A WATER-ROCK INTERACTION STUDY IN KINETIC MODE FOR THE *ARENARIE DI SAN VITO* FORMATION (SARDINIA, ITALY)

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Abstract

This study, aimed at investigating the role of chemical weathering on the *Arenarie di S.Vito* formation through use of reaction path modeling, enlightens the important role played by apatites, especially during the early steps of water-rock interaction, although they are present in very small amounts in the bedrock. The importance of apatites stems from their relatively fast dissolution kinetics, with respect to relevant silicates. This causes an early release of both major constituents (Ca, P and F) and trace elements, including As.

Introduction

The definition of geochemical baselines is of utmost interest to evaluate the impact of mining activity on different geo-environmental matrices, including waters. Equally important is the understanding of the processes fixing these geochemical baselines. Reaction path modeling (Helgeson, 1968) of chemical weathering can be suitably used to investigate this matter, provided we gather enough data on the solid reactants and products, the aqueous solution and the required boundary conditions. An exercise of this kind was recently carried out in the framework of the project Geobasi, devoted to the geochemical mapping of the Muravera sheet of the new geological map of Italy. The geological formation of the *Arenarie* (which is Italian for sandstones) *di San Vito* is chiefly constituted by micaceous and quartz-rich metasandstones and crops out over half of the area of the entire sheet, especially in its southern part. Thanks to this geological homogeneity, a conspicuous number of stream water and shallow groundwater samples, unaffected by interaction with other lithologies, and soil samples were gathered during the project Geobasi (Cidu et al., 2007; Scarciglia et al., 2007). These data represent the analytical counterparts of the outcomes of geochemical modeling and are needed to test its validity. The main results gathered so far are presented in this communication.

Methods

The chemical and mineralogical characteristics of the *Arenarie di San Vito* were evaluated through the study of two samples, coded ASV and ASV_P1, collected from an outcrop near P. to su Tramatzu and the bedrock of the P37 Geobasi profile, which is located in the Lower Flumendosa Valley near the Muravera town (Sanebidad), respectively. Sample ASV is chiefly made up of quartz, muscovite, a daphnite-rich chlorite, and fluorapatite, whereas the main primary phases of sample ASV_P1 are quartz, muscovite, albite, a clinochlore-rich chlorite, and francolite accompanied by small amounts of galena. Zircon, monazite, xenotime, and Ti oxides are also present as accessory primary minerals in both samples but were not included in geochemical modeling owing to their high durability.

Bulk rock analyses for major oxides and several trace elements were carried out in three different laboratories, i.e., Actalab (Vancouver, Canada), ALS Chemex (Ojebyn, Sweden) and OMAC (Loughrea, Ireland). The stoichiometry of main primary minerals was determined by means of SEM-EDS and EPMA-WDS analyses whereas trace element contents were measured by means of LAM-ICP-MS analysis. These analytical data allowed us to assess not only the composition of the solid reactants, but also the moles of each primary mineral in the two rock samples and their initial reactive surfaces, based on simple geometric considerations and the assumption of an effective porosity of 0.3 and an average grain size of 0.5 mm.

Reaction path modeling of chemical weathering was performed by means of the software package EQ3/6, v. 8.0 (Wolery and Jarek, 2003) in time mode, that is specifying the dissolution rates of primary minerals (adopting kinetic laws consistent with Transition State Theory, TST) and the surface of contact between each solid reactant and 1000 g of aqueous solution. Owing to the assumptions involved in the estimation of these surfaces (see above), they are minimum values, whereas the times computed by the computer simulation represent maximum values. The approach of the double solid reactant, suggested by Marini (2007) for a single reactant, was adopted and extended to all the primary mineral phases whose trace element contents are known. The double solid reactant includes both a solid phase whose thermodynamic properties are known (either a pure mineral or a solid mixture) and a special reactant (*sensu* EQ6), that is any material of known stoichiometry and unknown thermodynamic stability. TST-based dissolution rates can be defined for the former but not for the latter, unless each simulation is run twice: in the first run only pure minerals and solid mixtures are involved, thus obtaining the relative rates for each solid reactant throughout the reaction path; in the repeated run the relative rates are

assigned to the special reactants accompanying each pure mineral or solid mixture. The uncertainty on the recomputed relative rates turned out to be < 4% .

EQ6 simulations were carried out at 15°C, 1.013 bar, fixing f_{CO2} at 10^{-1} and 10^{-2} bar for sample ASV and at 10^{-2} and 10^{-3} bar for sample ASV_P1, in separate runs. These conditions were chosen to reproduce the available geochemical data for waters and soils. In contrast, no constraint was posed on f_{O2}, which is computed by the code during the progressive dissolution of solid reactants.

The initial chemical composition of the aqueous solution was chiefly derived from the rainwater sample collected in south-western Sardinia on March 31, 1988 (Caboi et al., 1990), whose Cl content, 39 mg/L, is close to the median Cl value of the non-polluted stream waters sampled in the Muravera sheet (Cidu et al., 2007). The concentrations of K and trace elements were obtained through dilution of average seawater to a Cl content of 39 mg/L, and SiO_2 concentration was set to 1.04 mg/L, based on the geometric mean of the Capo Carbonara rainwaters (Frau et al., 1996). The initial O_2 content was assumed to be fixed by equilibrium with the atmosphere.

The thermodynamic database data0.cmp of EQ3/6 was modified to include several metal-arsenate and metal-arsenite aqueous complexes (Marini and Accornero, 2007) and some relevant solid phases. Among these, a pivotal importance is played by PO_4-schwertmannite, and to a lower extent AsO_4- and CrO_4- schwertmannite as well. The thermodynamic data of schwertmannites were evaluated assuming that the Gibbs free energy of the exchange reactions involving two schwertmannites and two anions is equal to that of the exchange reactions involving the corresponding Fe(III) minerals and the same anions. Francolite and an Mg-free illite (called illite-K) were also included in the database. The solubility data of the former were taken from Perrone et al. (2002). The Gibbs free energy of the latter, compositionally similar to the illite described by Garrels (1984), was computed assuming ideal mixing between muscovite and pyrophyllite and molar fractions of 0.8 and 0.2, respectively.
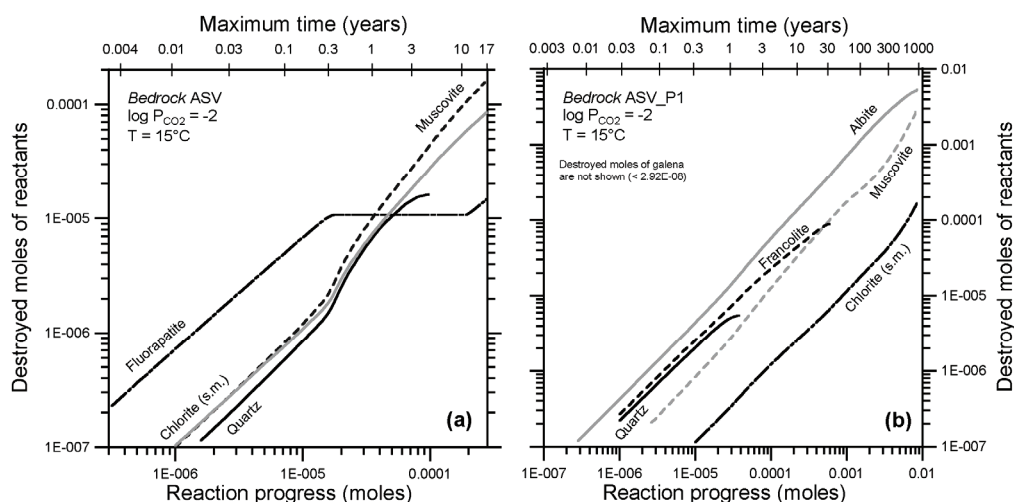
Figure 1. Destroyed moles of primary solid phases during the progressive dissolution of (a) sample ASV and (b) sample ASV_P1 in local meteoric water at the specified conditions.

To avoid the production of undesired secondary solid phase in the EQ6 simulations, only some solid phases (pure minerals and/or ideal solid mixtures) were allowed to precipitate. Product minerals were assumed to attain instantaneous equilibrium, which means to hypothesize that the dissolution of reactants is the rate-limiting step of the overall process.

The rate parameters for the dissolution of quartz and silicate minerals were taken from Marini (2007). The kinetic constants and the reaction orders for the different dissolution mechanisms of francolite and fluorapatite were derived from Guidry and Mackenzie (2003). The kinetics of galena dissolution was described by means of an H^+-governed mechanism (e.g., Zhang et al., 2004) and an Fe^{3+}-promoted mechanism (Rimstidt et al., 1994).

Results and Discussion

In the ASV case (Figure 1a), fluorapatite is the most important primary mineral supplying chemical substances to the system, at least during the early steps of the simulation. Upon attainment of saturation with respect to fluorapatite, the dissolution of muscovite and chlorite prevails over that of quartz. Fluorapatite becomes undersaturated and dissolves again close to the end of the simulation. In contrast, the ASV_P1 case (Figure 1b)

is dominated by albite dissolution throughout the run, with relatively important contributions from the dissolution of quartz, francolite, and muscovite, whereas chlorite and galena have subordinate roles.
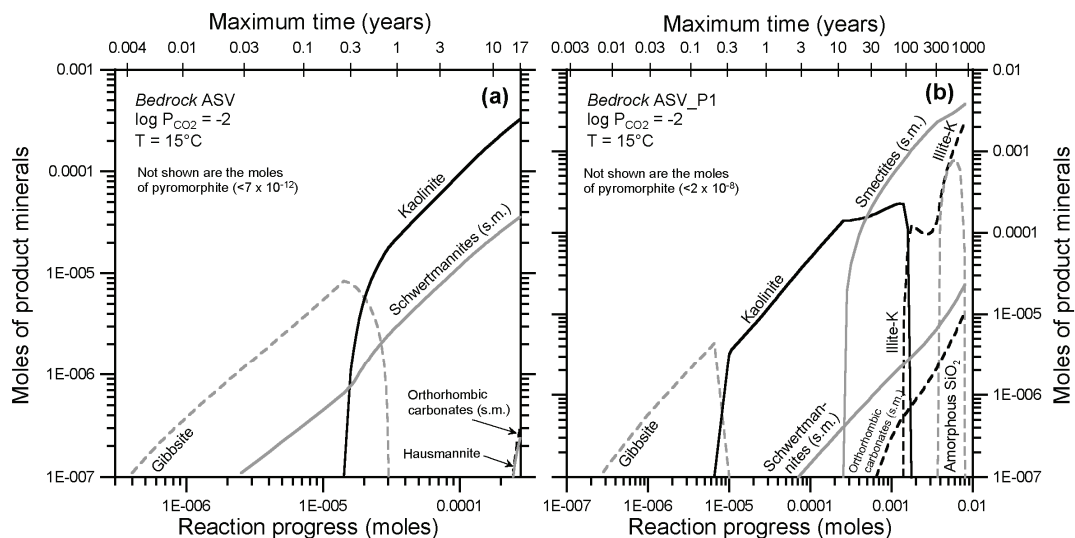
Figure 2. Moles of secondary phases produced during the progressive dissolution of (a) sample ASV and (b) sample ASV_P1 in local meteoric water at the specified conditions.

Based on these differences in the destroyed primary minerals, the differences in the authigenic minerals are not surprising (Figure 2). In fact, smectites and illite-K are produced during the dissolution of samples ASV_P1, whereas precipitation of prevailing kaolinite occurs during the dissolution of samples ASV, under similar values of the reaction progress. The stabilization of smectites and illite-K, in the case of sample ASV_P1, is the obvious consequence of the decomposition of albite and, to a lower extent, of muscovite too, which determines the supply to the system of important amounts not only of Si and Al but also of Na and K, allowing the production not only of kaolinite but of other clay minerals as well.
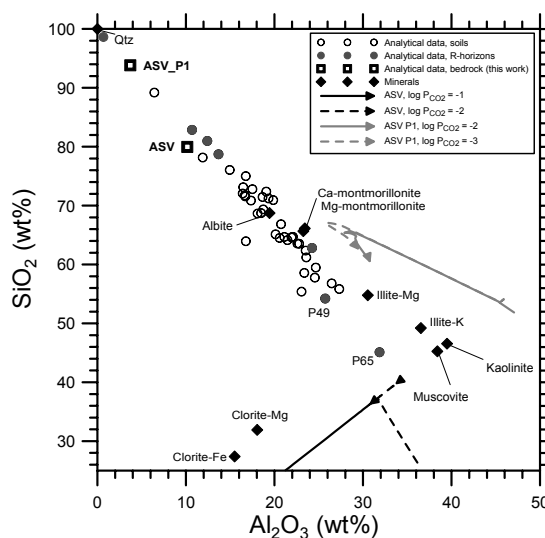

Figure 3. Plot of SiO_2 vs. Al_2O_3 showing the analytical data of soils, bedrock samples and minerals and the results of reaction path modeling for the chemical weathering of samples ASV and ASV_P1.

The moles and the chemical composition of the secondary minerals predicted by geochemical modeling were expressed as weight percentages of major oxides and compared with the analytical data available for soils developed on the *Arenarie di San Vito* formation (Scarciglia et al., 2007) by means of simple binary diagrams, such as the SiO_2 vs. Al_2O_3 plot (Figure 3). In this plot, soil samples define a tight linear trend (R = -0.939),

indicating that the increase in Al_2O_3 concentration in soils, with respect to the content of rocks, is accompanied by a concurrent decrease in SiO_2, as expected during chemical weathering, owing to the preferential removal of SiO_2 operated by the aqueous solutions percolating through the soils (hypothesis 1). Alternatively, variations in Al_2O_3 and SiO_2 concentrations could be attributed to the presence in these soils of bedrock minerals unaffected or partly affected by alteration (hypothesis 2). Besides, some R horizons belonging to soil profiles are Al_2O_3-rich themselves, suggesting the existence of a strong pristine chemical variability within this formation, whose understanding requires further consideration. Although it is not possible to discriminate between the two hypotheses, Figure 3 (and other binary plots, not reported) suggests that the results of geochemical modeling could be consistent with the analytical data of soils, accepting hypothesis 2.

The concentrations of major and trace elements predicted by geochemical modeling were compared with the analytical data available for the stream waters and groundwaters interacting with the *Arenarie di San Vito* formation (with Cl < 45 mg/L), by means of simple binary plots in which alkalinity is taken as reference variable. As an example, the alkalinity plots for Ca and As are shown in Figure 4.
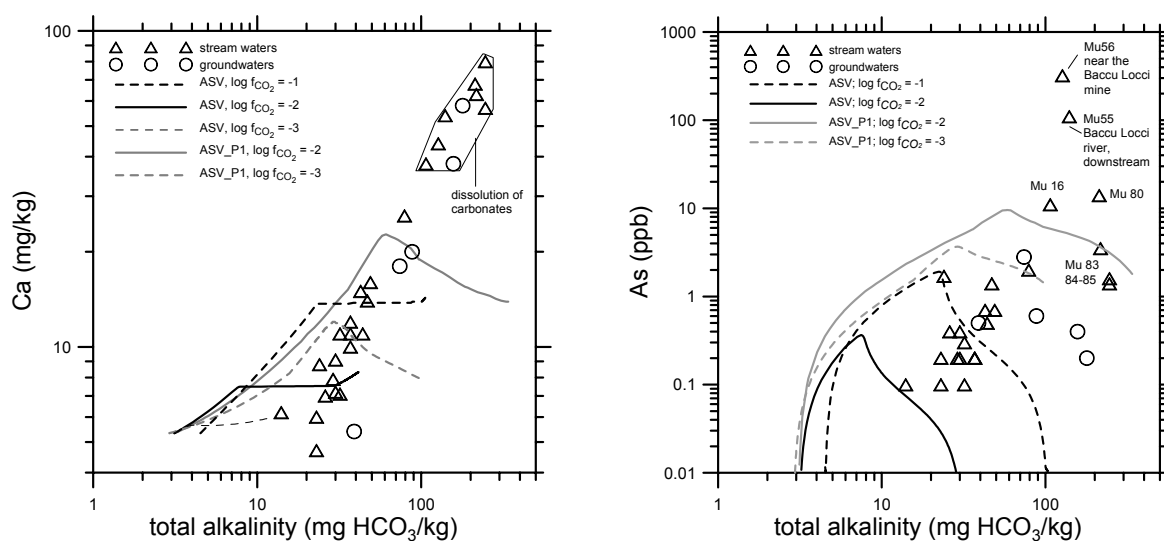
Figure 4. Plots of (a) Ca and (b) As vs. alkalinity showing the analytical data of stream waters and groundwaters interacting with the *Arenarie di San Vito* formation and the results of geochemical modeling for the chemical weathering of samples ASV and ASV_P1.

The main compositional changes of the aqueous solution result from the increase in Ca and alkalinity (Figure 4a), which are initially controlled by the dissolution of fluorapatite and francolite in samples ASV and ASV_P1, respectively. In the case of sample ASV, Ca stabilizes at 8-13 mg/L (depending on f_{CO2}), upon attainment of saturation with fluorapatite, and exhibits a very slight increase near the end of the simulation, when fluorapatite becomes undersaturated (due to PO_4 sequestration in schwertmannites) and dissolves again. In the case of sample ASV_P1, Ca attains maximum concentrations of 12-20 mg/L, at saturation with francolite, and decreases afterwards owing to sequestration in smectites rich in Ca-montmorillonite. In contrast to the previous case, the aqueous solution remains oversaturated with apatite (francolite) in the late steps of the simulation, due to the high concentrations of dissolved PO_4, whose sequestration in schwertmannites is relatively limited.

Theoretical trends reproduce satisfactorily the analytical data for the water samples collected in the southern part of the study area, whereas the samples collected in its northern part have higher Ca and alkalinity, because of interaction with carbonate rocks, probably resulting from the erosion of the *Monte Cardiga* formation.

According to the geochemical model, As is released through weathering of primary minerals (chiefly the apatites and to a lesser extent the phyllosilicates, especially ripidolite) and is sequestered into the solid mixture of schwertmannites. This is mainly composed by the PO_4 endmember, apart from the initial steps of the simulations, in which the importance of the AsO_4 component is similar to or even higher than that of the PO_4 endmember. In the ASV runs (Figure 4b), aqueous As attains maximum concentrations of 0.3 - 1.5 ppb and decreases afterwards below the analytical detection limit (<0.01 ppb) owing to incorporation in the solid mixture of schwertmannites, representing the second most important authigenic mineral after kaolinite. In the ASV_P1 runs, dissolved As increases up to 3 - 10 ppb and experiences a slight late decrease, due to limited sequestration in precipitating schwertmannite. The results of geochemical modeling reproduce satisfactorily the analytical data

for the waters interacting with the *Arenarie di S.Vito* formation, whereas the few samples receiving mine drainage are characterised by higher As contents.

Conclusions

One of the most interesting and innovative results of this study, aimed at investigating the role of chemical weathering on the *Arenarie di S.Vito* formation, is the pivotal role played by apatites, especially during the early steps of water-rock interaction, although these minerals are present in almost negligible amounts in the two considered rock samples: 0.08 and 0.145 wt. % for ASV and ASV_P1, respectively. The importance of apatites is due to their relatively fast dissolution kinetics, with respect to that of relevant silicate minerals (white micas, chlorites, quartz and albite), especially in the case of fluorapatite. This comparatively high reactivity brings about an early release not only of major constituents (Ca, P and F), but also of trace elements, such as Al, Si, Cl, Sr, Mn, Fe and of course As, whose fate is of utmost interest because of its toxicity for living beings. This considerable release of P and, to a lesser extent, of As to the aqueous solution has caused several problems in performing reaction path modeling of water-rock interaction, due to the poor knowledge of both the stability constants of metal-arsenate and metal-arsenite aqueous complexes and the thermodynamic stability of P-bearing secondary minerals, whose precipitation is a *sine qua non* condition to limit the dissolved PO_4 concentration into a range of values comparable with that measured in natural waters. Both gaps have been partly filled, in the framework of this study, but further researches are urgently needed for a better understanding of this important matter.

Acknowledgements

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