

In situ and micro-Raman spectroscopy for the identification of natural Sicilian zeolites

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Abstract

Zeolites are present in numerous outcrops of volcanites of different ages in Sicily (Italy). Some of these outcrops are important because they constitute the ideal genesis conditions of some of these minerals, which represent geological indicators of chemical and geothermal gradients involved during their formation. For this purpose, a group of zeolites coming from areas of the Ionian coast and Palagonia village (Eastern Sicily) was investigated by means of Raman spectroscopy. In the geological record, these areas have been influenced by intense volcanic events that produced mineralization of hydrothermal origin. Sicilian zeolite samples were analysed in situ using different mobile Raman apparatus, directly on the outcrops of Aci Castello and the nearby Lachea Island, or in local collections where they are preserved. Some of these samples have been then analysed using laboratory micro-Raman to compare the results and identify the zeolite types. The strength and weakness points of each instrument have been highlighted. Often, the Raman spectra of zeolites are affected by broad fluorescence, making them of difficult interpretation. However, satisfying results were obtained with portable devices, whose identifications were confirmed by micro-Raman, discerning zeolites of different groups, such as analcime, chabazite, natrolite and phillipsite. The use of portable instruments has demonstrated the possibility to obtain identification of zeolites and related minerals both on site and in the laboratory, whose results match with the geological setting of the considered areas.

KEYWORDS

in situ measurements, natural zeolites, portable Raman spectroscopy, Sicily, volcanism

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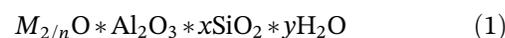
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1 | INTRODUCTION

The Sicilian geology is extremely complex and widely studied due to relevant tectonic events that affected the Mediterranean area.^[1] The Eastern sector of the island displays interesting outcrops of volcanites combined with zeolite minerals, as a consequence of important volcanic events. In detail, the area close to Palagonia and Mineo villages, located in the Hyblean area, represents one of the earliest (200 to 1 My) volcanism manifestations, in submarine conditions, in the eastern part of the island, during the upper Pliocene, generating the Militello - Mount Calielli formation. This latter is characterized by the presence of palagonite, basaltic breccia, pillow lavas, hyaloclastites and zeolites that substitute the volcanic glass and fill in the vesicles (Figure 1a).^[3-7] Next, the Ionic coast, extending from Aci Castello to Aci Trezza (Catania), represents the beginning of Etnean volcanism in submarine conditions, dated around 500 ky,^[8] characterized by peperites (i.e., mixing of pillows lava and sediments) with zeolites inside^[2] (Figure 1b).

Zeolites, from ancient Greek meaning 'boiling stones',^[9] are very interesting materials: natural ones inform us about geological events according to their geothermal or chemical gradient's information,^[10,11] whereas on the other hand, they play an important role in industrial processes such as water purification,^[12]

agriculture,^[13] medicinal applications,^[14] ion exchangers and molecular sieves^[15] thanks to their chemical structure.^[16] Moreover, they are used as precursors in alkaline activation process for the production of noncementitious binders (geopolymers^[17-19]); they can also be present in pyroclastic materials used as raw materials for alkaline activation, as for example, Mount Etna ashes^[20-23] or Lipari's pumices (Aeolian island-Sicily).^[24] Zeolites have an aluminosilicatic framework based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all oxygens, forming intracrystalline channels or interconnected voids, filled with water molecules and cations.^[16,25-28] Chemically, zeolites are represented by the empirical formula shown in Equation 1.



where M is any alkaline cation, n represents the valence of the cation, x is the number of Si tetrahedra ($2 \leq x < 10$) and y is the number of water molecules in the voids of the zeolite.^[25]

Natural Sicilian zeolites are formed following abundant volcanic activity pre- and post-Mount Etna volcano formation, which has influenced their formation mainly through alteration phenomena of hydrothermal type.^[16] This process is generated by the interaction of sea water

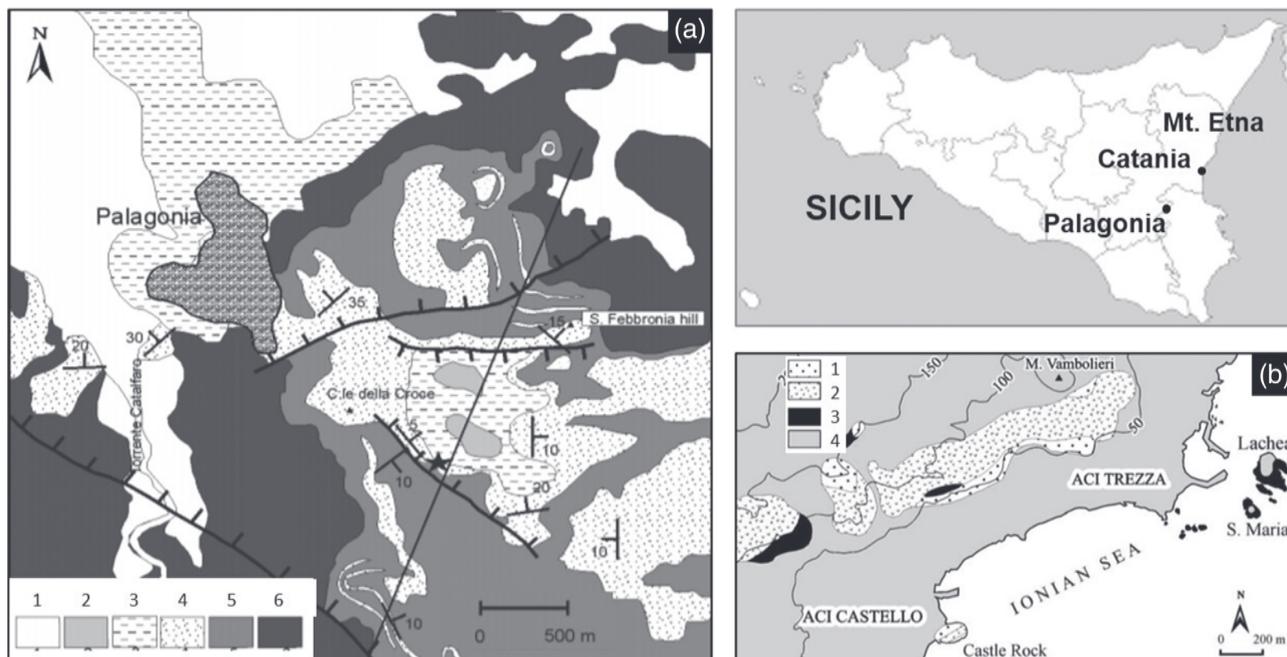


FIGURE 1 Localization of outcropping areas with the corresponding geological maps: a) geology of Ionian east coast. Legend: 1) pillow lavas and pillow breccia; 2 = volcanoclastic deposits; 3 = subvolcanic rocks with columnar joints; 4 = alkaline volcanic and sedimentary rocks^[2]; (b) geology of Palagonia area.^[3] Legend: 1) recent and terrace alluvial deposits; 2) 'Panchina' (Middle Pleistocene); 3) Sandy claystone; 4) Emilian Calcarenes and sands; 5) Poggio Vina Formation; 6) Militello - Mount Calielli volcanism (Late Pliocene)

with lava ejected in submarine conditions,^[29,30] modifying, after thousands of years, the volcanic glass in zeolite minerals. All zeolites are light coloured, of whitish, yellowish, bluish or pinkish shades. They occur in rocks as masses and, sometimes, especially in volcanic rocks, as crystalline aggregates. The zeolites outcropping in Sicily are listed in Table 1.

Typically, Sicilian zeolites belong to groups based on sodium exchangers cations: analcime,^[2] chabazite-Na,^[27] mesolite^[31] and phillipsite-Na,^[32] outcropping in the East coast of Catania between Aci Castello and Aci Trezza, whereas natrolite (or tetranatrolite) examples are found around Palagonia.^[7,33] Generally, zeolites are composed of complex secondary building units based on four-, five- or six-membered rings of SiO_4^{4-} and AlO_4^{5-} tetrahedra.^[34,35] They are often formed by hydrothermal interaction of tholeiitic, rhyolitic or alkali olivine basalts with alkali or alkali-earth containing solutions. The parent rock composition and porosity, and the hydrothermal solution's chemical composition, pH and temperature are the main parameters determining the type of zeolite. However, chemical, pH and temperature gradients may vary locally and through minerals crystallization, causing different paragenesis in the same environment^[36,37] and across adjacent amygdales.^[35,38–40] In this scenario, Gunter et al.^[37] have observed natrolite fibres displaying a mesolite termination, whereas Triana et al.^[36] report, in alkaline and tholeiitic basalts, the coexistence of natrolite with chabazite, of natrolite with analcime, as well as fan/radial aggregates of different varieties of fibrous zeolites (natrolite, mesolite & scolecite).

TABLE 1 Chemical information on the main natural zeolites outcropping in Sicily according to mindat.org

Mineral name	General chemical formula
Analcime	$\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$
Chabazite-Na	$(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Sr}, \text{Mg})_2[\text{Al}_2\text{Si}_4\text{O}_{12}]_2 \cdot 12\text{H}_2\text{O}$
Chabazite-K	$(\text{K}_2, \text{Ca}, \text{Na}_2, \text{Sr}, \text{Mg})_2[\text{Al}_2\text{Si}_4\text{O}_{12}]_2 \cdot 12\text{H}_2\text{O}$
Chabazite-Ca	$(\text{Ca}, \text{K}_2, \text{Na}_2)_2[\text{Al}_2\text{Si}_4\text{O}_{12}]_2 \cdot 12\text{H}_2\text{O}$
Faujasite-Na	$(\text{Na}_2, \text{Ca}, \text{Mg})_{3,5}[\text{Al}_7\text{Si}_{17}\text{O}_{48}] \cdot 32\text{H}_2\text{O}$
Gismondine-Ca	$\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$
Gmelinite-Na	$\text{Na}_4(\text{Si}_8\text{Al}_4\text{O}_{24}) \cdot 11\text{H}_2\text{O}$
Gmelinite-Ca	$\text{Ca}_2(\text{Si}_8\text{Al}_4\text{O}_{24}) \cdot 11\text{H}_2\text{O}$
Gonnardite	$(\text{Na}, \text{Ca})_2(\text{Si}, \text{Al})_5\text{O}_{10} \cdot 3\text{H}_2\text{O}$
Mesolite	$\text{Na}_2\text{Ca}_2\text{Si}_9\text{Al}_6\text{O}_{30} \cdot 8\text{H}_2\text{O}$
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
Phillipsite-Na	$(\text{Na}, \text{K}, \text{Ca}_{0,5}, \text{Ba}_{0,5})_{4-7}[\text{Al}_{4-7}\text{Si}_{12-9}\text{O}_{32}] \cdot 12\text{H}_2\text{O}$
Phillipsite-Ca	$(\text{Ca}_{0,5}, \text{K}, \text{Na}, \text{Ba}_{0,5})_{4-7}[\text{Al}_{4-7}\text{Si}_{12-9}\text{O}_{32}] \cdot 12\text{H}_2\text{O}$

Even though these associations have been observed, the comprehension of the exact geochemical mechanisms is not trivial and not easily reproducible under laboratory conditions.^[35,41] The crystallization order is well-known (chabazite, analcime, phillipsite & natrolite), as the initial formation of Na-zeolites followed by Ca-containing ones^[35,37,41]; moreover, some indications have been reported on the petrogenetic conditions leading to specific paragenesis.^[35] Nevertheless, as chemical variations and intergrowths have been observed at the microscopic scale by optical and electron microscopy, and chemically characterized by electron microprobe,^[36,37] it appears that obtaining structural information with spatial resolution and chemical sensitivity is essential.

X-ray diffraction (XRD) is the classical technique for zeolites identification and discrimination.^[42] Analyses are carried out under lab conditions and generally with powdered samples. More recently, non-destructive analytical tools, for example, Raman spectrometry are used in mineralogy, allowing to obtain vibrational spectroscopic data and identification of minerals either on very small specimens, particles or inclusions (commonly of micrometric dimension), and even outdoors. This has become possible thanks to the development of miniature instrumentation, which is being used in several scenarios and areas,^[43–45] and appears to be more challenging.

Raman spectroscopy represents an advantageous and fast technique for the detection of minerals.^[46] It has also been shown that this technique permits to identify and characterize organic minerals in the geological record. Nevertheless, zeolites were previously successfully investigated, and assignment of the Raman bands of common zeolites was carried out.^[47–49] All the previous papers concerning Raman spectroscopy of zeolites report results obtained using Ar (514 nm), frequency-doubled Nd:YAG laser (532 nm) or exceptionally also 488 nm (Ar-ion laser).^[48–50]

Generally, the Raman spectra of zeolites are affected by fluorescence, making them of difficult interpretation.^[51] However, some studies on zeolites pointed out the usefulness, also, of portable Raman equipment aimed at overcoming the limitations of traditional autoptic observations of physical features (e.g. shape and colour), generally used for the identification of minerals in situ.^[44,45,48–50] The previous experience using miniature instrumentation showed that near-infrared excitation was better to investigate a series of zeolites (thomsonite, stilbite, natrolite, euclase & phenakite) compared to 532-nm excitation.^[48–50] However, those investigations were carried out using a first generation portable Raman spectrometer with green excitation and the system generated measurement artefacts in several situations.

Generally, zeolites of the same group (e.g. natrolite-mesolite) have similar Raman spectra in the low-wavenumber range ($100\text{--}1200\text{ cm}^{-1}$) and differ from each other in the OH-related vibrations. Therefore, these latter represent the most distinctive signals for a univocal identification. Complete spectra of zeolites in both spectral ranges are often lacking in literature data. In this work, Raman spectroscopy was applied to analyse Sicilian zeolites, directly on the outcrops of Aci Castello and the nearby Lachea Island through portable devices, as well as for the identification of zeolites belonging to a private collection with samples from Palagonia and Ionian coast. In this latter case, a micro-Raman spectrometer was also used. Moreover, portable devices were also used in laboratory conditions to compare the results with the corresponding analyses in situ. Therefore, the main aim of this work was to evidence in this geographical-geological context the strength and weakness points of each instrument used for the comparison of spectra obtained in different spectral ranges, measurement set-ups and measurement conditions. Moreover, the versatility of portable devices for field applications, also in non-ideal conditions and the potentiality to recognize very similar phases of zeolites belonging to the same subgroup, have to be underlined, with the aim to attract interest towards in situ Raman applications.

2 | MATERIALS AND METHODS

Different spot analyses were performed on the outcrops of Aci Castello and the nearby Lachea Island using two portable devices: a DeltaNu spectrometer (equipped with a 785-nm laser, maximum output power of 120 mW, wavenumber range of $200\text{--}2000\text{ cm}^{-1}$) and an EnSpectr RaPort one (equipped with a 532-nm laser, maximum output power 30 mW, 0.5-mm spot size, $100\text{--}4000\text{ cm}^{-1}$ spectral range with a spectral resolution of $\sim 8\text{ cm}^{-1}$). Differently, some zeolites, coming from Palagonia and the Ionian coast (Aci Castello and Aci Trezza), belonging to a private collection were analysed with the same portable devices and with a Jasco NRS-3100 micro-Raman ($50\times$ long working distance objective) with (1) a 532-nm source, approximately 8-mW laser power on the sample, $0.5 \times 6\text{ mm}$ slit, 10 accumulations of 120 s each and (2) a 785-nm source, approximately 10-mW laser power on the sample, $0.5 \times 6\text{ mm}$ slit, 20–40 accumulations of 30–60 s each. For portable instruments, no calibration is required before measurements, although it has been checked with reference standard materials; differently, for the laboratory, one this was done using the 520.7 cm^{-1} Raman band of silicon before each experimental session. However, only portable devices could be used for sample

zeo 5 due to its considerable size, unsuitable for the micro-Raman instrument.

The in situ measurements were particularly challenging as geometrical constraints and direct sunlight/shadow had to be taken into account. Moreover, different laser wavelengths and combinations of time, accumulations and laser power were tested by performing quick measurements ($<25\text{ s}$): On the basis of these quick tests, evaluated directly on site, the acquisition conditions were optimized and only the best spectra (in terms of signal-to-noise ratio [SNR]) were kept. The Raman signals were then collected with longer acquisition times both in the low-wavenumber range (T–O–T bending and stretching vibrations) and in the OH stretching region. Samples were also acquired covering the observed variability of zeolite minerals for testing under laboratory conditions. Table 2 lists information on collection's zeolites together with their pictures, whereas most of the analysed crystals during in situ analyses are transparent trapezohedra embedded in the dark volcanic rock. Other sampled minerals occurring in small geodes showed the aspect of clusters of whitish prismatic crystals or spherical aggregates of needle-like crystals.

The zeolites of the collection were selected according to the presence of different crystalline aggregates, taking into account their shape and dimensions to avoid any damage to the specimens during the measurements (Table 2).

Baseline correction was performed with *LabSpec* software. Spectra of the aluminosilicatic vibrations region (below 1200 cm^{-1}) are given for all samples. The OH vibrations range ($3000\text{--}3700\text{ cm}^{-1}$) were obtained from the RaPort and Jasco instruments with 532-nm lasers.

The Raman identification of zeolitic phases was performed through comparison with literature data.^[34,48,52]

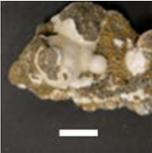
3 | RESULTS AND DISCUSSION

Representative spectra obtained with all the different instruments are reported in the low-wavenumber range ($200\text{--}1200\text{ cm}^{-1}$) in Figures 2–7, S1, S3, S4 and S5, whereas for the ones obtained with the green laser, also the OH-vibration range is given ($3000\text{--}3700\text{ cm}^{-1}$) in Figures 2, 4, 7 and S2. Moreover, band positions are reported in Table 3.

3.1 | In situ measurements

At different locations, different spectra were obtained. Raman spectra acquired with RaPort instrument on Lachea island show bands at approximately 300, 390 and

TABLE 2 Main information and macroscopic observation of zeolites analysed

Sample	Locality	Description	
Zeo 1	Palagonia	White hemispherical structures made of thin needle-like prismatic crystals	
Zeo 2	Aci Castello	Irregular clusters of transparent/whitish crystals	
Zeo 4	Palagonia	Large opaque white surface	
Zeo 5	Aci Trezza	Transparent crystals (crystal aggregate)	
Zeo 6	Palagonia	Small white spherical structures	
Zeo 8	Palagonia	White hemispherical structures made of thin needle-like prismatic crystals	
Zeo 9	Palagonia	Small white spherical structures with granular shape	
Zeo 16	Aci Castello	White structures made of thin needle-like prismatic crystals	
Zeo 16 new	Aci Castello	White and transparent structures with granular shape	
Analcime	Aci Castello	Transparent and dark crystals (crystal aggregate)	

Note: In each picture, the white scale bar is 1 cm.

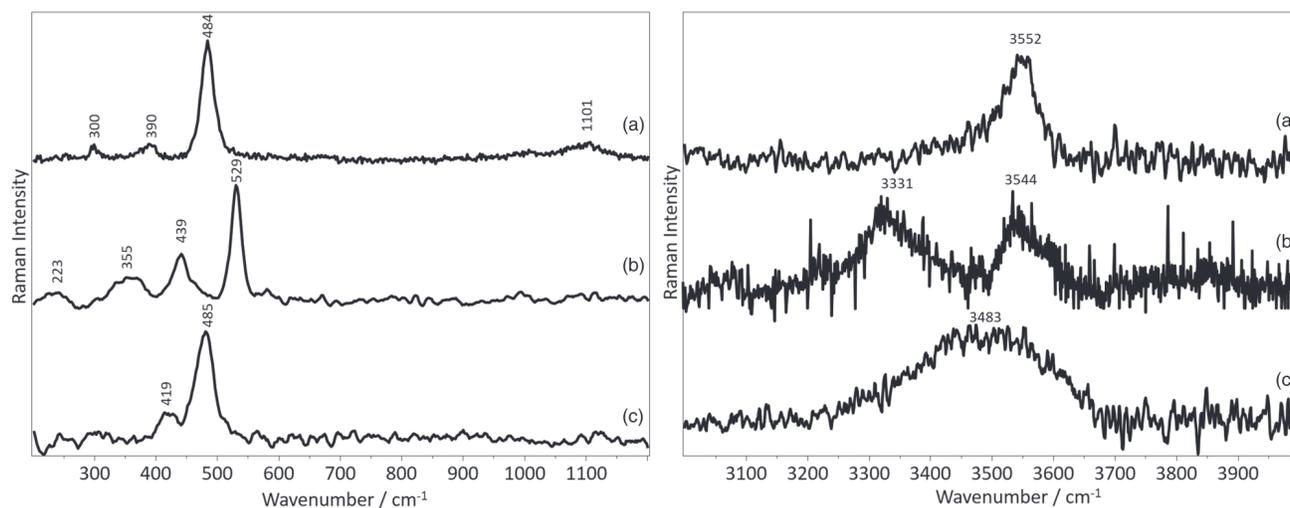


FIGURE 2 Spectra collected with RaPort (532 nm) device in outdoor conditions on locations of the Ionian coast. Legend: analcime (a); natrolite (b); phillipsite (c)

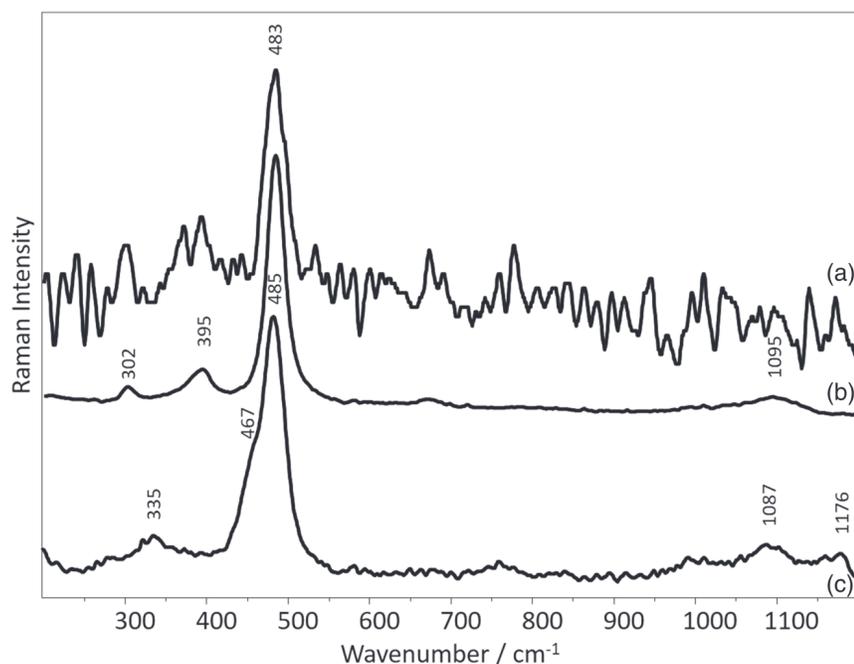


FIGURE 3 Spectra collected with DeltaNu (785 nm) device on: analcime sample in outdoor (a) and in laboratory (b) conditions; spectrum of chabazite sample (c) in laboratory conditions

484 cm^{-1} (Figure 2, spectrum a), moreover, in the green laser excited spectrum a broad band centred at 1101 cm^{-1} is also visible (Figure 2, spectrum a). These bands (Table 3), compared with literature,^[34] correspond to analcime Raman signals. On Lachea island, the low-wavenumber region also allowed the identification of natrolite (Figure 2, spectrum b, 223, 355, 439 and 529 cm^{-1}) and of phillipsite (Figure 2, spectrum c, 419 and 485 cm^{-1}). The OH-spectra shown in Figure 2, obtained on site with the RaPort instrument, show different Raman signatures, confirming the identification obtained from the low-wavenumber region: Analcime has a relatively sharp band (ca. 200 cm^{-1} at the baseline)

at approximately 3550 cm^{-1} (Figure 2, spectrum a), natrolite has two bands centred at approximately 3330 and 3540 cm^{-1} (ca. 250 and 200 cm^{-1} at the baseline, respectively) (Figure 2, spectrum b), phillipsite a very broad band (ca. 500 cm^{-1} at the baseline) at approximately 3480 cm^{-1} (Figure 2, spectrum c).

The spectra obtained with DeltaNu instrument on site and in the laboratory on samples from Lachea and Aci Trezza boulders are shown in Figure 3. The identification of analcime (Figure 3, spectra a and b; Table 3) has been possible both on site and in less severe conditions inside the laboratory, respectively, thanks to the main band at 485 cm^{-1} and to the weaker signals at 302, 395 and

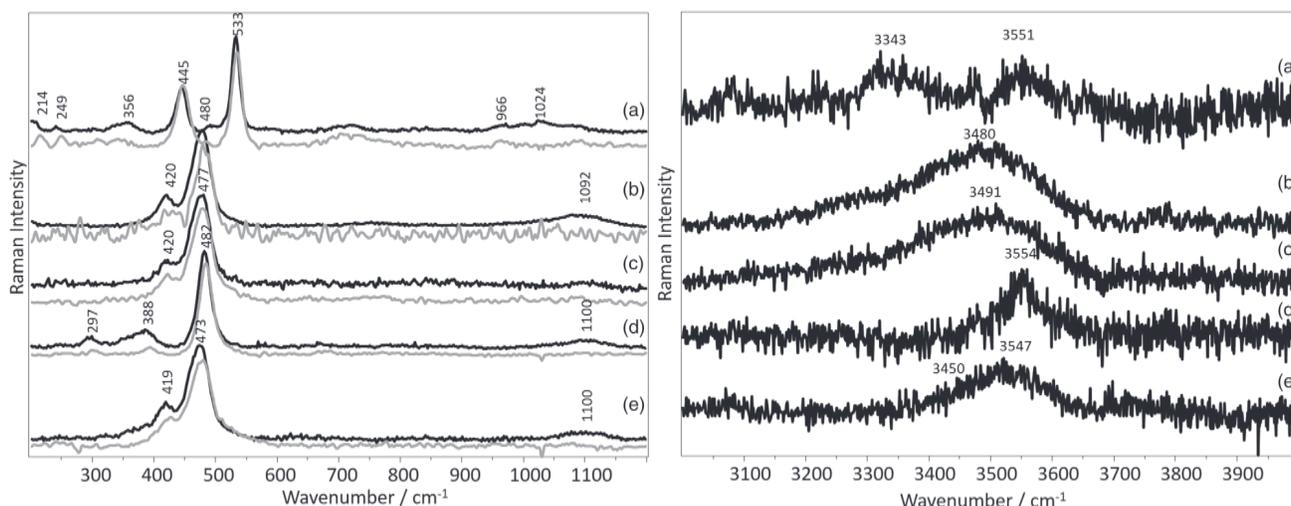
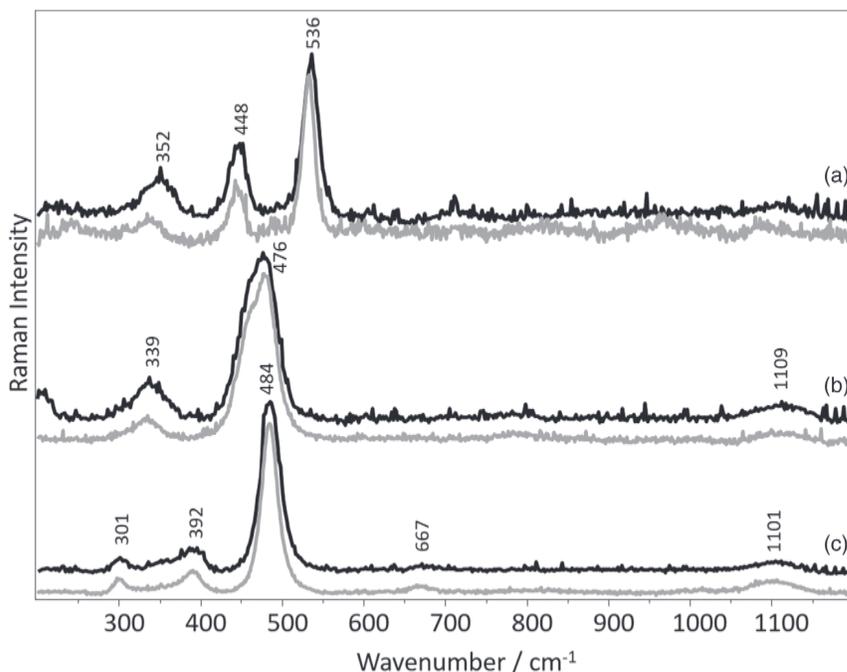


FIGURE 4 Spectra collected with RaPort (532 nm; black) and DeltaNu (785 nm; grey) devices in the 200–1200 cm^{-1} range. Spectra collected with RaPort device are also shown for the OH range. Legend: Zeo 1 (a); Zeo 2 (b); Zeo 4 (c); Zeo 5 (d); Zeo 6 (e)

FIGURE 5 Spectra collected with micro-Raman Jasco device with two different laser sources: 785 nm (black) and 532 nm (grey). Legend: Zeo 1 (a); Zeo 9 (b); analcime from Lachea island (c)



1095 cm^{-1} , only visible in the better quality spectrum (Figure 3, spectrum b). In the latter case, the SNR is greatly improved. Moreover, a sample taken to the lab (Figure 3, spectrum c; Table 3) allowed the identification of chabazite thanks to the bands at 335, 483 (with a shoulder at 467), 1087 and 1176 cm^{-1} .

3.2 | Private collection samples

For the zeolite samples of the private collection, both portable and laboratory instrumentation could be used, except for Zeo 5 that was too big for the microscope stage.

The acquired spectra are reported in Figure 4 for the low-wavenumber region with both portable devices and for the OH region with RaPort, and in Figures 5, 6 and 7 with the micro-Raman spectrometer. The Raman band positions are reported in Table 3.

3.3 | Portable instruments

Figure 4 reports representative spectra acquired on the private collection samples with the two different portable instruments used in laboratory conditions. Sample Zeo 1 (Figure 4, spectra a) is identified as a member of the

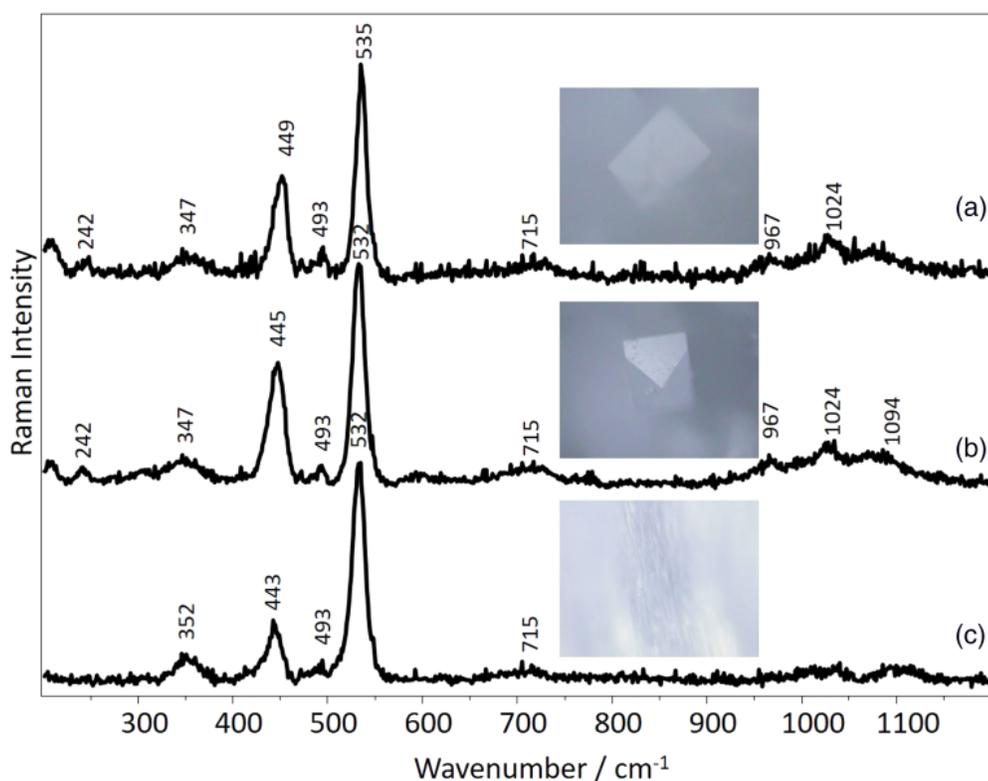


FIGURE 6 Spectra acquired on Zeo 8 sample in the 200–1200 cm^{-1} range by means of micro-Raman Jasco device (532 nm). Legend: I spot analysis (a); II spot analysis (b); III spot analysis (c)

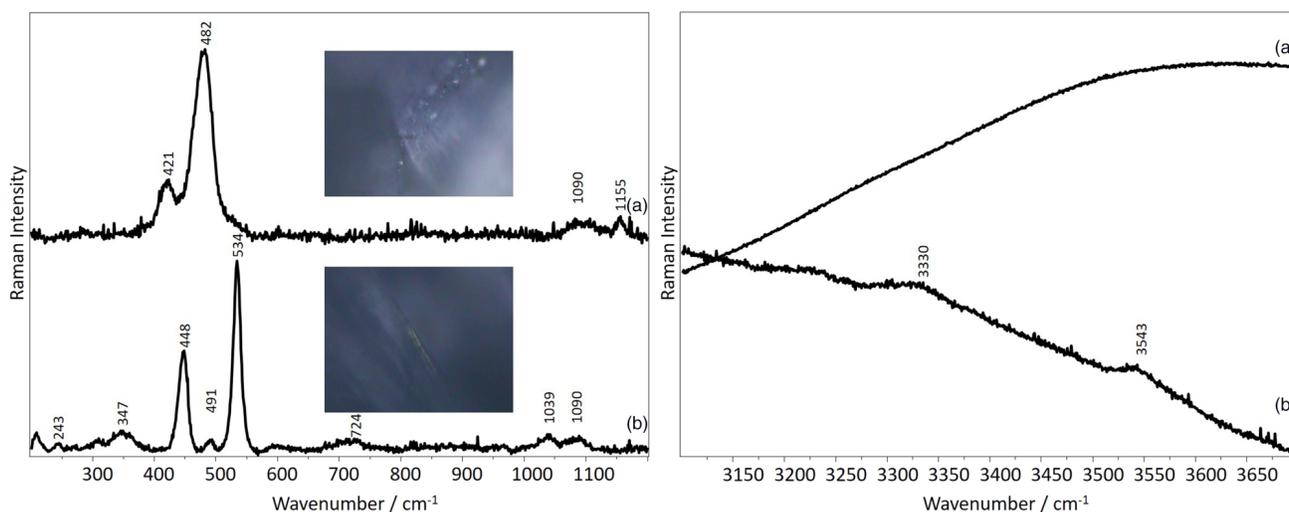


FIGURE 7 Spectra collected in 200–1200 and 3000–3700 cm^{-1} range with micro-Raman Jasco device (532 nm). Legend: Zeo 16 new (a); Zeo 16 (b)

natrolite group based on the bands at 356, 445, 533, 1024, 3343 and 3551 cm^{-1} . Sample Zeo 2 (Figure 4, spectra b), with bands at 420, 480, 1092 and 3480 cm^{-1} is identified as phillipsite. The same identification applies to sample Zeo 4 (Figure 4, spectra c). Sample Zeo 5 (Figure 4, spectra d), with bands at 297, 388, 482, 1100 and 3554 cm^{-1} is interpreted as analcime. Finally, also sample Zeo 6 (Figure 4, spectra e) is interpreted as phillipsite showing bands at 419, 473, 3450 and 3547 cm^{-1} .

3.4 | Micro-Raman instrument

Figure 5 shows spectra acquired on the private collection samples with the micro-Raman instrument using both lasers. The low-wavenumber spectra acquired on sample Zeo 1 (Figure 5, spectra a) are given for comparison with the spectra obtained with the portable devices (Figure 4, spectra a): The band positions are generally in good agreement (Table 3) and confirm the capability of both