To simulate the evolution of groundwaters interacting with granulitic rocks of the lower crust exposed in the southern sector of the Calabrian region, reaction path modeling was performed by means of the EQ3/6 software package version 8.0a. Low-salinity waters issuing from granulite have Na–Cl to Na-HCO₃ composition, about neutral pH (mean value of 6.7), outlet temperatures of 7.7 to 14.2°C, oxidant redox potentials from 100 to 182 mV, and electrical conductivity from 72.1 to 196.9 μS/cm. The mineral constituents of local granulite are plagioclase, amphibole, biotite, clinopyroxene, garnet, and orthopyroxene. Simulations were carried at constant temperature of 11.8°C (which reproduces the average temperature of local groundwaters) fixing the fugacity of CO₂ at 10⁻².₄ bar (mean value), 10⁻².₀ bar (mean value +1 σ), and 10⁻².₈ bar (mean value -1 σ). The analytical contents of major elements in groundwaters were satisfactorily reproduced by modeling and are fully consistent with the secondary minerals produced by weathering processes affecting the same rocks.

1. Introduction

The chemical composition of natural water is derived from many different sources of solutes, including aerosols and gases from the atmosphere, erosion and weathering of soil and rocks, and dissolution or precipitation reactions occurring below the land surface. However, human activities play an important and not negligible role on the chemical composition of natural waters. Some of the processes of dissolution or precipitation of minerals can be closely evaluated by means of principles of chemical equilibrium whereas other processes are irreversible and require consideration of reaction mechanisms and rates [1–4]. During water–rock interaction, the major, minor, and trace constituents are leached from primary minerals and enriched into local groundwaters. At the same time, during the progressive dissolution of the rocks, the aqueous solution may attain saturation with respect to different secondary solid phases, potentially acting as sinks of various elements and species [5–9]. For these reasons, the fate of the chemical components of interest during weathering of rocks is a rather complex theme, whose understanding requires the use of reaction path modeling [10–20]. In this work, the EQ3/6 software package, version 8.0a [21], was used to study the weathering processes that occurred on the granulite rocks of the Serra Massif. Reaction path modeling was performed using some needful information, comprising (i) relevant thermodynamic and kinetic data, (ii) chemical composition and abundance of each primary solid phase of interest, (iii) chemical composition of the initial aqueous solution, and (iv) chemical composition of the aqueous solution during water–rock interaction. Items (i) to (iii) are needed to implement reaction path modeling, whereas item (iv) is used to evaluate its validity, through comparison of computed results with analytical data.

2. Geological Background

The Calabrian belt, known as the Calabrian-Peloritan Arc [22], belongs to a fold belt linking the NW-SE Apennines...
structure with W-E-trending structures of Sicily and Northern African Maghrebian regions [23].
On the basis of radiometric, petrological, and seismic data [24], the Calabrian Peloritan Arc (CPA) has been considered to have a pre-Hercynian lower crustal segment thrust into the middle crust during the Hercynian orogeny and uplifted during the Europe-Apulia collision in Oligocene-Early Miocene ([22, 25] and references therein).

CPA is divided into two main sectors: (i) the northern sector, in which fall the Sila Massif and Coastal Chain, and (ii) southern sector, in which fall Aspromonte and Serre Massifs. The two sectors are separated by a strike-slip tectonic line cross along the Catanzaro trough [26]. The study areas fall in the Serre Massif which is made up mainly of high- and low-grade metamorphic rocks that discontinuously overlay the late Hercynian granitoids, granodiorites, and tonalites. All the sequences are sometimes covered by unmetamorphosed Cenozoic sedimentary deposits [27]. In the studied area (Figure 1), granulite-facies crop up extensively. These rocks can be associated with two distinct tectonic units belonging to the Monte Gariglione and Polia-Copanello complexes of the Sila Unit ([22, 28]; Bonardi et al., 2001). The two lithostratigraphic units [29] consist in (i) the lower unit mainly made up of metabasic rocks, predominantly layered metagabbro, and meta-anorthosite with small and subordinate ultramafic bodies and in (ii) the upper unit made up of migmatitic aluminous paragneiss, orthopyroxene-bearing felsic granulite, and marbles that sometimes include quartz monzo-gabbro-norite sills and/or dikes. Surrounding the investigated area, the granulite-facies rocks and phyllonitic rocks are separated by the Curinga-Girifalco Line of Alpine age [29].

3. Methods

3.1. Water Sampling and Analytical Techniques. A total of 30 spring water samples and 4 local rainwaters were collected in the study area (Figure 1) and analyzed for major components. During the collection samples, unstable parameters, such as temperature, pH, and oxidation-reduction potential (Eh) as well as electrical conductivity (EC), were measured in the field by using portable instruments. Total alkalinity was also determined in the field by acidimetric titration utilizing HCl 0.01 N as titrating agent. Waters were filtered in situ through a 0.4 μm pore-size polycarbonate membrane filter (Nuclepore). Samples for the determination of anions were stored without further treatment. Samples for the determination of cations were stored without further treatment. Samples for the determination of cations were acidified, by addition of suprapure acid (1% HNO₃) after filtration and stored. New polyethylene bottles were used for all the samples. In the laboratory, the concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, F⁻, Cl⁻, SO₄²⁻, and NO₃⁻ were determined by high-performance liquid chromatography (HPLC, Dionex DX 1100). All the chemical data were determined in the laboratory of the Department of
3.2. Chemical Characterization of Rocks and Minerals. The mineralogical and chemical characteristics of the granulite considered as a dissolving reactant in this work is based on the study of Apollaro et al. [30] who collected and analyzed several granulite samples from the lower crust exposed in the southern sector of the Calabrian region.

Apollaro et al. [30] carried out modal analyses on granulite-bearing plagioclase rock lithotypes (e.g., [31, 32]) to determine the volume percentages of main and accessory minerals by optical microscopy of thin sections using a mechanical stage. Granulite rocks have a coarse-grained
texture and are plagioclase-rich (60%) with minor amounts of amphibole (10%), biotite (10%), clinopyroxene (8%), garnet (8%), and orthopyroxene (4%).

3.3. Geochemical Modeling. Reaction path modeling of progressive dissolution of granulite in rainwater was carried out by means of the software package EQ3/6, version 8.0a [21], utilizing the thermodynamic database of Wolery and Jove-Colon [33]. Three simulations were performed in kinetic (time) mode, under a closed system with secondary solid phases and an open system with CO₂, adopting different, constant P CO₂ values (10⁻².⁰, 10⁻².⁴, and 10⁻².⁸ bar) and at constant temperature of 11.8°C (which reproduces the average temperature of local groundwaters).

Based on the mineralogical and petrographic data, the dissolving granulite was considered to be constituted by plagioclase, amphibole, biotite, clinopyroxene, garnet, and orthopyroxene. Kinetic parameters and surface area were specified for each primary (dissolving) solid phase because reaction path modeling was performed in time mode (Table 3). Kinetic parameters were obtained from the compilation and critical review of available laboratory dissolution experiments [34]. Thermodynamic data of some minerals such as anorthite, K-feldspar, albite, annite, phlogopite, muscovite, 1.4 nm clinohlore, magnesite, calcite, rhodochrosite, siderite, witherite, stontianite, and aragonite were evaluated by a review work of Helgeson et al. [35]. Thermodynamic data of clay minerals (Mg, Na, K, and Ca end members of beidellite, saponite, and montmorillonite) and 1.4 nm clamosite and celadonites were calculated by Wolery and Jove-Colon [33] and references therein. Those of vermiculites such as Me-Al vermiculites, Me-Fe vermiculites, Me-Mg-Al vermiculites, and Me-Mg-Fe vermiculites with Me=Na, K, Mg, and Ca were evaluated by Apollaro et al. [36, 37]. From Perri et al. [38], thermodynamic data of illite were obtained, and those of ferrihydrites are from the work of Majzlan et al. [39].

Four chemical analyses of rainwaters collected in the study area (Table 2) were used to compute the chemical composition of the initial aqueous solution (mean value).

4. Water Chemistry

4.1. Water Classification. Low-salinity waters issuing from granulite have about neutral pH (mean value of 6.7), outlet temperatures of 7.7° to 14.2°C, oxidant redox potentials from 100 to 182 mV, and electrical conductivity from 72.1 to 196.9 μS/cm. Based on the triangular plots of major anions and major cations (Figure 2), the waters show a Na-Cl to Na-HCO₃ composition.

In the binary diagram of pH vs. P CO₂ (Figure 3(a)), most of the waters are within the soil range (0.002–0.04 bar; [40]); only 2 samples are positioned below the lower soil threshold.

Therefore, in the area, CO₂ is prevalingly contributed by biogenic shallow sources, such as the decay of organic matter and root respiration occurring in the rhizosphere. The plot of the calcite saturation index vs. pH (Figure 3(b)) shows that undersaturation with calcite is a common condition for all waters.

Table 3: Geometrical surface areas and masses of solid phases of interest.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Vol %</th>
<th>Initial surface area (cm²)</th>
<th>Vm (cm³/mol)</th>
<th>Mass (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>60</td>
<td>84000</td>
<td>100.11</td>
<td>13.98462</td>
</tr>
<tr>
<td>Amphibole</td>
<td>10</td>
<td>14000</td>
<td>139.2</td>
<td>1.67625</td>
</tr>
<tr>
<td>CPX</td>
<td>8</td>
<td>11200</td>
<td>100.25</td>
<td>1.86201</td>
</tr>
<tr>
<td>OPX</td>
<td>4</td>
<td>5600</td>
<td>138.665</td>
<td>0.67309</td>
</tr>
<tr>
<td>Garnet</td>
<td>8</td>
<td>11200</td>
<td>272.92</td>
<td>0.68396</td>
</tr>
<tr>
<td>Biotite</td>
<td>10</td>
<td>14000</td>
<td>152.27</td>
<td>1.53237</td>
</tr>
</tbody>
</table>

![Figure 2: Triangular plots of major anions and major cations for the 30 groundwater samples from the study area.](image)

5. Interpretation of Reaction Path Modeling

Analytical data of the groundwater from the granulitic aquifer of the lower crust exposed in the southern sector of the Calabrian region were compared with results of reaction path modeling. For the waters of interest, alkalinity is used as a reaction progress variable (Xi) instead of pH for the following reasons [13]: (i) the progressive
dissolution of primary solid phases, driven by conversion of aqueous CO$_2$ to HCO$_3^-$ ion, causes a continuous increase in alkalinity, (ii) precipitation of calcite, which would cause a decrease in alkalinity, is limited (see Section 4.1), and (iii) the alkalinity consumption due to acidity produced by oxidative dissolution of pyrite is negligible, as indicated by the generally low SO$_4$ concentrations.

Indeed, during water-rock interaction, due to the appearance of different secondary mineral assemblages acting as pH buffers (e.g., [41–44]), pH changes are quite irregular and less continuous.

Figure 4 shows a close-to-linear relation between Xi and alkalinity, with a good correspondence for all different pCO$_2$ values considered.

The simulations show a progressive dissolution dominated by plagioclase followed by a minor amount of amphibole, clinopyroxene, and biotite and negligible amounts of orthopyroxene and garnet for all the investigated pCO$_2$ (Figure 5).

As already shown by Apollaro et al. [30], the differences in the type and amount, along the reaction path of the secondary minerals (Figure 6), mainly reflect the different dissolutions of primary minerals and, therefore, a different contribution during the reaction, of chemical elements.

The two main secondary solid phases forming during granulite dissolution, appearing at alkalinity close to 5mg HCO$_3$/L, are kaolinite and vermiculites with minor amount of hydroxides. Kaolinite, vermiculites, and hydroxides act as sinks of Al, Si, and Fe released by primary dissolved minerals. Carbon dioxide partial pressure has a significant influence on the first appearance of product phases for all these minerals except kaolinite. The lower the pCO$_2$, the earlier all the secondary phases begin to precipitate.

Consistently with the undersaturation with calcite, there is no solid carbonate.

5.1. The Aqueous Solution. The theoretical path of granulite dissolution, at constant pCO$_2$ of 10$^{-2.0}$, 10$^{-2.4}$, and 10$^{-2.8}$ bar,
indicates that the water-rock interaction is dominated by dissolution of plagioclase, amphibole, and clinopyroxene and much less from biotite, orthopyroxene, and garnet (Figure 5). The concentration of aqueous Ca and Mg (Figure 7) increases owing to dissolution of plagioclase, amphibole, and clinopyroxene, and the amount of Ca and Mg incorporated in precipitating secondary minerals is negligible. Variable pCO₂ does not affect the Ca/HCO₃ and Mg/HCO₃ ratio at the three pCO₂ values, and there is a very good agreement between reaction path modeling results and the analytical data (Figure 7).

The binary plots of Na versus alkalinity and K versus alkalinity (Figure 8) highlight that the dissolved Na and K concentrations increase slightly through the whole simulation, since the amounts of Na and K contributed by dissolution of plagioclase and biotite are minimal, and a part of K and Na is incorporated in the vermiculites at all pCO₂ (Figure 6). As already shown by Apollaro...
et al.,[13] Na and K versus alkalinity plots in low TDS groundwaters are poorly informative because these two alkali metals are probably controlled by varying contributions of atmospheric-marine salts rather than the water-rock interaction.

The binary plots of SiO$_2$ versus alkalinity (Figure 9) highlight that the concentration of aqueous SiO$_2$ increases during the dissolution of granulite because all minerals present in the rocks contain SiO$_2$ and the amount of SiO$_2$ incorporated in precipitating kaolinite and vermiculite is subordinate. Similar to Ca and Mg, variable pCO$_2$ does not affect the SiO$_2$/HCO$_3$ ratio and there is a very good agreement between analytical data and results of reaction path modeling.

6. Conclusion

Geochemical prospecting carried out in the granulitic rocks exposed in the southern sector of the Calabrian region (Southern Italy) has allowed identification of several springs...
hosted in a very extensive shallow hydrogeological metamorphic complex. To evaluate the irreversible water-rock mass exchanges occurring during the evolution of rainwaters to groundwaters, a reaction path modeling in kinetic (time) mode was performed, under a closed system with secondary solid phases and an open system with CO₂, adopting
The results of reaction path modeling show that the release of major dissolved constituents to shallow groundwaters is mainly controlled by weathering of plagioclase accompanied by minor amounts of amphibole, clinopyroxene, and biotite and negligible amounts of orthopyroxene and garnet. Computed contents of key dissolved components (Ca, Mg, Na, K, and SiO$_2$) are comparable with analytical data, although not all the details are reproduced, probably due to insertion in the model of the average composition of primary minerals, in spite of their nonnegligible chemical variations and to the fact that some elements such as Na and K are controlled by varying contributions of atmospheric-marine salts rather than the water-rock interaction.

Since the frequent worldwide occurrence of this type of rock, it can be said that this kind of research is of widespread interest and these results can be transferred to other sites where granulite rocks occur.

**Data Availability**

The manuscript is a data self-contained article, whose results were obtained from the laboratory analysis, and the entire data is presented within the article. However, if any additional information is required, these are available from the corresponding author upon request to the e-mail apollaro@unical.it

**Conflicts of Interest**

The author declares that he has no conflicts of interest.

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