measurements for H, F, and C (quantified as H₂O, F, and CO₂ wt.%, respectively) show contents 0.02–5.0 wt.% H₂O, 0.01–0.14 wt.% F, and 0.08–2.95 wt.% CO₂. Within the single crystals, the F and, to a lesser extent, CO₂ concentrations are homogeneous, whereas, in terms of H₂O, they range from relatively homogenous to strongly zoned. Single-crystal FTIR spectra of SGM can be grouped into sodalites and noseans/haüynes, according to the occurrence of the ¹²CO₂ absorption at 2340 cm⁻¹. The absorption due to H₂O or OH groups occurs as a very broad band extending from 3700 to 3000 cm⁻¹. FTIR data show the presence of CO₃²⁻ in all samples. The collected data allow us to fully characterize the SGM from Somma-Vesuvius, and also provide some constraints regarding their genesis. These data can contribute to a more detailed understanding of the crystal chemistry of

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SGM, their geological environments of formation, and possibly of the technological characteristics of their synthetic analogues.

Keywords: sodalite-group minerals, Somma-Vesuvius volcano, EPMA, SIMS, FTIR.

INTRODUCTION

Sodalite-group minerals are typical constituents of alkaline magmatic, hydrothermal, and some rare meta-evaporitic rocks (Parat *et al.* 2011, Hettmann *et al.* 2012). They are characterized by a tetrahedral framework structure with the general formula $M_{7-8}(T_{12}O_{24})X_{1.5-2}$. The structural framework T site is occupied by Si and Al (with minor substitution by Fe^{3+} or Be^{2+}). The extraframework M site contains mainly Na and Ca (less K, Mg, Fe^{2+} , Mn, Zn), whereas the extraframework X site can contain different chemical species, such as Cl^- , SO_4^{2-} , CO_3^{2-} , S_2^{2-} , S_3^{2-} , OH^- , H_2O , and CO_2 (Ballirano & Maras 2005, Bellatreccia *et al.* 2009). This group can be subdivided into three subgroups, the sodalite, tugtupite, and danalite subgroups, respectively represented by the following endmembers:

- sodalite $Na_8[Al_6Si_6O_{24}]Cl_{12}$, nosean $Na_8[Al_6Si_6O_{24}](SO_4) \cdot H_2O$, haiyue $Na_6Ca_2[Al_6Si_6O_{24}]_8(SO_4, Cl)_{1-2}$, lazurite $(Na, Ca)_{7-8}[Al_6Si_6O_{24}](Si_4, S, Cl) \cdot H_2O$;
- tugtupite $Na_4[BeAlSi_4O_{12}]Cl$;
- danalite $Fe_4[Be_3Si_3O_{12}]S$, helvite $Mn_4[Be_3Si_3O_{12}]S$, and genthelvite $Zn_4[Be_3Si_3O_{12}]S$.

The topological symmetry of the sodalite framework is cubic, whereas the rare mineral tugtupite has a tetragonal real structure (due to the $BeAl \rightleftharpoons AlAl$ substitution in the lattice). These minerals show a zeolite-like arrangement with two structural cavities per unit cell (Fischer & Baur 2009), consisting of layered structures containing an array of six-membered rings of TO_4 ($T = Si, Al$, or Be), and belong to the cancrinite-sodalite supergroup (Bonaccorsi & Nazzareni 2015). The presence of an ABC sequence generates the sodalite-group minerals, whereas an ABAB sequence gives rise to the cancrinite group (Della Ventura *et al.* 2008, Ballirano 2012). The extraframework chemical species, *i.e.*, the large cations, molecules, anions, or anionic groups, are often referred as guests and fill the pores of the hosting framework (Balassone *et al.* 2012). The extra-tetrahedral molecules in these structures can play a key role in both petrogenetic processes and technological applications, *i.e.*, gaseous H_2 and CO_2 molecular species storage (van der Berg *et al.* 2005, Bellatreccia *et al.* 2009, Della Ventura *et al.* 2008). The chemistry of the X site (CO_3 , SO_4 , H_2O , Cl , and Br) has also been

used to constrain the compositions and origins of coexisting fluids and the pressure-temperature environmental conditions (Hammerli *et al.* 2014, Cooper *et al.* 2015). Hence, quantification of light elements (*i.e.*, hydrogen and carbon) and their speciation (*i.e.*, OH^- , H_2O , CO_3^{2-} , CO_2) can have important implications in many geological fields. Recently, research has been carried out on halogen concentrations (F, Cl, Br, I) in scapolite-group minerals and sodalite by LA-ICP-MS and XRF, indicating their role as geological fluid tracers in the Earth's crustal processes (Hammerli *et al.* 2014, Pan & Dong 2003). Finally, the chemical zoning in haiyue has been investigated to constrain the evolution of volatile concentration in quartz-undersaturated magmatic systems (Tracy 2003, Di Muro *et al.* 2004, Parat *et al.* 2011, Cooper *et al.* 2015).

At the Somma-Vesuvius volcanic complex, the SGM occur in different lithotypes, ranging from lavas to contact metamorphic rocks, and in many types of xenoliths (Russo & Punzo 2004, Petti *et al.* 2010, Balassone *et al.* 2012, 2015). Many remarkable SGM samples, hereafter referred to as sodalite (a pure sodalite, *i.e.*, mostly containing chlorine as a volatile species), nosean (here indicating, for the sake of simplicity, a wide range of sulfur-rich varieties roughly approaching nosean compositions), and haiyue (generally represented by the Ca-S-richest varieties), are gathered in the "Vesuvian Collection" of the Università di Napoli Federico II mineralogical museum (Italy). They were catalogued as "sodalite" or "haiyue" in the past, and have never been studied before.

The present study includes a detailed characterization of 39 SGM samples from various rocks related to the alkaline potassic to ultrapotassic products of the Somma-Vesuvius volcano by using a combination of analytical techniques, including scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), secondary ion mass spectrometry (SIMS), and single-crystal Fourier transform infrared micro-spectroscopy (μ -FTIR) with focal plane array (FPA) imaging. A main focus was to evaluate the concentrations of the main cations and the major (Cl, S) and minor volatiles (H_2O , CO_2 , F), and to examine possible relationships with the genetic environment. The SIMS and FTIR methods are particularly pivotal in characterizing the real volatile contents of these zeolite-like minerals (Ottolini *et al.*

1994, 2002, Bellatreccia *et al.* 2006, Bonaccorsi *et al.* 2007, Della Ventura *et al.* 2005, 2007).

SAMPLE DESCRIPTION

The Mineralogical Museum of Naples (MMN) holds a vast collection of about 3000 samples from the Somma-Vesuvius volcano (the so-called “Vesuvian Collection”), which represents an inestimable heritage for the scientific community, due to their provenance from old and in some cases now-inaccessible outcrops (Ghiara & Petti 2008). Among the Museum samples, feldspathoid-bearing specimens, like the SGM, are of particular interest for their rarity and the gem-quality varieties of crystals. As reported in the MMN archives, the sodalite-bearing rocks were collected mostly during the eighteenth and early nineteenth century, and until now they have been poorly described and studied.

Table 1 reports the original MMN numbering and classification of the SGM examined in this study. Following the museum catalogues, a restricted number of SGM-bearing specimens originate from ejecta associated with the AD 1872 and 1906 lavas and Vesuvian historical lavas (*e.g.*, AD 1631). All other specimens are xenoliths without a clear sampling site, apart from a generic Mt. Somma occurrence reported for five samples. However, for all these latter specimens we can assume that their provenance is likely associated with the Plinian eruptions of Avellino (~3.9 ka BP), Pompei (AD 79), and Pollena (AD 472), which brought the largest amount of ejecta to the surface (Gilg *et al.* 2001, Balassone *et al.* 2012 and reference therein). The xenoliths range from alkali syenite nodules to metamorphic rocks, represented by skarns, hornfelses, thermally metamorphosed carbonates, and composite rocks.

Crystals identified as sodalites and haüynes generally occur in cavities or at the surface of ejecta and lava (Fig. 1A, B). Their dimensions vary from a few millimeters to some centimeters. Locally prismatic pseudo-hexagonal crystals have been found. This morphology is not rare for sodalite from Vesuvius and had previously been observed in the literature (Russo & Punzo 2004). A particular green variety of nosean (Fig. 1A), the so-called “molibdosodalite” (Zambonini 1935), is described in seven MMN specimens studied here. Indeed, as shown by previous studies (Ballirano & Maras 2005, Balassone *et al.* 2012), this variety corresponds to nosean, and is molybdenum-free. SEM micrographs of the studied SGM generally show well-developed morphologies, commonly with a rhombic dodecahedral habit (Fig. 1C, D).

METHODS

Thirty-nine SGM crystals were hand-picked using a binocular microscope for the instrumental analysis described below. SEM observations were done with a JEOL-JSM 5310 instrument (CISAG Laboratory, Università di Napoli Federico II). EPMA were obtained using a Cameca SX50 WDS instrument (CNR-IGAG, Rome) with the following experimental conditions: 15 nA sample current, 10 kV accelerating voltage, 10 µm beam diameter. The standards were: wollastonite (Si, Ca), titanite (Ti), corundum (Al), magnetite (Fe), periclase (Mg), jadeite (Na), and orthoclase (K). In each sample, several points (6–10) were analyzed. Data were corrected using the PAP program (Pouchou & Pichoir 1991). Relative uncertainty of the analytical measurements is 1% for major elements, 4% for minor elements, and 10% for F.

SIMS analysis was performed on 14 crystals from the set (four sodalites, seven noseans, and three haüynes) using the Cameca IMS 4f ion microprobe installed at CNR-IGG (Pavia). A static 20 nA, mass filtered $^{16}\text{O}^-$ primary beam accelerated to 12.5 kV was focused on the sample surface to obtain a ~25 µm beam diameter. Positive secondary ions from the sample were extracted with a 4.5 kV accelerating voltage and transferred into the mass spectrometer by the 25 µm secondary-ion optics. Secondary ions were “energy filtered” in the electrostatic sector with an emission energy in the range ~75–125 eV. Entrance and exit slits were left wide open. $^1\text{H}^+$, $^{12}\text{C}^+$, $^{19}\text{F}^+$, and $^{30}\text{Si}^+$ ion signals were detected after the 900 s waiting time required to obtain steady-state sputtering conditions. Acquisition times were 6 s for $^1\text{H}^+$, 8 s for each of $^{12}\text{C}^+$ and $^{19}\text{F}^+$, and 3 s for $^{30}\text{Si}^+$ for each of the three analytical cycles. Unknown crystals and standards were left to degas for several days in the ion probe sample-chamber (SC) before obtaining analyses (Ottolini *et al.* 1995, 2002). There were three analytical sessions for the whole sample set. The H_2O background was tested on a nominally (CNR-IGG) anhydrous pyrope, resulting in $0.0075 \pm 0.0035(1\sigma)$ wt.% H_2O . Inner reference materials used for H, C, and F quantification in sodalite and haüyne are represented by the sodalite LM11 (SiO_2 36.68 wt.%, H_2O 0.47 wt.%, F 0.06 wt.%, CO_2 0.35 wt.%) and haüyne H34 (SiO_2 32.62 wt.%, H_2O 0.16 wt.%, F 0.03 wt.%, CO_2 0.42 wt.%) samples previously characterized by Bellatreccia *et al.* (2009). Ion probe bombardment was done close to the micro-areas previously investigated by electron microprobe, and in doing so we tried to match as much as possible the chemical information from both techniques at the various selected areas of the crystals. We have to consider, however, that the SIMS crater is much larger

TABLE 1. SAMPLE INFORMATION FOR SGM FROM SOMMA-VESUVIUS IN THE MINERALOGICAL MUSEUM OF NAPLES UNIVERSITY

Sample ID	Sample description ^a	SGM species ^b	Host rock	Assemblage ^c
<i>"sodalites"</i> ^a				
D3	white sodalite	Sdl	xenolith, Mt. Somma	Kfs, Cal, Ves, Spl
D259	sodalite	Sdl	xenolith	Cpx, Grt, Mi
D740	white sodalite	Sdl	xenolith	Cal, Ves, Hu, Wo, Grt
D751	green-yellowish sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Ves, Mi
D752	white sodalite	Sdl	xenolith	Cal, Mi, Kfs
D756	hyaline sodalite	Sdl	xenolith	Kfs, Mel, Mag
D763	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Mei, Ves
D765	white sodalite	Sdl	xenolith	Kfs, Amp, Grt
D766	hyaline sodalite	Sdl	xenolith	Kfs, Amp
D768	hyaline sodalite	Sdl	xenolith	Kfs, Cpx, Mag
D772	hyaline sodalite	Nsn	xenolith	Kfs, Mi
D773	green sodalite	Nsn	xenolith	Kfs, Mi
D777	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Mi, Cal, Cpx
D778	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Mi, Ms, Hem
D781	white to colorless sodalite	Sdl	xenolith	Kfs, Mag
D782	white-light yellow sodalite	Sdl	xenolith	Cal, Kfs, Mag, Amp, Mi
D784	well-crystallized geodic sodalite	Nsn	xenolith	Cal, Lct, Ms
D785	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Mi, Kfs, Cpx
D786	white-light green geodic sodalite	Nsn	xenolith	Cal, Ms
D789	white sodalite	Sdl	xenolith, Mt. Somma	Ves, Amp
D795	green-bluish sodalite	Nsn	xenolith	Grt, Mel
D797	green sodalite	Nsn	xenolith	Cpx, Mi, Wo
D1581	white sodalite	Sdl	xenolith	Cpx, Amp, Ar
D1621	white sodalite	Sdl	xenolith	Ves, Gr, Hu
D1626	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Kfs, Ne, Amp, Mi
E1558	green sodalite (<i>"molibdosodalite"</i>)	Nsn	xenolith	Ves, Mi, Cal
E5707	sodalite	Nsn	xenolith, Vesuvius (AD 1872)	Lct, Kfs, Hem
E5926	white sodalite	Nsn	xenolith, Mt. Somma	Ves, Ol, Mi
E6264	iridescent sodalite	Sdl	lava, Vesuvius (AD 1631)	Lct, Cpx, Mi, Pl, Ol
E6265	iridescent sodalite	Sdl	lava, Vesuvius (AD 1631)	Lct, Cpx, Mi, Pl, Ol
<i>"hauyynes"</i> ^a				
150	blue hauýne	Hyn	xenolith	Cpx, Mi, Spl
22123	dark blue hauýne	Nsn	xenolith, Vesuvius (AD 1906)	Kfs, Cpx, Lc, Mag
A3149	deep blue hauýne	Hyn	xenolith	Lct, Cpx, Mi
C3488	light blue hauýne	Hyn	xenolith	Cpx, Lct
C3489	light blue hauýne	Hyn	xenolith, Mt. Somma	Cpx, Mi
D803	light blue-gray hauýne	Hyn	xenolith	Cpx, Lct, Ms
D804	blue-green hauýne - xenolith	Hyn	xenolith	Pl, Cpx, Mi
D1810	deep blue hauýne	Hyn	xenolith, Mt. Somma	Cal, Lct
E5918	hauýne	Nsn	xenolith, Mt. Somma	Kfs, Mi

^a Museum cataloging. The terms "sodalites" and "hauýnes" refer to the old museum classification (see text).

^b Species determined in this work; Sdl = sodalite; Nsn = nosean; Hyn = hauýne (see Table 2).

^c Amp = clinoamphibole, Ar = aragonite, Cal = calcite, Cpx = clinopyroxene, Grt = garnet (grandites), Hem = hematite, Hu = humite, Kfs = K-feldspar, Lct = leucite, Mag = magnetite, Mei = meionite, Mel = melilite, Mi = mica (biotite-phlogopite), Ne = nepheline, Ol = olivine, Pl = plagioclase, Spl = spinel, Ves = vesuvianite, Wo = wollastonite.

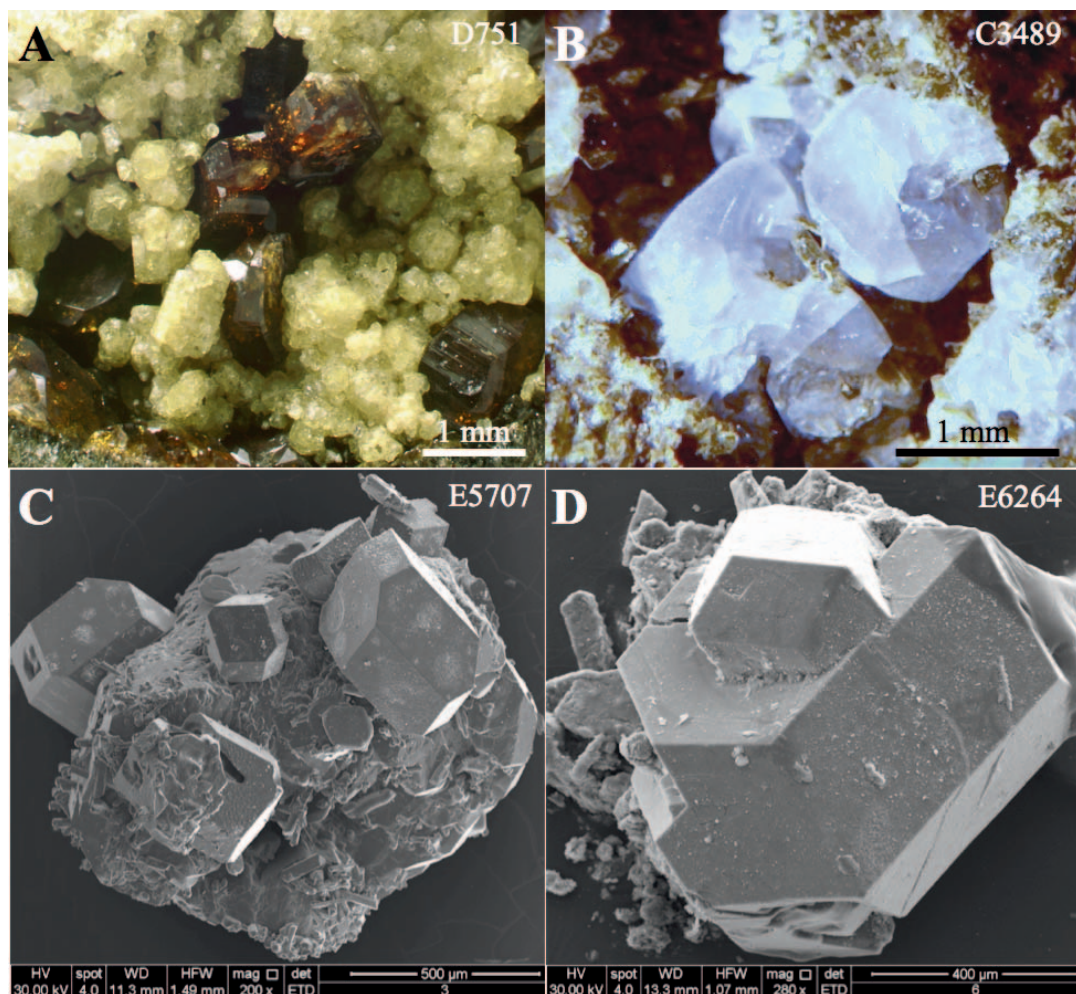


FIG. 1. (A, B) Hand-specimen pictures and (C, D) SEM micrographs of selected sodalite group minerals from the collection of the Mineralogical Museum (Università di Napoli Federico II); (A) light green-yellowish nosean (the so-called “molibdosodalite”), with euhedral brown vesuvianite crystals; (B) light-blue haüyne with light-green clinopyroxene crystals; (C) euhedral nosean crystals with aggregates of prismatic K-feldspar; (D) sodalite with a dodecahedral habit.

than the EPMA spot (in this study, $\sim 25 \mu\text{m}$ ion-beam $\varnothing$ versus $\leq 5 \mu\text{m}$ electron-beam $\varnothing$).

μ -FTIR spectra of 21 samples were collected at the Laboratori Nazionali di Frascati (Italy), Istituto Nazionale di Fisica Nucleare (LNF-INFN), using a Bruker Hyperion 3000 microscope attached to a VERTEX 70v FTIR spectrometer with a globar IR source. The studied samples were fragments from the same crystals analyzed by EPMA and SIMS, except for three samples (D259, D752, and E5918) which are different individuals of the same species occurring in the rock specimens. The sample chamber was constantly evacuated with a gentle nitrogen flux during

data collection. Single-spot μ -FTIR spectra were acquired with a LN₂-MCT (liquid nitrogen cooled-mercury cadmium telluride) detector and a beam size of $20 \mu\text{m}$. The nominal resolution was 4 cm^{-1} and 128 scans were averaged for both background and sample. μ -FTIR images were acquired from 13 samples using a LN₂-MCT 64×64 pixel FPA (focal plane array) of detectors. The IR images were acquired in the range $4000\text{--}800 \text{ cm}^{-1}$ at a nominal resolution from 8 to 16 cm^{-1} using a $15\times$ objective lens; 64 spectra were co-added (for both reference and sample). With this setting a single FPA image covers $170 \times 170 \mu\text{m}^2$ at a spatial resolution of $3\text{--}5 \mu\text{m}$ (Della Ventura *et al.*

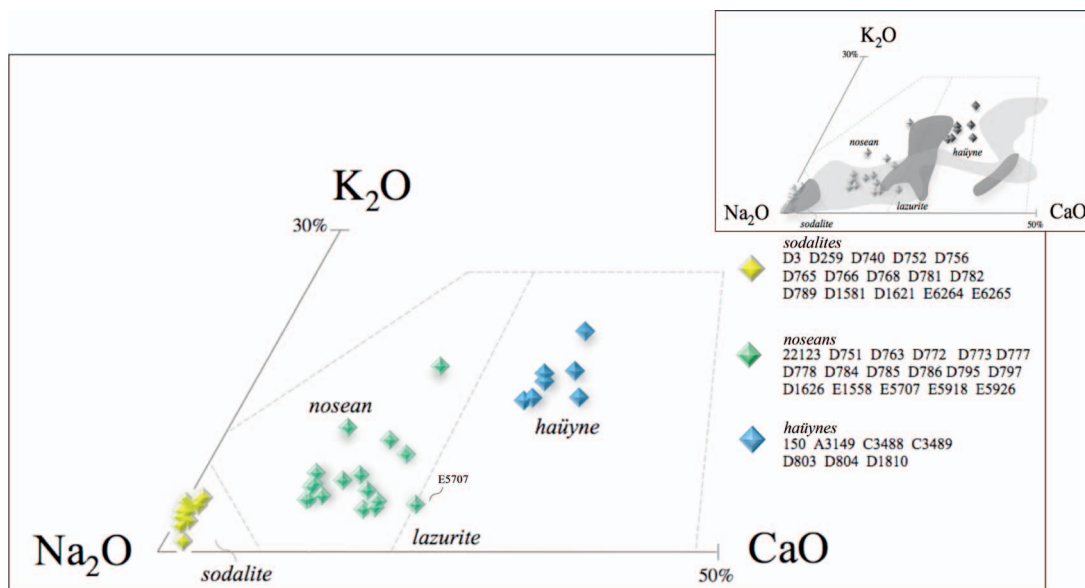


FIG. 2. Compositional fields recalculated to cation percentages (Lessing & Grout 1971) for the sodalite group minerals in this study. The top-right inset shows the SGM compositions of this work compared to literature data for Somma-Vesuvius (dark-grey area; Balassone *et al.* 2012) and Mt. Vulture rocks (light-grey area; Melluso *et al.* 2011).

2010, 2014). Samples were prepared as doubly polished sections with thicknesses varying from 70 to 350 μm ; the sample thickness was measured using a Mitutoyo electronic micrometer with a precision of $\pm 5 \mu\text{m}$. To avoid organic contamination the samples were washed in acetone and then heated at 300 $^{\circ}\text{C}$ for ~ 6 h (Balassone *et al.* 2012).

Eighteen samples were examined with a Bruker-Nonius Kappa CCD single-crystal X-ray diffractometer (CNR-IC, Bari), equipped with a charge-coupled device (CCD detector), using monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature and COLLECT software (Nonius 2002). Refinement of cell parameters and space group determination were done using EVAL (Duisenberg 1992), SADABS (Sheldrick 2002), and SIR2011, the updated version of the package SIR2008 (Burla *et al.* 2007). Cell data for the remaining crystals were obtained by powder diffraction using the X'Pert diffractometer at CNR-INNOVA S.C.R.L. (Pozzuoli), and the data were processed with the *UnitCell* least-square refinement software (Holland & Redfern 1997) using 22 to 25 X-ray reflections.

The mineral assemblage of the host rocks was investigated by combining optical microscopy, X-ray powder diffraction, and quantitative EDS microanalysis (JEOL-JSM 5310 instrument, DiSTAR microanalysis laboratory).

RESULTS

EPMA and XRD

The chemical compositions of the studied minerals are given in Table 2. Plotted in the $\text{CaO-Na}_2\text{O-K}_2\text{O}$ triangular diagram, the SGM species of the MMN can be classified as 15 sodalites, 17 noseans, and seven haiiyynes (Fig. 2). Sample E5707, classified as “sodalite” in the MMN catalogue, lies between the fields of nosean and haiiyne/lazurite.

The same conclusions illustrated in Figure 2 can be derived using a plot of Na versus (Ca + K) (in *apfu*) (Fig. 3). The studied SGM follow the negative correlation due to the exchange vector $8\text{Na}^+ \rightleftharpoons 6\text{Na}^+ + (\text{Ca}^{2+}, 2\text{K}^+)$; sodalites plot close to the ideal composition of sodalite/nosean (*M* site fully occupied by 8 Na cations), whereas the noseans and haiiyynes cover a more scattered area around the haiiyne ideal composition, *i.e.*, the *M* site occupied by 2 (Ca + K) *apfu* and 6 Na *apfu*, up to Na values of *ca.* 3.9 *apfu* and 3.7 (Ca + K) *apfu*. This feature was also observed by Balassone *et al.* (2012) for the sodalite-group minerals found in the K-feldspar-rich xenoliths of Somma-Vesuvius. It can be noted that sample D795, classified as nosean, plots in an intermediate position between the nosean and haiiyne clusters.

When plotting the data onto the Cl versus SO_4^{2-} diagram (Fig. 4), most of the sodalite samples lie very

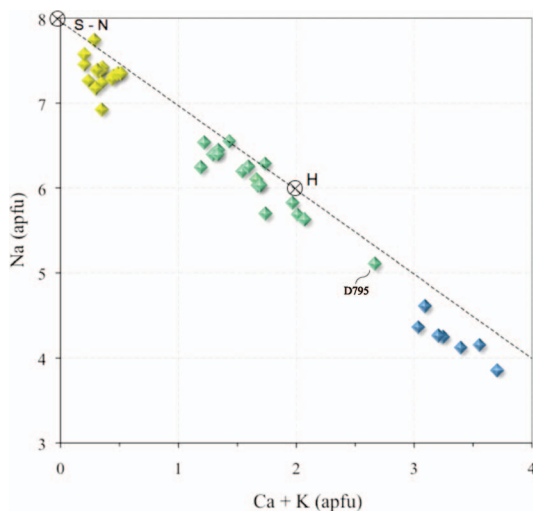


FIG. 3. The cationic compositions (expressed in atoms per formula unit, *apfu*) of the studied samples, plotted on a Na versus (Ca + K) diagram. S, N, and H are ideal sodalite, nosean, and haüyne, respectively [the dotted line represents the $8\text{Na}^+ \rightleftharpoons 6\text{Na}^+ + (\text{Ca}^{2+}, 2\text{K}^+)$ exchange vector]. Symbols as in Figure 2.

close to the related ideal composition; the noseans and haüynes are more scattered in a compositional field between $\text{Cl} < 1$ *apfu* and $\text{SO}_4^{2-} > \text{ca. } 0.75$ *apfu*. Moreover, samples 150 and D803 (which falls in the haüyne field of Fig. 2) plot close the nosean group, whereas sample E5707 (the “borderline” sample of Fig. 2) lies in the haüyne cluster.

Sodalite in the present study shows Si/Al in the range 1.0 to 1.08 (Table 2). Nosean and haüyne have Si/Al in the ranges 0.98–1.05 and 0.96–1.09, respectively. Iron, Ba, and Sr are present in trace amounts (see Table 2).

Figure 5 shows the *a* lattice parameters listed in Table 2 plotted against $\text{K}/\Sigma_{\text{cations}}$ (Fig. 5). In this diagram the sodalites plot in a more restricted area compared to the other SGM samples, with lower *a* values, between *ca.* 8.88 and 8.98 (Å), and $\text{K}/\Sigma_{\text{cations}}$ in the range 0.01–0.05. The noseans and haüynes follow the correlation trend of Ballirano & Maras (2005), with a larger scatter for both *a* and $\text{K}/\Sigma_{\text{cations}}$ values.

SIMS

The results of the SIMS study of minor volatiles occurring in selected SGM samples, *i.e.*, H, C, and F (quantified as H_2O , CO_2 , and F wt.%, respectively), are reported in detail in Table 3. For each sample, from

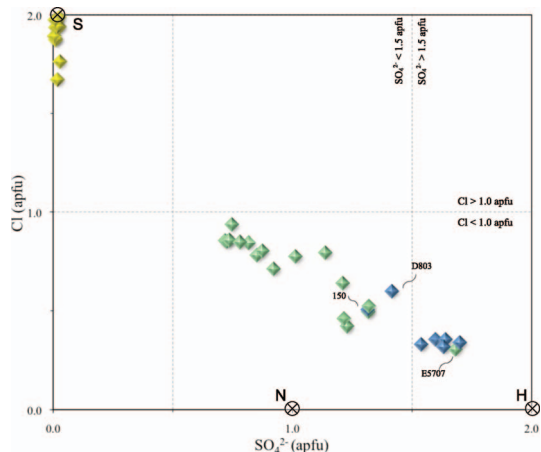


FIG. 4. Major anion composition (in *apfu*) of the studied SGM samples measured by EPMA. The anionic contents of ideal sodalite, nosean, and haüyne are indicated by S, N, and H, respectively. Symbols as in Figure 2.

three to five ion-probe analyses were done, close to the EPMA spots, as explained in the METHODS section. The average concentrations expressed in wt.% (Table 3) are also reported in Table 2, and are used for calculations of the crystal-chemical formulae.

With reference to the variation intervals of maximum and minimum amounts of the volatile species, H, C, and F, we can point out that CO_2 contents lie between 0.08 and 2.95 wt.%, whereas the H_2O concentrations vary in a greater range, *i.e.*, 0.02–5.00 wt.%. The fluorine amounts are very low in all samples (0.010–0.141 wt.% F).

If we consider the average concentration ranges as detected in the three mineral varieties, we have:

- sodalite, 0.25–0.91 wt.% CO_2 , 0.1–0.2 wt.% H_2O , 0.01–0.03 wt.% F
- nosean, 0.17–2.48 wt.% CO_2 , 0.02–3.31 wt.% H_2O , 0.02–0.11 wt.% F
- haüyne, 0.12–1.35 wt.% CO_2 , 0.16–0.69 wt.% H_2O , 0.03–0.09 wt.% F.

It can be noted that the noseans show wider ranges of all the minor volatiles. Figure 6A shows the correlations between the average contents of CO_3^{2-} versus H_2O , calculated in *apfu* (see Table 2). We can observe a well-defined positive trend, with the exception of noseans D785 and E5918 falling far from the sample cluster, due to their particularly high H_2O average amounts. In this Figure we can also see the higher contents of CO_3^{2-} (*ca.* 0.6 *apfu*) in the sample set, which are typical of noseans D772 and D795.

TABLE 2. COMPOSITIONS AND UNIT FORMULAE FOR SOMMA-VESUVIUS SODALITE-GROUP MINERALS IN THIS STUDY

Sample ID	D3	D259	D740	D751	D752	D756	D763	D765
<i>n</i>	7	6	7	8	6	10	9	8
	Sdl	Sdl	Sdl	Nsn	Sdl	Sdl	Nsn	Sdl
wt. %								
SiO ₂	37.86	37.46	37.91	35.00	37.27	37.28	34.72	38.39
Al ₂ O ₃	31.47	30.00	32.15	29.46	29.78	31.29	28.81	31.28
FeO _{tot}	0.02	0.06	0.15	0.02	0.13	0.05	0.03	0.15
MgO	bdl	0.01	bdl	bdl	0.06	0.01	0.01	bdl
CaO	0.54	0.52	0.32	5.46	0.29	0.29	6.24	0.06
SrO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.02
BaO	0.02	0.02	0.03	bdl	0.02	0.01	bdl	0.01
Na ₂ O	23.76	22.90	23.66	18.56	23.07	23.07	16.78	23.20
K ₂ O	1.10	1.70	0.91	2.47	1.45	1.47	3.81	1.42
SO ₃	0.23	0.12	0.08	6.60	0.22	0.22	7.03	0.16
Cl	6.49	7.04	6.98	2.68	7.07	7.07	2.40	6.18
F	0.01	0.03	bdl	0.01	0.03	0.01	bdl	bdl
CO ₂	bdl	0.43	bdl	bdl	0.26	bdl	bdl	bdl
H ₂ O	bdl	0.12	bdl	bdl	0.18	bdl	bdl	bdl
-O≡Cl,F	1.46	1.60	1.61	0.01	1.60	1.59	0.54	1.39
Total	100.04	98.81	100.62	99.65	98.23	99.18	99.29	99.48
Number of ions (<i>apfu</i>) on the basis of 12 T cations								
Si (<i>apfu</i>)	6.06	6.17	6.00	6.02	6.18	6.03	6.07	6.12
Al	5.94	5.83	6.00	5.98	5.82	5.97	5.93	5.88
Σ	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Fe	0.00	0.01	0.02	0.00	0.02	0.01	0.00	0.02
Mg	-	0.00	-	-	0.02	0.00	0.00	-
Ca	0.09	0.09	0.05	1.00	0.05	0.05	1.16	0.01
Sr	-	-	-	-	-	-	-	0.00
Ba	0.00	0.00	0.00	-	0.00	0.00	-	0.00
Na	7.38	7.32	7.26	6.19	7.42	7.24	5.69	7.17
K	0.23	0.36	0.18	0.54	0.31	0.30	0.85	0.29
Σ	7.70	7.78	7.52	7.74	7.81	7.60	7.70	7.50
SO ₄	0.03	0.02	0.01	0.85	0.03	0.03	0.92	0.02
Cl	1.76	1.97	1.87	0.78	1.99	1.94	0.71	1.67
F	0.01	0.02	-	0.01	0.02	0.01	-	-
CO ₃	-	0.10	-	-	0.06	-	-	-
H ₂ O	-	0.07	-	-	0.10	-	-	-
Σ	1.79	2.16	1.88	1.64	2.19	1.97	1.63	1.69
Si/Al	1.02	1.06	1.00	1.01	1.06	1.01	1.02	1.04
a(Å)	8.8880(2)	8.9100(1)	8.8820(2)	9.0680(1)	8.9000(1)	8.9220(2)	9.1100(3)	8.9351(4)
V(Å ³)	702.12(3)	707.18(6)	700.70(2)	746.65(7)	705.00(3)	746.64(3)	756.06(8)	733.63(5)

Note: *n* = numbers of spot-analyses averaged for each sample. Sdl, sodalite; Nsn, nosean; Hyn, haüyne. bdl, below detection limit.

CO₂, H₂O, and F contents measured by SIMS (average values from Table 3) are reported for selected fourteen samples (in bold). Cell parameters and volumes, obtained from both single crystal (in italics) and powder diffraction data, are given (1σ standard deviations are indicated in parentheses).

Figures 6B and 6C show the variation of major volatiles (in *apfu*), i.e., SO₄²⁻ and Cl, obtained by electron microprobe analysis, versus (H₂O + CO₃²⁻), respectively. In Figure 6B we can identify two distinct sample clusters including the sodalites *s.s.* and all the others. Noseans and haüynes show a slightly negative

correlation of SO₄²⁻ versus (H₂O + CO₃²⁻) whereas sodalites, here represented by four samples, plot close to zero. Two distinct sample clusters are also observed in Figure 6C, in which we can recognize a clear positive correlation of Cl versus (H₂O + CO₃²⁻) for the noseans and haüynes.

TABLE 2 (CONTINUED). COMPOSITIONS AND UNIT FORMULAE FOR SOMMA-VESUVIUS SODALITE-GROUP MINERALS IN THIS STUDY

Sample ID	D766	D768	D772	D773	D777	D778	D781	D782
<i>n</i>	6	6	7	7	10	10	9	6
	Sdl	Sdl	Nsn	Nsn	Nsn	Nsn	Sdl	Sdl
wt. %								
SiO ₂	37.49	37.87	34.33	35.61	33.66	33.57	37.84	37.25
Al ₂ O ₃	31.23	31.10	27.77	29.46	28.96	29.12	29.78	31.45
FeO _{tot}	0.14	0.20	0.05	0.01	0.03	0.01	0.21	0.01
MgO	0.03	bdl	0.03	bdl	0.01	0.01	0.01	bdl
CaO	0.57	0.55	5.73	4.43	7.05	6.99	0.61	0.75
SrO	bdl	0.01	bdl	bdl	bdl	bdl	bdl	bdl
BaO	bdl	bdl	0.01	bdl	bdl	bdl	bdl	0.02
Na ₂ O	23.24	23.53	17.37	19.32	17.76	17.58	23.02	23.80
K ₂ O	1.66	1.91	2.55	2.25	1.48	1.69	1.95	0.36
SO ₃	0.10	0.04	6.08	6.84	9.25	9.17	0.09	0.16
Cl	6.85	6.93	2.78	2.78	1.40	1.53	6.94	7.23
F	bdl	bdl	0.05	0.02	0.40	bdl	0.03	0.03
CO ₂	bdl	bdl	2.48	bdl	bdl	bdl	bdl	bdl
H ₂ O	bdl	bdl	0.31	bdl	bdl	bdl	bdl	bdl
-O≡Cl,F	1.54	1.56	0.65	0.06	0.48	0.34	1.57	1.66
Total	99.77	100.58	98.90	100.12	99.52	99.33	98.93	99.49
Number of ions (<i>apfu</i>) on the basis of 12 <i>T</i> cations								
Si (<i>apfu</i>)	6.06	6.10	6.14	6.07	5.96	5.93	6.23	6.02
Al	5.95	5.90	5.86	5.93	6.04	6.07	5.78	5.99
Σ	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Fe	0.02	0.03	0.01	0.00	0.00	0.00	0.03	0.00
Mg	0.01	-	0.01	-	0.00	0.00	0.00	-
Ca	0.10	0.09	1.09	0.81	1.33	1.32	0.11	0.13
Sr	-	0.00	-	-	-	-	-	-
Ba	-	-	0.00	-	-	-	0.00	0.00
Na	7.28	7.35	6.03	6.39	6.10	6.03	7.34	7.45
K	0.34	0.39	0.58	0.49	0.33	0.38	0.41	0.07
Σ	7.74	7.86	7.72	7.69	7.77	7.73	7.89	7.66
SO ₄	0.01	0.01	0.82	0.88	1.23	1.22	0.01	0.02
Cl	1.88	1.89	0.84	0.80	0.42	0.46	1.94	2.00
F	-	-	0.03	0.01	0.22	-	0.02	0.02
CO ₃	-	-	0.61	-	-	-	-	-
H ₂ O	-	-	0.19	-	-	-	-	-
Σ	1.89	1.90	2.48	1.69	1.87	1.67	1.96	2.04
Si/Al	1.02	1.03	1.05	1.02	0.99	0.98	1.08	1.00
a(Å)	9.0800(4)	8.9390(2)	9.0900(1)	9.0110(3)	9.0700(4)	8.8950(3)	8.9001(1)	8.8830(5)
V(Å ³)	748.61(2)	726.33(6)	750.46(9)	731.68(5)	745.93(1)	703.78(6)	736.80(2)	700.94(2)

Within the single crystals (Table 3), the H₂O amounts show a higher variability compared to the CO₂ and F concentrations. This feature is particularly noticeable in noseans D785 and E5926 (a highly fractured grain) whose H₂O concentrations are in the range 1.01–5.0 and 0.16–1.21 wt.%, respectively. The CO₂ content strongly varies only in the sodalites D1621, with a range 0.35–1.97 wt.%. Other inferences related to the volatile distribution in single grains are discussed in the following paragraphs.

μ-FTIR

As observed by Balassone *et al.* (2012), the single-crystal FTIR spectra of SGM can be divided into two types on the basis of the occurrence of a peak at 2340 cm⁻¹ due to the antisymmetric stretching mode (*v*₃) of ¹²CO₂ (Della Ventura *et al.* 2005, 2007, 2008, Bellatreccia *et al.* 2009). The presence of H₂O, CO₂, and CO₃²⁻ obtained from FTIR study is reported in Table 4.

TABLE 2 (CONTINUED). COMPOSITIONS AND UNIT FORMULAE FOR SOMMA-VESUVIUS SODALITE-GROUP MINERALS IN THIS STUDY

Sample ID	D784	D785	D786	D789	D795	D797	D1581	D1621
<i>n</i>	9	8	8	7	8	7	7	8
	Nsn	Nsn	Nsn	Sdl	Nsn	Nsn	Sdl	Sdl
wt. %								
SiO ₂	35.70	34.90	35.61	37.34	33.53	35.50	37.46	37.30
Al ₂ O ₃	29.36	28.30	29.62	30.77	27.30	29.67	29.71	30.00
FeO _{tot}	0.01	0.01	0.01	0.04	0.04	0.03	0.12	0.02
MgO	0.11	bdl	bdl	0.01	0.05	bdl	bdl	0.01
CaO	4.53	4.30	4.55	0.77	6.37	5.03	0.30	0.43
SrO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
BaO	bdl	0.01	bdl	0.02	0.05	bdl	0.02	0.01
Na ₂ O	19.57	18.30	19.81	23.93	14.41	19.35	22.99	23.07
K ₂ O	2.40	1.72	1.82	0.33	6.12	1.95	1.40	1.12
SO ₃	5.63	5.51	5.78	0.15	7.40	6.11	0.14	0.07
Cl	2.97	2.90	2.97	7.03	2.50	2.93	7.14	7.05
F	bdl	0.03	bdl	bdl	0.11	bdl	0.03	0.01
CO ₂	bdl	1.90	bdl	bdl	2.40	bdl	0.25	0.91
H ₂ O	bdl	3.31	bdl	bdl	0.55	bdl	0.14	0.20
-O≡Cl,F	0.67	0.67	0.67	1.58	0.61	0.66	1.62	1.59
Total	99.88	100.52	99.50	98.84	100.22	99.91	98.08	98.61
Number of ions (<i>apfu</i>) on the basis of 12 T cations								
Si (<i>apfu</i>)	6.07	6.14	6.06	6.09	6.12	6.05	6.20	6.16
Al	5.93	5.86	5.94	5.91	5.88	5.96	5.80	5.84
Σ	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Fe	0.00	0.00	0.00	0.01	0.01	0.00	0.02	0.00
Mg	0.03	-	-	0.00	0.01	-	-	0.00
Ca	0.82	0.81	0.83	0.13	1.24	0.91	0.05	0.08
Sr	-	-	-	-	-	-	-	-
Ba	-	0.00	-	0.00	0.00	-	0.00	0.00
Na	6.45	6.24	6.54	7.57	5.10	6.39	7.38	7.39
K	0.52	0.39	0.40	0.07	1.43	0.42	0.30	0.24
Σ	7.82	7.43	7.76	7.79	7.79	7.73	7.75	7.71
SO ₄	0.72	0.72	0.74	0.02	1.01	0.78	0.02	0.01
Cl	0.86	0.85	0.86	1.94	0.77	0.85	2.00	1.97
F	-	0.02	-	-	0.06	-	0.02	0.01
CO ₃	-	0.46	-	-	0.59	-	0.06	0.21
H ₂ O	-	1.94	-	-	0.34	-	0.08	0.11
Σ	1.57	3.99	1.60	1.96	2.78	1.63	2.17	2.30
Si/Al	1.02	1.05	1.02	1.03	1.04	1.02	1.07	1.05
a(Å)	9.0280(5)	9.0000(3)	9.0550(5)	8.8960(2)	9.0700(4)	9.0214(7)	8.9621(2)	8.9000(3)
V(Å ³)	735.83(3)	729.64(4)	742.45(2)	704.10(4)	746.95(6)	734.21(2)	744.90(2)	703.99(5)

The spectra of noseans (Figs. 7 and 8) show the ¹²CO₂ absorption at 2340 cm⁻¹, with a very weak but well-resolved band at 2274 cm⁻¹ assigned to the ν₃ mode of the ¹³CO₂ molecule (Fine & Stolper 1985). From 1900 to 2200 cm⁻¹ a broad multi-component absorption occurs, which can be assigned to the first overtone and/or combination modes of the tetrahedral T-O bonds and to the first overtone of the antisymmetric stretching mode (ν₃) of the SO₄²⁻ group (Bellatreccia *et al.* 2009).

In the 2400 to 2600 cm⁻¹ range there are some very weak absorptions due to the combination modes of CO₃²⁻ groups (Della Ventura *et al.* 2007). Very weak bands are also observed at 2900 cm⁻¹ and 3056 cm⁻¹, which can be attributed to H₃O⁺ groups and to the second overtone and/or combination modes of the SO₄²⁻ tetrahedral units, respectively (Beran *et al.* 2010).

From 2800 to 3700 cm⁻¹ there is a very broad absorption consisting of several overlapping compo-

TABLE 2 (CONTINUED). COMPOSITIONS AND UNIT FORMULAE FOR SOMMA-VESUVIUS SODALITE-GROUP MINERALS IN THIS STUDY

Sample ID	D1626	E1558	E5707	E5926	E6264	E6265	150	22123
<i>n</i>	9	10	8	7	10	6	8	7
	Nsn	Nsn	Nsn	Nsn	Sdl	Sdl	Hyn	Nsn
wt. %								
SiO ₂	33.46	33.67	33.20	34.32	39.00	37.93	32.34	34.33
Al ₂ O ₃	28.75	28.54	26.07	28.13	30.32	30.06	27.53	27.10
FeO _{tot}	0.02	0.03	0.77	0.03	0.23	0.29	bdl	0.28
MgO	bdl	bdl	0.57	0.01	0.01	0.02	bdl	0.06
CaO	6.60	6.68	8.02	4.29	0.02	0.14	9.67	6.90
SrO	bdl	0.02	0.13	bdl	bdl	bdl	0.04	0.11
BaO	bdl	0.03	0.02	0.03	0.13	bdl	0.17	0.02
Na ₂ O	18.20	18.08	15.99	18.99	22.23	24.39	12.14	16.03
K ₂ O	2.12	1.42	1.50	2.73	1.70	1.27	4.77	3.20
SO ₃	8.52	9.86	11.94	6.75	bdl	bdl	9.46	9.30
Cl	2.63	1.63	0.97	2.11	7.42	bdl	1.61	2.16
F	bdl	0.03	0.07	0.07	bdl	bdl	0.03	0.09
CO ₂	bdl	bdl	0.17	1.39	bdl	bdl	1.35	0.12
H ₂ O	bdl	bdl	0.03	0.51	bdl	bdl	0.69	0.16
-O≡Cl,F	0.59	0.38	0.25	0.50	1.67	1.63	0.37	0.52
Total	99.74	99.61	99.20	98.86	99.39	99.70	99.43	99.34
Number of ions (<i>apfu</i>) on the basis of 12 <i>T</i> cations								
Si (<i>apfu</i>)	5.97	6.00	6.23	6.10	6.26	6.20	5.99	6.22
Al	6.04	6.00	5.77	5.90	5.74	5.80	6.01	5.78
Σ	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Fe	0.00	0.00	0.12	0.00	0.03	0.04	-	0.04
Mg	-	-	0.16	0.00	0.00	0.01	-	0.02
Ca	1.25	1.27	1.61	0.81	0.00	0.02	1.91	1.33
Sr	-	0.00	0.01	-	-	-	0.00	0.01
Ba	-	0.00	0.00	0.00	0.01	-	0.01	0.00
Na	6.29	6.25	5.82	6.55	6.92	7.74	4.36	5.63
K	0.48	0.32	0.36	0.62	0.35	0.27	1.13	0.74
Σ	8.02	7.85	8.08	7.99	7.31	8.07	7.41	7.77
SO ₄	1.14	1.32	1.68	0.90	-	-	1.32	1.26
Cl	0.79	0.49	0.31	0.64	2.02	2.00	0.51	0.66
F	-	0.02	0.04	0.04	-	-	0.02	0.05
CO ₃	-	-	0.04	0.34	-	-	0.34	0.03
H ₂ O	-	-	0.02	0.30	-	-	0.43	0.10
Σ	1.93	1.83	2.09	2.22	2.02	2.00	2.61	2.10
Si/Al	0.99	1.00	1.08	1.03	1.09	1.07	0.99	1.07
a(Å)	9.0397(5)	9.0380(1)	9.0900(6)	9.0200(1)	8.9470(3)	8.9491(3)	9.0920(5)	9.0225(1)
V(Å ³)	738.69(7)	744.91(4)	750.46(9)	734.99(4)	744.66(4)	741.24(3)	751.60(7)	735.21(3)

nents which can be assigned to H₂O ν_3 , ν_1 , and OH stretching modes and to the first overtone of the H₂O ν_2 bending mode (at ~ 3200 cm⁻¹).

Finally, at ~ 3700 cm⁻¹ a very weak but frequently well-resolved peak occurs, due to the first overtone of the ¹²CO₂ ν_3 mode (Della Ventura *et al.* 2009, 2012).

Sodalite type spectra (Figs. 7 and 8) show in the 1900 to 2200 cm⁻¹ range a group of intense and partially overlapped absorptions which can be assigned to the first overtone and/or combination modes of the tetrahedral T–O bonds.

In almost all sodalite spectra there is a very weak band at 2342 cm⁻¹ due to the ¹²CO₂ ν_3 mode.

In the range from 2350 to 3100 cm⁻¹ there are some weak absorptions: (1) from 2350 to 2600 cm⁻¹ there is a group of well resolved absorptions due to the combination modes of the CO₃²⁻ groups (Della Ventura *et al.* 2007); (2) the bands at 2742 cm⁻¹, 2890 cm⁻¹, and the weak doublet between 3020 and 3060 cm⁻¹ could be tentatively attributed to some combinations and/or overtones modes of the CO₃²⁻

TABLE 2 (CONTINUED). COMPOSITIONS AND UNIT FORMULAE FOR SOMMA-VESUVIUS SODALITE-GROUP MINERALS IN THIS STUDY

Sample ID	A3149	C3488	C3489	D803	D804	D1810	E5918
<i>n</i>	10	8	6	9	8	10	9
	Hyn	Hyn	Hyn	Hyn	Hyn	Hyn	Nsn
wt. %							
SiO ₂	31.04	31.09	31.75	32.50	32.10	32.20	34.24
Al ₂ O ₃	27.48	27.03	26.97	27.20	26.81	27.70	27.21
FeO _{tot}	0.22	0.12	0.14	0.14	0.14	0.08	0.05
MgO	0.15	0.23	0.17	0.19	0.10	0.09	bdl
CaO	11.14	10.10	10.80	9.79	9.57	9.87	4.33
SrO	0.19	0.17	0.14	0.03	0.03	bdl	bdl
BaO	bdl	bdl	0.00	bdl	0.06	0.05	bdl
Na ₂ O	11.23	10.43	11.33	12.78	11.62	11.88	16.20
K ₂ O	4.76	6.80	5.73	4.86	5.51	5.34	3.88
SO ₃	11.98	11.18	11.58	10.15	11.56	11.09	9.69
Cl	1.06	1.10	1.10	1.90	0.99	1.05	1.72
F	bdl	0.04	0.12	bdl	0.09	0.08	0.02
CO ₂	bdl	0.80	bdl	bdl	0.65	bdl	0.88
H ₂ O	bdl	0.21	bdl	bdl	0.17	bdl	2.84
-O≡Cl,F	0.24	0.26	0.30	0.43	0.26	0.27	0.40
Total	99.01	99.04	99.57	99.11	99.14	99.16	100.66
Number of ions (<i>apfu</i>) on the basis of 12 <i>T</i> cations							
Si (<i>apfu</i>)	5.87	5.93	6.00	6.04	6.05	5.96	6.20
Al	6.13	6.07	6.00	5.96	5.95	6.04	5.80
Σ	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Fe	0.04	0.02	0.02	0.02	0.02	0.01	0.01
Mg	0.04	0.07	0.05	0.05	0.03	0.03	-
Ca	2.25	2.05	2.18	1.94	1.92	1.95	0.84
Sr	0.02	0.02	0.02	0.00	0.00	-	-
Ba	-	-	0.00	-	0.00	0.00	-
Na	4.12	3.86	4.15	4.61	4.25	4.26	5.68
K	1.15	1.65	1.38	1.15	1.32	1.26	0.89
Σ	7.62	7.67	7.79	7.78	7.55	7.51	7.42
SO ₄	1.70	1.60	1.64	1.42	1.63	1.54	1.31
Cl	0.34	0.36	0.36	0.60	0.32	0.33	0.52
F	-	0.02	0.07	-	0.05	0.05	0.01
CO ₃	-	0.21	-	-	0.17	-	0.22
H ₂ O	-	0.13	-	-	0.11	-	1.71
Σ	2.04	2.32	2.07	2.02	2.28	1.92	3.77
Si/Al	0.96	0.98	0.99	1.01	1.01	0.99	1.07
a(Å)	9.1282(4)	9.1266(5)	9.1049(7)	9.0999(8)	9.1140(2)	9.1132(2)	9.0648(4)
V(Å ³)	760.61(8)	760.19(6)	754.80(4)	753.55(7)	757.06(3)	756.84(1)	744.86(5)

groups (Schroeder *et al.* 1962, Plyler 1929, Genge *et al.* 1995).

Lastly, the absorption due to H₂O and/or OH groups occurs as a very broad band extending from 3700 to 3000 cm⁻¹ and peaking at around 3449 cm⁻¹.

Mapping of H and C: inhomogeneous versus homogeneous arrangements

A more thorough survey of minor volatile distribution in the single SGM crystals can be made by

combining SIMS and μ-FTIR-FPA imaging for selected samples.

Concerning the volatile distribution as inferred by SIMS, in Figure 9 we display the variation of C and H along one or two transects in six representative sodalite, nosean, and haüyne grains (see also Table 3). A virtually homogenous distribution of both volatiles is displayed in Figure 9L (haüyne C3488), whereas moderately inhomogeneous distributions of CO₂ and H₂O are observed in nosean E5918 (Fig. 9F) and in haüyne D804 (Fig. 9N).

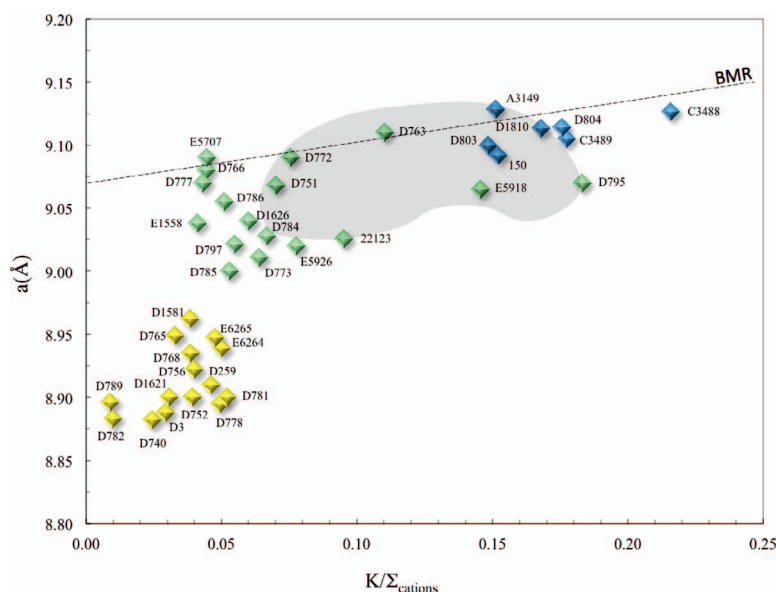


FIG. 5. Correlation between the a cell-edge (Å) and the cationic content in SGM. The grey area refers to Vesuvian S-sodalites from Balassone *et al.* (2012). The dotted line (BMR) represents the regression found for haüyne compositions by Ballirano & Maras (2005). Symbols as in Figure 2.

An inhomogeneous distribution of H or C can be seen in Figures 9B, 9D, and 9H. In particular, the micro-areas investigated by SIMS reveal an inhomogeneous distribution of CO_2 in sodalite D1621 (Fig. 9B), whereas the H_2O is almost constant. Instead, a significant variation of H_2O contents, in comparison with CO_2 amounts at the same spots, is shown by nosean D785 (Fig. 9D) and haüyne 150 (Fig. 9H).

It is worth noting that the higher values of CO_2 and H_2O are related to SIMS spots falling close to fractured areas, as observed in sodalite D1621 (Fig. 9A).

Further reasoning about the volatile species distribution in the single crystals can be made by considering the μ -FTIR FPA imaging. Moreover, a comparison between the SIMS and FTIR data is also possible, taking into account the following aspects:

- (1) SIMS technique cannot discriminate the different speciations of C (*e.g.*, CO_2 and CO_3^{2-}). The SIMS data for carbon (quantified as CO_2 wt.%) must therefore be interpreted as representative for the overall C distribution in the crystal. The same reasoning holds for H, whose speciation is not available by SIMS methods, and for which H is conventionally quantified as H_2O wt.%;
- (2) FTIR and SIMS may be considered as not-to-scale techniques, because SIMS is a higher spatial

resolution technique compared with FTIR spectroscopy in transmission mode; μ -FTIR probes a sample volume that is very large compared the volume probed by SIMS; nevertheless, these two techniques can be regarded as complementary: SIMS yields high-precision *in situ* quantitative data for minor-to-trace volatile contents, whereas FTIR imaging provides the spatial distribution of these species, highlighting possible (optically visible or not) fractures, inclusions, alteration, *etc.*, which could affect the quantitative analysis at a small to very-small scale.

Figure 10 illustrates the results of μ -FTIR FPA analyses for selected SGM samples, collected from the doubly polished slabs previously used for micro-spectroscopic data collection and imaging of H_2O , CO_2 , and CO_3^{2-} . Nosean D785 shows an inhomogeneous distribution of both H_2O and CO_2 contents that are also inversely related each to other, whereas the CO_3^{2-} distribution seems to be more homogeneous. Nosean E5918 displays some inhomogeneity in both C and H distributions. Data from μ -FTIR mapping for samples D785 and E5918 agree qualitatively with the SIMS results (see Fig. 9D and 9F, and Table 3). μ -FTIR FPA imaging of haüyne 150 shows an inhomogeneous distribution of both CO_2 and H_2O , at least in part associated with fractures visible in the

TABLE 3. WATER, CARBON DIOXIDE, AND FLUORINE CONTENTS (wt.%) DETERMINED BY SIMS FOR SELECTED SGM SAMPLES OF SOMMA-VESUVIUS

Sample ID	Species	SIMS spot #	F	CO ₂	H ₂ O	Sample ID	Species	SIMS spot #	F	CO ₂	H ₂ O
D259	Sdl	a	0.026	0.51	0.15	D5707	Nsn	a	0.054	0.16	0.02
		b	0.025	0.42	0.13			b	0.043	0.17	0.03
		c	0.026	0.39	0.13			c	0.056	0.17	0.03
		d	0.027	0.39	0.12			Average	0.051	0.17	0.03
		e	0.036	0.45	0.10			1σ	0.007	0.004	0.003
		Average	0.028	0.43	0.12			1σ%	13.8	2.5	10
		1σ	0.005	0.05	0.02						
		1σ%	16.4	11.4	15.5						
D752	Sdl					E5926	Nsn	a	0.072	1.34	1.21
								b	0.067	1.44	0.23
		a	0.029	0.27	0.16			c	0.07	1.47	0.16
		b	0.029	0.24	0.17			d	0.056	1.31	0.42
		c	0.028	0.26	0.19			Average	0.066	1.39	0.51
		Average	0.029	0.26	0.18			1σ	0.007	0.08	0.48
		1σ	0.001	0.01	0.01			1σ%	10.8	5.7	94.7
		1σ%	3.1	5.2	8.2						
D772	Nsn					150	Hyn	a	0.029	1.35	0.65
		a	0.051	2.47	0.36			b	0.029	1.42	0.99
		b	0.063	2.51	0.34			c	0.031	1.35	0.49
		c	0.057	2.47	0.30			d	0.031	1.31	0.45
		d	0.045	2.48	0.25			e	0.028	1.32	0.86
		Average	0.054	2.48	0.31			Average	0.029	1.35	0.69
		1σ	0.008	0.02	0.05			1σ	0.001	0.04	0.23
		1σ%	14.3	0.8	15.4			1σ%	4.2	3.3	33.8
D785	Nsn	a	0.032	2.02	3.55	22123	Nsn	a	0.141	0.14	0.13
		b	0.034	1.82	3.70			b	0.075	0.12	0.16
		c	0.028	1.77	5.00			2b	0.075	0.08	0.19
		d	0.033	1.98	1.01			c	0.071	0.13	0.18
		Average	0.032	1.90	3.31			Average	0.09	0.12	0.16
		1σ	0.0029	0.12	1.67			1σ	0.034	0.03	0.03
		1σ%	9.1	6.2	50.4			1σ%	37	22	15.3
D795	Nsn	a	0.136	2.24	0.57	C3488	Hyn	a	0.045	0.79	0.19
		b	0.123	2.95	0.58			b	0.038	0.80	0.23
		c	0.075	2.03	0.51			c	0.044	0.81	0.21
		Average	0.111	2.41	0.55			Average	0.042	0.80	0.21
		1σ	0.030	0.48	0.04			1σ	0.004	0.01	0.02
		1σ%	28.9	20	6.8			1σ%	8.5	1.4	10
D1581	Sdl	a	0.026	0.23	0.14	D804	Hyn	a	0.096	0.66	0.14
		b	0.028	0.26	0.15			b	0.093	0.64	0.20
		c	0.028	0.25	0.13			c	0.082	0.65	0.18
		Average	0.027	0.25	0.14			Average	0.09	0.65	0.17
		1σ	0.001	0.01	0.01			1σ	0.008	0.01	0.03
		1σ%	2.7	5.8	5.9			1σ%	8.7	2.2	17.7
D1621	Sdl	a	0.014	1.97	0.14	E5918	Nsn	a	0.023	0.79	2.86
		b	0.011	0.40	0.26			b	0.024	0.80	2.46
		c	0.010	0.35	0.20			c	0.023	1.08	2.63
		Average	0.012	0.91	0.20			2a	0.013	0.69	3.05
		1σ	0.002	0.92	0.06			2b	0.014	1.03	3.18
		1σ%	20	101	29			Average	0.020	0.88	2.84
								1σ	0.006	0.17	0.3
								1σ%	28	19	10

Note: Sdl, sodalite; Nsn, nosean; Hyn, haüyne.

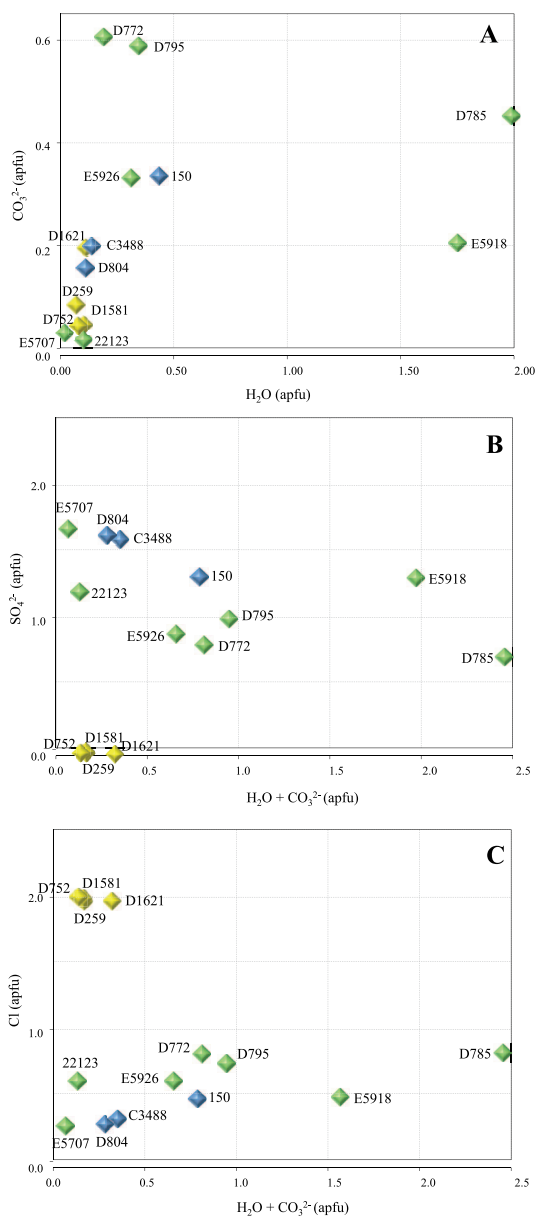


FIG. 6. Plot of volatile contents in apfu: (A) CO₃²⁻ versus H₂O, derived from SIMS analysis for selected SGM crystals. Average SIMS values for C are expressed as CO₃²⁻ (see Tables 2 and 3). (B) SO₄²⁻ versus (H₂O + CO₃²⁻). (C) Cl versus (H₂O + CO₃²⁻), where sulfur and chlorine concentrations were obtained by means of EPMA (see Table 2). Symbols as in Figure 2.

TABLE 4. H₂O, CO₂, AND CO₃²⁻ CONTENTS DEDUCED FROM FTIR INVESTIGATIONS FOR 21 SGM SAMPLES

Sample ID	SGM species	Composition
D259	Sdl	H ₂ O, low CO ₂ , (CO ₃) ²⁻
D752	Sdl	H ₂ O, very low CO ₂ and (CO ₃) ²⁻
D782	Sdl	H ₂ O, very low (CO ₃) ²⁻
D789	Sdl	H ₂ O, CO ₂ , (CO ₃) ²⁻
D1581	Sdl	Very low H ₂ O and CO ₂ and (CO ₃) ²⁻
D1621	Sdl	H ₂ O, (CO ₃) ²⁻
D772	Nsn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D777	Nsn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D785	Nsn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D795	Nsn	H ₂ O
E5707	Nsn	H ₂ O
E5926	Nsn	H ₂ O, CO ₂ , (CO ₃) ²⁻
150	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
21123	Nsn	H ₂ O
A3149	Hyn	Low H ₂ O, CO ₂ , very low (CO ₃) ²⁻
C3488	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
C3489	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D803	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D804	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
D1810	Hyn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻
E5918	Nsn	H ₂ O, CO ₂ , very low (CO ₃) ²⁻

Note: Sdl, sodalite; Nsn, nosean; Hyn, haüyne. Samples also analyzed by SIMS are in bold.

crystal slab; CO₃²⁻ seems more homogeneous and not affected by microcracks in the grain. Haüyne D804 displays a relatively homogeneous H and C distribution (Fig. 9N), whereas some inhomogenities observable in μ -FTIR FPA mapping could be due to thickness variations of the analyzed slabs.

DISCUSSION

On the basis of chemical features of major cations and anions obtained by EPMA, the investigated Somma-Vesuvius sodalites are nearly close to ideal composition, and do not show significant solid solution with the S-bearing varieties, as previously observed by Parat *et al.* (2011 and references therein). Both noseans and haüynes are more scattered compared to their ideal compositions and show a moderate solid solution that is more evident when the Cl and S contents are taken into account. As stated by Balassone *et al.* (2012), the nomenclature of the sodalite group can sometimes show some shortcomings, as in the case of a few nosean and haüyne samples (*i.e.*, E5707, D795, D803, and 150) whose classification is not straightforward. For example,

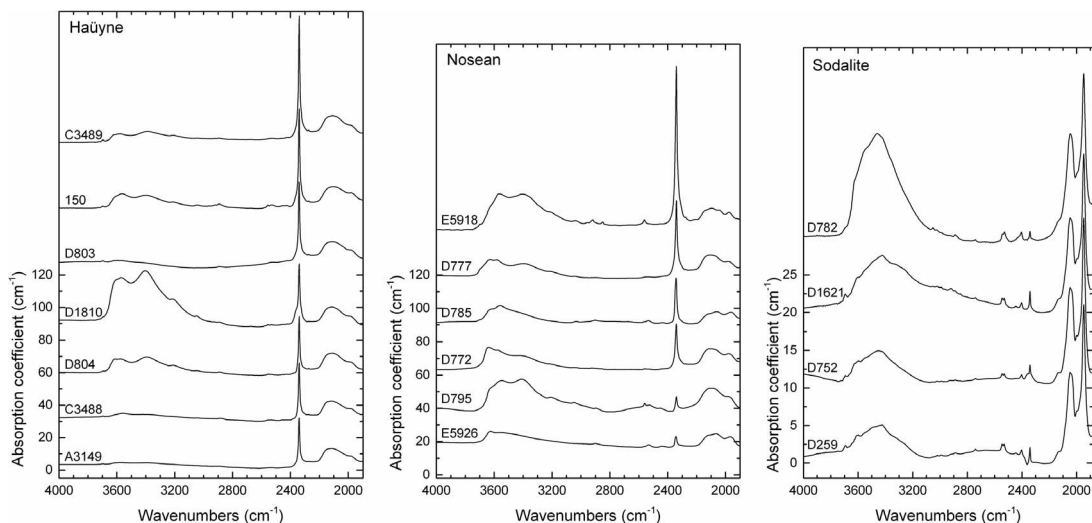


FIG. 7. Single-crystal FTIR spectra of studied SGM. Spectra are plotted with the same abscissa scale for direct comparison.

sample D795 can be better described as an intermediate phase of the SGM group corresponding to a Cl-rich häüyne than an intermediate member between häüyne and a hypothetical (H_2O)-dominant phase. Indeed, when the unit-cell parameters of the investigated samples are correlated with their respective major cations, we see that noseans show the widest range, varying from the häüyne field up to values approaching the sodalite field.

As regards minor volatile components, the inhomogeneous distribution of H_2O and CO_2 indicated by both SIMS and μ -FTIR techniques in some crystals may be due to various factors, such as mineral zoning, presence of microfractures and/or grain boundaries (more affected by fluid action), and fluid inclusions in the crystal, which are not directly evident by the analytical methods used here. Fluid/melt inclusion-enriched häüyne phenocrysts have been investigated by various authors (Cooper *et al.* 2015 and references therein).

If we consider the relationships between the SGM and the related host rocks, most of the samples are xenoliths, and, though our results are biased by an unequal distribution of lithotypes, we can observe that the two SGM samples associated with historical lavas of Vesuvius, *i.e.*, noseans E5707 and 22123 (related to the AD 1872 and AD 1906 eruptions, respectively), incorporate low values of H_2O and CO_2 if compared to the xenolithic occurrences of likely older eruption times. Instead, variable up to higher volatile contents are contained in SGM from

“older” xenoliths. At the Somma-Vesuvius volcanic complex sodalite is not a common mineral in the juvenile products assemblages (Santacroce 1987). The experimental work of Scaillet *et al.* (2008) constrained the stability field for this mineral in the Vesuvius magmas to 200 MPa, 850 °C, and 0.4 wt.% vapor phase. This paper also establishes the storage pressure for the 1906 AD eruption to be lower (80 MPa) than in the previous volcanic history (see Table 1 in Scaillet *et al.* 2008). The 1872 and 1906 AD olivines and clinopyroxenes include melt inclusions with CO_2 and H_2O contents higher than in the older rocks (Marianelli *et al.* 2005). Therefore, degassing likely occurred in the 1872–1906 AD magmas before their extrusion. In spite of the paucity of collected data, we speculate that SGM were trapped in the uprising magma and pervaded by fluids escaping from the melt. In accepting this speculative hypothesis, the H_2O and CO_2 contents of sodalite from xenoliths are dependent on the composition and decompression history of the hosting magma, thus furnishing additional information on the volcanic processes occurring at Somma-Vesuvius.

CONCLUSIONS

The crystal-chemical data set of the investigated SGM and the determination of their absolute concentrations of volatile components (H, C, and F) by SIMS can contribute to the knowledge of the crystal chemistry of these minerals, in particular suggesting that H_2O can be present as a main component in

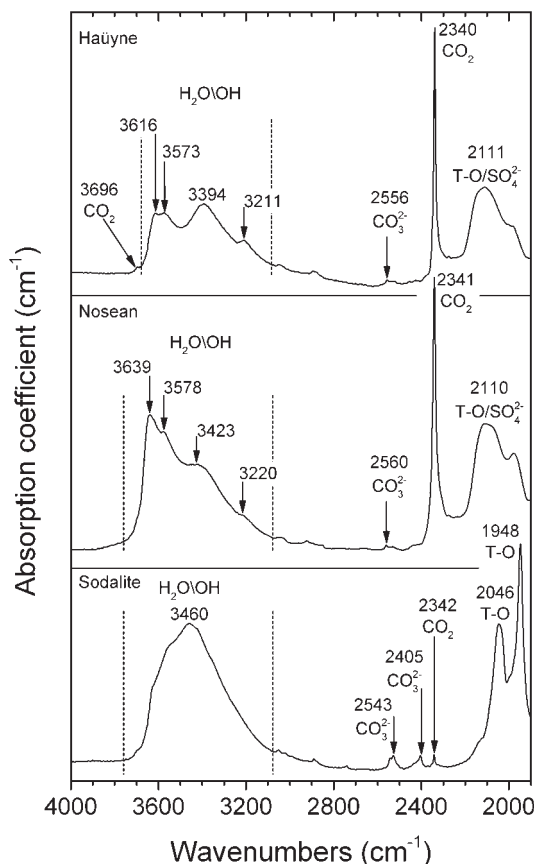


Fig. 8. Single-crystal FTIR typical spectra of haüyne (top, sample D804), nosean (middle, sample D772), and sodalite (bottom, sample D782). For the very weak features occurring between 2700 cm^{-1} and 3100 cm^{-1} , please see the text.

nosean-like compositions. Hassan & Grundy (1989) described the crystal structure of nosean containing 0.91 wt.% H_2O , showing that its cage contains both $[\text{Na}_4\text{SO}_4]^{2+}$ and $[\text{Na}\cdot\text{H}_2\text{O}]^{4+}$ ordered clusters in a 1:1 ratio. Deer *et al.* (2004) reported nosean compositions with variable H_2O (0–4.24 wt.%). Nosean samples from Somma-Vesuvius display a larger range and indeed higher H_2O (and CO_2) amounts. In particular, the inverse correlation observed for C and S in nosean and haüyne can be justified by the expected $\text{CO}_3^{2-} \rightleftharpoons \text{SO}_4^{2-}$ substitution at their extraframework *X* site.

Our data can also help in interpreting the magmatic and hydrothermal/metasomatic processes attending the cooling magma body. SGM are fairly common mineral phases in alkaline-peralkaline rocks and play an important role in the volatile evolution. It is known

that the formation of sodalite itself can have a major influence on volatile contents and on the redox state of peralkaline melts (Stormer & Carmichael 1971, Markl *et al.* 2010, Hettmann *et al.* 2012, Giehl *et al.* 2014, Wang *et al.* 2014). In addition to their geological importance, SGM and sodalite-type lattices are microporous structures and hence are of interest as advanced materials for many industrial applications (see for example the general reviews of Ferraris & Merlino 2005, Krivovichev 2008, and Pabby *et al.* 2015). Sodalite-type compounds bridge the fields of mineralogy and material science, due to their ion exchange properties at 60–300 $^{\circ}\text{C}$, as similarly established for the cancrinite group, clay minerals, and narrow-pore zeolites (Pekov *et al.* 2008). Natural minerals form in geological environments which are generally chemically heterogeneous, so they can be useful for modeling chemical substitution mechanisms in synthetic analogues. Hence, a specific knowledge of the pore content of the microporous SGM lattices can be useful for experimental studies and applicative purposes.

Finally, the results of this investigation emphasize that a combination of independent techniques (in this case SIMS and FTIR) can be particularly helpful in correctly determining the volatile distribution within a single crystal. Inhomogeneous distributions seen in some samples suggest care is necessary when bulk H and C values are considered for both crystal-chemical issues and spectroscopic determination of concentrations of hydrous and/or carbon-bearing species in minerals and glasses, especially in relation to calibration procedures.

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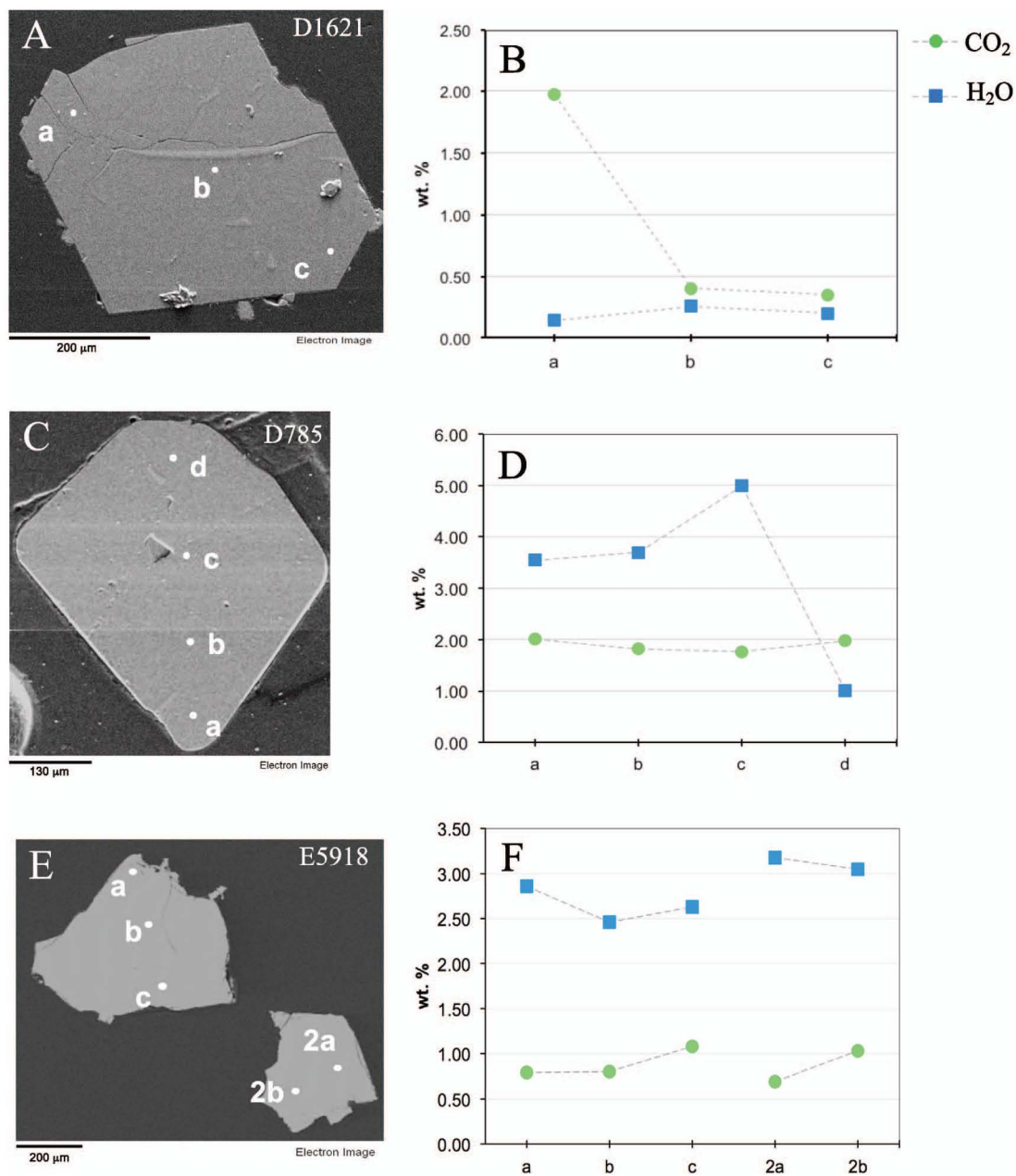


FIG. 9. (A, C, E, G, I, M) SEM-BSE images of selected SGM samples, and (B, D, F, H, L, N) the related SIMS values of CO₂ and H₂O (wt.%) at the selected spots.

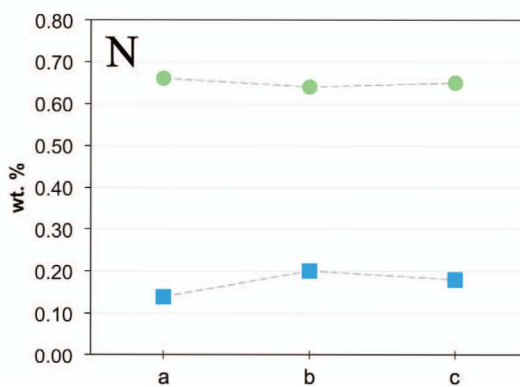
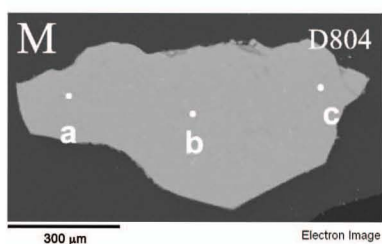
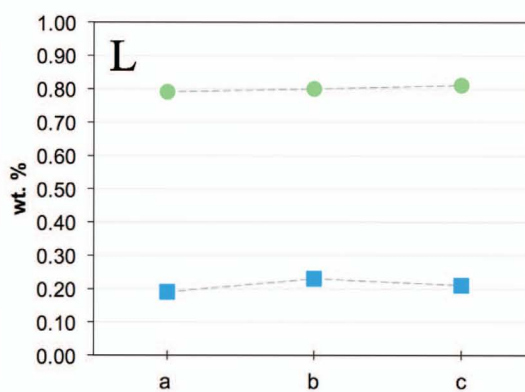
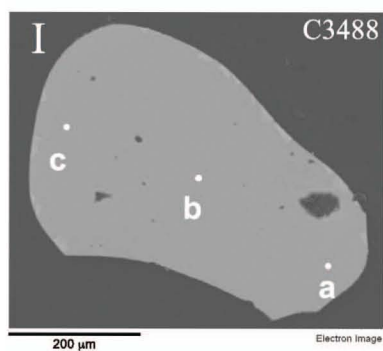
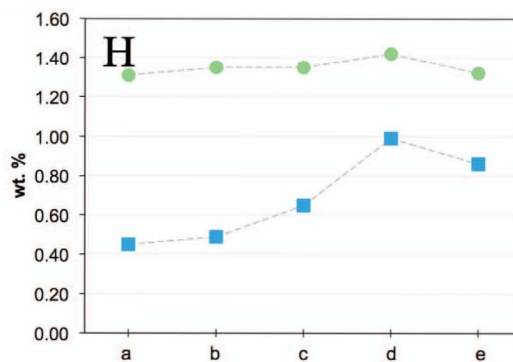
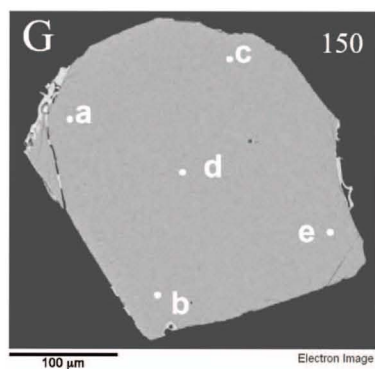


FIG. 9. (continued)

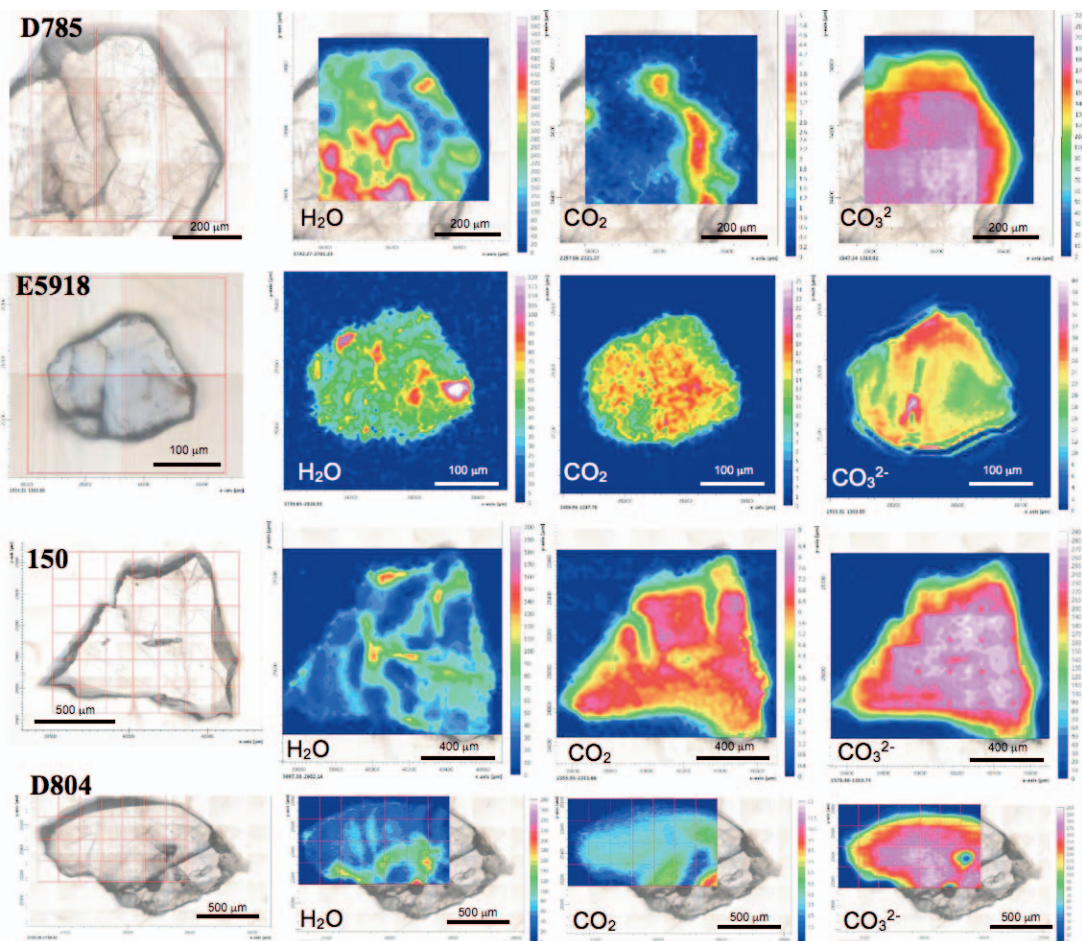


FIG. 10. μ -FTIR-FPA imaging of H_2O , CO_2 , and CO_3^{2-} distribution in selected SGM samples. Signal integration range: 3742–2700 cm^{-1} (H_2O), 2358–2321 cm^{-1} (CO_2), and 1556–1321 cm^{-1} (CO_3^{2-}).

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