

Geochemical modeling of diagenetic reactions: a thermodynamic and kinetic approach

B. Madé

*Ecole Nationale Supérieure des Mines de Paris, Centre
d'Informatique Géologique, URA CNRS 1367, F-77305
Fontainebleau Cedex, France*

**M. Ben Baccar
B. Fritz**

*Centre de Géochimie de la Surface, CNRS, F-67084 Strasbourg
Cedex, France*

The kinetic and thermodynamic geochemical model KINDISP (KINetic of DISsolution and Precipitation) describes the interactions between minerals and aqueous solutions. The general laws included in the model are based on the Thermodynamics of Irreversible Processes. KINDISP model has been used to simulate the diagenetic albitization of K-feldspar and plagioclase in sandstone reservoirs in terms of fluid chemistry and temperature.

Introduction

Weathering and hydrothermal processes are always very complicated thus, geochemical codes have been developed to simulate the water-rock interactions. The first generation of codes is based on purely thermodynamic laws without reference to the time dependence of chemical reactions and then the dissolution path calculations refer to the irreversible dissolution of reactants and reversible precipitation of products. The system evolution is followed according to the reaction progress ξ which has been introduced for chemical systems by Gibbs.

Recent experimental studies on the kinetics of mineral dissolution have allowed us to take into account dissolution rate data for the major minerals (silicates, carbonates). More recently, a new geochemical code has been generated, which is based on thermodynamic potential and kinetic laws. The system evolution is followed according to the reaction time.

Description of geochemical code

In the KINDISP code (KINetic of DISsolution and Precipitation), in addition to the potential evolution laws based on thermodynamic principles (Fritz, 1981), kinetic laws are introduced to simulate the water-rock interactions (Madé, 1991). The general laws used to characterize the mineral dissolution and precipitation kinetics are deduced from the thermodynamics of irreversible

processes and theoretical works applied to geochemistry (Lasaga, 1981; Aagaard and Helgeson, 1982; Steefel and Van Cappellen, 1990). In KINDISP, the dissolution and precipitation of minerals are controlled either by aqueous molecular diffusion of elementary entities or by surface reactions (adsorption-desorption of reactant and/or product species) (Madé and Fritz, 1992).

The precipitation constants can be determined from the thermodynamic equilibrium constant and the constant of the intrinsic dissolution rate by using the principle of microscopic reversibility which is applicable if the global reaction is taken to be reversible. Thus, for a total reversible reaction with n opposed elementary reactions ρ the microreversibility principle is written:

$$K_{\rho_{1n}} = \prod_{x=1}^n \frac{\overrightarrow{k}_x}{\overleftarrow{k}_x}$$

where $K_{\rho_{1n}}$ is the thermodynamic equilibrium constant of the global reaction ρ_{1n} ; \overrightarrow{k}_x is direct kinetic constant of elementary reaction and \overleftarrow{k}_x is inverse kinetic constant of elementary reaction. Thus, for a mineral m , we can write:

$$\log k_{pm} = \log k_{dm} - \log K_m$$

with k_{dm} and k_{pm} , dissolution rate constant and precipitation rate constant, respectively.

Application

Diagenetic albitization of K-feldspar and plagioclase is a common diagenetic phenomenon in numerous sedimentary basins. The geochemical code KINDISP is used to simulate these albitization reactions in terms of fluid chemistry and temperature. The model shows that albitization of K-feldspar is enhanced by increasing temperature, and is most likely to occur at 120–150°C. Kinetic modeling of this reaction predicts

the instability of quartz, which is generally considered a K-feldspar albitization product. Albitization of plagioclase is shown to decrease with increasing temperature. For low p_{CO_2} conditions it probably occurs between temperatures of 60 and 100°C, while for higher values of p_{CO_2} it continues at temperatures greater than 100°C.

The water-rock interaction modeling approach has confirmed at a given $a_{\text{K}}/a_{\text{Na}}$ ratio, the albitization of K-feldspar is enhanced by increasing temperatures. With a closed-system approach the kinetic modeling of albitization reactions suggests a short time span. These reactions seem to be related to the removal of reacting solution and thus an opening of the system to circulating solutions (Ben Baccar *et al.*, 1993).

Conclusions

The geochemical model KINDISP has been used to simulate a number of natural or induced phenomena of which the following are some examples:

–modeling of the alteration of granite by meteoric water at 25°C which, by comparison between the chemistry of the simulated water and that of the natural water, has made it possible to estimate the reaction time needed by the latter to reach its present composition (Madé and Fritz, 1990);

–modeling of the formation of bauxites and ferruginous crusts providing the means of estimating the time needed for the formation of laterite layers (Del Nero, 1992);

–modeling of the alteration of granite at higher temperatures (100 and 150°C) for a study of radioactive waste disposal in a granitic medium (Madé and Fritz, 1993);

–modeling of experiments on hydrothermal alteration of sandstone (Bertrand, 1992) and of glass for nuclear disposal, R7T7 (Advocat, 1991), which permitted an initial validation of the model;

–recently, the strontium isotopes ($^{86}\text{Sr}/^{87}\text{Sr}$) were included in the KINDISP model, thus making it possible to describe the origin of an

aqueous solution on the basis of its isotopic signature (Fritz *et al.*, 1992).

References

- Aagaard, P. and Helgeson, H.C. (1982) *Amer. Jour. Sci.*, **282**, 3, 237–85.
- Advocat, T. (1991) Les mécanismes de corrosion en phase aqueuse du verre nucléaire R7T7. Ph-D dissert., Strasbourg, 211p.
- Ben Baccar, M. Fritz, B. and Madé, B. (1993) *Jour. Sed. Petrol.*, **63**, 6, 1100–9.
- Bertrand, C. (1992) Etude expérimentale et modélisation thermodynamique et cinétique de l'altération hydrothermale d'un grès. Ph-D dissert., Strasbourg, 188p.
- Del Nero, M. (1992) Modélisation thermodynamique et cinétique de la formation des bauxites et des cuirasses ferrugineuses. Ph-D dissert., Strasbourg, 219p.
- Fritz, B. (1981) *Mem. Sci. Geol.*, **65**, Strasbourg, 197p.
- Fritz, B., Richard, L., and Mc Nutt, R.H. (1992) Geochemical modeling of Sr isotopic signatures in the interaction between granitic rocks and natural solutions. In: *Proc. Intern. Symp. WRI-7*, (Kharaka, Y. and Maest, A. eds.), Balkema, Rotterdam, 927–30.
- Lasaga, A.C. (1981) Rate laws of chemical reactions. In: *Kinetics of Geochemical Processes*, (Lasaga, A.C. and Kirkpatrick, R. eds.), *Rev. Mineral.*, **8**, 1–68.
- Madé, B. (1991) Modélisation thermodynamique et cinétique des réactions géochimiques dans les interactions eau-rochebl. Ph-D dissert., Strasbourg, 308p.
- Madé, B. and Fritz, B. (1990) *Chem. Geol.*, **84**, 1–4, 100–4.
- Madé, B. and Fritz, B. (1992) Theoretical approach and modelling of the dissolution and precipitation of minerals under kinetic control. In *Proc. Intern. Symp. WRI-7*, (Kharaka, Y. and Maest, A. eds.), Balkema, Rotterdam, 101–5.
- Madé, B. and Fritz, B. (1993) *Proc. Intern. Conf. Safewaste' 93, SFEN*, 3, 430–43.
- Steeffel, C.I. and Van Cappellen, P. (1990) *Geochim. Cosmochim. Acta*, **54**, 10, 2657–77.