

MODELLING OF WATER-ROCK INTERACTIONS IN CARBONATE AQUIFERS: INSIGHTS FROM A CASE STUDY IN THE MADONIE AREA (SICILY)

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Weathering reactions between natural waters and the minerals that constitute the soils and underlying rocks are the major geologic control on natural water chemistry. The chemical action of water, oxygen, carbon dioxide and other components cause the chemical dissolution of primary minerals and the release of dissolved constituents to natural waters. As a result of these processes, the chemical features of groundwaters are strictly dependent on the characteristics of the host rocks.

This research attempts at a comprehensive and systematic characterization of water-rock interaction processes taking place in the aquifers of the Madonie area.

The Madonie is one of the main massifs in Sicily and is located in the centre of the Mediterranean region. The study area is characterized by several distinct kinds of landscape, resulting from heterogeneous outcropping lithologies as well as from the tectonic and modelling action of morphodynamic factors.

The hydrogeology of the Madonie area is characterized by the presence of both of carbonate rocks, generally acting as aquifers and clayey Flysch deposits.

The characteristics of outcropping rocks, the density of fractures and other structural features, the morphogeological setting, and the presence of karst processes, all contribute to the complex hydrogeological setting of the Madonie area.

Carbonate outcrops are of particular hydrogeologic interest because they represent the highly productive reservoirs.

Previous geochemical researches in the Madonie area focused on the isotopic composition of springs and rains (*e.g.*, Mangano *et al.*, 1970; Hauser *et al.*, 1980; Favara *et al.*, 1984). More recently, the first hydrogeochemical results on the chemistry of major elements dissolved in groundwaters were presented by Cusimano *et al.* (1992). These Authors suggested that the Madonie springs can be clustered into four homogeneous groups: springs with $\text{Ca/Mg} > 1$, typical of calcite-dominated hydrostructures of the Panormide Unit; springs with $\text{Ca/Mg} < 1$, characteristic of dolomite hydrostructures of the Panormide Unit; springs with low salinity, typical of Flysch aquifers; and springs with high salinity, related to seawater ingression.

The gap of data on the abundance and distribution of major, minor and trace elements in the area is the first reason for this work. Here, we report data collected from 241 different sites, including springs and wells, during an extensive hydrogeochemical survey. Analytical data are used to produce geochemical maps, and to draw geochemical considerations on compositional diversity in the Madonie area.

Water-rock interaction is the principal processes controlling the cycling of chemical elements in the Madonie groundwaters. In fact, the wide compositional range of groundwaters mostly reflects variable extents of weathering of carbonate rocks (see below). Limestones represent the main sedimentary rocks cropping out in the study area, and they are also highly productive reservoirs. As such, the mineralogical

and chemical characterization of the Madonie limestones is an indispensable step for understanding the chemical evolution of local groundwaters.

Previous studies on the petrography and geochemistry of outcropping rocks in the study area have been limited in number; therefore, a sampling survey of the main rocks in the area, and their geochemical characterization (through optical microscopy, SEM-EDS observations, XRF whole rock analyses and LA-ICP-MS determinations on selected minerals) have been required to fulfil the objectives of this work. In fact, major, minor and trace elements data described below have been used as input parameters in the reaction path simulations that are to define the solid reactant.

In this work, we have also collected 21 rock samples from different lithologies cropping out in this study area, with a special focus on limestones, which represent the prevalent sedimentary formations and are also highly productive reservoirs. The mineralogical and chemical characterization of the Madonie limestones is an indispensable step for an understanding of the chemical evolution of local groundwaters.

Microscopic characterization reveals that carbonate clasts are generally rounded to sub-angular or have irregular shapes. In general, the Madonie carbonate rocks are characterized by different fossil associations.

Selected samples were subsequently studied by scanning electron microscopy (SEM) to ascertain mineral textures, textural relationships, and element distributions in mineral phases. EDS has been used for quantitative mineral chemistry. SEM images allowed to characterise the textural features of the carbonates, and confirmed the results of optical observations, in that clasts essentially consist of carbonate minerals with variable proportions of secondary minerals. In thin and polished sections of carbonate rocks, apatite grains with size ranging from some microns to 100 microns are relatively common. Cryptocrystalline apatite crystals are associated with accessory amounts of pyrrhotite, quartz and Fe-oxides.

Petrographic and geochemical analyses have also been carried out in dolostone showing the typical feature of euhedral crystals.

Geochemical characteristics of the Madonie sediments have been first evaluated through detailed investigation by X-Ray Fluorescence (XRF). Whole rock chemistry of limestones shows significant variability in the amounts of SiO₂ (0.284-5.413 wt.%), Al₂O₃ (0.1-2.6 wt.%), P₂O₅ (0.008-1.01 wt.%), MgO (1.1-31.4 wt.%), MnO (0.05-0.96 wt.%) and CaO (21.0-54.4 wt.%).

Earth alkalis (Mg and Ca) are manifestly the two major components of the studied rocks. The variable MgO and CaO concentrations reflect variable proportions of calcite and dolomite in the rocks. Variations in Fe₂O₃ content are likely due to variable amounts of pyrite and Fe-oxides in the samples, and subordinately to presence of a siderite and ankerite component in carbonate minerals.

Scanning electron microscopy reveals a notable compositional homogeneity in the selected samples, highlighting the need of spot analyses to complement whole-rock determinations. High-resolution electronic images, obtained by SEM-EDS, were then used to select adequate areas where to perform Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS).

The present study has proposed the first detailed geochemical mapping of the distribution of major, minor and trace elements in the Madonie area. Geochemical data acquired in this work allow understanding the processes controlling the abundance and mobility of metals in this groundwater system.

The wide compositional range of groundwaters circulating in the Madonie area is initially investigated by the study of major element abundance.

An initial assessment of the chemical composition of groundwaters of the Madonie area is obtained from the Langelier Ludwig (L-L) diagram of Fig. 1.

Waters samples have been differentiated in six families, according to their composition. Groundwaters circulating in carbonate aquifers have a typical bicarbonate alkaline-earth composition.

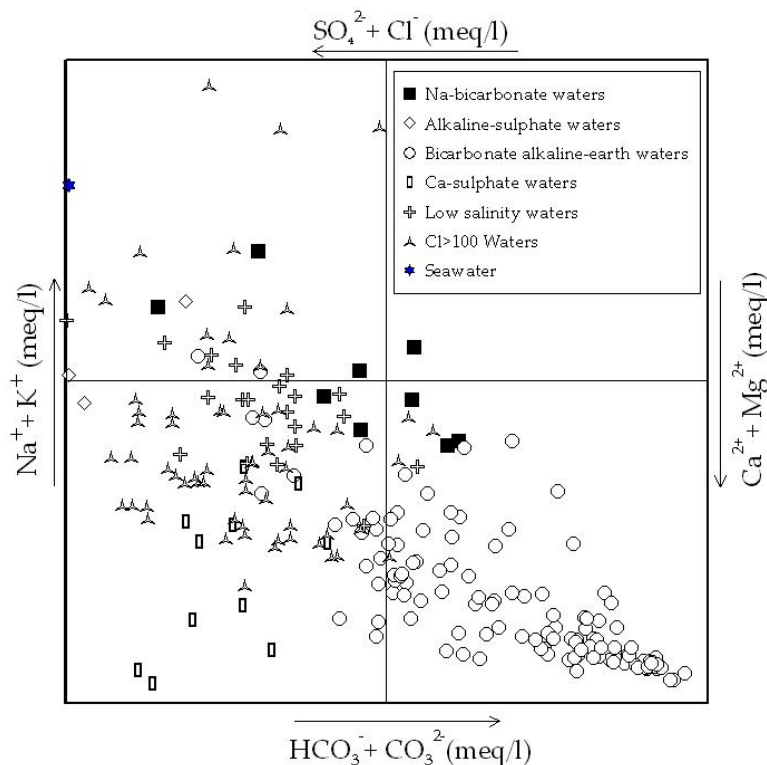


Fig. 1 - Square diagram of Langelier-Ludwig.

These samples have been collected in areas where the carbonate rocks of the Imerese and Panormide Formations crop out. A few waters, coming from the Flysch Numidico Units, also cluster in the bicarbonate alkaline-earth group. A common feature of these sediments is the presence of clays interposed between the quartz-arenaceous levels. The apparent incongruity between water composition and lithology can be explained either by the presence of carbonates in form of calc-arenaceous levels, calcirudites and silty breccias Mesozoic, called Wildflysch (Ogniben, 1963), or by dissolution of limestone cement in quartz-arenaceous sediments.

Some samples of this group show a trend towards the point representative of seawater point, suggesting a some extent, mixing with seawater. These samples have been collected near the seacoast.

The Na-bicarbonate waters are depleted in calcium and magnesium, and enriched in sodium and potassium, compared to the bicarbonate alkaline-earth waters described above. The enrichment in sodium and potassium displayed by these waters is likely the result of ionic exchange processes. These processes are very common in the water circulation in the phreatic aquifers (Stumm & Morgan, 1996), where clayey sediments remove calcium and magnesium and release sodium and potassium. A small group of samples are characterized by high sulphate contents and prevalence of Ca among the cations; in fact, these Ca-sulphate waters stretch toward the bottom-left corner of Fig. 1, their chemical characteristics likely reflecting leaching of the Messinian evaporites.

The group of low salinity waters is characterized by conductivities between 44 $\mu\text{S}/\text{cm}$ and 564 $\mu\text{S}/\text{cm}$, and by an average pH of 6.6. These samples have measured bicarbonate concentrations of 0.1-76.3 mg/l , and are mostly distributed in Fig. 1 in the compositional domain of chloride-sulphate waters. Their low conductivity can be explained by minor water-rock interaction because of very short residence time in the aquifer system. As such, low-salinity waters can be interpreted as shallow infiltrated rain waters weakly modified by water-rock interactions. The remaining groundwaters display a fair compositional trend toward seawater composition. These samples (hereafter referred as $\text{Cl} > 100$ waters) are characterized by chloride contents higher than 100 mg/l , and are likely produced through mixing with seawater. This is also consistent with their coastal location.

The chemical characteristics of Madonie groundwaters typically evolve under oxidizing redox conditions (range from 200 to 500 mV), consistent with the superficial groundwater system; in contrast reducing redox conditions are less frequent and often found for natural waters with significant residence times in aquifers. The water samples have conductivity between 31.7 $\mu\text{S}/\text{cm}$ and 8220 $\mu\text{S}/\text{cm}$; their total dissolved solids (TDS) content is higher near the coast area, where contribution from saline components (seawater) becomes important.

The good correlation between sodium and chloride of Fig. 2 and the high contents of these dissolved constituents are an indications of significant seawater contribution in several samples. The same diagram also indicates that groundwaters consistently plot along a mixing line between low salinity (meteoric) waters and seawater, suggesting the presence of a marine component in virtually all the waters of the study area. It is likely of atmospheric derivation at the low Na, Cl contents, whereas it is ascribable to seawater ingression at the high Na, Cl concentrations.

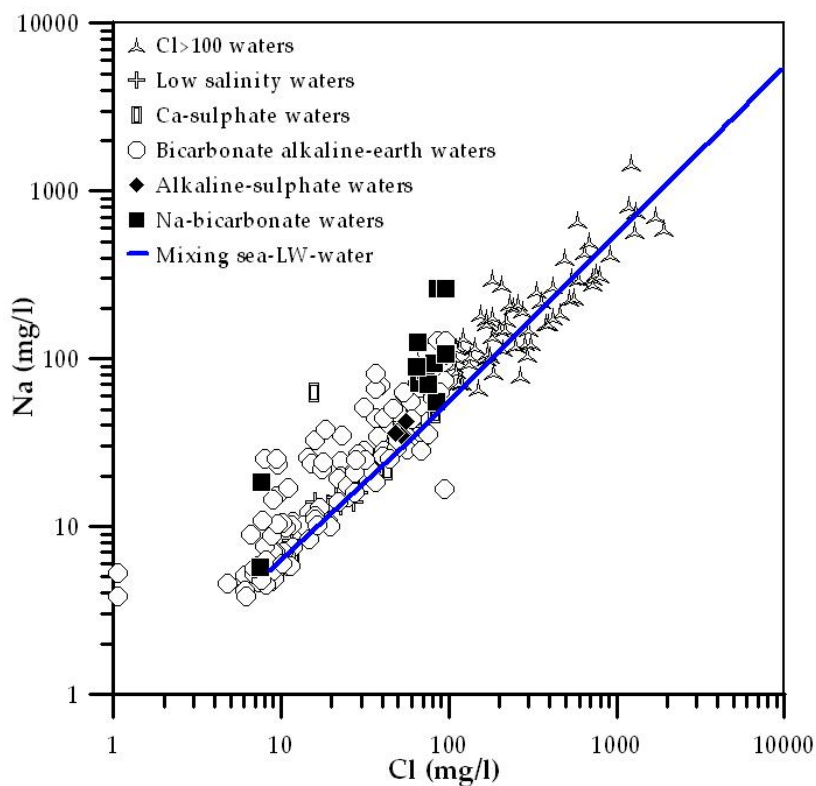


Fig. 2 - Na-Cl scatter diagram. The figure demonstrates that the groundwaters of the “ $\text{Cl} > 100$ group” are contaminated by seawater.

In fact, groundwaters collected in coastal area display a fair compositional trend toward seawater composition. The significance of seawater ingress is also consistent with the Na and B distribution maps; the amount of both elements increasing from inner sites toward the coast.

The wide compositional range of groundwaters circulating in the Madonie area is also related to lithological feature of host rocks, and particularly to variable extents of water-rock interaction. Calcium and bicarbonate excess concentrations in groundwaters suggest the occurrence of other process as in addition to seawater mixing, namely water-rock interaction in carbonate aquifers.

Simple thermodynamic considerations suggest that congruent carbonate dissolution takes place in the investigated area. Relationships between carbonate and groundwaters are illustrated in the HCO_3/pH plot of Fig. 3 which shows the evolution trend of groundwaters from under-saturated waters to saturated and slightly oversaturated conditions.

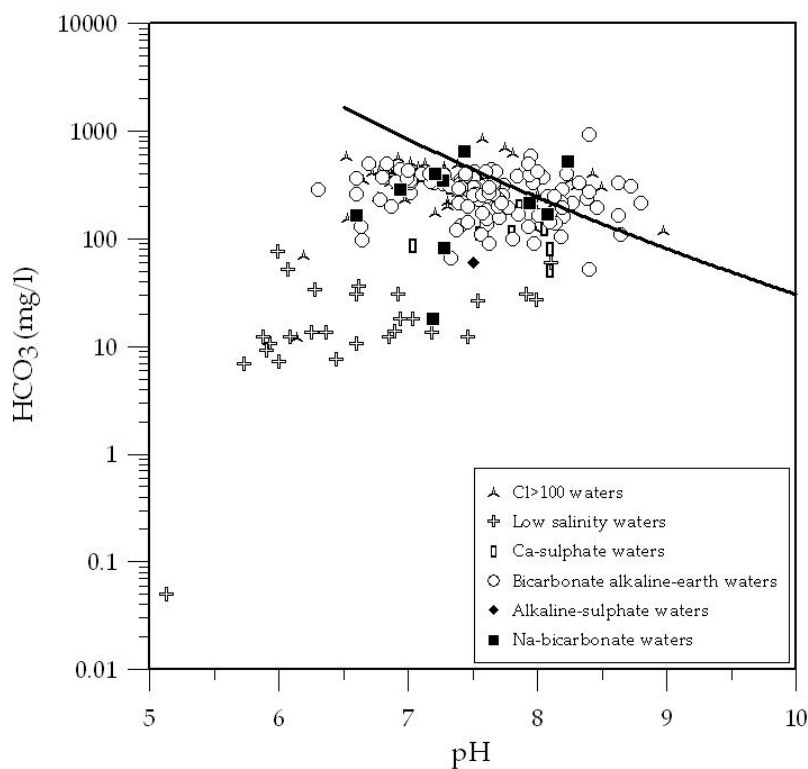


Fig. 3 - HCO_3 -pH scatter diagram with the theoretical equilibrium curve for calcite. The figure suggests that the inverse relationship between pH and HCO_3 contents for most groundwaters from the study area is related to attainment of saturation with calcite (and dolomite).

Ca and HCO_3 concentrations ($\approx 500 \text{ mg/l}$) are higher in the northern sector than in the southern one; this allows hypothesizing that the weathering process is more important in the northern area. High values of PCO_2 associated to the lower pH values confirm the presence of aggressive water with respect to carbonates.

The contribution of solutes from the weathering process is confirmed by the good correlation between Ca and Mg (Fig. 4), suggestive of a common origin for the two elements. The Mg/Ca ratio of groundwaters falls within the range of Mg/Ca ratios of the two main carbonate lithologies in the area, namely the limestones of the Imerese Unit (black line), and the dolostones of the Quacella Formation (grey line), respectively. This shows that leaching of carbonate rocks is the main source of calcium and magnesium in the groundwaters samples.

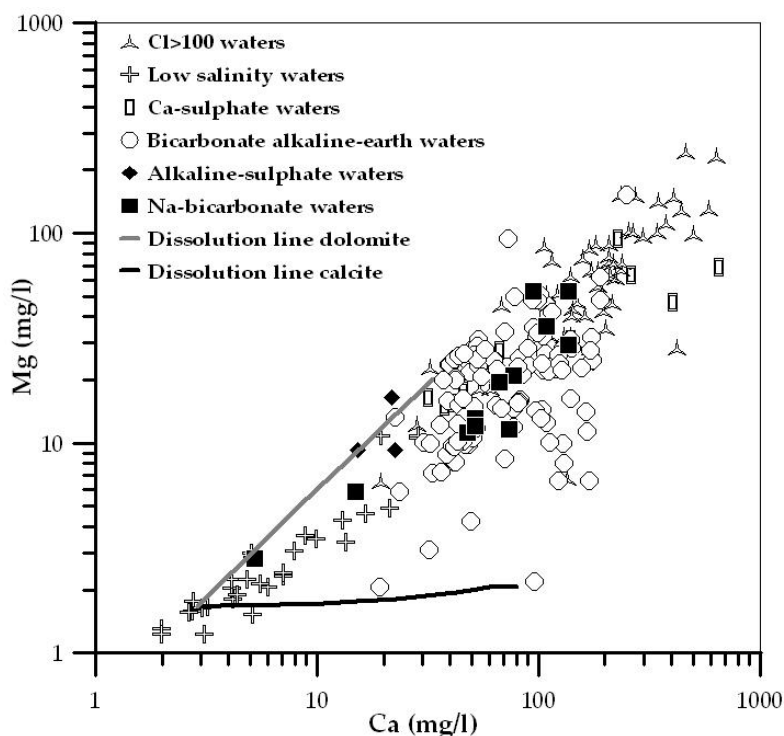


Fig. 4 - Diagram of Mg^{+2} vs. Ca^{+2} . Dissolution lines were computed at the average temperature (14.6°C) by reaction path modelling, carried out by mean of the EQ3/6 software package, version 7.2b (Wolery & Daveler, 1992).

Also we report a study of trace metals in Madonie groundwater. Minor elements (Fe, Sr and Mn) display a concentration range from 0.1 $\mu\text{g/l}$ up to 10 mg/l, whilst trace elements (Ag, Pb, Sb and Cd) are comprised between 0.01 and 0.1 $\mu\text{g/l}$, and ultra-trace elements from 0.01 up to 1 $\mu\text{g/l}$.

The abundance and distribution of minor and trace elements in the Madonie aquifers reflects the variable extent of water-rock interaction, and eventually the presence of additional sources of chemical elements (*i.e.*, anthropogenic pollution).

Correlation diagram of median concentration of metals in groundwaters (C_g , in $\mu\text{g/l}$) vs. average content in carbonates from the Madonie area (C_r , in mg/kg) suggests that carbonate leaching is a controlling factor on groundwater chemistry. This is confirmed by a fair correlation between Ca and Sr and U. However, metal partitioning between aqueous solution and rock-forming minerals also depends on their geochemical behavior. Al, Fe, Mn and Cr are typically depleted in groundwaters, compared to more mobile elements (*e.g.* alkalis), supporting their affinity for the solid phase during water-rock interaction.

The geochemical mobility of chemical elements during the water-rock interaction is related to their speciation, namely the partitioning of an element among its different chemical species. Speciation computation and mineral-solution equilibria are important to understand the processes controlling the abundance and mobility of major and trace elements in the groundwater system. Speciation calculations indicate control of environmental parameters (mostly the pH and redox potential) on trace element mobility in waters. Most water types are typical of oxidant redox conditions (range from 200 to 500 mV), consistent with the superficial groundwater, favouring low aqueous mobility of Fe and Mn; while reducing redox conditions are less frequent, and often found for natural waters with significant residence times in aquifers.

The chemical fractionation of elements during the water-rock interaction processes is closely related to the relative tendencies of primary minerals to dissolve and of secondary minerals to form. The

primary minerals release their own chemical constituents, whereas the secondary minerals behave as a possible sink for the elements. This process was quantitatively evaluated in this work by use of reaction path modelling, carried out by EQ3/6 code adopting the Double Solid Reactant Method (DSRM) (suggestion of Accornero and Marini (2007)). Theoretical simulations were performed in time mode, using as solid reactant either a carbonate solid solution (representative of Mg-calcites of the Imerese units) or a dolomite, each one with its associated special reactant (dissolving at the same rate, as required by the DSRM). Based on these input parameters (also including a guess of the composition of the original solution at in open-system conditions at f_{CO_2} ranging from $10^{-1.5}$ to 10^{-3}), a sequence of model solution were calculated upon increasing extents of reaction (*e.g.*, on increasing values of the overall reaction progress ξ); which were then compared with observed composition of natural waters, highlighting a general agreement.

Fig. 5 shows the cumulative moles of reactant minerals that are dissolved during the model runs, plotted against corresponding pH 's of the model solutions. The diagram highlights that, as the model reaction progresses (the overall progress variable increases from bottom to top in the diagram), the reactant minerals are increasingly dissolved, and the pH increases from acidic conditions at the onset of the reaction, to basic conditions at the end of the simulation. The diagram also shows that, independently on the composition of the reactant (Mg-calcites or dolomite), and at all f_{CO_2} investigated, the pH does not vary significantly in the first part of the simulations, whereas it shows a remarkable shift towards basic conditions in the second part of the runs, when important amounts of the solid reactants are dissolved.

Upon advancement of the irreversible model reaction path, a set of secondary minerals sequentially attains saturation with the model solution, and these “stable” minerals are allowed to precipitate and act as sinks of selected chemicals from the model solution. The sequence of “model” secondary minerals that are formed is similar in all model runs, albeit the actual amount (cumulative moles) of any given mineral formed changes with composition of the reactant and f_{CO_2} . Taking the runs

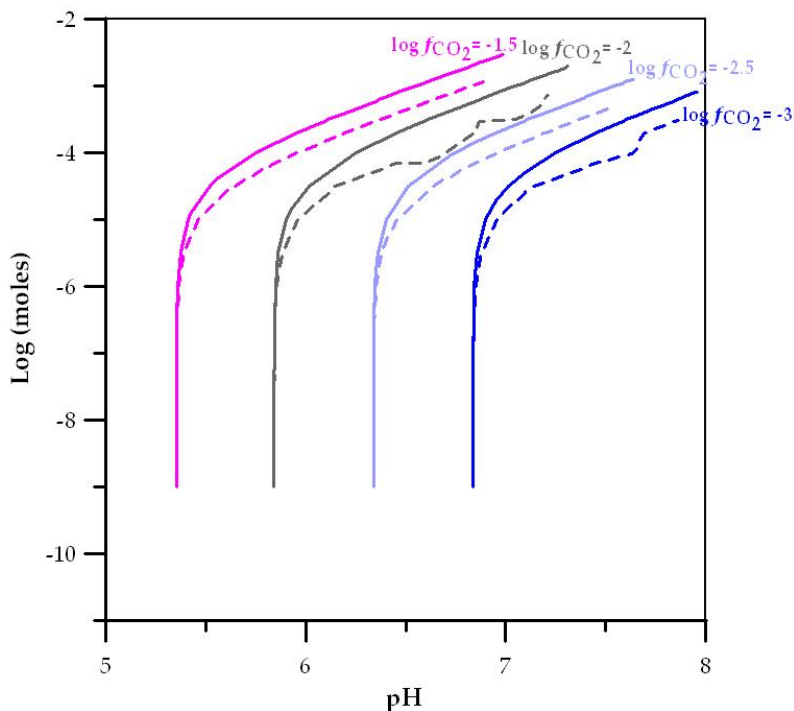


Fig. 5 - Cumulative moles of primary solid phases destroyed through weathering of Mg-calcites (solid lines) and dolomite (dashed lines) at 14.6°C and CO_2 fugacity of 10^{-3} , $10^{-2.5}$, 10^{-2} and $10^{-1.5}$ bar.

calculated at $f_{\text{CO}_2} = 10^{-2}$ bar as reference (Fig. 6), the run calculated with the Mg-calcites as the reactant (solid lines) indicates that kaolinite and ferrihydrite are the first-formed and most abundant secondary minerals along the reaction path; implying that these minerals act as principal sinks for the elements Si, Al (kaolinite), Fe, Mn, Cr, Zn, Co, Cu, and Ni (ferrihydrite).

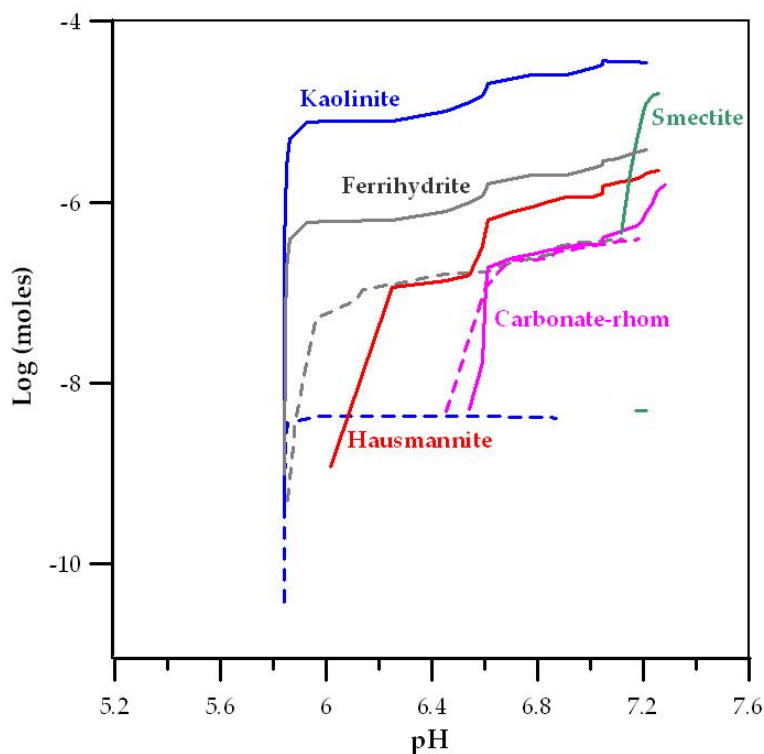


Fig. 6 - Cumulative moles of secondary minerals solid phases precipitated through weathering of Mg-calcites at 14.6°C and CO_2 fugacity of 10^{-2} bar.

Upon increasing extent of reaction, as the pH becomes more basic, the minerals hausmannite, the ortho-rhombic carbonate solid solution, and smectite, also become progressively stable. It is noteworthy that the sequence of secondary minerals formed in the reaction path modelling is consistent with the set of minerals that have shown to attain saturation in natural samples.

In a second set of simulations, also carried out using the DRSM, the presence of fluoro-apatite and pyrite in the mineral assemblage of the leached carbonate rock was also taken into account, revealing that these accessory minerals provide a negligible contribution to the mineralisation of natural waters.

The measurements and simulations presented here represent a step forward in the interpretation of water-rock interaction processes in the carbonate environment, and should contribute to stimulate farther studies in this relevant field of geochemistry.

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