Permian Hydrothermal Alteration Preserved in Polymetamorphic Basement and Constraint for Ore- genesis (Alpi Apuane, Italy)

Simone Vezzoni 1, Diego Pieruccioni 2*, Yuri Galanti 3, Cristian Biagioni 2 and Andrea Dini 1

1 Istituto di Geoscienze e Georisorse, CNR, Via Moruzzi 1, I-56124 Pisa, Italy; simone.vezzoni@igg.cnr.it (S.V.); a.dini@igg.cnr.it (A.D.)
2 Dipartimento di Scienze della Terra, Università di Pisa, Via Santa Maria 53, I-56126 Pisa, Italy; cristian.biagioni@unipi.it
3 Dipartimento di Pistoia, ARPA Toscana, Via dei Baroni 18, I-51100 Pistoia, Italy; y.galanti@arpat.toscana.it
* Correspondence: diego.pieruccioni@dst.unipi.it

Received: 13 September 2020; Accepted: 29 September 2020; Published: 5 October 2020

Abstract: The reconstruction of the polymetamorphic history of basement rocks in orogens is crucial for deciphering past geodynamic evolution. However, the current petrographic features are usually interpreted as the results of the metamorphic recrystallization of primary sedimentary and/or magmatic features. In contrast, metamorphic rocks derived by protoliths affected by premetamorphic hydrothermal alterations are rarely recognized. This work reports textural, mineralogical and geochemical data of metasedimentary and metaigneous rocks from the Paleozoic succession of the Sant’Anna tectonic window (Alpi Apuane, Tuscany, Italy). These rocks were recrystallized and reworked during the Alpine tectono-metamorphic event, but the bulk composition and some refractory minerals (e.g., tourmaline) are largely preserved. Our data show that the Paleozoic rocks from the Alpi Apuane were locally altered by hydrothermal fluids prior to Alpine metamorphism, and that the Permian magmatic cycle was likely responsible for this hydrothermal alteration. Finally, the Ishikawa Alteration Index, initially developed for magmatic rocks, was applied to metasedimentary rocks, providing a useful geochemical tool for unravelling the hydrothermal history of Paleozoic rocks, as well as a potential guide to the localization of hidden ore deposits in metamorphic terranes.

Keywords: basement; Permian magmatism; hydrothermal alteration; ore genesis; Alpi Apuane

1. Introduction

Polymetamorphic basement complexes may show a large variety of lithotypes that are usually interpreted as primary variations in sedimentary inputs and/or in the composition of magmas that fed igneous bodies, as well as metasomatic changes experienced during metamorphism/subduction (e.g., [1,2]). Little attention has been given to the possibility that some peculiar lithotypes actually derive from the metamorphism of hydrothermally-altered protoliths formed during magmatic-hydrothermal events preceding the last metamorphic event (e.g., [3,4]). The identification of hydrothermal alterations predating metamorphism is relevant for the reconstruction of old magmatic-hydrothermal systems and the correct interpretation of past geodynamic settings (e.g., [5]). In addition, they can be used as potential guides to the localization of hidden ore deposits.

Hydrothermal alteration (triggered or not by magmatism) can produce very peculiar mineralogical assemblages and geochemical fingerprints, significantly deviating from the usual sedimentary and/or magmatic realms. These features can still be recognized after metamorphic recrystallization. It is well-known that low-grade metamorphism can be a nearly isochemical process, and thus, the mobility of chemical components is largely restricted to volatiles (e.g., [6–9]).
Consequently, the metamorphic processes can modify the texture and mineralogy of the protoliths, but the bulk composition and some refractory minerals (e.g., tourmaline, zircon) are commonly preserved.

This contribution provides geochemical and mineralogical evidence that a pre-Alpine hydrothermal event related to an ore-forming event is recorded within the Paleozoic succession of the Alpi Apuane, affecting both the Cambrian-Early Ordovician phyllitic rocks and the felsic magmatites of Permian age.

2. Geological Background

2.1. Regional Geology

The Northern Apennine (Italy) is a collisional belt related to the convergence between the Europe and Adria plates active since Late Cretaceous ([10] and references therein). The Alpi Apuane is the largest tectonic window of the Northern Apennine in which the deepest structural levels are exposed (Figure 1). The tectonic units are representative of the distal part of the Adria continental margin (Tuscan Domain) and they lie below the westerly-derived oceanic Ligurian and sub-Ligurian accretionary wedge units ([11–13] and references therein).

Figure 1. Geological sketch map (modified after Carmignani and Kligfield [11]) of the Alpi Apuane massif with location of the main orebodies (modified after Lattanzi et al. [14]).
Three main stratigraphic (Tuscan Nappe) and tectono-metamorphic units (Massa and Apuane units) are traditionally distinguished in the Alpi Apuane region, all of which are derived from the Adria paleo-margin. The Tuscan Nappe is formed by Mesozoic carbonate, i.e., siliceous rocks and Tertiary deep-water and turbiditic sequences mainly detached from their original basement along the decollement level of the former Carnian and Norian evaporites (e.g., [15,16] and reference therein). The Massa Unit consists of a Paleozoic metasedimentary and metavolcanics basement and an upper Permian-Upper Triassic metasilicoclastic succession (Figure 1; e.g., [16,17]). The Apuane Unit includes a litho-stratigraphic sequence made up of a Paleozoic basement (e.g., [18]) intruded by post-Variscan magmatic rocks (Fornovolasco Metarhyolite Fm; [19–21]), unconformably overlain by an Upper Triassic-Oligocene metasedimentary succession (Figures 1 and 2; e.g., [16]).

Figure 2. Geological map of the Sant’Anna tectonic window (modified after Conti et al. [22]) with locations of the main abandoned mines. The “Filladi Inferiori” and Fornovolasco Metarhyolites samples are also shown.

The Tertiary tectonic evolution of the Alpi Apuane includes an early stage of underplating and antiformal stacking, associated with peak metamorphism and isoclinal folding (D1 event according to Carmignani and Kligfield [11]). This stage was followed by deformation associated with
Geosciences 2020, 10, 399

syncontractional exhumation, during which folding and subhorizontal crenulation cleavage was developed (D2 event according to Carmignani and Kligfield [11] and Molli and Vaselli [23]). The latest stages of geological evolution, associated with the final exhumation and uplift of the Alpi Apuane, were characterized by brittle faulting (low- and high-angle faults) during “postorogenic” regional extension of the inner part of the Northern Apennine wedge (e.g., [24–26]).

In the metamorphic units of the Alpi Apuane, peak conditions are roughly estimated between 350–450 °C and 0.4–0.8 GPa ([27] and references therein). The early deformation D1 occurred during early Miocene at 27–20 Ma [28], whereas synmetamorphic D2 structures developed at temperatures higher than 250 °C and predated cooling at 11 Ma, according to zircon fission-track ages [29].

The Sant’Anna tectonic window is located in the southern sector of the Alpi Apuane (Figure 1). Notwithstanding its small exposed area, it is a key zone for the study of ore deposits. Indeed, several small pyrite ± baryte ore bodies, associated with Pb-Zn-(Ag) and iron oxides ores, occur in this area and were formerly exploited in some mines (Pollone, Verzalla, Monte Arsiccio, and Zulfiello; Figure 2). Its complex tectonic setting is characterized by the occurrence of the polymetamorphic Paleozoic basement, intruded by post-Variscan magmatic rocks, and the Triassic-to-Oligocene metasedimentary cover belonging to the Apuane Unit. Ore bodies are located within the Paleozoic succession or close to the contact with Triassic metadolostone (e.g., [30,31]). The metamorphic rocks are overlain by the Tuscan Nappe (Figure 2).

2.2. The Paleozoic Succession of Sant’Anna Tectonic Window

The Paleozoic succession of Sant’Anna tectonic window (southern Alpi Apuane) is formed by two geological formations: the “Filladi Inferiori” and the Fornovolasco Metarhyolite Fms (Figure 2).

The “Filladi Inferiori” Fm is made up of light- to dark-grey quartzite, dark-grey and/or grey-greenish phyllitic quartzite and phyllite, interpreted as a metamorphic product of an original alternance of quartzitic sandstone and pelite [16,32,33]. The top of this formation is locally marked by the presence of a discontinuous layer of matrix-supported metamorphic paraconglomerate that contains quartzitic pebbles and grains of magmatic quartz and feldspar in a quartzitic-feldspathic matrix [18,33]. In the southern Alpi Apuane, a peculiar tourmalinite-bearing facies, spatially associated with orebodies, has been referred as the “Fornovolasco Schists” Fm; it was attributed to a different lithostratigraphic unit (e.g., [34]). However, this interpretation has been strongly debated (e.g., [19]). A Cambrian-early Ordovician depositional age was proposed through the correlation with the Paleozoic successions of Sardinia (e.g., [18,35]); this dating was recently confirmed by Paoli et al. [36] and Pieruccioni et al. [37], who suggested a depositional age between early Cambrian and middle-late Ordovician Ordovician times, based on LA-ICP-MS U-Pb zircon data.

The Fornovolasco Metarhyolite Fm is formed by fine-grained massive subvolcanic rocks with a granular to porphyritic texture, locally showing the widespread occurrence of cm-sized tourmaline + quartz orbicules [19,20]. On the basis of LA-ICP-MS U-Pb zircon dating, Vezzoni et al. [20] dated this formation to Permian (c.a. 270 Ma). The Fornovolasco Metarhyolite Fm occurs as decimeter-sized lensoid bodies embedded within the “Filladi Inferiori” Fm, commonly associated with the facies previously referred to as “Fornovolasco Schists” [21,34].

2.3. The Alpi Apuane Ore District

The Alpi Apuane hosts several small polymetallic orebodies [14,38] (Figures 1 and 2) discontinuously exploited almost from the Renaissance to the end of the 1980s. The main orebodies widely crop out in the southern Alpi Apuane and are preferentially hosted in the “Filladi Inferiori” Fm. Among them, the pyrite ± baryte ± Fe-oxides deposits are the most important ones, representing the volumetrically largest orebodies. The pyrite, baryte, and Fe-oxides ores are an example of metamorphosed orebodies (following the definition reported in e.g., [8,39]) in which the primary mineralogy and texture were modified by the Alpine metamorphism and associated polyphasic deformation (e.g., [40] and references therein). Previous authors debated the origin and age of the ore (e.g., [41] and references therein), and recently, a magmatic-hydrothermal origin, likely Permian age, was suggested [20] on the basis of the following observations:
i. the discovery of tourmaline-bearing Permian felsic shallow-intrusive rocks (Fornovolascocorhyolite Fm) [19,20] spatially associated with the orebodies;

ii. the elemental association of Tl, Hg, As, and Sb in pyrite ores, a typical geochemical feature of low-temperature hydrothermal systems (e.g., [40–42]);

iii. Pb isotope data [41], showing similar values with late Paleozoic-Triassic ores of Sardinia.

However, the effects of hydrothermal activity on the rocks hosting the orebodies are largely unknown, and the occurrence of tourmaline veins have been considered as the only evidence of these hydrothermal processes (e.g., [20,34,41]).

3. Materials and Methods

In total, 61 samples of phyllites and quartzitic phyllites belonging to the “Filladi Inferiori” Fm [18,22] were collected in the Sant’Anna tectonic window (Figure 2). The samples were collected following the method of the channel sampling (e.g., [43]). The channels were 50 cm long and ca. 5 cm wide, and were cut perpendicular to the main foliation, avoiding quartz veins, tourmalinite levels, and sulfide enriched-volumes. The samples were collected using a grid of around 150 m × 150 m covering the whole outcrop of the Paleozoic succession of Sant’Anna tectonic window. Finally, an oriented block sample was collected near all the channels and sixteen thin sections covering the whole petrographic and geochemical variability of the “Filladi Inferiori” Fm were made. For the sake of comparison, all samples, thin sections, and geochemical data of the Fornovolaskocorhyolite Fm, reported in Vezzoni et al. [20], were used. The database of metarhyolite samples was increased by other samples and thin sections and bulk geochemical data. Sample locations and geochemical data are reported in Table S1.

The petrographic features of the rock samples were investigated by optical microscopy. Chemical analyses of “Filladi Inferiori” Fm samples were performed at ACTLABS (Ancaster, Ontario, Canada). Major and trace elements were determined by ICP-OES and ICP-MS, respectively, following lithium metaborate/tetraborate fusion and dissolution with diluted HNO3. Additional samples of the Fornovolaskocorhyolite Fm were analyzed for major and trace elements at the Dipartimento di Scienze della Terra, University of Pisa. Major elements were determined by XRF Philips PW1480 using fused glass discs following the method reported in Tamponi et al. [44]. Trace elements were determined by ICP-MS (VG PQII Plus STE). Samples were dissolved in perfluoralkoxy (PFA) vials at about 120 °C with a HF + HNO3 mixture following the standard lab protocols.

The distribution of Ishikawa Alteration Index (AI, see chapter 3 for further details) has been gridded and contoured throughout the study area using the Natural Neighbor interpolation method [45] available in Surfer software code [46]. We opted for this method because it provides reliable results with data sets that have an inhomogeneous distribution of data. The Natural Neighbor interpolation estimates the grid node value by finding the closest subset of input data points to a grid node and then applying weight to each. The Natural Neighbor method does not extrapolate the Z-grid values beyond the range of data and does not generate nodes in areas without data. In order to take into account the anisotropic distribution of the different lithotypes (controlled by the Alpine deformation as constrained by geological mapping) and the variable density of data, an anisotropy ratio of 1.5 was used coupled with an anisotropy angle of 45° E and 40° W, respectively, in the southeastern and in the northern sector of the study area. This approach provided a contour map of the distribution of the AI that is remarkably consistent with the real distribution of the geological formations (whitish and/or tourmalinized schists, ores, metarhyolites) as also reported in the geological map of Orberger [47].
4. Results

4.1. “Filladi Inferiori” Fm

4.1.1. Field and Petrographic Investigation

The prominent feature of the “Filladi Inferiori” Fm of the Sant’Anna tectonic window is the wide variability in color, texture, and modal mineralogy (Figure 3). Two end-members facies have been recognized: (i) a tourmaline-poor to tourmaline-free facies (FAF; Figure 3a,b) and (ii) a whitish facies with variable abundance of tourmaline (w-FAF; Figure 3c,d). The whitish facies was recognized in other area of the southern sector of the Alpi Apuane (e.g., [19,34]).

![Figure 3](image_url)

**Figure 3.** Polished slabs of “Filladi Inferiori” specimens from Sant’Anna tectonic window. (a) Phyllitic quartzite with alternance of quartz- and white mica+chlorite-rich levels with deformed milky quartz vein. (b) Phyllitic quartzite with intermediate features between least (e.g., a) and most altered (e.g., c,d) samples. See text for further details. (c,d) Whitish quartzitic phyllites with levels and pods of tourmaline and pyrite. AI: Alteration Index of Ishikawa. Mineral abbreviation: Py, pyrite; Qz, quartz; Tur, tourmaline; Wmca, white mica.

We observed a continuous transition between the FAF and w-FAF end-members, at all scale of observation, from field to hand- (Figure 3) and microscale (Figure 4). The FAF facies consists of light-to dark-grey fine-grained quartzite, dark-grey and/or grey-greenish phyllitic quartzite, and phyllite. At the macroscale, this facies is characterized by a pervasive foliation and a very fine-grained texture and, sometimes, it shows alternance of centimeter layers with different colors (e.g., Figure 3a,b). Deformed smoky and milky quartz veins are common (Figure 3a), as are late and vuggy quartz veins (Figure 3b). At the microscale, it consists of an alternation of millimeter-sized granoblastic and lepidoblastic levels. The granoblastic levels are dominated by quartz with minor albite and rare carbonates, while the lepidoblastic levels are mainly formed by fine-grained oriented white mica and a variable amount of “chlorite” and carbonaceous materials (Figure 4a,b). Common accessory minerals are opaque minerals associated with rare sulfides (typically pyrite) and tourmaline supergroup minerals (hereafter tourmaline). Tourmaline shows clastic texture, and their crystal size does not usually exceed 60 μm in length (Figure 4b). Rarely, tourmaline porphyroclasts (up to 3 mm) occur.
Figure 4. Petrographic features of the “Filladi Inferiori” from Sant’Anna tectonic window. (a) Alternance of granoblastic and lepidoblastic levels in a phyllitic quartzite. (b) Albite crystals in a granoblastic level. Note the occurrence of small clastic tourmaline crystals. (c) Tourmaline pod aligned along the main foliation with pyrite crystals. (d) Folded levels with granoblastic and lepidoblastic texture. (e,f) Tourmaline porphyroclasts associated with pyrite in a white mica + quartz matrix. Mineral abbreviation: Ab, albite; Carb, carbonates; Chl, chlorite; Py, pyrite; Qz, quartz; Tur, tourmaline; Wmca, white mica.

The w-FAF facies is represented by quartzitic-phyllites and quartzite with a characteristic whitish color due to the occurrence of abundant quartz and large crystals of white mica, up to 3 mm across. The mica crystals are iso-oriented, developing a penetrative foliation (Figure 3c,d). The w-FAF facies is ubiquitously associated with pyrite and baryte and contains variable amounts of tourmaline-rich veinlets and bodies, from millimeters to decimeters in size. Furthermore, the w-FAF facies is spatially associated with the main orebodies of the Sant’Anna tectonic window as, for instance, those previously exploited at the Pollone and Monte Arsiccio mines. At the microscale, the w-FAF consists of granoblastic levels, mainly formed by quartz, and lepidoblastic layers of white mica associated with variable amounts of “chlorite”, and rare carbonaceous materials. Petrographic investigation reveals the absence of feldspars, while pyrite and baryte are widespread, even if their modal abundance is highly variable. Tourmaline can be found as very small relics (<50 μm), or as zoned
euhedral to anhedral porphyroclasts, up to 5 mm, sometimes forming tourmalinite levels and pods (Figure 4e,f).

4.1.2. Geochemistry

The “Filladi Inferiori” Fm can be classified using chemical methods for (meta-)sedimentary rocks (Figure 5a–c). For the sake of comparison, the geochemical data of “Filladi Inferiori” Fm outside the study area available in literature (from Andreotti [48] and Dini [49]; green cross symbols) were reported.

![Classification diagrams](image)

**Figure 5.** Classification diagrams for metasedimentary (a–c) and magmatic rocks (d–f) with data from “Filladi Inferiori” and Fornovolasco Metarhyolites Fms, respectively. (a) Ternary diagram modified from Turekian [50]. (b,c) Classification diagrams from Herron [51]. (d) Ternary AFM diagram from Irvine and Baragar [52]. (e) TAS diagram from Le Bas et al. [53]. (f) Zr/TiO₂ × 0.0001 vs SiO₂ diagram modified from Winchester and Floyd [54].

The classification diagrams stress the intraunit variability in SiO₂, Al₂O₃, and FeO₉ tot associated with a very low (CaO + MgO) concentration (Figure 5a–c). The samples have a SiO₂ concentration varying from ≈ 55 to 83.5 wt%, whereas the Al₂O₃ concentration ranges between 10.5 and 23.5 wt%. The FeO₉ tot concentration is low and comprises between 1.0 to 8.5 wt%. The Na₂O/K₂O ratio is generally low to very low, with a negative correlation between Na₂O and K₂O concentration range from around 0.2 to 3.3 wt% and 1.9 to 6.5 wt%, respectively. In particular, the w-FAF samples have a Na₂O/K₂O ratio lower than 0.1, a value considered the common lowest limit for sedimentary rocks (see [51,55]). These samples also show the higher Alteration Index (AI) values (Figure 5b). This index
was defined by Ishikawa et al. [56] to quantify the intensity of sericite and chlorite alteration in magmatic rocks that occurs in the footwall rocks proximal to Kuroko hydrothermal deposits (see [57] for further details); it is expressed by the following formula:

\[ AI = \frac{1000 + (K_2O + MgO)}{(K_2O + MgO + Na_2O + CaO)} \]  

(1)

The AI can be used for the geochemical discrimination between FAF and w-FAF facies. Indeed, the former has lower AI values than the latter. For this reason, the use of AI in the plots (e.g., Figures 6 and 7) shows us immediately which facies the sample belongs to.

Figure 6. (a–f) Major elements variability plots of the “Filladi Inferiori” and Fornovolasco Metarhyolites Fms. (a) Alteration box plot (see text for further details), (b) SiO₂ vs AI, (c) L.O.I. (Loss On Ignition) vs SiO₂, (d) MgO vs SiO₂, (e) Na₂O vs Al₂O₃, and (f) K₂O vs Al₂O₃. The composition of the main rock-forming minerals is also reported (see text for further details). The red and blue areas represent the composition of rock-forming minerals exclusively by variable proportion of Ab, Wmca, Chl, and quartz, for “Filladi Inferiori” and Fornovolasco Metarhyolites Fms, respectively. Mineral abbreviation: Ab, albite; An₄₀, plagioclase “Andesine”; Cc, calcite; Chl, chlorite; Qz, quartz; Wmca, white mica. The major elements are expressed in wt%.

Figure 6 shows the major elements and L.O.I. variations integrated by the chemical compositions of the main rock-forming minerals. The wt% of these phases are recalculated from the quartz, albite, “andesine” (An₄₀), and calcite stoichiometric formula, whereas selected chemical electron microprobe (EPM) data measured on white mica and “chlorite” [47,58] from “Filladi Inferiori” samples were used. The plots in Figure 6 indicate that the variability of the major elements is restricted within the albite-muscovite-chlorite-quartz field in agreement with the petrographic investigation. Furthermore, the
alteration box plot, a combination of the AI and the Chlorite-Carbonate-Pyrite Index (CCPI) plotted in the x-axis and y-axis, respectively, is reported (Figure 6a) [57]. The CCPI is based on major elements and was defined as:

\[
CCPI = \frac{100 \times (MgO + FeO)}{(MgO + FeO + Na_2O + K_2O)}
\]  

(2)

where FeO is the total FeO + Fe₂O₃ concentration of the rock. The CCPI was developed for geochemical exploration perspective (e.g., [59–61]), with a focus on Volcanic-Hosted Massive Sulfide (VHMS) deposits. This index is related to the hydrothermal fluid temperature and water/rock ratios. The CCPI varies between around 25 and 60, not showing obvious correlations with the AI.

Finally, the K and Rb concentrations show a positive correlation with the AI (Figure 7a,b); a similar but more scattered correlation occurs also for Ba, Tl (Figure 7c,d) and other metals and metalloids (Cu, Zn, As, Ag, Sb, Pb, Bi; not reported in figure).

![Plots showing correlation trends between Al and K2O, Rb, Ba, and Tl](image)

**Figure 7.** Plots showing correlation trends between (a) K₂O, (b) Rb, (c) Ba, and (d) Tl vs. Al. The major and trace elements are expressed in wt% and ppm, respectively.

4.2. **Fornovolasco Metarhyolite Fm**

4.2.1. **Field and Petrographic Investigation**

Field evidence and petrographic investigation of the Fornovolasco Metarhyolite Fm are described by Vezzoni et al. [20]. In addition to the main rock bodies cropping out close to the Fornovolasco hamlet [19,21], several smaller bodies occur in the Sant’Anna tectonic window (Figure
They are decimeter- to decameter-sized and are usually flattened on the main field foliation. The primary magmatic features are variably preserved. The Fornovolasco Metarhyolite bodies are preferentially hosted in the w-FAF, spatially associated with pyrite-baryte ore, tourmaline-rich veins, and tourmalinite. However, they were also found embedded in the FAF facies. Similar field relationships were observed in all the southern Alpi Apuane [20].

Usually, the metarhyolite bodies hosted in the FAF facies show well-preserved primary features characterized by granular to porphyritic texture with tourmaline-quartz orbicules, up to 4 cm, surrounded by a leucocratic halo. The primary mineralogical features are partially preserved, as shown by phenocrysts of quartz (sometimes showing magmatic embayments), feldspars (usually completely sericitized), “biotite” (locally replaced by “chlorite”), white mica, and tourmaline minerals (see [20] for further details). In contrast, the rock bodies embedded within the w-FAF facies are usually more altered and strongly deformed. In addition, they can be more commonly associated with baryte + pyrite orebodies, as well as tourmalinite layers. At the mesoscale, these samples can be identified due to the occurrence of dark-blue to black tourmaline-rich spots in a whitish foliated matrix. The tourmaline-rich spots are a textural feature distinguishing them from all the other rocks occurring in the Sant’Anna tectonic window. In thin section, the primary magmatic texture (e.g., porphyritic texture; Figure 8a,b) is largely lost, and only the spots are partially preserved with euhedral quartz in dendritic-to-radiated-aggregates of tourmaline crystals. The tourmaline crystals are strongly fractured, and the tourmaline-rich spots are wrapped by foliation (Figure 8c,d). The matrix consists essentially of granoblastic quartz and lepidoblastic white mica with large grain-size, i.e., commonly up to 3 mm, associated with a minor “chlorite”. The altered rock hosts dispersed pyrite and baryte as accessory phases and trace amounts of other sulfides and sulfosalts.

Figure 8. Petrographic features of the Fornovolasco Metarhyolite. (a) Porphyritic texture, showing phenocrysts of quartz, altered feldspars (sericite), biotite (partially altered in chlorite), and tourmaline. (b) Quartz and feldspar phenocrysts in a recrystallized white mica + quartz matrix. (c,d) Tourmaline + quartz porphyroclasts wrapped by the Alpine schistosity highlighted by white mica crystal orientation. Mineral abbreviation: Ab, albite; alt-Fld, altered feldspar phenocrystal; Bt, biotite; Chl, chlorite; Qz, quartz; Tur, tourmaline; Wmca, white mica.

4.2.2. Geochemistry

The classification of the Fornovolasco Metarhyolite Fm has been recently discussed [20], whereas in this paper, the geochemical variability of this rock is investigated. The classification diagrams (Figure 5d–f) show the variability of the concentration of major elements while the considered immobile elements in the Zr/TiO₂ × 0.0001 vs SiO₂ are substantially constant. This variability is mainly
related to the alkali content, that is correlated with the alteration of the sample. The less altered samples (those having lower AI values) have an alkali content of around 6 wt%, a value typically found in calc-alkaline rhyolites. In contrast, the altered samples (those having higher AI values) show a lower alkali content (around 4 wt%). It is worth noting that the alteration is related to lower Na₂O and higher K₂O concentrations. Thus, the AI can be used for the geochemical discrimination of least and most altered samples, like in the “Filladi Inferiori” Fm.

The major elements and CCPI show similar trends to those observed for the “Filladi Inferiori” Fm (Figure 6), although some components have a lower variability (e.g., SiO₂, MgO, L.O.I.). As previously described for the “Filladi Inferiori” Fm, the observed major elements variability falls within the albite-muscovite-chlorite-quartz field, in agreement with the petrographic investigation (for white mica and chlorite EPM data see [20]).

Potassium and Rb concentrations show a clear positive correlation with the AI (Figure 7a,b) while Ti and Ba show a more complex trend, although the higher values are related to the most altered samples (Figure 7c,d).

5. Discussion

5.1. Pre-Alpine Hydrothermal Alteration Recorded by Alpi Apuane Paleozoic Rocks

As reported above, several ore deposits occur in the Sant’Anna tectonic window. Usually, the genesis of hydrothermal ore deposits may be associated with a pervasive alteration of the country rocks (e.g., [62–65]). However, only the occurrence of a widespread tourmalinization is currently recognized as evidence of a hydrothermal process related to ore genesis (e.g., [41,66]). No other hydrothermally-altered rocks, typically associated with orefields, have been reported so far.

However, the data reported in this work clearly indicate the occurrence of different facies in the Paleozoic rocks characterized by several degrees of hydrothermal alteration. This is particularly evident for the Permian meta-rhyolite belonging to the Fornovolasco Metarhyolite Fm, which may play a central role in the identification of the hydrothermal alteration affecting these rocks. The main factors which make it possible to use metarhyolite to assess the occurrence of hydrothermal processes recorded in the Alpi Apuane are:

i. Permian metarhyolite experienced only the Alpine metamorphic event;
ii. the geochemistry of a calc-alkaline rhyolitic rock is less variable than that of a sedimentary protolith like the “Filladi Inferiori” Fm (Figure 5);
iii. several diagrams for the investigation of hydrothermal alteration were developed for igneous rocks (e.g., [63]).

The two different facies recognized within the Fornovolasco Metarhyolite Fm may be related to different alteration degrees. Indeed, one facies is characterized by a relatively well-preserved magmatic texture and mineralogy and display low AI values, associated with high Na₂O/K₂O ratios, typical of calc-alkaline rhyolite. The other facies is typically strongly deformed and foliated, and few remnants of the pristine magmatic textures and mineralogical features are preserved. These rocks display the highest AI values, with a K₂O enrichment and a strong depletion in Na₂O.

Both rock facies can be classified as (meta-)rhyolite/rhyodacite-dacite on the basis of the immobile elements (Figure 5), whereas, taking into account the mobile elements (i.e., the alkali content), they show a strong data dispersion (TAS and AFM diagrams; Figure 5). However, the very low Na₂O concentration is not compatible with an “unaltered” rhyolite (e.g., [67] and reference therein), supporting the occurrence of post-crystallization hydrothermal alteration.

Since this process does not affect the facies having low AI values, and both facies suffered the Alpine metamorphism, we hypothesize that the Alpine metamorphism has not significantly affected the geochemistry of the protoliths. This could be in agreement with previous works suggesting a limited fluid-rock interaction during synmetamorphic processes in the Alpi Apuane metamorphic complex (e.g., [68–71]). This assumption was valid for the metasedimentary Triassic-Miocene cover, whereas Cortecchi et al. [69] suggested extensive fluid flow in the basement units. However, these
latter authors recognized the possibility that this extensive fluid flow could pre-date the Apennine orogeny. Indeed, other data supported the existence of only small vein systems of Alpine age that represented localized drainage systems in the basement rocks (e.g., [72]). The metamorphism of the Alpi Apuane was therefore substantially isochemical, and thus, the chemistry of the pre-Alpine history may be preserved.

To support this interpretation, we report a litho-geochemical approach based on major element variability—the alteration box plot (Figure 9). This diagram was developed to discriminate among geochemical trends due to diagenetic and/or hydrothermal alteration [57].

![Figure 9. Alteration box plot for metasedimentary (“Filladi Inferiori” Fm) and metaigneous (Fornovolasco Metarhyolites Fm) samples. The red arrow represents the typical effect of sericite alteration. Fields for diagenetic (lower left) and hydrothermal (upper right) alteration are also reported (see [57] for further details).](image)

The first end-member plot in the less altered rhyolitic field of the alteration box plot, while the other one falls toward the right side of the plot, in agreement with the common hydrothermal processes that shift the bulk composition toward this side [57]. A petrographic investigation suggests that the geochemical shift is related to the disappearance of albite and the modal increase of white mica, explaining the decrease and increase of Na₂O and K₂O concentrations, respectively. The role of “chlorite” and pyrite is less evident, as shown by the slight increase in the CCPI (the most sensible index for the increase of these phases), while quartz is weakly enriched, as observed in the TAS diagram (Figure 5).

The metarhyolite bodies are hosted within the “Filladi Inferiori” Fm. It is therefore reasonable to look for hydrothermal alteration also in this formation. Indeed, the tourmalinization and the presence of pyrite disseminations and pods support this hypothesis. In addition, two different facies, interpreted as the results of the different alteration degrees, have been observed. The FAF facies is the least hydrothermally altered, and occurs in a distal position with respect to the main orebodies and metarhyolite bodies outcropping in the Sant’Anna tectonic window. The features are similar to those described in other outcrops of the Alpi Apuane [16,32,33], where these rocks are characterized by the occurrence of albite and the absence of significant amounts of pyrite and tourmaline pods and veins (Figure 3a,b). The samples from the FAF facies have low Al (50–65), associated with a variable CCPI (25–60). A transition between this facies and the w-FAF was observed. The latter is characterized by the presence of tourmaline-rich veins and pods associated with a dispersed baryte + pyrite mineralization. The w-FAF is spatially associated with the orebodies and is characterized by the highest Al values (>85) and variable CCPI (30–60). The CCPI variability could be a relic of the primary inhomogeneity of the sedimentary protolith as supported by:

i. field and petrographic data (e.g., alternance of centimeter-thick layers with different colors, variable modal “chlorite” content in the less altered samples; Figures 3a–c and 4a–d);
ii. similar variability of the CCPI value for both FAF and w-FAF facies (Figure 9).

In summary, the hydrothermal processes yielded similar mineralogical and geochemical features both on the Fornovolasco Metarhyolite and on the “Filladi Inferiori” Fms. This similarity is probably derived from the simple and similar main mineralogy of the two rocks. Both formations were affected by two main hydrothermal processes, corresponding to (i) tourmalinization, and (ii) sericitization. The former is easily recognizable in the field due to the occurrence of millimeter- to decimeter-sized tourmalinite bodies. These particular hydrothermal rocks are usually associated with the whitish color of the host rocks, making it possible to distinguish among the most altered samples (i.e., w-FAF facies). The whitish color is indeed one of the main field features of the w-FAF, resulting from the modal increase of white mica and quartz. The mineral proportion explains the significant increase of the Al with no or moderate increase in the CCPI (Figure 9) and the largely constant Al:O concentration during the alteration (Figure 6f). Finally, the slight increase of Si:O is more evident for the Fornovolasco Metarhyolite samples (Figures 5 and 6; e.g., TAS diagram). These features are typical of sericite alteration (e.g., [57]). The relative timing of tourmalinization and sericitization is not clear. In similar ore deposits, tourmalinization postdated sericitization in a “short” time interval (e.g., [73]). However, further studies are needed to clarify this issue in the Alpi Apuane.

5.2. Constraint on the Permian Age of Hydrothermal Alteration

The hydrothermal alteration recognized in the Paleozoic rocks occurs only in the pre-Triassic “Filladi inferiori” and Fornovolasco Metarhyolite Fm.

There are further constraints on the actual dating of this hydrothermal process. Indeed, tourmalinization and sericitization affecting the Fornovolasco Metarhyolite, dated at ca. 270 Ma [20], give a lower limit for the hydrothermal event. The higher limit is given by the occurrence of tourmalinite clasts in the upper Carnian-lower Norian metasedimentary rocks of the Alpi Apuane (e.g., [19,74]), as well as the occurrence of Ba-rich mineralized clasts in the Late Triassic–Lower Jurassic formation [75]. This suggests that hydrothermally-altered rocks were partially exposed and eroded at least during the Middle–Late Triassic. Taking also into account that no evidence of hydrothermal alteration is recorded in the Upper Triassic–lower Miocene rocks, the hydrothermal event should be likely constrained between the emplacement of the metarhyolite bodies and the pre-Carnian metasiliciclastic rocks. However, we hypothesize that the hydrothermal alteration developed in a short-time interval with respect to the emplacement age of Fornovolasco Metarhyolite bodies, based on:

i. the type of hydrothermal alteration (i.e., tourmalinization) typically associated to shallow intrusion tourmaline-bearing felsic magmatism (e.g., [76,77]);
ii. the clear spatial distribution of hydrothermally altered “Filladi Inferiori” and Fornovolasco Metarhyolite bodies (Figure 10);
iii. comparison with other post-Variscan Permian ore deposits and magmatism in Europe with similar features (e.g., [78–81]);
iv. the description of several magmatic-hydrothermal systems in which the hydrothermal alteration follows, in a short-time interval, the emplacement of magmatic rocks (e.g., [82–84]).

Consequently, a Permian hydrothermal event may be recorded in the Alpi Apuane Paleozoic rocks. This seems to have close relationships both with the post-Variscan magmatic cycle and the ore genesis.

5.3. Hydrothermal Alteration and Ore Genesis

Among the different genetic models proposed for the ore deposits from the Alpi Apuane, recent data seem to support a hydrothermal origin, as suggested, for instance, by the association of Tl-Hg-As-Sb, typical of low-temperature hydrothermal systems [41]. The identification of hydrothermally-altered rocks in the mineralized areas of the Sant’Anna tectonic window allows us to refine this scenario. In fact, although a detailed geological mapping of the entire study area is still lacking, the
AI contour map (Figure 10) shows with a good approximation the real distribution of the w-FAF (higher AI values and widespread tourmalinization) within the Sant’Anna tectonic window, showing their close spatial relationship with both metarhyolite (in red) and the main ore bodies (in black, generally formed by baryte + pyrite with minor amount of Pb-Zn-Ag sulfides).

![Figure 10](image_url)

Figure 10. Sant’Anna tectonic window AI distribution map (see text for further details) based on geochemical data from “Filladi Inferiori” Fm. The main ores and Fornovolasco Metarhyolites bodies are also reported.

The w-FAF is the host rocks of the ore bodies, as previously reported by other authors (e.g., [34,47,72]). Our study has pointed out an increase in the alteration degree toward the ores. Figure 10 visualizes such a variation of the AI index around the ore bodies. The close spatial relationships between rock alteration and ore bodies suggest a genetic link between these two geological features. Indeed, the occurrence of alteration halos around the orebodies is a typical feature reported in hydrothermal ore-forming systems worldwide (e.g., [62–65]); it is characterized by a decrease in the alteration moving away from mineralization, as observed in the Sant’Anna tectonic window. These geological data allow us to hypothesize that the ore deposits could be genetically linked to a Permian hydrothermal event, very likely associated to the emplacement, in the shallow crust, of felsic magmatic bodies.

This interpretation is also supported by the correlation between the AI values and the Ba and TI concentrations in the samples (these two elements being the most characteristic elements of the Alpi
Apuane ores; [40,41]; Figure 7), as well as with other metals and metalloids (Cu, Zn, As, Ag, Sb, Pb, Bi) typically occurring in these mineralizations.

6. Conclusions

The pre-Alpine formations cropping out in the Sant’Anna tectonic window (Alpi Apuane, Italy) recorded the occurrence of a hydrothermal alteration event predating the Alpine metamorphism. This event locally produced tourmalinization and sericitization, affecting both the Cambrian-Early Ordovician phyllitic rocks (FAF), giving rise to whitish schists (indicated as w-FAF), and the felsic magmatites of Permian age. In contrast, the Triassic to Miocene metasedimentary cover was not involved in such an alteration process.

The age of the hydrothermal event is bounded between the age of the younger magmatic rocks (around 270 Ma) and the occurrence of tourmalinite clasts in the upper Carnian-lower Norian metasedimentary rocks of the Alpi Apuane. On the basis of field evidence, a Permian age is suggested, being related to the Permian magmatic cycle, in analogy with similar geological contexts.

The spatial distribution and geochemical features of hydrothermally altered rocks point to a genetic link with the ore bodies occurring in the Sant’Anna tectonic window, whose Permian age is thus hypothesized. This conclusion is possible owing to the near isochemical nature of the Alpine metamorphism in the Alpi Apuane, in agreement with previous authors (e.g., [68–71]), that preserved the original geochemical variability of the Paleozoic rocks.

At a larger scale, the present study reveals that the Alpi Apuane have recorded an hydrothermal post-Variscan event with similar features to those recognized in many ore districts in Europe (e.g., [77–81,85]). Further studies are needed to specify this scenario.

Finally, it is worth noting that the Ishikawa Alteration Index, originally developed for magmatic rocks, proved to be a useful geochemical tool for unravelling hydrothermal alteration, also in polymetamorphic basement rocks with sedimentary protoliths, resulting in a potential guide for the localization of hidden ore deposits.

Supplementary Materials: The following are available online at www.mdpi.com/2076-3263/10/10/399/s1, Table S1: major and trace element analyses of Filladi Inferiori and Fornovolasco Metarhyolite Fms.

Author Contributions: A.D. and S.V. conceived and designed the experiment; Y.G., D.P. and S.V. collected samples and field geological data on the Paleozoic rocks and prepared samples for geochemical analysis; S.V. performed ICP-MS analysis at the Dipartimento di Scienze della Terra—Università di Pisa; A.D. and D.P. realized the geostatistical interpolation of chemical data; S.V. wrote the original manuscript, with contributions by C.B., A.D. and D.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received support by MIUR (Ministero dell’Istruzione, dell’Università e della Ricerca) through the project SIR 2014 “THALMIGEN—Thallium: Mineralogy, Geochemistry, and Environmental Hazards”, granted to Cristian Biagioni (Grant No. RBSI14A1CV) and PRIN 2017 “TEOREM—deciphering geological processes using Terrestrial and Extraterrestrial ORE Minerals”, granted to Cristian Biagioni and Andrea Dini (prot. 2017AK8C32).

Acknowledgments: We wish to thank Giancarlo Molli for the fruitful discussions about the geology of the southern Alpi Apuane, Massimo D’Orazio and Rolando Matteoni for the ICP-MS analysis at the Dipartimento di Scienze della Terra - Università di Pisa. The constructive criticism of two anonymous reviewers helped us improving the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Von Raumer, J.F.; Bussy, F.; Schaltegger, U.; Schulz, B.; Stampflı, G.M. Pre-Mesozoic Alpine basements—Their place in the European Paleozoic framework. Geol. Soc. Am. Bull. 2013, 125, 89–108, doi:10.1130/b30654.1.

2. Cavargna-Sani, M.; Epard, J.L.; Bussy, F.; Ulianov, A. Basement lithostratigraphy of the Adula nappe: Implications for Palaeozoic evolution and Alpine kinematics. Int. J. Earth Sci. 2014, 103, 61–82, doi:10.1007/s00531-013-0941-1.
3. Pawling, S.; Baumgartner, L.P. Geochemistry of a talc-kyanite-chloritoid shear zone within the Monte Rosa granite, Val d’Ayas, Italy. Schweize. Mineral Petrog. Mitt. 2001, 81, 329–346, doi:10.5169/seals-61696.

4. Franz, L.; Romer, R.L.; De Capitani, C. Protoliths and phase petrology of whiteschists. Contrib. Miner. Pet. 2013, 166, 255–274, doi:10.1007/s00410-013-0874-5.

5. Funedda, A.; Naitza, S.; Buttai, C.; Cocco, F.; Dini, A. Structural Controls of Ore Mineralization in a Polydeformed Basement: Field Examples from the Variscan Baccu Locci Shear Zone (SE Sardinia, Italy). Minerals 2018, 8, 456, doi:10.3390/min8100456.

6. Kruger, F.; Geringer, G.; Havenga, A. The geology, petrology, geochronology and source region character of the layered gabbronitonic Oranjerivier Complex in the Kibaran Namaqua mobile belt, South Africa. J. Afr. Earth Sci. 2000, 30, 675–687, doi:10.1016/s0899-5362(00)00045-2.

7. Vernon, R.H. A Practical Guide to Rock Microstructure; Cambridge University Press: Cambridge, UK, 2004; p. 422.

8. Stanton, R.L.; Stanton, R.L. On limits to distances of movement of matter during regional metamorphism: An investigation of nine samples from high-grade metamorphic terranes. Can. Mineral. 2006, 44, 985–1024, doi:10.2113/gscanmin.44.5.985.

9. Bailie, R.; Gutzmer, J.; Rajesh, H. Lithogeochemistry as a tracer of the tectonic setting, lateral integrity and mineralization of a highly metamorphosed Mesoproterozoic volcanic arc sequence on the eastern margin of the Namaqua Province, South Africa. Lithos 2010, 119, 345–362, doi:10.1016/j.lithos.2010.07.012.

10. Marroni, M.; Meneghini, F.; Pandolfi, L. A Revised Subduction Inception Model to Explain the Late Cretaceous, Double-Vergent Orogen in the Precollisional Western Tethys: Evidence From the Northern Apennines. Tectonics 2017, 36, 2227–2249, doi:10.1002/2017tc004627.

11. Carmignani, L.; Kligefield, R. Crustal extension in the northern Apennines: The transition from compression to extension in the Alpi Apuane Core Complex. Tectonics 1990, 9, 1275–1303, doi:10.1029/tc09i006p01275.

12. Carmignani, L.; Decandia, F.A.; Disperati, L.; Fantozzi, P.L.; Kligefield, R.; Lazzarotto, A.; Liotta, D.; Mecheri, M. Inner Northern Apennines. In Anatomy of an Orogen: The Apennines and Adjacent Mediterranean Basins; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2001; pp. 197–213.

13. Molli, G. Northern Apennine–Corsica orogenic system: An updated overview. Geol. Soc. Lond. Spec. Publ. 2008, 298, 413–442, doi:10.1144/sp298.19.

14. Lattanzi, P.; Benvenuti, M.; Costagliola, P.; Tanelli, G. An overview on recent research on the metallogeny of Tuscany, with special reference to the Apuan Alps. Mem. Soc. Geol. Ital. 1994, 48, 613–625.

15. Ciaparica, G.; Passeri, L. The palaeogeographic duplicity of the Apennines. Boll. Soc. Geol. Ital. 2002, 1, 67–75.

16. Conti, P.; Carmignani, L.; Massa, G.; Mecheri, M.; Patacca, E.; Scandone, P.; Pieruccioni, D. Note Illustrative della Carta Geologica d’Italia alla Scala 1:50.000, Foglio 249 Massa—Carrara; ISPRA: Roma, Italy, 2019; p. 290.

17. Ciaparica, G.; Passeri, L. Panoramica sulla geologia delle Alpi Apuane alla luce delle più recenti ricerche. Mem. Soc. Geol. Ital. 1982, 24, 193–208.

18. Conti, P.; Di Pisa, A.; Gattiglio, M.; Mecheri, M. The Pre-Alpine Basement in the Alpi Apuane (Northern Apennines, Italy). In Pre-Mesozoic Geology in the Alps; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 1993; pp. 609–621.

19. Pieruccioni, D.; Galanti, Y.; Biagiioni, C.; Molli, G. Geology and tectonic setting of the Fornovolasco area, Alpi Apuane (Tuscany, Italy). J. Maps 2018, 14, 357–367, doi:10.1080/17445647.2018.1476985.

20. Vezzoni, S.; Biagioni, C.; D’Orazio, M.; Pieruccioni, D.; Galanti, Y.; Petrelli, M.; Molli, G. Evidence of Permian magmatism in the Alpi Apuane metamorphic complex (Northern Apennines, Italy): New hints for the geological evolution of the basement of the Adria plate. Lithos 2018, 104–123, doi:10.1016/j.lithos.2018.08.003.

21. Pieruccioni, D.; Galanti, Y.; Biagiioni, C.; D’Orazio, M.; Molli, G.; Vezzoni, S. Fornovolasco (Alpi Apuane, Tuscany, Italy): Type locality for the Permian felsic magmatism in the Northern Apennines. Int. J. Earth Sci. Geosites 2020, 109, 2133–2134, doi:10.1007/s00531-020-01887-9.

22. Conti, P.; Massa, G.; Mecheri, M.; Carmignani, L. Geological map of the Stazzema area (Alpi Apuane, Northern Apennines, Italy); Litografia Artistica Cartografica: Firenze, Italy, 2010.

23. Molli, G.; Vaselli, L. Structures, interference patterns, and strain regime during midcrustal deformation in the Alpi Apuane (Northern Apennines, Italy). Geol. Soc. Am. Bull. 2006, 414, 79–93, doi:10.1130/2006.2414(05).
24. Ottria, G.; Molli, G. Superimposed brittle structures in the late-orogenic extension of the Northern Apennine: Results from the Carrara area (Alpi Apuane, NW Tuscany). *Terra Nova* **2000**, *12*, 52–59, doi:10.1111/j.1365-3121.2000.00272.x.

25. Molli, G.; Corteci, G.; Vaselli, L.; Ottria, G.; Cortopassi, A.; Dinelli, E.; Mussi, M.; Barbieri, M. Fault zone structure and fluid–rock interaction of a high angle normal fault in Carrara marble (NW Tuscany, Italy). *J. Struct. Geol.* **2009**, *32*, 1334–1348, doi:10.1016/j.jsg.2009.04.021.

26. Molli, G.; Carlini, M.; Vescovi, P.; Artoni, A.; Balsamo, F.; Camurri, F.; Clemenzzi, L.; Storti, F.; Torelli, L. Neogene 3-D Structural Architecture of the North-West Apennines: The Role of the Low-Angle Normal Faults and Basement Thrusts. *Tectonics* **2018**, *37*, 2165–2196, doi:10.1029/2018tc005057.

27. Molli, G.; Brovarone, A.V.; Beyssac, O.; Cinquini, L. RSCM thermometry in the Alpi Apuane (NW Tuscany, Italy): New constraints for the metamorphic and tectonic history of the inner northern Apennines. *J. Struct. Geol.* **2018**, *113*, 200–216, doi:10.1016/j.jsg.2018.05.020.

28. Klugfield, R.; Hunziker, J.; Dallmeyer, R.; Schamel, S. Dating of deformation phases using K-Ar and 40Ar/39Ar techniques: Results from the northern apennines. *J. Struct. Geol.* **1986**, *8*, 781–798, doi:10.1016/0191-9617(86)90025-8.

29. Fellin, M.G.; Reiners, P.W.; Brandon, M.T.; Wüthrich, E.; Balestrieri, M.L.; Molli, G. Thermochronologic evidence for the exhumation history of the Alpian Apuan metamorphic core complex, northern Apennines, Italy. *Tectonics* **2007**, *26*, doi:10.1029/2006tc002085.

30. Carmignani, L.; Dessau, G.; Duchì, G. Una mineralizzazione sin-tettonica: Il giacimento di Valdicastello (Alpi Apuane). Rapporti tra tettonica e minerogenesi in Toscana. *Boll. Soc. Geol. Ital.* **1975**, *94*, 725–758.

31. Carmignani, L.; Dessau, G.; Duchì, G. I giacimenti a barite, pirite e ossidi di ferro delle Alpi Apuane. Studio minerogenetico e strutturale. Nuove osservazioni sui giacimenti polimetallici. *Boll. Soc. Geol. Ital.* **1976**, *95*, 1009–1061.

32. Barberi, F.; Giglia, G. La serie scistosa basale dell’Autoctono delle Alpi Apuane. *Boll. Soc. Geol. Ital.* **1965**, *84*, 41–92.

33. Tucci, P. Le metamorfiti della “Serie scistosa basale” del Monte Corchia (Alpi Apuane). *Period. di Mineral.* **1980**, *49*, 57–148.

34. Pandeli, E.; Bagnoli, P.; Negri, M. Fornovolasco schists of the Apuan Alps (Northern Tuscany, Italy): A new hypothesis for their stratigraphic setting. *Boll. Soc. Geol. It.* **2004**, *123*, 53–66.

35. Gattiglio, M.; Mecccheri, M.; Tongiorgi, M. Stratigraphic correlation forms of the Tuscan Paleozoic basement. *Rend. Soc. Geol. Ital.* **1989**, *12*, 435–446.

36. Paoli, G.; Stokke, H.H.; Rocchi, S.; Sirevaag, H.; Ksienzyk, A.K.; Jacobs, J.; Köslér, J. Basement provenance revealed by U–Pb detrital zircon ages: A tale of African and European heritage in Tuscany, Italy. *Lithos* **2017**, *277*, 376–387, doi:10.1016/j.lithos.2016.11.017.

37. Pieruccioni, D.; Vezzoni, S.; Petrelli, M. A petrographic and U-Pb geochronological approach to the reconstruction of the pre-alpine history of Alpi Apuane (Tuscany). *Atti Soc. Tosca. Sci. Nat. Mem. Ser. A* **2018**, *125*, 69–80, doi:10.2424/ASTSN.M.2018.24.

38. Carmignani, L.; Dessau, G.; Duchì, G. I giacimenti minerari delle Alpi Apuane e loro correlazioni con l’evoluzione del gruppo montuoso. *Mem. Soc. Geol. Ital.* **1972**, *11*, 417–431.

39. Marshall, B.; Vokes, F.M.; Larocque, A.C.L. Regional metamorphic remobilization: Upgrading and formation of ore deposits. *Rev. Econ. Geol.* **2000**, *11*, 19–38.

40. Biagioni, C.; D’Orazio, M.; Vezzoni, S.; Dini, A.; Orlandi, P. Mobilization of Tl-Hg-As-Sb-(Ag, Cu)-Pb sulfosalt melts during low-grade metamorphism in the Alpi Apuane (Tuscany, Italy). *Geology* **2013**, *41*, 747–750, doi:10.1130/g34211.1.

41. D’Orazio, M.; Biagioni, C.; Dini, A.; Vezzoni, S. Thallium-rich pyrite ores from the Apuan Alps, Tuscany, Italy: Constraints for their origin and environmental concerns. *Miner. Deposita* **2017**, *52*, 687–707, doi:10.1007/s00126-016-0697-1.

42. George, L.L.; Biagioni, C.; D’Orazio, M.; Cook, N.J. Textural and trace element evolution of pyrite during greenschist facies metamorphic recrystallization in the southern Apuan Alps (Tuscany, Italy): Influence on the formation of Tl-rich sulfosalt melt. *Ore Geol. Rev.* **2018**, *102*, 59–105, doi:10.1016/j.oregeorev.2018.08.032.

43. Dominy, S.C.; Glass, H.J.; O’Connor, L.; Lam, C.; Pureverger, S.; Minnitt, R. Integrating the Theory of Sampling into Underground Mine Grade Control Strategies. *Minerals* **2018**, *8*, 232, doi:10.3390/min8060232.

44. Tamponi, M.; Bertoli, M.; Innocenti, F.; Leoni, L. X-Ray fluorescence analysis of major elements in silicate rocks using fused glass discs. *Atti Soc. Tosca. Sci. Nat. Mem. Ser. A* **2003**, *108*, 73–79.
45. Sibson, R. A brief description of natural neighbor interpolation. In *Interpreting Multivariate Data*; Barnett, V., Ed.; John Wiley: Hoboken, NJ, USA; Chichester, UK, 1981; pp. 21–36.
46. Golden Software. *Surfer 12, Full User's Guide*; Golden Software Inc.: Golden, CO, USA, 2014; p. 1056.
47. Orberger, B. Les Gisements de Barytine-Pyrite-Oxydes des fer de la Région de Santa Anna (Alpes Apuanales, Toscane, Italie). PhD Thesis, Institute National Polytechnique de Lorraine, Vandeuve-lès-Nancy, França, 11 February 1985.
48. Andreotti, P. Composizione Chimica Delle Formazioni del Basamento Toscano: Implicazioni Stratigrafiche e Minerogenetiche. Master's Thesis, Università degli Studi di Firenze, Florence, Italy, July 1990.
49. Dini, A. Contributo Alla Minerogenesi dei Giacimenti Mercuriferi Apuani. Master’s Thesis, Università di Pisa, Italy, 1992.
50. Turekian, K.K. The Oceans, Streams, and Atmosphere. In *Handbook of Geochemistry*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 1969; Volume 1, pp. 297–323.
51. Herron, M.M. Geochemical Classification of Terrigenous Sands and Shales from Core or Log Data. *J. Sediment. Res.* **1988**, *58*, 820–829, doi:10.1036/212F8E77-2B24-11D7-864800102C1865D.
52. Irvine, T.N.; Baragar, W.R.A. A Guide to the Chemical Classification of the Common Volcanic Rocks. *Can. J. Earth Sci.* **1971**, *8*, 523–548, doi:10.1139/e71-055.
53. Le Bas, M.J.L.; Maitre, R.W.L.; Streckeisen, A.; Zanettin, B.; Rocks, I.S.O.T.S.O.I. A Chemical Classification of Volcanic Rocks Based on the Total Alkali-Silica Diagram. *J. Petrol.* **1986**, *27*, 745–750, doi:10.1093/petology/27.3.745.
54. Winchester, J.; Floyd, P. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chem. Geol.* **1977**, *20*, 325–343, doi:10.1016/0009-2541(77)90057-2.
55. Pettijohn, F.J.; Potter, P.E.; Siever, R. *Sand and Sandstone*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 1987; p. 553.
56. Ishikawa, Y.; Sawaguchi, T.; Iwaya, S.; Horiuchi, M. Delineation of prospecting targets for Kuroko deposits based on modes of volcanism of underlying dacite and alteration halos. *Mining Geol.* **1976**, *26*, 105–117, doi:10.11456/shigenchisshitsu1951.26.105.
57. Large, R.; Gemmell, J.B.; Paulick, H.; Huston, D.L. The Alteration Box Plot: A Simple Approach to Understanding the Relationship between Alteration Mineralogy and Lithogeochemistry Associated with Volcanic-Hosted Massive Sulphide Deposits. *Econ. Geol.* **2001**, *96*, 957–971, doi:10.2113/gsecongeo.96.5.957.
58. Costagliola, P.; Benvenuti, M.; Lattanzi, P.; Tanelli, G. Metamorphogenic barite-pyrite (Pb–Zn–Ag) veins at pollone, Apuane Alps, Tuscany: Vein geometry, geothermobarometry, fluid inclusions and geochemistry. *Miner. Pet.* **1998**, *62*, 29–60, doi:10.1007/bf01173761.
59. Morton, R.L.; Franklin, J.M. Two-fold classification of Archean volcanic-associated massive sulphide deposits. *Econ. Geol.* **1987**, *82*, 1057–1063, doi:10.2113/gsecongeo.82.4.1057.
60. Lydon, J.W. Volcanogenic massive sulphide deposits, Part 2: Genetic models. *Geosci. Can.* **1988**, *15*, 43–65.
61. Schardt, C.; Cooke, D.R.; Gemmell, J.B.; Large, R. Geochemical Modeling of the Zoned Footwall Alteration Pipe, Hellyer Volcanic-Hosted Massive Sulfide Deposit, Western Tasmania, Australia. *Econ. Geol.* **2001**, *96*, 1037–1054, doi:10.2113/gsecongeo.96.5.1037.
62. Large, R.; McGoldrick, P.J. Lithogeochemical halos and geochemical vectors to stratiform sediment hosted Zn–Pb–Ag deposits, 1. Lady Loretta Deposit, Queensland. *J. Geochem. Explor.* **1998**, *63*, 37–56, doi:10.1016/s0375-6742(98)00113-2.
63. Large, R.; Allen, R.L.; Blake, M.D.; Herrmann, W. Hydrothermal Alteration and Volatile Element Halos for the Rosebery K Lens Volcanic-Hosted Massive Sulphide Deposit, Western Tasmania. *Econ. Geol.* **2001**, *96*, 1055–1072, doi:10.2113/gsecongeo.96.5.1055.
64. Leach, D.L.; Sangster, D.F.; Kelley, K.D.; Large, R.R.; Garven, G.; Allen, C.R.; Gutzmer, J.; Walters, S. Sediment-Hosted Lead-Zinc Deposits: A Global Perspective. In *One Hundredth Anniversary Volume*; Society of Economic Geologists: Lancaster, PA, USA, 2005; pp. 561–607.
65. Cooke, D.R.; Baker, M.; Hollings, P.; Sweet, G.; Chang, Z.; Danyushevsky, L.; Gilbert, S.; Zhou, T.; White, N.C.; Gemmell, J.B.; et al. New Advances in Detecting the Distal Geochemical Footprints of Porphyry Systems—Epidote Mineral Chemistry as a Tool for Vectoring and Fertility Assessments. In *Building Exploration Capability for the 21st Century*; Society of Economic Geologists: Littleton, CO, USA, 2014; pp. 127–152.
66. Benvenuti, M.; Lattanzi, P.; Tanelli, G. Tourmalinite-associated Pb-Zn-Ag mineralization at Bottino, Apuane Alps, Italy: geologic setting, mineral textures, and sulfide chemistry. Econ. Geol. 1989, 84, 1277–1292, doi:10.2113/econgeo.84.5.1277.

67. Sheth, H.C.; Torres-Alvarado, I.S.; Verma, S.P. What Is the “Calc-alkaline Rock Series”? Int. Geol. Rev. 2002, 44, 686–701, doi:10.2747/0020-6814.44.8.686.

68. Cortecchi, G.; Orlandi, P. Oxygen- and carbon-isotopic composition of gypsum-calcite-dolomite crystals and metamorphic marble assemblages. Chem. Geol. 1975, 15, 309–314, doi:10.1016/0009-2541(75)90041-8.

69. Cortecchi, G.; Leone, G.; Pochini, A. Stable isotope composition and geothermometry of metamorphic rocks from the Apuane Alps, Northern Tuscany, Italy. Miner. Petrogr. Acta 1994, 37, 51–62.

70. Montomoli, C.; Ruggieri, G.; Carosi, R.; Dini, A.; Genovesi, M. Fluid source and pressure–temperature conditions of high-salinity fluids in syn-tectonic veins from the Northeastern Apuan Alps (Northern Apennines, Italy). Phys. Chem. Earth 2005, 30, 1005–1019, doi:10.1016/j.pce.2005.01.003.

71. Molli, G. Deformation and fluid flow during underplating and exhumation of the Adria continental margin: A one-day field trip in the Alpi Apuane (Northern Apennines, Italy). In Deformation, Fluid Flow, and Mass Transfer in the Forearc of Convergent Margins: Field Guides to the Northern Apennines in Emilia and in the Apuan Alps (Italy); Geological Society of America: Boulder, CO, USA, 2012; Volume 28, pp. 35–48.

72. Biagioni, C.; Dini, A.; Orlandi, P.; Moëlo, Y.; Pasero, M.; Zaccarini, F. Lead-Antimony Sulfosalts from Tuscany (Italy). XX. Members of the Jordanite–Geocrinites Series from the Pollone Mine, Valdocastello Carducci: Occurrence and Crystal Structures. Minerals 2016, 6, 15, doi:10.3390/min6010015.

73. Mlynarczyk, M.S.J.; Sherlock, R.L.; Williams-Jones, A.E. San Rafael, Peru: Geology and structure of the world’s richest tin lode. Miner. Deposita 2003, 38, 555–567, doi:10.1007/s00126-002-0334-z.

74. Cavaretta, G.; Franceschelli, M.; Fandeli, E.; Puxeddu, M.; Valori, A. Tourmalinates from the Triassic Verrucano of the Northern Apennines, Italy. In Contributions to the Geology of Italy with Special Regard to the Paleozoic Basement. A Volume Dedicated to Tommaso Cocozza; Carmignani, L., Sassi, F.P., Eds.; Siena Publishing: Siens, Italy, 1992; pp. 335–338.

75. Franceschelli, M.; Puxeddu, M.; Gattiglia, M. Geochemistry and origin of chloritoid schist from the Alpi Apuane, Italy. Evidence of a prevailing lateritic signature. Eur. J. Miner. 2003, 15, 575–588, doi:10.1127/0935-1221/2003/0015-0575.

76. Samson, I.M.; Sinclair, W.D. Magmatic hydrothermal fluids and the origin of quartz-tourmaline orbicules in the Seagull Batholith, Yukon territory. Can. Mineral. 1992, 30, 937–954.

77. Dini, A.; Mazzarini, F.; Musumeci, G.; Rocchi, S. Multiple hydro-fracturing by boron-rich fluids in the Late Miocene contact aureole of eastern Elba Island (Tuscany, Italy). Terra Nova 2008, 20, 318–326, doi:10.1111/j.1365-3121.2008.00823.x.

78. Blundell, D.; Arndt, N.; Cobbold, P.R.; Heinrich, C.A. Geodynamics and ore deposit evolution in Europe: Introduction. Ore Geol. Rev. 2005, 25, 5–11, doi:10.1016/j.oregeorev.2005.07.031.

79. Martin, S.; Toffolo, L.; Moroni, M.; Montorfano, C.; Secco, L.; Agnini, C.; Nimis, P.; Tumiati, S. Siderite deposits in northern Italy: Early Permian to Early Triassic hydrothermalism in the Southern Alps. Lithos 2017, 276–295, doi:10.1016/j.lithos.2017.04.002.

80. Cugeroni, A.; Oliot, E.; Chauvet, A.; Bordes, J.G.; Laurent, A.; Le Goff, E.; Cenki-Tok, B. Structural Control on the Formation of Pb-Zn Deposits: An Example from the Pyrenean Axial Zone. Minerals 2018, 8, 489, doi:10.3390/min8110489.

81. Ostendorf, J.; Henjes-Kunst, F.; Seifert, T.; Gutzmer, J. Age and genesis of polymetallic veins in the Freiberg district, Erzgebirge, Germany: Constraints from radiogenic isotopes. Miner. Deposita 2018, 54, 217–236, doi:10.1007/s00126-018-0841-1.

82. Von Quadt, A.; Ermi, M.; Martinek, K.; Moll, M.; Peytcheva, I.; Heinrich, C.A. Zircon crystallization and the lifetimes of ore-forming magmatic-hydrothermal systems. Geology 2011, 39, 731–734, doi:10.1130/g31966.1.

83. Waters, P.J.; Cooke, D.R.; Gonzales, R.I.; Phillips, D. Porphyry and Epithermal Deposits and 40Ar/39Ar Geochronology of the Baguio District, Philippines. Econ. Geol. 2011, 106, 1335–1363, doi:10.2113/econgeo.106.8.1335.
84. Vezzoni, S.; Dini, A.; Rocchi, S. Reverse telescoping in a distal skarn system (Campiglia Marittima, Italy). *Ore Geol. Rev.* **2016**, *77*, 176–193, doi:10.1016/j.oregeorev.2016.03.001.

85. Zanchi, A.; Zanchetta, S.; Berio, L.; Berra, F.; Felletti, F.; Volpi, V.; Civile, D.; Forlin, E.; Facchin, L.; Burca, M.; et al. Low-angle normal faults record Early Permian extensional tectonics in the Orobie Basin (Southern Alps, N Italy). *Ital. J. Geosci.* **2019**, *138*, 184–201, doi:10.3301/ijg.2018.35.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).