

GEOCHEMICAL MODELING OF WATER-ROCK INTERACTION IN THE OPHIOLITIC AQUIFERS OF NORTHERN CALABRIA (S-ITALY)

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INTRODUCTION

This doctoral thesis is aimed at investigating the weathering processes of the metabasalts and serpentinites cropping out in Northern Calabria through geochemical modeling and at determining the dissolution rate of relevant mineral phases by means of laboratory dissolution experiments on well characterized whole-rock samples.

EXPERIMENTAL WORK

In this study, sixty-nine spring samples were collected in November 2011 and July 2012.

At each site, temperature, *pH*, *Eh* and electrical conductivity (EC) were measured in the field by use of portable instruments (see the methodology in Critelli *et al.*, 2012). Chemical analyses were performed in the laboratory of the Di.BEST of the University of Calabria to determine the abundance of major, minor and trace elements in these groundwaters. Major anions and cations were determined by ion-chromatography, using a HPLC DIONEX DX 120, whereas trace elements were determined by a quadrupole Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Perkin Elmer/SCIEX, Elan DRCE) with a collision reaction cell capable of reducing or avoiding the formation of polyatomic spectral interferences.

Chemical characteristics of rocks and minerals

The compositional features of groundwaters depend on the extent of water-rock interaction and the mineralogy of local rocks. Therefore, the mineralogical and chemical characterization of metabasalts and serpentinites cropping out in the study area represents a mandatory step to better understand the chemical evolution of local groundwaters. As such, five representative samples from metabasalts and seven from serpentinites were selected, on the basis of macroscopic characteristics, for mineralogical and chemical analyses.

Primary mineral phases of the studied rocks were identified through both optical microscopy of thin sections and X-ray Diffraction (XRD) analysis using a Bruker D8 Advance XRD Diffractometer.

Point analyses on single primary minerals were carried out on polished carbon-coated thin sections through an Environmental Scanning Electron Microscope FEI QUANTA 200 equipped with a X-ray EDS suite comprising a Si/Li crystal detector model EDAX-GENESIS-4000. This technique allowed us to determine the stoichiometry of the main primary phases, whereas trace element contents were measured by Laser Ablation ICP-MS (LA-ICP-MS).

Whole-rock analyses were performed by X-ray fluorescence spectroscopy (XRF) using a Philips PW 1480 XRF spectrometer. X-ray counts were converted into concentrations by a computer program based on the matrix correction method described by Franzini *et al.* (1975). The certified international reference materials AGV-1, BCR-1, BR, DR-N, GA, GSP-1 and NIM-G were used as monitors of data quality.

XRD analysis and optical microscopy of thin sections revealed that metabasalts are made up of actinolite, chlorite, albite and epidote, with small quantities of phengite and calcite. According to Liberi *et al.* (2006), Na-amphibole, prehnite and titanite are also present in these rocks, as accessory phases. However, their effect on water chemistry is expected to be minor to negligible owing to their very small amounts and high durability, especially for titanite. The paragenesis of serpentinites is composed of antigorite with subordinate magnetite. The weight percentages of primary minerals in the two bulk rocks were evaluated by Apollaro *et al.* (2011)

based on the median concentrations of major oxides in the two lithotypes of interest (given by XRF analysis) and in each solid phases (obtained by SEM-EDS analysis).

The analysis of primary minerals have been performed on both metabasalts and serpentinites and showed that the computed oxide content is in satisfactory agreement with the corresponding XRF analytical data. Therefore, it can be concluded that the estimated weight percentages of primary minerals have acceptable precision for the purposes of this investigation.

The concentrations of trace elements in relevant minerals were acquired through LA-ICP-MS for metabasalts only, as hydrochemical data indicate that local groundwaters interact chiefly with these rocks and less commonly with serpentinites.

The chemical and mineralogical characteristics of samples coded A19 (metabasalt) and A10 (serpentinite) were evaluated in detail (Apollaro *et al.*, 2011; Bloise *et al.*, 2012, 2014), as these two samples were selected and utilized to determine the kinetic parameters of metabasalt and serpentinite through dissolution experiments.

The same approach mentioned above was used to estimate the weight percentages of primary minerals and to determine their stoichiometry in both samples A19 and A10. Again, the computed oxide contents resulted to be in satisfactory agreement with the corresponding XRF analytical data, suggesting that estimated weight percentages of primary minerals have adequate precision for the aims of this study.

Apparatus and analytical procedures of laboratory experiments for the determination of dissolution rates

The dissolution rates of the metabasalt sample A19 and the serpentinite sample A10 have been investigated by means of laboratory experiments at the Lawrence Berkeley National Laboratory (LBNL; Berkeley, CA, USA) and at the Géosciences Environnement, Toulouse, France).

Experiments have been performed under known conditions of temperature, pH, and composition of inlet solutions by means of mixed flow reactor systems. A continuously-stirred mixed flow reactor (or flow-through reactor; Chou & Wollast, 1984) consists of a plastic reaction vessel of known volume, which is continuously stirred with a floating Teflon-coated magnetic stirrer (Pokrovsky & Schott, 2000). Stirring is controlled by a stirplate located directly beneath the bath.

As described by Marini (2006), the input solution is continuously pumped through the reaction vessel at a constant flow rate, Q . The molal concentrations of some relevant solutes, produced by rock dissolution, are monitored both in the inlet solution, m_{in} , and in the outlet solution, m_{out} . The dissolution experiment is run until m_{out} attains a constant value, or steady-state value, which is used to compute the steady-state whole rock dissolution rate.

The experiments were performed on the cleaned 80-150 μm size fraction. In detail, samples were initially ground using a jaw crusher and then an agate mortar and pestle. The finely grained materials were dry sieved to obtain the 80-150 μm size fraction.

The Brunauer-Emmett-Teller (BET) specific surface areas of the cleaned and dried 80-150 μm size fractions were determined to be $0.461 \text{ m}^2\text{g}^{-1}$ for the metabasalt sample A19 and $17.04 \text{ m}^2\text{g}^{-1}$ for the serpentinite sample A10, based on a 11 point krypton and nitrogen adsorption, respectively, using a Quantachrome Gas Sorption System located at the Géosciences Environnement Toulouse.

Dissolution experiments were performed at a constant temperature of 25 °C keeping the mixed-flow reaction vessel immersed in a water bath. Input fluids of ionic strength 0.01 mol/kg were prepared using deionized water and Merck reagent grade HCl, NaOH, NaHCO₃, and NaCl. They were stored in compressible polyethylene containers during the experiments and injected into the reaction vessel using a Gilson peristaltic pump at constant flow rate.

In each dissolution experiment, an amount of rock powder weighted on an analytical balance was allowed to react in the stirred vessel with the fluid of fixed input composition.

The exit solutions were collected at regular intervals of time to ascertain the achievement of constant concentrations (*i.e.*, steady-state conditions). Outlet solutions were filtered at 0.45 μm and acidified with

concentrated supra-pure HNO₃ prior to their analysis by ICP-MS (Al, Ca, Fe, Cr, and Mn), AAS (Mg), and colorimetry (Si). All chemical analyses were carried out in the laboratory of the GET.

Experimental determination of the release rates for metabasalt

Five metabasalt dissolution experiments were carried out in this study at 25 °C and at various pH (2.0, 3.2, 6.3, 7.2, and 12.0). The reactive fluid concentrations of Si, Mg, Ca, Al, Fe, K, Sr, Cr, and Mn were regularly measured. These concentrations were used to calculate the release rate of each element ($r_{i,BET}$).

Each dissolution experiment was run for a relatively long time, until attainment of steady-state conditions, as indicated by the temporal evolution of Si and Mg concentrations.

The logarithm of the steady-state release rate of Si exhibited a U-shaped variation with pH, since it decreased with increasing pH at acidic condition but it increased slightly with increasing pH at alkaline conditions. These results have been observed also in Gudbrandsson *et al.* (2011) on crystalline basalt and are in agreement with the characteristic dissolution behaviour exhibited by most aluminum-silicates minerals. The dependence of the logarithm of the steady-state release rate of Mg on pH is not characterized by the typical U-shaped variation as the logarithm of the release rate decreases with increasing pH also under alkaline conditions, probably due to the precipitation of brucite. The possible occurrence of this process is suggested by speciation-saturation calculations carried out using EQ3/6 and is in agreement with what has been observed by Pokrowsky & Schott (2004).

Experimental determination of the release rates for serpentinite

Five serpentinite dissolution experiments were performed in this study at 25 °C and at various pH (2.0, 3.1, 5.8, 7.3, and 8.9). Again, the reactive fluid concentrations of Si, Mg, Ca, Al, Fe, K, Sr, Cr, and Mn were regularly measured in order to calculate the release rate of each element. As for the metabasalt dissolution experiments, attainment of steady-state conditions required a comparatively long time.

The logarithms of the release rates, generated from Si and Mg outlet concentrations, are characterized by a significant decrease from acidic conditions to pH = 7 and by a subsequent increase in weakly alkaline solutions.

Incidentally, taking into account that both Mg and Si released by this lithotype come only from antigorite dissolution, the release rates of Mg and Si and the dissolution rates of antigorite differ by the stoichiometric coefficient of Mg and Si in antigorite. In principle, the calculation of the dissolution rate of antigorite is a very simple matter. In practice, things might be complicated by occurrence of non-stoichiometric dissolution.

Therefore, the Mg/Si ratio in the outlet solution has been monitored and, at pH 8.9, it was observed a preferential release of Si with respect to that of Mg which leads to the formation of a Mg-rich surface layer. The formation of this layer was confirmed by decreasing the pH of the inlet solution from 8.9 to 2, which resulted in a sharp increase in the Mg/Si ratio of the outlet solution, owing to dissolution of the Mg-rich surface layer. This interpretation is in agreement with the pH dependence of the dissolution rates and surface speciation of brucite and quartz, as discussed by Schott *et al.* (2009).

GEOCHEMICAL MODELING

In this study, reaction path modeling of chemical weathering of metabasalts and serpentinites from Northern Calabria (Italy) was performed using the EQ3/6 software package, version 8.0 (Wolery & Jarek, 2003), adopting the Double Solid Reactant Method (DSRM; Accornero & Marini, 2008; Lelli *et al.*, 2008; Apollaro *et al.*, 2011). In this way, it was possible to simulate the progressive dissolution of metabasalts and serpentinites in local meteoric waters as well as the concurrent rock-to-water release of major, minor, and trace elements.

Reaction path has been modeled in kinetic (time) mode, under closed system with a defined set of secondary solid phases, which were allowed to precipitate, and under open system with CO₂. An updated version of the thermodynamic database data0.ymp.R5, whose characteristics are described by Wolery & Jove-Colon (2007), was used (see also Apollaro *et al.*, 2013a, 2013b).

Simulations were carried out at constant temperature of 11.4 °C, which reproduces the average temperature of local groundwaters. Fugacity of CO₂ was fixed, in different runs, at either 10^{-2.5} bar (mean value), 10^{-1.9} bar (mean value + 1σ), or 10^{-2.9} bar (mean value - 1σ).

The solid reactants considered to model the dissolution of average metabasalt were (in order of decreasing importance) calcite, amphibole, epidote, albite, chlorite, and phengite, whereas those considered to simulate the dissolution of mean serpentinite were antigorite and magnetite.

To model the dissolution of the metabasalt, the precipitation of the following solid reactants was allowed: gibbsite, kaolinite, α-cristobalite, and hausmannite as well as several solid solutions. Precipitation of talc and magnesite was also permitted, and indeed it occurred, during simulation of serpentinite-water interaction. These minerals were selected based on the general understanding of chemical weathering (*e.g.*, Berner & Berner, 1996; Langmuir, 1997; Appelo & Postma, 1999) to avoid the production of undesired minerals.

The theoretical concentrations of calcium and magnesium, the two most important cations provided to the aqueous solution by progressive dissolution of metabasalts and serpentinites, obtained from the geochemical modeling have been compared with their analytical counterpart, referring to local shallow groundwaters, through binary correlation diagrams (Figs. 1 and 2), in which alkalinity is reported on the X-axis, as a proxy for the reaction progress variable.

The theoretical paths of metabasalt dissolution, independent of the adopted f_{CO_2} , indicate that the concentration of aqueous Ca increases owing to calcite dissolution, as long as the aqueous solution is undersaturated with calcite (Fig. 1a). Maximum dissolved Ca concentration depends on f_{CO_2} and reaches values of 89.2, 53.5, and 38.4 mg/L at f_{CO_2} of 10^{-1.9}, 10^{-2.5}, and 10^{-2.9} bar, respectively. In contrast, dissolved Ca content decreases upon attainment of calcite saturation, as the amount of Ca incorporated in precipitating trigonal carbonates is higher than that supplied to the aqueous solution by amphibole and epidote destruction. The computed trend of serpentinite dissolution (Fig. 1b), at any f_{CO_2} , is characterized by nearly constant Ca concentration, due to the absence of Ca-bearing mineral in the considered serpentinite. Analytical data for all the Ca-HCO₃ groundwaters are in agreement with the theoretical paths of metabasalt dissolution, whereas the Mg-HCO₃ springs are situated close to the computed trend of serpentinite dissolution.

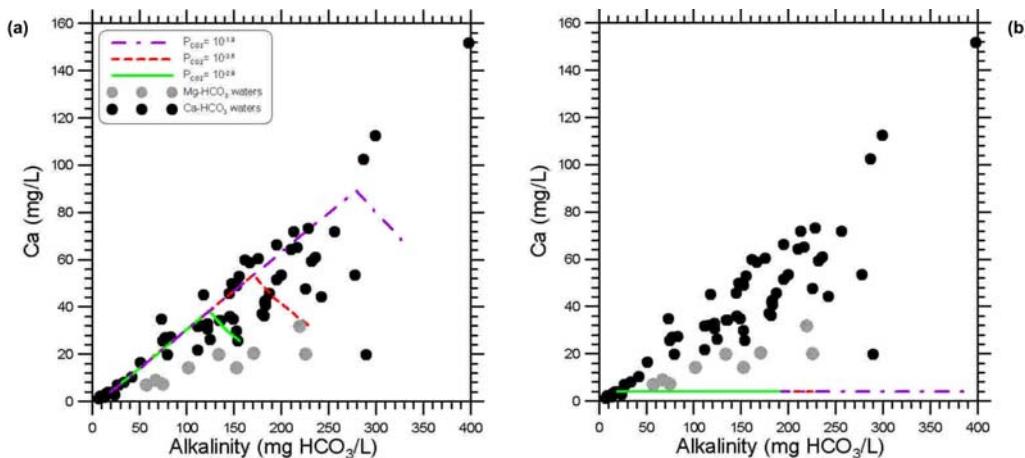


Fig. 1 - Plot of Ca vs. alkalinity showing the analytical data (water-rock derived concentrations) for the waters from the study area (closed circles) as well as the results of reaction path modeling for the dissolution of (a) metabasalts and (b) serpentinites under different f_{CO_2} values (see legend).

Dissolved Mg remains constant during the first calcite-dominated stage of metabasalt dissolution, at all f_{CO_2} values, since Mg supplied by amphibole, chlorite and phengite destruction is completely insignificant (Fig. 2a). Upon attainment of calcite saturation, dissolution of these silicates, especially the tremolite-rich

amphibole, becomes important causing a considerable increase in dissolved Mg, according to relatively steep trends. Dissolution of serpentinite (Fig. 2b) is described by paths of constant slope, which is somewhat smaller than that of the second stage of metabasalt destruction. In addition, the three paths for different f_{CO_2} values are superimposed. Again, analytical data for all the Ca-HCO₃ spring waters are explained by the model results for metabasalt dissolution, whereas the Mg-HCO₃ samples are positioned on the simulated paths of serpentinite dissolution.

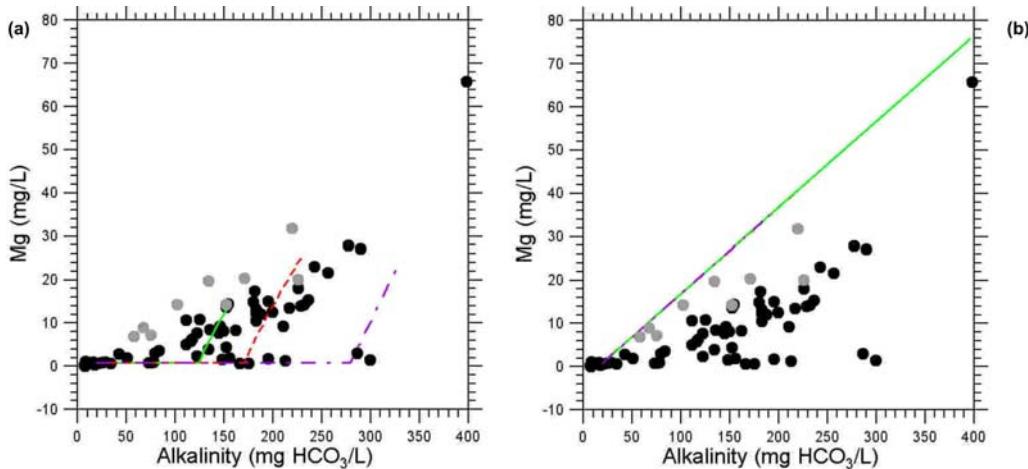


Fig. 2 - Plot of Mg vs. alkalinity showing the analytical data (water-rock derived concentrations) for the waters from the study area (closed circles) as well as the results of reaction path modeling for the dissolution of (a) metabasalts and (b) serpentinites under different f_{CO_2} values (same legend as for Fig. 1).

The same approach was applied to investigate the rock-to-water release of several trace elements (see Apollaro *et al.*, 2011 for further details).

CONCLUSIONS AND IMPLICATIONS

The rock-to-water release of major, minor, and several trace elements as well as their fate in the aqueous solution was simulated for the shallow aquifer systems of Northern Calabria, chiefly hosted in metabasalts and subordinately in serpentinites, by means of the EQ3/6 software package. Accepting that the model provides a sufficiently reliable picture of the natural system under investigation, the following conclusions can be drawn.

i) Most groundwaters, belonging to the Ca-HCO₃ facies, are produced through interaction of meteoric waters with metabasalts, whereas the only Mg-HCO₃ spring water is generated through dissolution of serpentinites. Therefore, water circuits appear to be mainly hosted into metabasalts, representing the prevailing and most permeable lithotype, and subordinately in less abundant and less permeable serpentinites.

ii) A tremolite-rich amphibole is the only important, active source of dissolved Cr. This fact was rarely recognized in previous studies, that usually emphasized the provenance of Cr from other solid phases (*e.g.*, chromite, Cr-magnetite, a chromite-silicate mixture, enstatite, augite, and chlorite). In addition, accepting that dissolved Cr is prevailingly present in the hexavalent form, as suggested by the measured total Cr concentrations and literature data, Cr(VI) speciation results to be dominated by CrO₄²⁻ ion (52 – 78 mol%), followed by the neutral complexes CaCrO₄[°] (14-32%) and MgCrO₄[°] (2-12%) which are more mobile and more bio-available, being less affected by electrostatic sorption onto charged solid surfaces with respect to charged solutes. Owing to the common occurrence of ophiolitic rocks worldwide, as already recalled above, these results obtained for the study area are of global interest.

iii) In addition to Cr, also the contents of other dissolved trace elements (*e.g.*, Ba, Cu, Ni, Pb, Sr, and Zn) are explained by progressive dissolution of local rocks and, consequently, contributions related to anthropogenic pollution can be excluded.

Furthermore, a significant effort was devoted to determine whole-rock dissolution rates. In fact, several laboratory experiments in mixed-flow reactors, at 25 °C and different pH values, were carried out during the one-year research period profitably spent at both the Lawrence Berkeley National Laboratory (California, USA) and at the Géosciences Environnement Toulouse (Toulouse, France).

To appreciate and contextualize the innovative nature of this experimental work, it must be recalled that many laboratory studies aimed at the determination of the dissolution rates of separate (single) minerals were carried out so far, especially during the last thirty years, after the pioneering work of Chou & Wollast (1984) on the dissolution rate of albite by mean of a fluidized bed reactor. In contrast, the dissolution rates of individual minerals in multi-mineralic rocks are poorly known as they were investigated in a limited number of works (*e.g.*, Yokoyama & Banfield, 2002; Evans & Banwart, 2006; Gudbrandsson *et al.*, 2011). The lack of this information motivated the laboratory experiments which were performed, as part of this thesis, to study the dissolution kinetics of a metabasalt and a serpentinite cropping out in the area of interest in order to retrieve the rates of each constituting mineral phases.

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