The Vesuvianite Gems of the Val d’Ala (Piedmont, Italy)

Franca Piera Caucia 1, Luigi Marinoni 1, Maurizio Scacchetti 2, Maria Pia Riccardi 1,* and Omar Bartoli 3

1 DiSTA—Università degli Studi di Pavia, via Ferrata 9, I-27100 Pavia, Italy; francapiera.caucia@unipv.it (F.P.C.); luigitito.marinoni@unipv.it (L.M.)
2 Società Reggiana di Scienze Naturali I-42100, via G. Puccini 4, I-42124 Reggio Emilia, Italy; mauscacchetti@alice.it
3 DiGS—Università degli Studi di Padova, via Gradenigo 6, I-35131 Padova, Italy; omar.bartoli@unipd.it
* Correspondence: mariapia.riccardi@unipv.it

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Abstract: In Val d’Ala (Western Alps in Piedmont, Italy), the most interesting rocks for mineralogical research are represented by rodingite (rich in mineralized veins and fractures) associated with serpentinite in the eclogitized oceanic crust of Piedmont Zone, south of Gran Paradiso Massif. Among the vein-filling minerals, vesuvianite is well appreciated for its potential as gem-quality materials, even though it has never been characterized in detail. This study provides a gemological characterization of eleven vesuvianite crystals from different localities of the Val d’Ala. The refractive index (1.717–1.708) and density (1.705–1.709) values of our vesuvianite are in the range of those in the literature. Scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) established that the samples are pretty compositionally homogeneous in terms of major elements, while trace and rare earth elements (REE) contents are more variable. All REE patterns are characterized by pronounced positive Eu anomalies. The variations in color (from olive green to dark green with chocolate (reddish-brown color shades and polychrome bands) are due to the relevant presence of Fe and, to a lesser extent, Ti and Cr. The X-ray powder diffraction (XRPD) analyses and SEM/EDS quantitative study indicate that the other phases associated with vesuvianite are represented by diopside, garnet, clinohlore.

Keywords: vesuvianite; gemstones; geochemistry; Val d’Ala (Italy); SEM/EDS quantitative analysis; XRPD

1. Introduction

Vesuvianite is the most famous name for the “idiocrase” gem; it is a sorosilicate, whose formula is very complex but a common end member can be as follows: Ca_{19}(Al,Mg,Fe)_{13}Si_{18}O_{68}(OH,F,\text{O})_{10} [1–4]. This mineral is generally found as prismatic crystals of various lengths, from transparent to translucent, and shows various colors, including green yellow, pink and brown. The green is due to the presence of Fe and Cr, while the pink is due to Mn [1,2]. The name “vesuvianite” was proposed by the German mineralogist Abraham Gottlieb Werner, because it was discovered for the first time in Mount Vesuvius, while the name “idiocrase” derives from the Greek word meaning “mixed form”, as the crystals generally have several different habits [3].

Vesuvianite crystals are morphologically complex; its composition is similar to the grossular. Vesuvianite usually occurs in different geological settings like skarn deposits and limestone that underwent contact or regional metamorphic processes, serpentinites and ultramafic rocks,
rodingites and also in altered alkali syenites. The ornamental stone known as “californite” is a mixture of vesuvianite and grossular and is similar to green jadeite. The most important deposits of vesuvianite in the world are found in Canada (Asbestos, Jeffrey mine and St. Hilaire in Quebec, Long Lake mine and York River in Ontario), in Kenya (Magadi mine), USA (California, for californite), Mexico (Cerro de los Muertos and Laguna del Jaco, Chihuahua), Japan, Pakistan (Hindubagh mine in Baluchistan), Australia (Bowling Alley Point, Nundle New South Wales), and Turkey (Kızdere-Rize, Keşan-Elažığ, Susurluk-Balkesir regions) [1,2]. Concerning Italy, several different studies have been carried out on vesuvianite from the Somma-Vesuvius volcano near Naples [4,5], the volcanic groups of Latium in Central Italy [6,7], in the Alps in Aosta valley [8,9], Val d’Ala in Piedmont [10–13], and the Dolomites [14,15]. The vesuvianite from the regions of Piedmont and Val d’Aosta is considered among the most beautiful worldwide, and for this reason it is highly sought after by collectors. In particular, the Curbassere deposits in Val d’Ala and those of Bellecombe in Aosta Valley have provided truly valuable samples of this mineral. Piedmont vesuvianite is present in rodingites, metamorphic rocks rich in Ca-silicates, derived from the transformations of mafic rocks (gabbro or basalt) intruding inside ultramafic mantle rocks (peridotites) and affected by serpentinization processes in an oceanic and orogenic environment [16,17]. Rodingites are composed by grossular and other Ca-silicates like diopside, vesuvianite, epidote and chlorite, formed by the enrichment in Ca and depletion in Si at the expense of gabbros and basalts intruded in peridotites, when the latter underwent the serpentinization processes. Rodingites occur as “boudin” or lenses of metric to decimetric thickness, are very heterogeneous, even in very close outcrops, and frequently show the original structure of the intrusive gabbroic bodies in the peridotites.

In this work, gem-quality vesuvianite from Val d’Ala (Turin, Italy) has been studied [2,10–13], to define its peculiar mineralogical and gemological properties, the chemical composition and the relationships with the colors of the gem and the composition of the host rock, the presence of solid inclusions, the most important differences with other vesuvianites from renowned deposits. The complete gemological, mineralogical and geochemical characterization represents the basis for the traceability of the gemstone, both for its recognition in ancient artefacts and for the traceability of the sources of supply when used in contemporary jewelry.

2. Materials and Methods

The samples investigated in this work were collected from the Val d’Ala, which represents the central furrow of the Lanzo valleys (Figure 1). These valleys occupy the southern part of the arch of the Graian Alps, between the Susa Valley to the south and the Orco Valley with the Gran Paradiso Massif to the north. Val d’Ala is about 30 km long, from the municipality of Ceres, up to the reliefs of the Uja Bessianese and Uja Ciamarella, close to the border with France. The different lithologies outcropping in this area, such as serpentinites, metagabbros, prasinites and eclogites, derive from the Alpine and Eocene metamorphic processes (56–34 M.y.) on oceanic lithospheric rocks, that formed after the separation of the paleo-European margin from the Adriatic. Metamorphic processes transformed basalts into prasinites or eclogites, gabbros into metagabbros and mantle peridotites into serpentinites [16,17]. Calcschists of probably the Cretaceous Age formed through the same previous metamorphic processes which, in this case, acted on the sedimentary sequences that deposited above the seafloor basaltic rocks. Gneisses belong to the complex of “Gneiss minuti” and derive from the high pressure metamorphic transformation of Permian granites (260 M.y.). The geological maps published so far do not show the presence of important tectonic lines work [17].

In this paper, we investigated 11 samples of vesuvianite from different localities in the Val d’Ala (Table 1, Figures 1 and 2). Some of these samples derive from places well known for the gemological variety of this mineral (Figure 2A, B). Testa Ciarva (Figure 2B) is a rocky massif with a rounded shape smoothed by the glacier located towards the bottom of the valley. The rodingite host-rocks of vesuvianite occurring in this locality show a variable size (up to 1 m) and contain beautiful samples of epidote, clinoclore, diopside, vesuvianite and garnet. The Testa Ciarva deposit has become famous both for the quality and the quantity of vesuvianite provided over the years and
was certainly the most exploited in the valley. Due to the past intense collecting activity, nowadays the area is totally forbidden for the sampling of minerals.

Figure 1. Geological map showing the distribution of vesuvianite-bearing rodingite along the Val d’Ala. Black stars indicate the location of samples analyzed in this work [16,17]. Map redrawn by [17].

Fontana del Preive is located in the lower part of the Rio Chianale valley near a water source, now completely dry, called “Fontana del Preive” in honor of a man-like rock in its vicinity, locally known as “Preive” (literally the Priest). The deposit of Mont Fort is near the village of Albaron; this locality is important for a variety of andradite called melanite, which is very dark due to the presence of titanium and also abundant small-sized vesuvianite crystals.
Figure 2. Images of some vesuvianite sampling locations of Val d’Ala, investigated in this work. (A) outcrop of Borne Brous, see also images A and B of sample 4 in Figure 3; (B) outcrop of Testa Ciara; see also images C, D and E of samples 1 and 2 in Figure 3.

Table 1. Samples investigated in this work.

| Samples* | Val d’Ala Localities | Mineralogical Description | Mineralogical Association |
|----------|----------------------|---------------------------|----------------------------|
| 1        | Testa Ciara          | Subhedral short crystals matched with poor matrix | Vesuvianite + clinochlore + diopside |
| 2        | Testa Ciara          | Euhedral prismatic crystal twinned with polychromy | Vesuvianite |
| 3        | Testa Ciara          | Subhedral crystals with matrix | Vesuvianite + clinochlore + diopside |
| 4        | Borne Brous          | Prismatic crystal twinned | Vesuvianite |
| 5        | Mont Fort (Balme)    | Small euhedral tabular crystals in matrix | Vesuvianite + clinochlore + diopside |
| 7        | Preive Fountain      | Matrix and few small tabular crystals | Vesuvianite + clinochlore + diopside |
| 8        | Pian Ciamarella—Balme | Subhedral crystals in matrix + small faceted gemstone | Vesuvianite + clinochlore + diopside + andradite |
| 9        | Uja di Mondovè       | Few small and short crystals on matrix plate | Vesuvianite + diopside |
| 10       | Vallonetto di Mondrone | Few small subhedral crystals in matrix | Vesuvianite + clinochlore |
| 11       | Monterosso d’Ala     | Matrix with few small prismatic crystals | Vesuvianite + clinochlore |
| 12       | Val d’Ala**          | Two samples. Bundle association of prismatic crystals | Vesuvianite |

*All vesuvianite samples are associated with rodingites included in serpentinites.** gift of a collector from Val d’Ala; unknown locality.

Standard gemological analyses were carried out in order to describe the optical properties, specific gravity and ultraviolet fluorescence. Density (gravity) was evaluated using a Presidium PCS100 Sensible hydrostatic balance (Gemmarum, Cavalese, Italy), the color with a Panton color
Refractive index was measured by the distant vision method using a Kruss refractometer (1.45–1.80 range) and a contact liquid with R.I. = 1.80. The ultraviolet fluorescence was investigated with a short (254 nm) and long (366 nm) wavelength ultraviolet Wood lamp. We determined the vesuvianite colors with ColorMeter RGB. The RGB color system constructs all the colors from the combination of the red, green and blue.

X-ray powder analyses (XRPD) were conducted to determine the mineralogical composition of some vesuvianite crystals and rock matrices. We used a Philips PW1800 Powder Diffractometer (Philips, Amsterdam, Netherlands), with Cu Kα radiation (λ = 1.5418 Å) and a scan speed of 1°/min, in the range between 2° and 65° 2θ. The samples for the analyses were previously ground in an agate mortar and reduced to a powder. Qualitative and semi-quantitative evaluation was performed with the program X Pert-High Score [18].

Textural observations (backscattered electrons images—BSE) were performed by means of a Tescan FE-SEM (Mira 3XMU-series), and the samples were analyzed for major elements with a Tescan VEGA TS Univac 5136 XM scanning electron microscope coupled with an EDAX Genesis4000 XMS Imaging 60 SEM-EDS at the University of Milano-Bicocca (Italy) under an electron beam of 20 kV high voltage, with 250 nm spot size and an absorption of current of 190 ± 1 pA, measured in a platinum Faraday cup. The quantification of main elements was calibrated on Astimaex Scientific standard. The measurements were processed using the EDAX Genesis software (2011, EDAX Inc., Mahwah, NJ, USA) and the data were obtained using the ZAF correction.

Trace elements analyses were performed on the same crystals by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS), using an Elan DRC-e mass spectrometer (2010, Perkin-Elmer SCIEX, Waltham, MA, USA) coupled with a Q-switched Nd: YAG laser source, with a fundamental emission (1064 nm) that was converted to 266 nm by two harmonic generators. Helium was used as a carrier gas, mixed with Ar gas downstream of the ablation cell. The calibration was performed using NIST SR 610 glass and Si as external and internal standards, respectively. The precision and accuracy estimated on the glass BRC2 standard were better than 10%. Three analyses per sample were collected using a spot size of 35 μm.

3. Results

The investigation of gemological properties was carried out on all the raw gemstones (0.18–0.98 ct; e.g., Figure 3). Since XRPD analyses are destructive, only 9 samples out of 11 were analyzed (excluding samples 11 and 12); for the same reason, LA-ICP-MS measurements were reduced to 10 samples (excluding sample 2).

3.1. Gemological Analyses

All the analyzed samples show a prismatic habit and are about 3 cm long (Figure 3); they show vitreous luster and a beautiful range of different shades and colors: from yellow green to chocolate (reddish-brown color), with intermediate colors like lime green, olive green, forest green, dark olive green. The most appreciated vesuvianite gemstones are those that are green or brown, with red shades. All the samples are inert to short and have long UV wave lengths.
Figure 3. Images of the different samples of vesuvianite from Val d’Ala investigated in this work. (A) sample 4: twinned crystal of vesuvianite (from Borne Brous); (B) sample 4: fragment of vesuvianite from Borne Brous with matrix rock. The crystal shows a squat morphology; (C) sample 2: crystal of vesuvianite with columnar habitus (from Testa Ciarva); (D) sample 1: association of columnar crystals of vesuvianite (from Testa Ciarva) with rock matrix; (E) sample 2: another specimen of vesuvianite from Testa Ciarva with prismatic habitus; (F) sample 6: tabular crystals of vesuvianite in the host rock (from Mont Fort); (G) sample 12: fragment of vesuvianite from Val d’Ala s.l. showing the presence of inclusions (photos by M. Scacchetti and R. Appiani).

An important gemological peculiarity was the polychromy, shown in the olive green and chocolate (reddish-brown) samples, in particular in sample 2 from Testa Ciarva, 4 from Borne Brous and 12 from Val d’Ala s.l. (Figure 3). The refractive index value varies between 1.075 and 1.720, while density (gravity) varies between 3.25 and 3.38. These values are in the range of those in literature [19–21]. It is noteworthy that the samples with the highest color saturation show higher refractive indexes (Table 2); sample 4 from Borne Brous has the lowest refractive indices <1.715>, <1.708> (Table 2). Regarding density (gravity), we observe that the sample from Monterosso d’Ala (11) shows the lowest values (3.25). These slight variations in density and refractive indices are probably related to the presence of chromophore elements and solid inclusions. The pleochroism is weak in the green-yellow (yellow-green at dichroscope) and light green (pale green-green), is moderate in the olive green samples (green-dark green) and more intense in the dark olive green (dark green-brown) and chocolate (reddish-brown) samples.

In transparent vesuvianite gems, the diagnostic of inclusions is important for the traceability of the material. The association of the mineralogical phases present within the mineral include more or fewer lamellar fibrous aggregates and, at high magnification, we observed more elongated phases consisting of phyllosilicates, such as clinohlore (Figure 4B), opaque inclusions (garnets) and prismatic diopside (Figure 4A, B). Many single crystals show multiple and rhythmic compositional zonings Figure 4C), manifested in light brown bands (perpendicular to the axis of greatest growth of the crystal). The analyzed crystals are all very fibrous (Figure 4D).
Table 2. Gemological data of vesuvianite from Val d’Ala.

| Samples | Dimensions (mm) | RI   | Gravity (g/cm$^3$) | Diaphaneity | Color (RGB) and Green Saturation |
|---------|-----------------|------|--------------------|-------------|---------------------------------|
| 1       | 17.4 × 4.6      | n.d. | 3.29               | Tl          | Green vivid 6                    |
| 2       | 5.8 × 19.9      | 1.718–1.709 | 3.38 | T | Light green (yellowish) 3       |
| 3       | 29.4 × 7.8      | n.d. | 3.39               | Tl          | Olive green 4                    |
| 4       | 22.5 × 2.8      | 1.715–1.708 | 3.33 | Tl | Chocolate (reddish-brown) 1     |
| 5       | 7.7 × 2.6       | 1.718–1.707 | 3.33 | T | Dark olive green 3              |
| 6       | 3.2 × 2.2       | 1.719–1.705 | 3.32 | T | Dark olive green 3              |
| 7       | 2.2 × 1.6       | 1.720–1.708 | 3.33 | Tl | Dark golden 2                   |
| 8       | 2 × 2           | 1.716–1.705 | 3.29 | Tl | Dark olive green 3              |
| 9       | 8 × 3.3         | 1.720–1.708 | 3.35 | Tl | Dark olive green 3              |
| 10      | 4 × 1.6         | n.d. | 3.25               | Tl          | Olive green vivid 5              |
| 11      | 6 × 19.1        | 1.718–1.709 | 3.37 | Tl | Dark olive green (brownish) 2   |

n.d.—not determined.

Figure 4. Different typologies of inclusions in the vesuvianite from Testa Ciarva (sample 2). (A) Inclusions of diopside with elongated shape (50X); (B) diopside and clinochlore (25X); (C) multiple and rhythmic compositional zonings formed by pale brown bands perpendicular to the crystal elongation. (50X); (D) vesuvianite crystal showing the structure composed by channels and tubes (75X). (photo by Angelo Leone).

3.2. X-ray Powder Diffraction (XRPD)

XRPD analyses were carried out on raw materials (vesuvianite crystal and, when present, host-rock), to determine the other mineral phases associated with vesuvianite. In all samples, vesuvianite is the most abundant phase and is associated with clinochlore; the latter is present in variable contents (between 0% and 23%, Table 3). Among the Ca-rich phases, the diopside is the most widespread, while the garnets with andradite and grossular varieties are present, respectively, in sample 8 from Pian Ciamarella–Balme and sample 3 from Testa Ciarva (Table 3).
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Table 3. Mineralogical compositions of raw materials obtained from XRPD analyses (%).

| Sample | Vesuvianite | Clinohlore | Diopside | Andradite | Grossular |
|--------|-------------|------------|----------|-----------|-----------|
| 1      | 55          | 20         | 25       | 0         | 0         |
| 2      | 80          | 10         | 10       | 0         | 0         |
| 3      | 33          | 23         | 18       | 0         | 26        |
| 4      | 90          | 10         | 0        | 0         | 0         |
| 5      | 78          | 10         | 12       | 0         | 0         |
| 6      | 83          | 10         | 7        | 0         | 0         |
| 7      | 54          | 23         | 14       | 10        | 0         |
| 8      | 90          | 0          | 10       | 0         | 0         |
| 9      | 90          | 10         | 0        | 0         | 0         |
| 10     | 90          | 10         | 0        | 0         | 0         |

3.3. Optical Microscope, Scanning Electron Microscope and SEM/EDS Microanalysis

The optical characteristics of vesuvianite crystals were determined through thin sections observation, under a transmitted light microscope. The transparent portions, without inclusions, show a marked compositional zoning (Figure 5A), as already observed in the gemological study. This type of microstructure is related to chemical variations, which occurred during the crystal formation phase. As a matter of fact, the zoning follows the growth lines of the crystal and is arranged according to the restrictions imposed by the crystalline structure. In the non-transparent portion (Figure 5A, B), it is possible to observe the distribution of inclusions within the vesuvianite crystal. Andradite is abundant between the poikilitic and the transparent zones of crystal (Figure 5C). In the most internal parts, the most abundant phase is the clinohlore (Figure 5D, E), often zoned, in aggregates of acicular fibrous crystals. OM and SEM observations are in agreement with gemological data and XRPD analyses.

Compositional data for the vesuvianite crystals are reported in Table 4. The major element composition shows good compositional homogeneity, even if the samples derive from different outcrops. There are some differences regarding Al₂O₃ contents that are lower in sample 12 (Val d’Ala) and MgO contents, which are higher in sample 3 from Testa Ciamarella and 7 from Preive Fountain. The most important chromophore elements are represented by Fe and, to a lesser extent, Ti. In particular, we observed that FeO is higher in sample 6 from Mont Fort, 9 from Uja di Mondovè and 11 from Monterosso d’Ala, while it is lower in sample 3 from Testa Ciara and 8 from Pian Ciamarella. TiO₂ is higher in sample 12 from Val d’Ala and 4 from Borne Brous.

Table 4. Mineral chemistry (wt.%) and mineral formula (apfu; based on 78O) of vesuvianite of the Val d’Ala.

| Wt.%   | 1    | 3    | 4    | 6    | 7    | 8    | 9    | 10   | 11   | 12   |
|--------|------|------|------|------|------|------|------|------|------|------|
| MgO    | 2.25 | 2.74 | 1.59 | 2.52 | 2.87 | 2.16 | 2.60 | 2.54 | 2.60 | 2.64 |
| Al₂O₃  | 17.05| 17.25| 17.10| 16.72| 17.12| 18.23| 16.75| 17.46| 16.43| 14.37|
| SiO₂   | 37.55| 37.65| 37.42| 37.53| 37.66| 37.63| 37.60| 37.55| 37.20| 37.20|
| CaO    | 34.93| 35.24| 34.61| 35.27| 35.48| 35.43| 35.34| 35.45| 34.94| 34.99|
| TiO₂   | 1.71 | 0.73 | 2.70 | 0.33 | 0.01 | 0.59 | 0.22 | 0.05 | 0.16 | 3.90 |
| MnO    | 0.02 | 0.05 | 0.00 | 0.05 | 0.11 | 0.00 | 0.06 | 0.02 | 0.16 | 0.02 |
| FeO₂   | 3.48 | 3.30 | 3.45 | 4.90 | 4.00 | 3.11 | 5.01 | 4.11 | 4.90 | 4.10 |
| NiO    | 0.11 | 0.11 | 0.10 | 0.15 | 0.15 | 0.15 | 0.16 | 0.18 | 0.11 | 0.17 |
| Total  | 97.10| 97.07| 96.97| 97.47| 97.40| 97.30| 97.73| 97.36| 96.50| 97.39|

| Wt. (apfu) | 1   | 3   | 4   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Mg (apfu)  | 1.60| 2.80| 1.20| 1.84| 2.16| 1.60| 1.92| 1.90| 1.96| 1.96|
| Al (apfu)  | 9.98| 10.14| 9.98| 10.24| 10.04| 10.70| 9.86| 10.26| 9.80| 8.54|
| Si (apfu)  | 18.60| 18.70| 18.80| 18.80| 18.60| 18.64| 18.70| 18.68| 18.70| 18.50|
| Ca (apfu)  | 18.66| 18.80| 18.60| 18.64| 18.94| 18.82| 18.84| 18.92| 18.90| 18.74|
| Ti (apfu)  | 0.65| 0.28| 1.00| 0.16| 0.00| 0.22| 0.08| 0.02| 0.06| 1.46|
| Mn (apfu)  | 0.08| 0.02| 0.20| 0.02| 0.04| 0.00| 0.00| 0.00| 0.00| 0.00|
| Fe³⁺ (apfu)| 1.32| 1.24| 1.28| 1.82| 1.50| 1.16| 1.88| 1.54| 1.86| 1.54|
| Ni (apfu)  | 0.04| 0.04| 0.04| 0.06| 0.06| 0.06| 0.06| 0.08| 0.04| 0.06|
Figure 5. Transmitted light microscopy images and SEM images (backscattered electrons (BSE)) of sample 6 (from Mont Fort). (A) thin section optical microscope observation of vesuvianite crystals (yellow grains) (crossed nicols); (B) same previous image observed through BSE; (C) andradite crystals in vesuvianite (BSE); (D) zoned clinohlore in vesuvianite (BSE); (E) aggregate of zoned clinohlore in vesuvianite crystal (BSE).

3.4. Laser Ablation-Inductively Coupled Plasma Mass Spectrometry

The minor and trace element composition of the investigated vesuvianite is reported in Table 5. Contrary to the major elements, the trace element composition is more variable without defined trends. The vesuvianite from Testa Ciarva (1, 2, 3 in Table 5) are distinguished by a higher content of light elements (Be and Li) and, for this feature, they can be correlated with sample 12 from Val d’Ala s.l. We also observed that Sr values vary between around 110 and 250 ppm, with the exception of the samples 6, 7 and 8 (respectively, Mont Fort, Preive Fountain, Pian Ciamarella—Balme), where Sr is much lower.

Some specific trace elements may affect the color saturation. The more “vivid” vesuvianite (1 and 3 from Testa Ciarva, 11 from Monterosso) contain greater quantities of Cr, and among these, sample 1 from Testa Ciarva shows values close to 150 ppm. V contents are higher in the dark olive green (6 Mont Fort, 9 Uja di Mondovè, 10 Valletta di Mondone) (Table 5).

Table 5. Minor and trace elements contents of the investigated vesuvianite.

| Elements (ppm) | 1   | 3   | 4   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Li            | 4.64 | 2.12 | 4.25 | 0.02 | 0.01 | 0.67 | 0.76 | 0.10 | 0.44 | 2.39 |
| Be            | 8.55 | 15.81 | 3.48 | 0.67 | 1.01 | 0.55 | 0.44 | 0.23 | 0.28 | 1.06 |
| B             | 32.27 | 40.17 | 38.81 | 25.22 | 31.93 | 35.45 | 19.54 | 21.54 | 23.17 | 37.33 |
| Sc            | 3.79 | 4.48 | 1.40 | 5.85 | 4.18 | 2.86 | 18.09 | 9.77 | 10.36 | 0.68 |
| V             | 36.37 | 31.73 | 29.33 | 99.06 | 72.50 | 17.45 | 106.15 | 92.60 | 63.90 | 22.37 |
| Cr            | 146.26 | 23.66 | 1.00 | 9.39 | 1.37 | 4.11 | 1.76 | 6.79 | 21.25 | 0.20 |
| Co            | 8.90 | 20.00 | 8.03 | 8.00 | 6.80 | 6.38 | 7.48 | 9.19 | 7.24 | 11.22 |
| Ni            | 55.97 | 21.24 | 22.65 | 33.71 | 38.76 | 29.17 | 22.25 | 23.82 | 27.70 | 43.62 |
| Zn            | 9.44 | 20.10 | 13.15 | 13.79 | 9.41 | 8.21 | 9.33 | 8.18 | 8.22 | 23.59 |
| Sr            | 114.20 | 213.13 | 131.49 | 15.62 | 55.17 | 41.17 | 251.60 | 226.83 | 130.58 | 111.79 |
| Y             | 7.34 | 24.18 | 3.70 | 1.62 | 0.07 | 3.38 | 1.03 | 0.03 | 5.20 | 0.51 |
| Zr            | 1.75 | 5.08 | 31.98 | 7.86 | 1.20 | 7.30 | 2.81 | 4.62 | 1.59 | 56.22 |
| Pb            | 0.88 | 4.92 | 0.08 | 0.04 | 0.07 | 0.27 | 0.14 | 1.13 | 0.31 | 0.46 |
3.5. **REE Distribution**

In Table 6 we report the REE abundances in the samples investigated in this work while in Table 7 the total REE contents in some vesuvianite worldwide. REE contents in our vesuvianite are variable but generally low: higher contents are found in sample 3 (Testa Ciavara), 4 (Borne Brous) and 8 (Pian Ciamarella). All patterns display a decrease in heavy rare-earth elements (HREE) (except for the samples 9, Uja di Mondovè, and 10, Valletta di Mondrone) and slight enrichment of light rare-earth elements (LREE). All REE patterns (Figure 6) are also characterized by a pronounced positive Eu anomaly that decreases with the increasing of the total REE content. The literature data show that vesuvianite in skarn and rodingite rocks coexists with Ca-rich garnets [19,20] and both minerals can contain significant concentration of REE.

**Table 6. REE abundances in the Val d’Ala vesuvianite. *Chondrite-normalized values [21].**

| ppm | 1   | 3   | 4   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| La  | 0.63| 32.78| 8.14| 0.13| 0.01| 2.77| 0.10| 0.01| 0.08| 0.50|
| Ce  | 2.01| 73.82| 29.63| 0.40| 0.01| 8.39| 0.17| 0.02| 0.22| 1.37|
| Pr  | 0.47| 10.25| 4.78| 0.06| 0.00| 1.52| 0.01| 0.00| 0.05| 0.22|
| Nd  | 3.68| 56.63| 22.98| 0.28| 0.00| 10.76| 0.05| 0.02| 0.31| 0.99|
| Sm  | 1.15| 10.76| 3.58| 0.09| 0.00| 3.18| 0.01| 0.01| 0.20| 0.15|
| Eu  | 1.34| 6.04| 5.41| 0.64| 0.00| 3.47| 0.12| 0.01| 0.66| 2.58|
| Gd  | 1.30| 10.41| 1.57| 0.12| 0.00| 2.06| 0.01| 0.00| 0.38| 0.08|
| Tb  | 0.23| 1.42| 0.17| 0.02| 0.00| 0.20| 0.01| 0.00| 0.09| 0.01|
| Dy  | 1.51| 7.32| 0.75| 0.22| 0.01| 0.92| 0.07| 0.00| 0.77| 0.06|
| Total | 10.81| 209.43| 77.01| 1.96| 0.03| 33.27| 0.55| 0.07| 2.76| 5.96|

| ppm | La* | Ce* | Pr* | Nd* | Sm* | Eu* | Gd* | Tb* | Dy* |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 2.65| 138.30| 34.36| 0.54| 0.03| 11.68| 0.43| 0.05| 0.33| 2.09|
| 3.27| 120.43| 48.33| 0.65| 0.01| 13.68| 0.27| 0.04| 0.35| 2.24|
| 5.02| 110.45| 51.51| 0.59| 0.00| 16.37| 0.14| 0.05| 0.51| 2.38|
| 8.06| 123.92| 50.28| 0.61| 0.01| 23.53| 0.11| 0.04| 0.69| 2.17|
| 7.79| 72.68| 24.19| 0.59| 0.00| 21.46| 0.06| 0.05| 1.32| 1.02|
| 23.88| 107.22| 96.09| 11.39| 0.03| 61.66| 2.20| 0.13| 11.71| 45.90|
| 6.52| 52.29| 7.89| 0.62| 0.01| 10.36| 0.05| 0.01| 1.92| 0.40|
| 6.28| 39.26| 4.70| 0.59| 0.00| 5.61| 0.15| 0.02| 2.40| 0.31|
| 6.12| 29.77| 3.04| 0.89| 0.02| 3.74| 0.28| 0.02| 3.14| 0.26|

| Table 7. REE abundances in the REE rich-vesuvianite worldwide. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| REE (ppm) | Hirao | Japan | REE (Oxides) | S. Benito | USA |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| La | 1546 | 2631 | LaO | 5.58 | 3.79 |
| Ce | 4022 | 2946 | CeO | 9.88 | 8.69 |
| Pr | 571 | 253 | PrO | 0.29 | 0.70 |
| Nd | 1928 | 642 | NdO | 1.23 | 1.37 |
| Sm | 310 | 101 | SmO | 0.07 | 0.19 |
| Eu | 56 | 406 | | | |
| Gd | 156 | 102 | GdO | 0.15 | -- |
| Tb | 18 | 21 | | | |
| Dy | 97 | 164 | | | |
| Ho | 14 | 41 | | | |
| Er | 34 | 126 | | | |
| Tm | 4 | 21 | | | |
| Yb | 23 | 152 | | | |
| Lu | 2 | 20 | | | |
| Total | 8781 | 7626 | Total | 17.19 | 14.74 |
4. Discussion and Conclusions

The values of physical properties (pleochroism, polychromy, density, refractive index) of vesuvianite investigated in this paper are well comparable with those of other vesuvianites from the most famous deposits of the world (Russia, Pakistan, Canada, United States) (Table 8).

Table 8. Gemological data of vesuvianite from other worldwide localities.

| Locality               | RI          | Gravity g/cm³ | Diaphaneity | Color                  | Morphology | Host Rock   |
|------------------------|-------------|---------------|-------------|------------------------|------------|-------------|
| Jeffrey Mine Canada [2]| 1.722–1.725 | 3.36          | T           | Pink, green, Brown    | Prismatic  | Rodingite   |
| S. Benito USA [1]      | 1.732–1.741 | 3.39          | T/Ti        | Red/gold, black       | Prismatic  | Altered greenstones |
| Lake Jaco Mexico [1]   | --          | -             | Ti          | Yellow-green          | Short prismatic | Skarn      |
| Yakuskaya Russia [2]   | 1.668–1.691 | 3.27          | Ti          | Cream                 | Tabular    | Skarn       |
| Bellecombe Italy [9]   | 1.714–1.738 | 3.36          | T/Ti        | Yellow-brown, Greenish-brown | Prismatic | Rodingites  |
| Vesuvio Italy [4,5]    | --          | 3.40          | Ti          | Greenish-brown, Orange-brown | Short prismatic | Skarn, Syenite |

The major element composition is similar to that of vesuvianite from Piedmont and Aosta Valley occurring in similar geological settings and is also well comparable to Val d’Ala samples reported by [11]. The mineralogical association of the host rocks is made of prevalent vesuvianite with chlorite and garnet. Vesuvianite generally grows at the expense of garnet and is locally zoned with Al increasing and (Ti + Mg) decreasing from core to rim, respectively [13]. The trace element composition of the investigated vesuvianite is very variable, which is consistent with the complex metasomatic and metamorphic processes that generated vesuvianite and host rock. The genesis of vesuvianite depends on several factors strictly dependent on local chemical equilibrium between the different phases. As a result, crystals are often zoned and the chemical variability can be observed at a microstructural level equilibrium between the different phases.

REE contents in the investigated samples are also very variable but commonly show a LREE enrichment with respect to HREE and a Eu positive anomaly. This is also confirmed by the studies in the literature on vesuvianite worldwide that indicate that REE abundances are very variable, while the patterns often show an enrichment of LREE with respect to HREE [1,2,4,6,7,19,22,23]. Often, all samples of lanthanide-rich vesuvianite are relatively enriched in Fe [2]. Vesuvianite in the skarns of
the Hirao Formation in Japan contains large amounts of REE, up to 8000 ppm (Table 6), and represents the phase that preferentially hosts these elements with respect to the other minerals, such as garnet, diopside and wollastonite [19]. Vesuvianite from San Benito County in California are exceptionally rich in REE (Table 6), about 17 wt.% (calculated as oxides); in the structure of the mineral, the REEs replace the Ca and, in decreasing order of abundance, are Ce, La, Nd, Pr, Gd, and Sm [1]. A metamorphic vesuvianite from Mexico shows contents of La and Ce of about 1000 ppm while the other REE are much lower [19]. In the mid-Miocene Zhibula Cu skarn of Gangdese Belt in Tibet vesuvianite contains several hundred ppm of REE that show LREE enrichment and either a positive or negative Eu anomaly. Additionally, in this case, vesuvianite would appear to be a host for alkali earths (Li, Na, K, Sr) and several transition metals, V, Cr, Zn, As, Sb, Th and U [23]. Our results suggest that REE distribution in vesuvianite may depend on fluid composition, as REE-enriched vesuvianite formed through the interaction with LREE-enriched and HREE-depleted fluids. Ca-garnets coexisting with vesuvianite in Val d’Ala [19,20] preferentially incorporate HREE rather than LREE, suggesting that LREE in fluids might preferentially accumulate in vesuvianite.

The relations between the color of vesuvianite and the chromophore elements are discussed in many works [2,24,25]. Vesuvianite generally presents a wide range of colors due to the great variety and quantity of trace elements. Investigations on vesuvianite from Jeffrey (Quebec) showed that the samples with low Ti contents are green, while those with more than 0.10 wt.% TiO₂ are brown [2,25].

Manning [25] suggested a loose classification of vesuvianite based on the color and transition-metal composition: blue, pink, lilac vesuvianite containing Cu²⁺, Mn³⁺or Cr³⁺; green vesuvianite with Fe³⁺chromophore on octahedral coordination; Fe²⁺ rich vesuvianite green-brownish or green-yellowish; brown vesuvianite with Fe³⁺and Fe²⁺. Groat et al. [2] highlighted that Cr³⁺ content in vesuvianite can be >6 wt.% and, in this case, the color is green vivid. Kobayashi and Kaneda [26] established that the green color is related to the charge transfer Fe³⁺ → Fe²⁺, and both the ions are octahedrally coordinated in the structure. According to these authors, in the yellowish-green samples, the color can be attributed to the presence of octahedral Fe²⁺and to the charge transfer Fe²⁺ → Fe³⁺. Also the presence of Mn³⁺(0.25–0.30 apfu) in the octahedral site, together with Fe²⁺ and Cr³⁺, can produce a red-brownish hue. Mn is also an important chromophore when Fe is poor—a small amount of Mn causes a pink or lilac color. Indeed, some crystals of vesuvianite from Jeffrey in Quebec are lilac-colored (Mn-rich). Cr is also a strong chromophore that causes a vivid green color.

The samples of vesuvianite examined in this work show a green color that is principally due to the presence of Fe. The relative abundances of Fe also generate a more or less pronounced dark tone: light green—sample 2; olive green—samples 3 and 11; dark olive green—samples 6, 7, 8, 9, 10. The abundance of Ti determines a lower or greater degree of green color saturation: higher quantities of this element lead to less saturation of the green color (Table 4). We observe that the vesuvianite from Borne Brous (sample4) and Val d’Ala s.l. (sample 12) show a reddish-brown (chocolate RGB; dark olive green brownish) color due to higher Ti contents (2.7 wt.%). The samples from Testa Cierva show a reddish-brown polychromy (Figure 4C) that is related to the variable contents of Ti (from 1.71 to 0.73 wt.%). As a matter of fact, the bands with a more pronounced reddish-brown color show higher Ti contents with respect to the other parts of the crystal. Lastly, we observe that the samples with higher Cr and Ni contents (sample 1 and 3 from Testa Cierva and sample from 11 Monterosso) present a more “vivid” color, which is a very important gemological property.

The differences between vesuvianite from Val d’Ala and other gem-quality vesuvianite in the world (Table 8) are the following:

1) The crystals are less transparent than those of Pakistan, California and United States; this is due to the presence of many inclusions, sometimes making them even opaque;
2) The refractive indices are lower than those of the most beautiful gems from Canada, the United States and Pakistan. The only exception is represented by the samples from Yakuskaya in Russia, which have the lowest refractive indices;
3) The vesuvianite of Val d’Ala often shows a peculiar polychromy, perpendicular to the lengthening of the crystal;
4) The crystals are frequently twinned, which is an uncommon characteristic in vesuvianite worldwide;

5) The vesuvianite of Val d’Ala is found in rodingite and therefore belongs to a geological context different from that of vesuvianite of Mexico and Russia (skarn), Mount Vesuvius (syenite, skarn), California (altered greenstones). The vesuvianite of the Val d’Ala is well known, especially among collectors; however, this mineral shows all the gemological characteristics to be commercially appreciated even by a wider public. The gemological defect that explains the scarce consideration of these gems is their common translucent diaphaneity related to the presence of inclusions (Figure 7).

Figure 7. Gems of vesuvianite from Val d’Ala. (A) “Emerald” rectangular cut; (B) “Emerald” trapezoidal cut (private collection; photo by Enrico Borghi).

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