

Water–Rock Interaction Processes Seen through Thermodynamics

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1811-5209/10/0006-0305\$2.50 DOI: 10.2113/gselements.6.5.305

The chemical composition of groundwater results from the reaction of mineral dissolution and precipitation. We can use the thermodynamic approach to predict water composition under conditions where water and newly formed minerals are in equilibrium. Although some minerals exist in a state of equilibrium with water, other minerals are always unstable. In the latter case, we can evaluate the extent of the overall irreversible mass transfer between minerals and water to quantify the mineral surface area participating in the water–rock interaction. This parameter is fundamental to basic and applied research in areas such as the geological sequestration of CO₂ and the safe geological storage of waste.

KEYWORDS: water–mineral interaction, thermodynamics, waste storage, CO₂ sequestration

INTRODUCTION

Water and other subsurface fluids are fundamental to several geological processes because they are always present in rock systems. Although the term *water–rock interaction* includes many possible processes in nature, such as river waters smoothing down rocks over time and ocean waves crashing onto a rocky shoreline, for geologists the term refers to the dominant chemical and thermal exchanges (reactions) that occur between groundwater and rocks.

Natural water interacting with rocks induces both alteration of thermodynamically unstable minerals and formation of new, stable minerals. Water composition reflects the balance between the two processes. The reactions that occur during these interactions not only cause transformations of minerals but also affect the chemical composition and the quality of water above and below the Earth's surface.

Using the thermodynamic equilibrium approach, it is possible to predict the evolution of water composition when macroscopic variables, such as temperature, pressure and affinity (also called the driving force of the reaction), can be modelled by simple laws with the help of kinetic equations. In this article I will discuss how evaluating the rate of the geochemical interaction between water and minerals can be used to predict the environmental impact of waste deposits over time.

BALANCING GEOCHEMICAL MASS TRANSFER IN WATER SYSTEMS

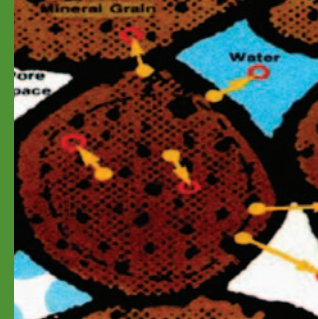
Garrels and Mackenzie (1967) explained that water composition can be described by a mineralogical transformation 'budget', balancing dissolution and precipitation. In the

particular case of granites in the Sierra Nevada, they showed that the concentration of each dissolved element results from the balance between mineral dissolution in the rock and precipitation of newly formed minerals under stable thermodynamic conditions. In their model, they estimated the contributions of dissolution and precipitation for each dissolved element by assuming that the sources of dissolved Na, Ca and Mg were albite, anorthite and mica, and that the sources of dissolved K were feldspar and mica. By identifying the newly formed clay minerals (kaolinite, smectite or, more rarely, gibbsite), they estimated the amount of dissolved Si and Al from the dissolution–precipitation net mass balance. Garrels and Mackenzie (1967) assumed that the observed precipitation of kaolinite or secondary minerals is the cause of the low amount of aluminium in natural water. However, as emphasized by Garrels and Mackenzie (1967), this simple and elegant mass balance representation cannot be applied to the majority of natural conditions because it is difficult to quantify the exact composition of minerals that are inherently chemically heterogeneous.

THE THERMODYNAMIC EQUILIBRIUM MODEL

The mass budget approach was interpreted by Helgeson (1968) as an energy budget. Helgeson assumed that the instability of the minerals in the parent rock (mainly igneous and metamorphic rocks) at the Earth's surface leads to a 'natural' dissolution process. Since water can reach equilibrium with newly formed minerals, he estimated the saturation index of the fluids with respect to newly formed clay minerals by calculating the ratio between the solute ionic activity product and the mineral solubility or stability constant. This approach assumes that there is an initial mineral dissolution resulting from the interaction with rainwater, where each dissolved element is assumed to be 'soluble' (or not controlled by newly formed minerals). At this stage of the process, the water is undersaturated with respect to clays or oxide minerals and the activity (effective concentration) of the dissolved ions results from the dissolution of the unstable minerals in the parent rock. Oxyhydroxides of aluminium and iron are very sparingly soluble, however, so they readily precipitate. In a second stage of the process, the activity of these dissolved elements is 'controlled' by the formation of new minerals. The silicon present in the water and originating from dissolution of aluminosilicate minerals in the parent rock may precipitate, forming oxides (SiO₂) or aluminosilicates (clay minerals) if the water is oversaturated with respect to these

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minerals. The chemical evolution of the water composition in equilibrium with different minerals can be represented by activity diagrams (Fig. 1).

Although the thermodynamic approach has a rigorous theoretical basis, caution must be used when applying it to real conditions for the simple reason that the model uses fixed hypothetical Gibbs free energy values for clay minerals, whereas naturally occurring clays have heterogeneous compositions, and therefore, can have significantly different thermodynamic properties. Nevertheless, we can use theoretical activity diagrams to represent the evolution of the mass transfer process, although these diagrams must be considered approximate.

THE 'CLOSED' SYSTEM

Water-rock systems with a very low water-to-rock ratio can be considered to be closed systems. In such systems, the amount of dissolved chemical elements is very low compared to the amount of those elements present in the parent rock, and equilibrium is achieved through a limited number of internal processes. Here, the water acts as a 'conveyor' of matter from unstable weathered minerals to the newly formed stable minerals. For this reason, water has been defined as the vector of mineralogical transformation in closed systems (Giggenbach 1984; Zuddas et al. 1995).

Whatever the equilibrium state between water and newly formed minerals is, ion activities in water are controlled by various mineralogical buffers (mineral associations that stabilize the water composition). The water composition in equilibrium with the stable mineral assemblage must satisfy the Duhem postulate, according to which the state of equilibrium in a closed system of fixed size is determined once only two properties are fixed (be they intensive or extensive – see glossary for definitions of these and many other terms in Richet et al. 2010 this issue). In a complex system with a large number of constituents, it is difficult to identify and characterize independent reactions. In geochemical systems, if the number of major elements can be limited to 12 (Si, Al, Na, K, Ca, Mg, Fe, S, Cl, C, H, O), the number of potential minerals containing these elements is extremely large. The number of independent chemical components can be estimated from a matrix defined by the number of atoms of every chemical element contained in a mol of mineral constituents according to the Brinkley rule (Michard 1987).

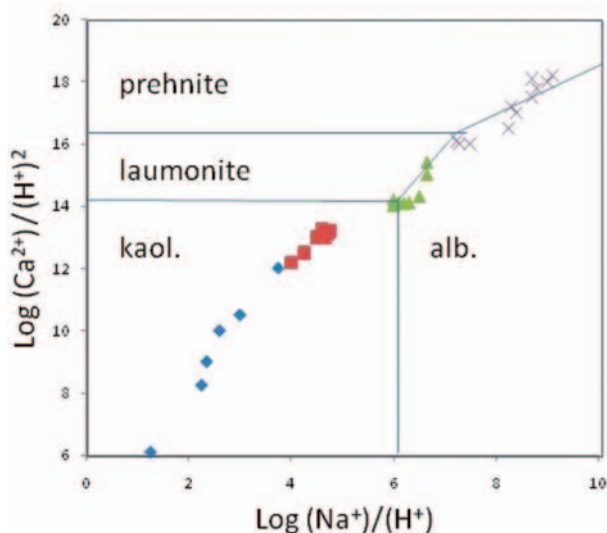


FIGURE 1 Activity diagram, $\log (\text{Ca}^{2+})/(\text{H}^+)^2$ versus $\log (\text{Na}^+)/(\text{H}^+)$, illustrating how water composition depends on the minerals with which the water is in equilibrium. The coloured symbols correspond to measured compositions of water groups (Grimaud et al. 1990). Mineral stability fields are calculated by the thermodynamic equilibrium approach.

As previously mentioned, chemical elements can be qualified as *controlled* (water incompatible) or *mobile* (water compatible). Controlled elements have an effective concentration in water high enough to be constituents of all newly formed minerals, while mobile elements are characterized by a strong affinity for water. In the case of mobile ions, the activity is not controlled by the solubility of newly formed minerals. Typically, in crystalline rocks, silica and aluminium are controlled elements, whereas chlorine and occasionally sulfates (present in rather low concentrations in both rock and incoming water) are generally mobile. The controlled versus mobile nature of a given element is not an intrinsic feature but rather is a function of the system characteristics. At the beginning of the interaction, when dissolution of the parent mineral is predominant, all dissolved ions behave as if they were mobile. As soon as the water becomes saturated with respect to mineral phases like Al-Fe oxyhydroxides, silica polymorphs or clay minerals, some of the elements become controlled by the solubility of these newly formed minerals.

Even in the case of water solutions with a high ionic strength, the thermodynamic description of the system is based on energy conservation, solution electrical neutrality and mass conservation. Contrary to controlled elements, which participate also in the mass action law, mobile ions participate only in the electroneutrality equation. As a result, their concentration cannot be deduced from water-mineral equilibrium constants, but it can be estimated if the amount of reacting water and the concentrations of the mobile ions in the rock are known. The ratio between these parameters is the water-rock ratio. Its determination is a real challenge to geologists in the field. If the mobile ion concentrations are known parameters (like temperature and pressure), the equilibrium water composition can be calculated with the assumptions that (1) the algebraic sum of the ionic charges representing the mobile and controlled ions is zero (electroneutrality equation) and (2) the phase rule is observed, so that the number of equilibrium minerals is equal to the number of controlled elements. A theoretical calculation (Fig. 2) shows that the water composition in equilibrium with some minerals (low-temperature albite, adularia, calcite, muscovite, quartz and prehnite at 60 °C) changes significantly as a function of the chlorine concentration. In particular, the concentrations of several major controlled elements increase when the chlorine concentration increases.

Geological Storage of Waste

Today, it is very important to predict the long-term stability of waste stored in the geological environment. From this perspective, characterizing the deep fluid environment of a potential storage site and understanding the fluid's genesis and evolution are fundamental to preventing the migration of toxic elements into the rock and groundwater. The ideal geological site for waste storage is one that behaves as a closed system. For this purpose, the composition of the deep waters in granite, in clay mines and at geothermal sites can effectively address the chemistry of confined systems.

In a study of the very old waters of the abandoned Stripa mine in Sweden, Grimaud et al. (1990) showed that different mineralogical buffers can be found at different chlorine concentrations when waters have the same temperature. Water at the Stripa mine has reacted with granitic rocks at low temperatures over a long period of time, probably for more than 20,000 years. After careful sampling and analysis of major and trace elements and isotope ratios by an international working group (Nordstrom et al. 1989; Moser et al. 1989; Fontes et al. 1989), Grimaud et al. (1990) divided the Stripa water into 4 mineral buffer groups: water with low pH (~7), with only Al and Si controlled; water with Ca, Mg and K controlled, but not Na; water with pH ~9 controlled by chalcedony, kaolinite,

albite, laumontite, adularia and calcite; and a more mature water with pH ~10, controlled by the same mineral association, except that kaolinite is replaced by prehnite.

Waters from several other cratonic areas, like the Canadian and Scandinavian shields, and from areas in western Europe underlain by Palaeozoic rocks behave according to the equilibrium model described by Grimaud et al. (1990). These waters are in equilibrium, yet buffered, with newly formed stable minerals under closed-system conditions. These naturally occurring closed systems are of particular interest as potential sites for the storage of chemical and nuclear waste since they are both closed and in equilibrium even after the deposition of waste. The thermodynamic approach reliably predicts water composition in systems governed by acid–base reactions, which are very rapid. Unfortunately, this approach does not work when redox reactions, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ transformations, occur because the slowness of these reactions prevents equilibrium from being reached in natural contexts (Michard et al. 1996; Appelo and Potsma 2007). Although redox equilibria are absent in natural systems, redox equilibrium modeling can be a useful tool. Although the models are not significant quantitatively, they are qualitatively instructive.

THE 'OPEN' SYSTEM

In open systems, the pH of water generally reflects the equilibrium CO_2 partial pressure that results from the ionic dissociation of carbonic acid. This acid is quite often the most abundant acid–base species. Because of the rock interaction, water composition changes from rain to groundwater and pH increases by 2–3 units. Thus pH variations may trace the advancement of the water–rock interaction, which can be considered as an acid–base titration: the weak acid is CO_2 (or carbonic acid) and the strong base is the rock.

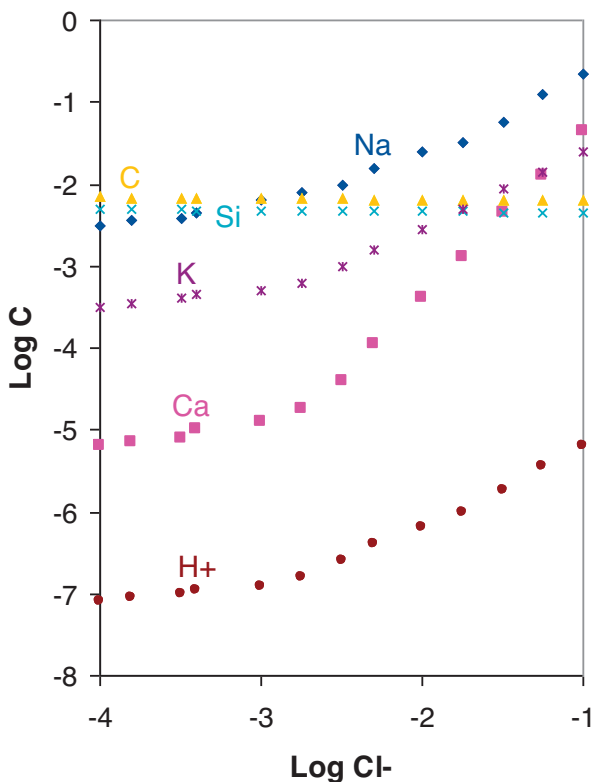


FIGURE 2 Influence of chlorine concentration on the composition of water in equilibrium with albite, adularia, calcite, muscovite, quartz and prehnite at 60 °C (Michard 1987). Points represent the logarithmic concentration (in mol/kg) for the element or the activity of H^+ .

From a thermodynamic point of view, open systems can be considered to be divided into discrete, neighbouring subsystems. The evolution of the water composition can thus be represented by a function called the degree of advancement of the process, ζ , using equilibrium conditions. Mathematically, this function is a truncated Taylor expansion representing the discrete set of open subsystems labelled by a coordinate vector (Lichtner 1985; Marini et al. 2000). The variable ζ is generally related to the length of time the water–rock interaction process has been going on. This age parameter can usually be estimated from radiometric dating based on tritium decay. Tritium (^3H) has a half-life of 4500 days; its abundance decays exponentially with time and is, in the simplest case, approximately related to ζ . If a linear relationship between analysed pH values and computed ζ is observed, the overall water–rock interaction process can be considered as the result of continuous rock titration (dissolution of Al-silicates and carbonates) driven mainly by the conversion of CO_2 to HCO_3^- and by the connection of natural waters with different CO_2 reservoirs. Since the majority of surface and subsurface waters are very close to saturation with respect to kaolinite and quartz (or other silica polymorphs), dissolved silica and aluminium are controlled by these two equilibrium constraints throughout the entire process. Consequently, the evolution of the fluid chemistry can be reconstructed from dissolution reaction paths calculated based on the degree of advancement of the irreversible mass-transfer process (Marini et al. 2000).

During water–rock interaction it is important to evaluate what part of the rock is interacting with water. Water–mineral reactions take place at the surface of the mineral in contact with water. However, only the part of the mineral surface that is in contact with the circulating waters participates in the reaction. This mineral surface is often called the 'reactive surface' and its area is difficult to estimate in natural conditions. Marini et al. (2000) propose a method for estimating the reactive surface area of the various minerals reacting with water by a mathematical model based on the calculation of the ζ functions. An experimental calibration of the Marini methodology was recently verified by Scislewski and Zuddas (2010). FIGURE 3 represents an estimation of the reactive surface area of albite during laboratory interaction of a granite-like rock with carbon dioxide–saturated fluids. The reactive surface area is not constant during water–rock interaction but, on the contrary, changes dramatically by 3 to 4 orders of magnitude during the investigated reaction time. These studies suggest that the reactive surface area of the mineral does not remain constant during the water–rock interaction processes. The decreasing reactive surface area observed in FIGURE 3 can be explained by the formation of new minerals

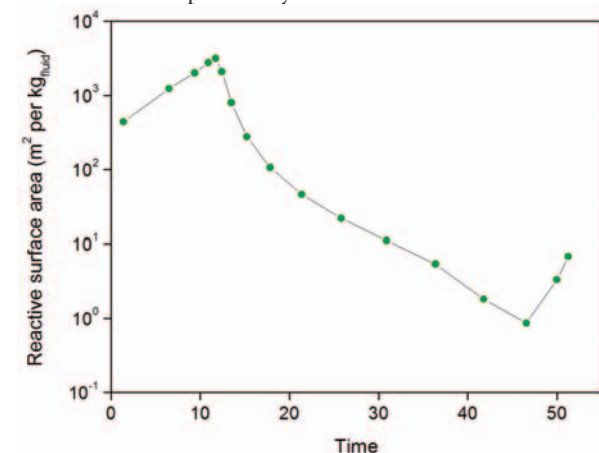
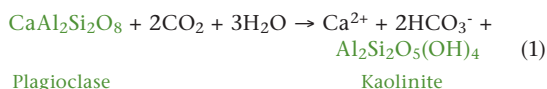


FIGURE 3 Evolution of the reactive surface area of albite as a function of time (years) recalculated from an experimental simulation of the interaction of granite-like rock with CO_2 -saturated fluids at 22 °C. DATA FROM SCISLEWSKI AND ZUDDAS 2010

coating the dissolving surfaces of the albite, thereby decreasing the surface exposed to the interacting water. The evaluation of the mineral reactive surface area during the water–rock interaction process is still a controversial topic in basic and applied research.

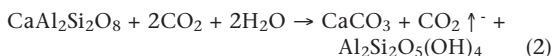
Geological Sequestration of CO₂

The geological sequestration of carbon dioxide is accomplished by artificially injecting CO₂ into natural aquifers. When CO₂ is introduced into groundwater, the initial pH decrease of the groundwater intensifies mineral-dissolution reactions. As soon as minerals begin to dissolve, water acidity is neutralized by the formation of bicarbonate ions. For example, in the case where anorthite (calcic end-member of the common mineral plagioclase) is dissolved and water reaches equilibrium with kaolinite (a typical mineral that buffers aluminium and silica in natural waters), we have:



This reaction shows that as mineral dissolution proceeds, CO₂ sequestration takes place by forming bicarbonate (HCO₃⁻) ions. The amount of anorthite surface area able to react is the main limiting parameter of CO₂ sequestration. The success of greenhouse gas reduction technology therefore depends on the available surface area of the minerals participating in the dissolution reaction (Friedmann 2007).

When water reaches equilibrium with calcite and a carbonate mineral is formed, the reaction becomes:



Equation (2) shows that when the concentrations of divalent ions such as calcium (or magnesium, or sodium, or iron) are controlled by the precipitation of carbonate minerals (here calcite), less gaseous CO₂ is sequestered: in this reaction, 2 moles of CO₂ are consumed (left part of the equation) and one mole is produced. This indicates that when mineral carbonation takes place, the overall fixation of gaseous CO₂ is reduced, as observed in nature and in the laboratory (Giammar et al. 2005; McGrail et al. 2006). Mineral carbonation is thermodynamically favoured

but proceeds slowly. Both in nature and in several artificial carbonation scenarios, the metal-silicate mineral dissolves and a metal carbonate may precipitate. In most cases, the dissolution rate of the silicate phase is slower than the corresponding carbonate precipitation rate. The key to optimizing sequestration is to accelerate mineral dissolution. Preliminary results (Scislewski and Zuddas 2010) suggest that changes in the amount of carbon sequestration in the mineralogical form are related to the amount of newly formed minerals that coat the dissolving mineral surface and in turn control the overall water–rock interaction process.

CONCLUSIONS

When rock minerals are exposed to acidified water, they may dissolve to produce clay minerals and zeolites or other small-sized minerals, such as insoluble oxides, hydroxides and colloidal suspensions. The chemical reactions that take place during these transformations can be used to define the conditions required for equilibrium when both reactants and products are stable. The application of the equilibrium thermodynamic laws allows us to define the environmental conditions under which each mineral is stable in a given compositional system and thus to potentially predict what happens to minerals when they are exposed to conditions outside their own stability field. The chemical composition and quality of water can be predicted using the solubility limits of certain mineral components, which may play a significant role in the composition of natural aqueous solutions.

One of the main questions concerns the effect of natural or artificial disruptions on the stability of the mineralogical buffers controlling the activity of the ions at equilibrium. This question may be solved when we have reliable analytical tools allowing us to evaluate how disruptions change the system entropy in natural water–rock interaction systems over time.

ACKNOWLEDGMENTS

This article benefited from discussions with Prof. G. Michard, Prof. D. Grimaud and Dr. P. Toulhoat and from a decade of participation in sponsored and informal water–rock interaction activities. I thank my research group for their support and thought-provoking discussions. ■

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