

Transformation reactions in phyllosilicates at low temperature: experimental approach

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Introduction

Clay minerals in sediments and sedimentary rocks, stable at Earth surface conditions, evolve to other phyllosilicates by the effect of higher temperature and pressure during diagenesis and metamorphism. New mineral assemblages are attained according with the new p,T,t conditions, under the of kinetic and thermodynamic control. Thermodynamics establishes which minerals are stable or in equilibrium at a determined pressure and temperature. However, most mineral assemblages do not correspond to equilibrium conditions, as reaction time is not long enough to reach equilibrium. In such cases, minerals react under kinetics control. In general, temperature and time ratio establish if the process is either under kinetic or thermodynamic control. High temperature favors equilibrium and low temperature conditions needs longer reaction time.

Low temperature reactions are usually controlled by kinetics. The system does not reach the most stable phases, but those more close to the initial minerals. The intermediate minerals act as precursors of the following ones and the system evolves gradually to the final state. The reaction path is a succession of intermediate states of apparent equilibrium. This behavior is described as the Oswald's step rule (Ostwald, 1887).

Experimental mineralogy and geochemistry provide a useful tool to the understanding of the mechanism of low temperature reactions. Laboratory experiments allow scientist to unravel the successive stages of a complex reaction. Mimic nature is not a simple task, as Earth crust processes are complex and many different variable are involved, as temperature, pressure, time, activity of water, gases and dissolved components. Although the experimental approach is a simplification of the natural reaction, this method permits to focus the interest on a particular aspect and to perform a detailed monitoring of the system reactivity and transformation.

In this study, we try to provide several examples to illustrate the contribution of experimental mineralogy and geochemistry to the understanding of the transformation of clay minerals under low temperature conditions.

Methods

Experimental studies of mineral transformation reactions are usually called alteration and synthesis experiments. They consist of the treatment of a solid with a solution under specific conditions of temperature, pressure and time. Special reactors are chosen for heating and pressurizing the system.

Depending on the aim of the study, starting materials can be ground rocks or minerals, oxides mixtures, glasses, ignited gels and hydrous gels. Amorphous materials as glasses and gels are more reactive than minerals or oxides. Transformation of minerals and oxides resembles in a greater extension the Earth crust environments.

The composition of the reacting solution is one of the keys of the experiment success, through the control of many parameters. The first one is pH, not only the initial pH, but also how pH can vary during the aging process. The pH influences the solubility of elements as well as minerals. Other variables to monitor are the concentrations of cations (e.g., Ca, K, Al, Fe, silica, etc.) and anions (Cl, SO_4^{2-} , CO_3^{2-} , etc.).

Temperature exerts a strong control on the reaction and, in most cases, it establishes if the system is under thermodynamic or kinetic control. Higher temperatures favor equilibrium and lower temperatures allow intermediate metastable products to form under a kinetic regime. Three ranges can be established according to temperature:

- < 100°C: very low temperature. Pressure is fixed to 1 atm.
- 100 – 250°C: low temperature hydrothermal conditions; usually pressure is the corresponding water vapor pressure.
- > 250°C: medium to high temperature experiments; pressure must be controlled independently of temperature.

Reactors of increasing complexity are used for higher temperature and pressure. Plastic containers are used below 250°C (Teflon). Below the water critical point, pressure can be fixed to saturation water pressure at the selected temperature.

The last and most critical variable to consider is time. Laboratory experiments and natural mineral transformations occur in different time frames. Normal tests last for days or months, but transformation of minerals under diagenesis or low temperature conditions need at less thousands of years to completion. Time and temperature are combined to mimic Earth crust reactions in laboratory. Increasing temperature may shorten the duration of the experiments, what assumes that reaction mechanism is not modified within the range of conditions.

Combination of the different variables in an adequate setup permits to focus the experiment on mineralogical, geochemical or crystallochemical aspects of the clay mineral transformation reactions.

Transformation of amorphous materials into clay minerals

Amorphous materials exhibit an exceptional reactivity. They correspond to volcanic glasses that transform into clay minerals by interaction with interstitial solutions. The neoformed mineral belong to the kaolinite and smectite groups. A great number of experiments of volcanic glass alteration have been performed.

Rhyolitic obsidian transforms into allophane and precursors of clay mineral in distilled water at temperatures below 200°C (Kawano and Tomita, 1992). The addition of AlCl₃ induces crystallization of boehmite, spherical kaolinite and precursors of smectites at acidic pH, whereas at pH>5 the dominant product is smectite and spherical kaolinite decomposed (Kawano and Tomita, 1993). Smectites and zeolites were formed with NaOH solution (0.1 to 10 mol/L), being Fe an important constituent of smectite (Tomita et al., 1993).

The obsidian undergoes incongruent dissolution with formation of a cation-depleted layer. Fiore et al. (1999) observed crystallization of proto-halloysite in leaching experiments at 82°C. Increasing temperature, obsidian reacts to form smectite crystals: Fe-rich smectite forms by in-situ rearrangement of the hydrated external layer of the glass and Mg-rich smectite precipitates directly from solution (Fiore et al., 2001).

Alteration of volcanic tuff to illite-smectite under hydrothermal conditions is described by de la Fuente et al. (2000). Tuff was altered in batch reactors with solutions with different Na/K ratios and total salt concentration. The neoformed phase consists of a random mixed-layer illite-smectite with 75% smectite. Initial dissolution of the glass permits precipitation of very thin, individual flakes of I/S on the glass surface and development of I/S honey-comb structure either covering large areas of the glass grains or resulting from the complete alteration of the grains. The major reaction mechanism seems to be direct transformation, although there also is evidence of glass dissolution and subsequent precipitation.

Amorphous gels are analogs of natural glasses. The gel reactivity and the wide range of compositions have made of them a versatile starting material to synthesize kaolinite and smectites of variable composition.

Kaolinite synthesis started in the 1930s following a trial and error process. A significant contribution was made by De Kimpe and co-workers, who prepared kaolinite from amorphous Al-Si gels in acid, neutral and alkaline solutions. The best crystals were formed by reaction with alkaline solutions that neutralize the gel acidity. In NaOH solutions intermediate zeolites and smectites are formed (De Kimpe, 1976). The use of KOH prevents precipitation of metastable phases (De Kimpe et al., 1981). In acidic conditions a low (alkali)/(H⁺) favors kaolinite crystallization (Eberl and Hower, 1975), as cations inhibit the reaction (Miyawaki et al., 1991). Tomura et al. (1985) point out the effect of temperature and time on the morphology and crystallinity of kaolinite (Figure 1) during the synthesis from oxides as starting material.

Huertas and co-workers investigated the kinetics and mechanism of kaolinite formation (Huertas et al., 1999). The gel-to-kaolinite reaction occurs through an intermediate metastable "phase" identified as spherical kaolinite (Figure 2). Although spherical kaolinite was observed previously (Rayner, 1962; Rodrique et al., 1972; Tomura et al., 1983), it was not identified as an intermediate product of the reaction. Spherical kaolinite forms by in-situ rearrangement of the Al-Si gel and later decomposed to give rise to platy kaolinite (Huertas et al., 2004). The spheres consist of radially arranged sectors of stacks of planar crystallites. They can be considered analogous of the spherical halloysite-kaolinite found in hydrothermal deposits of kaolin. Estimated crystallization rates are consistent with precipitation rates at room temperature.

Amorphous gels have also been used extensively to synthesize smectites of different composition (see Klopogge et al., 1999, for a review). Synthesis performed under moderate hydrothermal conditions are the most numerous and the most successful in terms of smectite yield. The presence of Mg seems to be essential for the formation of smectites. Trioctahedral smectites form at lower temperature and at shorter time than dioctahedral ones. Dioctahedral smectites are usually beidellite type, being high-purity montmorillonite difficult to obtain. Highly crystalline phases require extreme temperatures or pressures (Yamada et al., 1994). Metastable and accessory phases are often formed, in less extension at high temperature experiments (Figure 3).

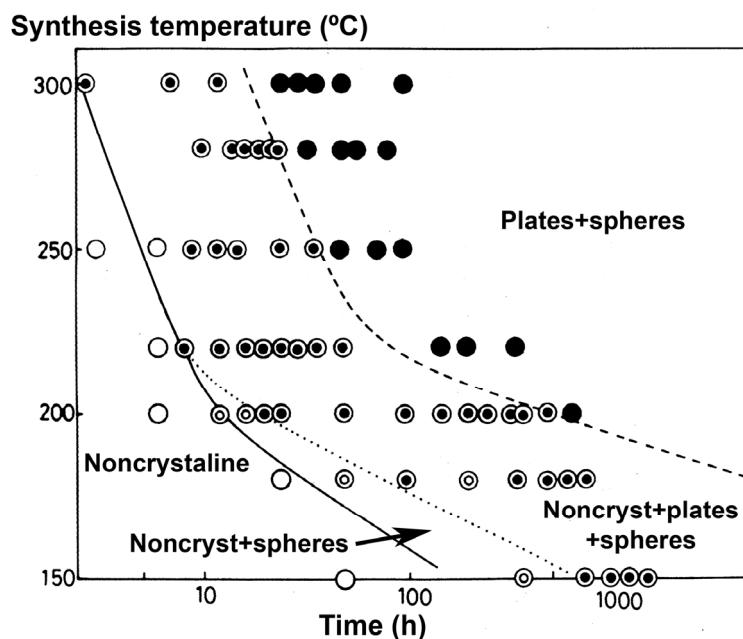


FIGURE 1. Variation of kaolinite morphology with synthesis temperature and time (modified from Tomura et al., 1985).

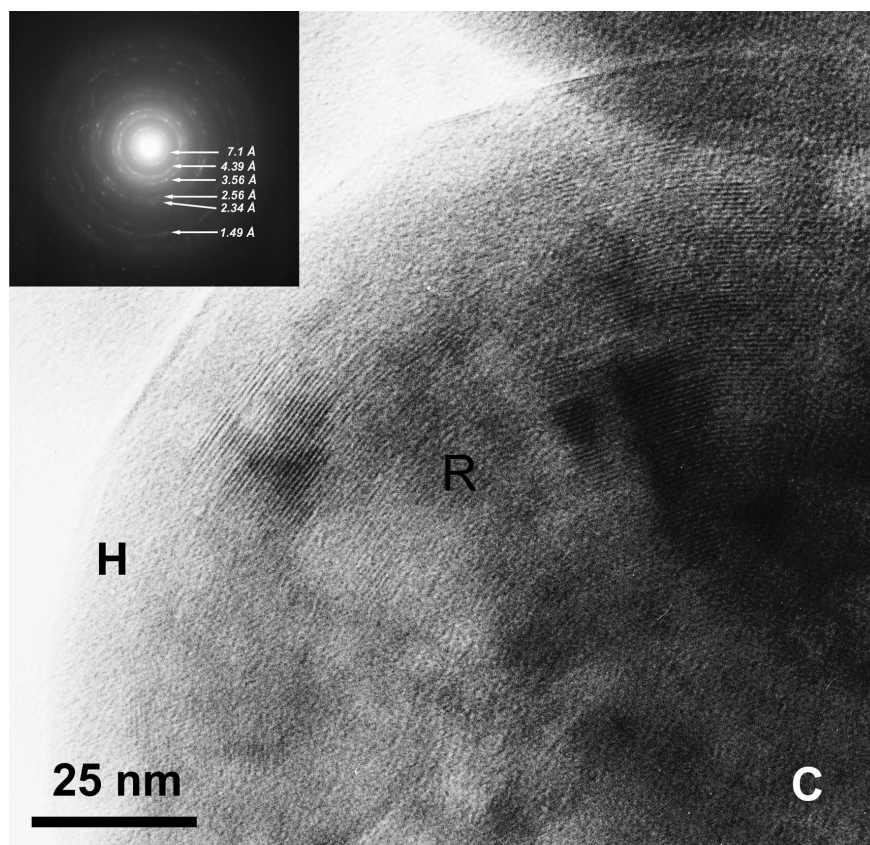


FIGURE 2. HRTEM image of an ultrathin section of spherical kaolinite. H: external halo; R: radial aggregates of kaolinite layers; C: core.

Formation of smectites having variable octahedral Al-Mg-Fe composition has been explored by several authors. Grauby et al. (1993) investigated the Al-Mg series. All synthesized clays were tetrahedrally charged thus leading to a solid-solution between beidellite and saponite, without compositional chemical gap at the particle scale. XRD revealed three types of coherent domains: dioctahedral (Al), trioctahedral (Mg) and intermediate. The apparent ditrioctahedral particle consisted of associated Al and Mg domains, exhibiting metastable behaviour as reaction time increases. Huertas et al. (2000) obtained smectites with a continuous composition between di and trioctahedral. Kaolinite also formed from the most Al gels. Kaolinite and Mg smectite seems to grow readily from the gels and they acts as templates for topotactic growth of dioctahedral particles. Montmorillonite type particles were found only in the experiment using the most aluminous gels.

The products derived from hydrothermal experiments in the Fe(III)-Mg series indicated a solid solution between the nontronite-saponite end-members (Grauby et al., 1994). The b parameter increases continuously with Mg-content. Analytical electron microscopy analyses of isolated particles show continuous evolution between the two end-members. However, IR data provide evidence for segregation of octahedral cation in local di and trioctahedral arrangements. The series can be considered as a continuous solid-solution from nontronites to saponites, with differentiated octahedral clusters.

Iriarte (2003) carried out a systematic study of the crystallogensis of clay minerals (kaolinite and smectites) in Si-Al-Mg-Fe gels. Under slightly alkaline conditions (pH 7-10), dioctahedral smectites (beidellite) crystallised from Al-rich gels with Fe and Mg. In all the series smectite was accompanied by a 7 Å phase of kaolinite type. From Mg-rich gels (pH 8-10) all synthesized

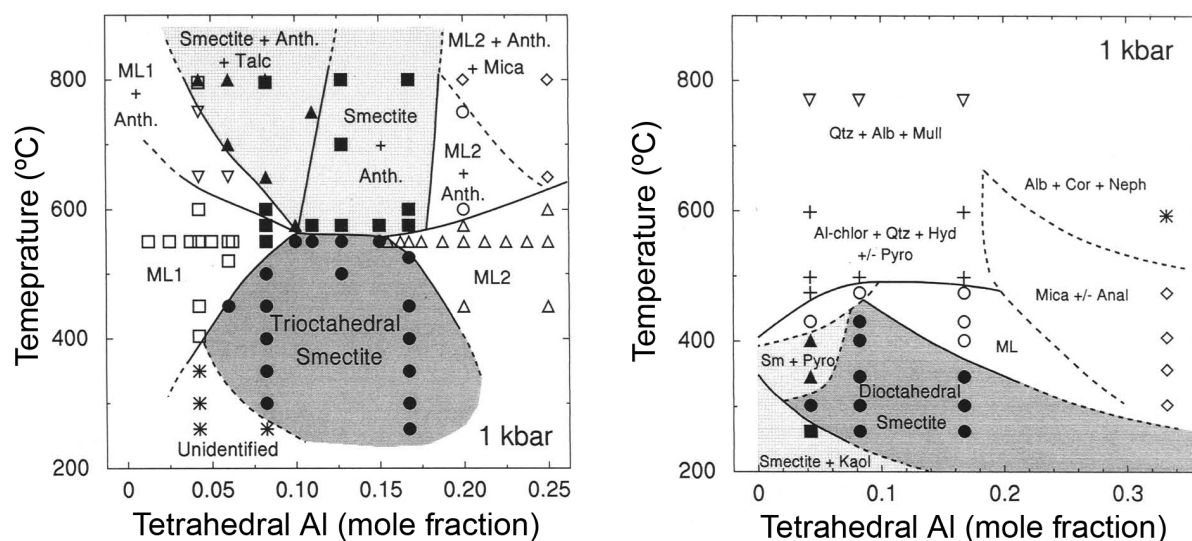


FIGURE 3. Synthesis fields of trioctahedral (left) and dioctahedral (right) smectites prepared by hydrothermal techniques (modified from Klopogge *et al.*, 1999).

phases were trioctahedral. Mixed-layer stevensite/kerolite formed from purely Mg or Mg-rich with Fe gels were the starting gels. However, when the starting Mg-rich gels contained Al, saponite and kerolite were synthesized.

There are also a great number of studies concerning the synthesis of phyllosilicates at temperatures above 350°C. They are a continuation of the investigations started by R. Roy and co-workers in the 1950s. They studied the mineral assemblages produced after treating a gel, a rock or a mineral mixture with a small quantity of water at high temperature (400-900°C) and pressure (0.3-2 kbar). At such conditions, reaction is controlled by thermodynamics and equilibrium is likely reached. The synthesis conditions are far away from diagenesis or low-temperature metamorphism. The scope of these papers were to investigate mineral assemblages in terms of the stability field, miscibility gaps, domain of solid solutions, etc. at high temperature and pressure.

More recently, J.L. Robert and co-workers have improved and extended Roy's methods to a wider range of p,T conditions. They synthesize phyllosilicates of variable composition from silicate gels and so provide materials to investigate their mineralogy and crystalchemistry.

At lower temperatures, such experiments contribute to define the equilibrium diagrams and stability temperature of phyllosilicates. However, the key point is to know whether the system reaches equilibrium. For example, Eberl and Hower (1975) established the kaolinite-pyrophyllite transition temperature (345-405°C) as a function of the Si/Al ratio of the starting gel.

The synthesis experiments using gels has permitted to explore the crystalchemistry of infrequent or rare clay minerals in nature. These experiments produce minerals whose content in elements usually in trace amount go further than those found in nature or even they can be described as new phases.

It is rare for the minerals of the kaolin group to contain appreciable amounts of elements other than Si and Al. The presence of Fe(III) in natural kaolinites has been known for many years, Fe-bearing kaolinites originating mainly in Fe-rich environments such as tropical soils or associated with Fe ores. Cr-kaolinites have been described associated with hydrothermal alteration of ultrabasic rocks. However, natural kaolinites do contain very small amount of Mg (less than 0.05 apfu on $O_5(OH)_4$, in Cr-halloysites). Kaolinites with important content of "infrequent" elements have been hydrothermally synthesized from gels and intensively ground kaolinite:

- Fe(III)-rich kaolinites (up to 0.6 apfu) were prepared and characterized by Angel et al. (1975), Petit and Decarreau (1990) and Iriarte et al. (2005). It forms a solid-solution with kaolinite.
- Cu-rich kaolinite: Samples with copper contents ranging from 0.1 to 7% and another one with the chemical composition of the Cu end-member were synthesized (Petit et al., 1995).
- Ga substituted kaolinite (10% Ga): Martin et al. (1998).
- Mg-rich (0.46 apfu), Ni-rich (0.64 apfu), and Mg-Ni-rich kaolinites: Bentabol et al. (2006a, 2007a). As by-product of the reactions, Al-serpentine and Ni-Al-serpentine also formed.
- Co-rich kaolinite (0.25 apfu) and Al-Co-serpentine: Bentabol et al. (2007b).

Cation substituted smectites have also been prepared (e.g. Co, Bruce et al., 1986; Ga, Martin et al., 1998). However, smectite structure is more flexible to accommodate “infrequent” cations than kaolinite structure. Thus the Al substitution in kaolinites are more relevant and indicate that the lack of these phases lay on the genesis, but not in the crystalchemical constraints.

Transformation of phyllosilicates

Diagenesis and metamorphism induce mineralogical and crystalchemical changes in phyllosilicates. Kaolinite, smectites or vermiculite disappears and illite, chlorite and micas, more stable under new p,T conditions, form. Smectite-to-illite reaction is the most relevant process involving clay minerals. Smectite illitization is an important reaction in burial diagenesis as it influences greatly the chemical and physical evolution of the sediments and smectite and smectite illitization have also been linked to oil formation and migration.

Authigenic precipitation of clay minerals during diagenesis in sandstones was simulated in gold/titanium cells (Figure 4) (Small, 1993). Al and Si were supplied by dissolution of a Si-Al gel in oxalate solution. Dissolution rates were determined after monitoring the decline of Al concentration and decomposition of oxalate. A core of sandstone free of authigenic clays was included as a substrate for illite nucleation. Kaolinite precipitation is faster than illite and should be equilibrium-controlled at all stages of burial. It is dependent of oxalate decomposition. Illite precipitation is kinetically controlled. Below a minimum temperature threshold of around 60°C for North Sea well sequences, illite precipitation rate is too slow relative to likely rates of fluid movements. After this threshold, illite precipitation can be considered kinetically feasible and will be controlled by the supply of illite saturated fluids.

Transformation of smectite into illite/smectite (I/S) or illite seems to be controlled by kinetics. Gels of beidellite composition and bentonite after hydrothermal treatment (260-490°C) react through a series of intermediate phases towards micas (Eberl and Hower, 1977). Gels initially convert in beidellite. Further transformation is conditioned by the interlayer cation. Potassium beidellite reacted through a series of intermediate I/S towards illite. Sodium beidellite evolves to beidellite without octahedral charge, rectorite and paragonite. Despite the effect of the chemistry of the interlayers, reaction mechanism follows Ostwald’s step rule: the first stage was a highly expandable clay, then transformed into a regularly interstratified structure, and the final product should be an illite or a paragonite.

Cuadros and Linares (1996) determined the kinetics of the smectite-illite transformation under hydrothermal treatment in batch reactors. They used a bentonite that initially contains approximately 15% of illite layers. The run conditions were combinations of the following variables: KCl concentration 0.025, 0.05, 0.1, 0.3, 0.5, and 1 mol/L; temperature 60, 120, 175 and 200°C; time 1, 5, 15, 30, 90, and 180 days; solid:solution ratio 1:5. Pressures were those corresponding to water vapor.

Transformation was detected only by XRD, up to 15%, while NMR, DTA/TG and FTIR did not show any appreciable transformation. Transformation to illite was observed, however, when aqueous silica concentration was examined, as the smectite-to-illite transformation releases silica. They derived the following equation:

$$-dSm/dt = kK^{1/4}Sm^n \quad \text{Eq. 1}$$

where Sm is the fraction of smectite in illite/smectite, t time, k the rate constant, and K potassium concentration in solution. The exact value for n could not be determined. After testing several possibilities (Figure 5) and in agreement with other studies, they suggest $n > 1$. The estimation of the apparent activation energy allowed them to suggest a solid transformation mechanism.

Cuadros (2006) used Eq. 1 with $n=5$ to fit to the experimental data from wells, reproducing both the illitization onset and the patterns of the plots of % smectite vs. depth. Because the actual concentration of K cannot be determined, he introduces the concept of “effective K concentration” that takes into account the effect of other cations (e.g., Ca) that compete for the smectite sites. These results support the validity of the equation used in the models. He also suggests that this equation can be used to assess K concentrations in sediments and K mobility within basins.

Montmorillonite is unstable in deep geological conditions. Beaufort et al. (2001) observed that the hydrothermal treatment (100 to 200°C) induces important structural modifications that finally will produce the conversion to illite. The reaction begins with development of tetrahedral substitution and formation of high-charge beidellite, and minor amount of saponite or stevensite-like phases. This reaction is accompanied by morphological changes which suggest that it proceeded by a dissolution-crystallization mechanism. This type of reaction may be considered as a first step in the overall illitization process of montmorillonite.

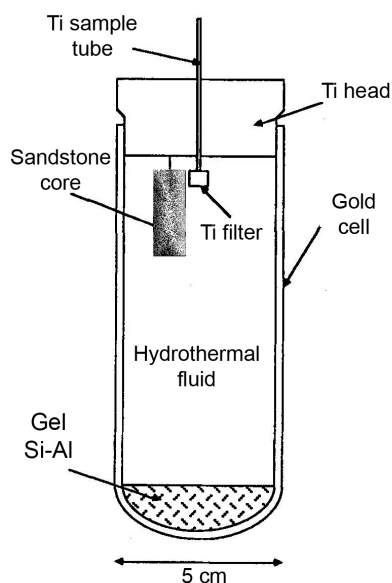


FIGURE 4. Experimental setup in experiments of illite precipitation in sandstones (modified from in Small, 1993).

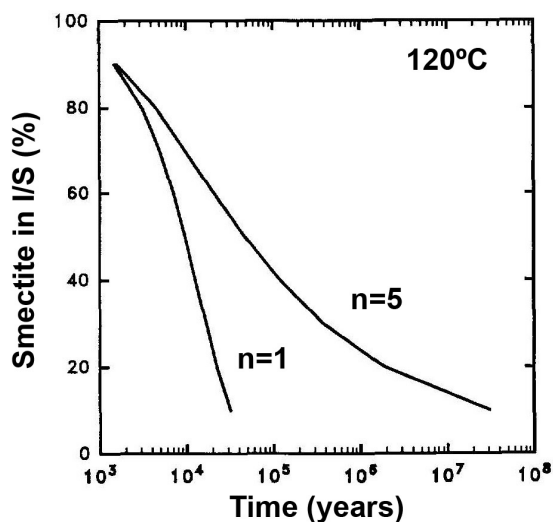


FIGURE 5. Kinetics of the smectite-to-illite conversion at 120°C for $n=1$ and 5 in Eq. 1 (modified from Cuadros and Linares, 1996).

The formation of illite layers occurred when 50% of the starting montmorillonite had reacted. The illite layers were interstratified with both low-charge and high-charge dioctahedral smectite.

Conversion of kaolinite to illite occurs during diagenesis-metamorphism. It has been investigated under hydrothermal conditions (e.g., Chermak and Rimstidt, 1990; Huang, 1993; Bentabol et al., 2006b). Polymorphic reaction kaolinite-to-dickite takes place during diagenesis, with relevance for oil reservoir in sandstones. These reactions are the topic for another contribution.

Laboratory experiments that involve transformation of clay minerals and their assemblages with related minerals as quartz, feldspars, iron oxides or carbonates are an important source of data to establish mineral stability fields and phase boundaries. The high degree of isomorphic substitution that smectites, illites or chlorites can host makes complex to derive equilibrium diagrams that reflex the changes in chemistry and mineralogy during diagenesis.

The experiments are designed according to the phase rules, allowing a number of solid phases to equilibrate with solutions to locate invariant points and curves at different temperatures by analyzing solutions in equilibrium with the solid assemblage. Sass et al. (1987) investigated the stability of illite/smectite in the system $K_2O-Al_2O_3-SiO_2-H_2O$ at 25-250°C (this is a simplified system, as smectites and illites contain small amounts of Mg and Fe). The experimental data were used to construct isothermal, isobaric activity diagrams. The stability regions were defined for kaolinite, boehmite and three other phases that are believed to be components of the studied illites (Figure 6). They conclude that at ~100°C illite and smectite are incompatible in the presence of K-feldspars. At low temperature illite-smectite equilibrium is metastable with respect to kaolinite-microcline equilibrium. At 90-110°C the decrease in Gibbs free energy of illite and smectite stabilize the assemblage illite-smectite-kaolinite respect to illite-smectite-microcline. With increasing temperature illite-smectite equilibrium is again metastable respect to microcline-kaolinite equilibrium, but kinetics constraints may prevent the reappearance of K-feldspar during

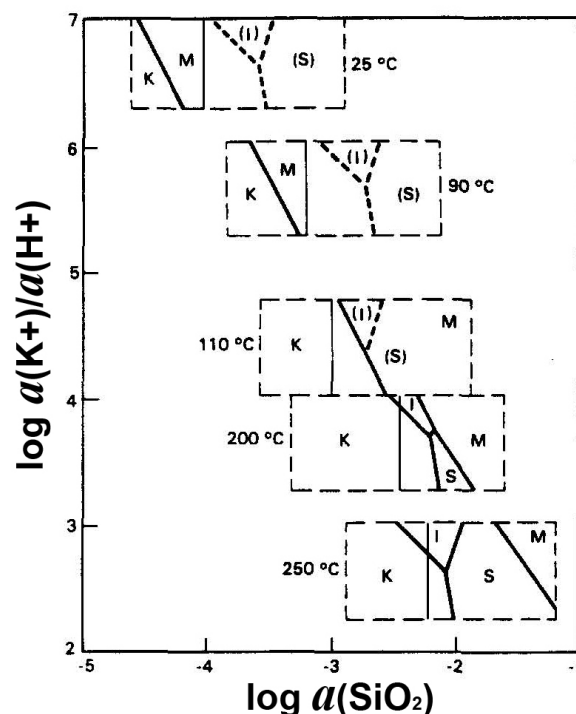


FIGURE 6. Phase relationships at selected temperatures derived from the experimental data and calculated phase boundaries for microcline-kaolinite (modified from Sass et al., 1987).

diagenesis. At 200°C and above illite and smectite may coexist stably with either kaolinite or microcline. However, smectite decomposition occurs when silica activities are controlled by quartz solubility.

Conclusive remarks

Experimental mineralogy and geochemistry is revealed a powerful tool to investigate clay mineral reactivity and transformations under low temperature conditions. Experiments can be designed to simulate natural scenarios in order to monitor periodically the variables involved in the process.

- Laboratory experiments can provide information on reaction mechanism, in particular on metastable intermediate phases that can disappear in natural reactions.
- Reaction rates can be derived from detailed monitoring of the process; kinetics models can be calibrated with natural processes.
- The magnitude of the duration of the reactions is very different in laboratory and in Earth crust. To accelerate reactions, conditions in the laboratory may be slightly different than in nature: higher temperature, concentrated solutions, more acid or alkaline pH, etc.
- In the laboratory, usually the reactions are under kinetic control. Temperature is increased to allow reactions to attained equilibrium.

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