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Conversion reactions from dioctahedral smectite to trioctahedral chlorite and their structural simulations

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ABSTRACT

The clay minerals are good indicators of rock history because their wide transformation variations are sensitive to the formation conditions, like temperature (T), pressure (P) and fluid composition. Accordingly, many geothermometers and fluid-rock interaction indicators based on mineral assemblages, illite polytypism and composition of chlorite have been proposed during the last 30 years. In this study, dioctahedral smectite dominated mudstone was tested hydrothermally in the 250–550 °C temperature range and 5–280 MPa pressure range, with reactions lasting 24 h, with a liquid/solid ratio of 1:1, and in saturated KCl solution. The mineralogical and chemical evolution of the clay minerals was characterized by using X-ray powder diffraction (XRD), X-ray fluorescence spectroscopy (XRF), field-emission scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and high resolution transmission electron microscopy (HRTEM). Molecular simulation was performed to determine the structure and behavior of interlayer cations and interlayer water changes of Na and Ca-rich smectite. We then obtained the transformation series as follows: from dioctahedral smectite to dioctahedral randomly interstratified illite/smectite to dioctahedral ordered illite/smectite to coexistence of dioctahedral and trioctahedral ordered illite/smectite and finally to trioctahedral chlorite and illite/smectite. This work illustrated the dioctahedral smectite alteration and transformation process and showed a continuous octahedral sheet transformation from dioctahedral smectite to trioctahedral chlorite. The series of clay minerals transformation provided an important experimental basis for understanding the geochemical conditions to which clay minerals were exposed to in the geological environment and will offer basic parameters for establishing a quantitative link between composition and formation conditions.

1. Introduction

Phyllosilicates exist in a wide variety of environments and rock types including volcanoclastic sediments, altered igneous rocks, and pelitic rocks which have gone through a diagenetic and a very-low-grade to low-grade metamorphism (Merriman and Peacor, 1999). Mineralogical reactions in phyllosilicates, particularly the low-temperature conversion of dioctahedral smectite to illite and trioctahedral smectite to chlorite, have attracted much interest in recent years. These two mineral transformations can be applied as a geothermometer and as an indicator of fluid-rock interaction. The reaction of dioctahedral

smectite to illite (S → I) occurs under increasing temperature during the burial process and is considered temperature dependent when adequate amounts of K⁺ ions are available (Dong et al., 2002). During the burial process, fine-grained sediments at low temperatures are usually rich in smectite, while deeply buried mud rocks are rich in illite (Burst, 1969; Perry Jr and Hower, 1972). The other transformation of trioctahedral smectite to chlorite (S → C) is also one of the most fundamental reactions in diagenesis and low-grade metamorphism of intermediate to mafic volcanic rocks and volcanogenic sediments (Murakami et al., 1999). The trioctahedral smectite-to-chlorite conversion has been characterized both as continuous with a gradual decrease in percentage

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of smectite (%S) (e.g., Chang et al., 1986; Bettison and Schiffman, 1988; Bevins et al., 1991) and as discontinuous with a stepwise decrease in % S (e.g. Inoue et al., 1984; Inoue and Utada, 1991; Schiffman and Staudigel, 1995; Murakami et al., 1999; Robinson and Zamora, 1999). Continuous conversion suggests the presence of randomly interstratified C/S whereas discontinuous conversion suggests its absence.

It is increasingly being recognized that phyllosilicates reactions exist not only in the burial and low-temperature metamorphism, but also in the subduction zones or slip faults. The characterization of clay minerals has also proved of interest to better understand fault tip propagation in crustal fault-zone or in subduction regions (Ferrage et al., 2011). Phyllosilicate diagenetic reactions release fluids (e.g., the smectite-illite transformation) (Vidal and Dubacq, 2009; Dubacq et al., 2011), that have a direct effect on the mechanical coupling process along the plate interface (Kameda et al., 2011) or it can have a strong impact on the rock rheology as fluid pressure can reduce the effective stress state and promote slip formation. However, the mineralogical properties of fault-related rocks can similarly affect fault behavior by inducing weak mineral phases at the interface (Schleicher et al., 2012). In the cores collected from the SAFOD project in Parkfield, California, and localized in fault-rock samples, the presence of smectite clay minerals has increasingly been confirmed as evidence for mineralogical weakening (Schleicher et al., 2006; Schleicher et al., 2010; Bradbury et al., 2011; Holdsworth et al., 2011).

Phyllosilicate transformations occur as a response to the burial process and are mainly controlled by temperature (T), pressure (P), time, and some chemical variables (Ferrage et al., 2011). When the faulting process starts, frictional heating induces a slight temperature rise, influencing pore fluid properties and geochemical bearing fluids along numerous faults (e.g., K^+) and makes the transformation of clay minerals become more complicated and slightly quicker than the normal burial-diagenetic or low-grade metamorphism (Abid et al., 2004; Kameda et al., 2011). However, the multiple transformation modes of clay minerals are probably related to specific environmental conditions that are not yet clearly defined. For these reasons, hydrothermal laboratory experiments are essential to assess the main parameters controlling the extent of illitization and chloritization as well as those that could lead to a better understanding of the series of transformation.

Traditionally, it has been considered that there is a compositional gap between dioctahedral and trioctahedral structures and there is no continuum in the composition of the octahedral sheet between the two groups (Cuadros, 2012). Therefore, the mechanisms that transform dioctahedral smectite into illite via interstratified illite/smectite (I/S) and trioctahedral smectite transformation into chlorite via interstratified chlorite/smectite (C/S) or corrensite are widely accepted by geoscientists. Numerous results are available from the literature on the experimental behavior of smectites under hydrothermal conditions, generally in the presence of chloride solutions (Eberl, 1978; Eberl et al., 1978; Yamada et al., 1998), however, compared to the amount of research effort devoted to the transformation of dioctahedral smectite to illite, studies about the transformation of dioctahedral smectite to trioctahedral chlorite or chlorite/smectite are still limited. The limited observations of dioctahedral smectite transforming into trioctahedral chlorite or chlorite/smectite can be attributed to the different chemical environments (Hillier and Velde, 1992) and the phase transformation of clay minerals under low temperatures, and the long burial time the transformation needs.

The main aim of this work is to investigate in detail the transformation process of dioctahedral smectite at the same liquid/solid (L/S) ratios, both through experiments and the simulation of the behavior at the atomic level in clay-mineral structural models by molecular simulations. Hence, dioctahedral Na, Ca-smectite-rich mudstones that originated from the Jiufengshan formation in the Dayangshu basin, east of Inner Mongolia in China were selected as the starting material. A continuous octahedral sheet transformation from dioctahedral smectite

to trioctahedral chlorite was obtained: from dioctahedral smectite to dioctahedral randomly interstratified illite/smectite to dioctahedral ordered illite/smectite to coexistence of dioctahedral and trioctahedral ordered illite/smectite and finally to trioctahedral chlorite and illite/smectite.

2. Experimental

2.1. Sample collection

To clarify clay mineral transformation process on the history of diagenesis, very-low grade and low-grade metamorphism in the area, dioctahedral Na, Ca-smectite dominated mudstone was selected as the starting material. The mudstone was originated from the Mesozoic Jiufengshan formation in the Dayangshu basin, located in the Arong Banner and Oroqen Banner, east of Inner Mongolia, with the geographic coordinates of 124°23'39.7"E, 50°01'14.7"N. They were influenced by early diagenesis processes and the temperature estimated for the diagenetic changes was below 100 °C. The mudstone was crushed in an agate mortar and directly studied by XRD. The analysis of the randomly oriented powder XRD showed that the primary mineral components were smectite with a small amount of muscovite, quartz and feldspar. The fractions separated from the uppermost part of the suspension were noted to contain smectite ($\pm 95\%$) and a small amount of illite and muscovite. The chemical composition of the fractions, as determined by X-ray fluorescence (XRF) method using a PANalytical AXIOS spectrometer, is shown in Table 1. Calculated on the base of O_{11} , the half structural formula of the suspension was: $(Ca_{0.143}Na_{0.137}K_{0.124}Mg_{0.073})_{0.477}(H_2O)_n\{(Al_{1.594}Mg_{0.246}Fe_{0.122}Ti_{0.038})_{2.00}[(Si_{3.515}Al_{0.485})_{4.000}O_{10}](OH)_2\}$. There were some substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet.

2.2. Hydrothermal experiments set-up

Weighed 0.2 g hand-crushed powder of mudstone samples, and then sealed them into a 2.5 cm long Ag capsule with a diameter of 0.5 cm. 0.2 ml [liquid/solid ratio (L/S) = 1:1] of saturated potassium chloride (KCl) solution was added into each capsule, and the capsules were sealed up at both ends and then loaded into the high-pressure autoclave. To increase the reaction rate, we increased the temperature and pressure to above that reported in the literature (smectite transformed to illite at about below $\sim 180^\circ C$, mixed-layer chlorite/smectite to 240 °C in the Nesjavellir geothermal field in Iceland). The experiments were conducted using a LECO hydrothermal apparatus (HR-1B-2-847, LECO Corp., US) with different conditions: 250 °C and 5 MPa, 350 °C and 65 MPa, 450 °C and 120 MPa, 550 °C and 265 MPa, 550 °C and 280 MPa, and each was maintained for 24 h. The temperature control was precise to $\pm 1^\circ C$ and accurate to $\pm 5^\circ C$. The relative samples are labeled as 1-250-5-KCl-24, 1-350-65-KCl-24, 1-450-120-KCl-24, 1-550-265-KCl-24 and 1-550-280-KCl-24, respectively. The reacted material and the solution were separated by centrifugation. To exclude excess electrolytes in the products, the obtained products were washed several times with deionized water until chloride-free (this was tested by using $AgNO_3$ solution), then dried at 60 °C and grounded before characterization.

Table 1

The chemical composition (in mass %) of smectite.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O
58.523	29.367	2.698	0.834	2.218	3.563	1.621	1.177

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