Illitization processes: Series of dioctahedral clays and mechanisms of formation

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Introduction

The series involving dioctahedral clay minerals is, with increasing temperature, or grade: smectite$\rightarrow$ mixed-layer illite/smectite (I/S) $\rightarrow$ illite. This sequential smectite-to-illite reaction via mixed-layered minerals ("smectite illitization") has been documented in low-temperature environments and is commonly associated with burial diagenesis, low-grade metamorphism, contact metamorphism, and hydrothermal alteration.

The smectite illitization developed as a function of burial depth is well displayed in the Tertiary sediments in the Gulf Coast of the United States. This sequence has been extensively studied, and the pioneer paper by Hower et al. (1976) is one of a series that brought definition to the mineralogical relations. In the cited paper, a curve was established (Figure 1) showing the proportion of illite layers in I/S as a function of depth. Such curve implies that smectite at shallow depths consists of disordered I/S with approximately 20% illite layers and with depth, the smectite layers are progressively replaced by illite-layers producing a decrease of expandability of I/S phases from 80 to 20% at a depth of 3700m. Little additional change occurs up to depths approaching 6000m. The data by Hower et al. (1976) indicate that the illitization process produces loss of Si, Na and H_2O and gain of K and Al.

The concept that the smectite illitization proceeds through mixed-layer I/S intermediates has been established regardless of geological environment (eg. Hower et al. 1976, for diagenesis, Inoue et al., 1978 for hydrothermal alteration). Most of the illitization studies, based on X-ray diffraction studies (XRD), describe that as I/S interstratified clays become illitic, the interlayer arrangements change from random (R0) to short-range (R1) ordered, and then to long-range (R3) ordered, where R is the Reichweite parameter (Jagodzinski, 1949). Some studies note that R2 I/S is uncommon, and where it has been described it is better explained by a mixture of R1 and R3 ordering (Srodon and Eberl, 1984). The illitization process implies polytypic changes evolving from turbostratic staking in smectitic I/S to 1Md or 1M in illitic I/S to $2M_1$ in pure illite (Inoue et al., 1987, Reynolds, 1993). It has been also described that the octahedral vacancy can occur in either the M1 (trans) or M2 (cis) octahedral site (Drits et al., 1993, Reynolds, 1993). Alternatively, some authors suggest the existence of a third component layer, which is often called a vermiculite or "high-charged smectite" layer, in I-S phases; however, whether its existence or not and whether the formation acts as an essential step during smectite illitization are unanswered (Drits et al., 1997, Meunier et al., 2000, Inoue et al., 2005).

The smectite-to-illite transition is complete in sequences where pelites have been subjected to sedimentary burial with associated overburden stress at depths in order 3000 meters; the illite formation indicates a late diagenesis stage (Merriman and Peacor, 1999).

As Altaner and Ylagan (1997) describe, the smectite illitization and the crystal chemistry of mixed-layer I/S depend on various variables which include temperature, compositions of fluid, time, and fluid/rock ratio during the formation of I/S minerals and chemical composition of the precursor materials (Altaner and Ylagan, 1997). Thus, these factors probably condition the type of I/S phases formed during the process. Despite extensive investigation over the last several decades characterizing smectite illitization sequences, many unresolved points remain,
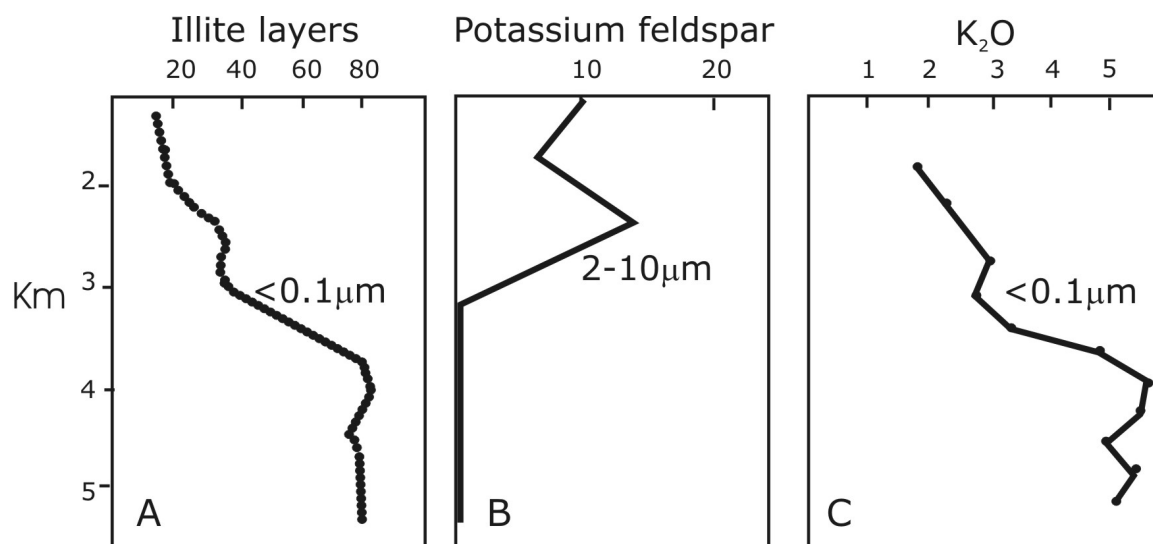
FIGURE 1. *Gulf Coast sediments (well 6), late Oligocene-Miocene. Vertical distribution of illite layers in I/S phases (<0.1 μm fraction) (A); K-feldspar percentage (2-10μm fraction) (B); K$_2$O (%) (<0.1μm fraction) (C). Modified from Hower et al. (1976).*

including the crystal chemical models of I/S mixed-layered structures and the illitization mechanism.

Characterization of the series of dioctahedral clays

Sediments and sedimentary rocks usually display complex mineral composition; they consist of mixtures of clays, which are characterized by fine-sized grains, non-clays phases and even amorphous components. This complexity makes more difficult the characterization and identification of the mineral associations. The use of XRD allows mineralogists to identify the presence of clays and mixed-layered phases, and to determine the proportion of the components in the mixed-layered mineral as well as the ordering of layer staking (e.g. Moore and Reynolds, 1997). In the case of I/S phases, the proportion of each type of layer is taken to represent the progress of the reaction from smectite to illite. However, the XRD patterns of mixed-layered clay display some of the most difficult problems of interpretation, particularly if, as is often the case, the mixed-layered species are present in physical mixtures that include the simple clay types. Multiple analyses are needed as well as computer-generated X-ray diffraction patterns to discriminate the clays.

The introduction of the transmission electron microscopy (TEM) to diagenesis and very low grade studies in the mid-80s has also permitted to enhance the characterization of clays and mixed-layer I/S minerals. The TEM techniques have a powerful advantage in that they simultaneously provide information in three ways: 1) textural information imaging over a broad range of magnifications up to near-atomic resolution; 2) crystal structure characterization through selected area electron diffraction (SAED); 3) quantitative chemical data from precise areas characterized by other means, using energy dispersive spectroscopic (EDS) techniques.

An essential problem in TEM investigation of mixed-layer I-S minerals is the collapse of expandable interlayers under high vacuum. This makes the distinction between smectite and illite layers in I/S very difficult, if not impossible. Recent improvements in imaging and sample preparation techniques have addressed this problem; as the permanent expansion of smectite interlayers using L.R. White resin (Kim et al., 1995, Bauluz et al., 2000, 2002, Yan et al., 2001, Tillick et al., 2001) and n-alkylammonium ions (Bell, 1986, Vali and Köster, 1986, Vali and

Hesse, 1990, Arroyo et al., 2006). Gutrie and Veblen (1989, 1990) have shown that smectitic and illitic interlayers can be distinguished from one another in overfocused images. They indicate that ambiguities may be still present in the interpretation of such images due to specimen orientation and microscope focus.

The XRD gives information on average layer staking within crystallites while the TEM gives information on layer stacking in local region within a crystallite. Thus, the two methods are complementary to one another in studies of mixed-layer I/S minerals.

Reaction mechanism for smectite Illitization

Reaction mechanism for smectite illitization can be classified into two broad categories: a) solid-state transformation (SST) and b) dissolution-crystallization (DC) (Figure 2).

SST mechanisms, which typically also involve fluid, that can act as catalysts and transport media (Veblen, 1992), involve gradual replacement of the parent mineral (e.g. smectite) by the daughter mineral (e.g. illite) in close topotactic contact. Such a model is sometimes referred to as a "layer-by-layer transformation". Other general features of an SST mechanism are similar polytypes for the parent and daughter crystals as well as daughter crystals with similar size and shape as the parent (Baronnet, 1992). Pollard (1971) displays an SST model for smectite illitization in which Al and Si diffuse through the hydrous interlayer and the tetrahedral sheet distorts while Al replaces Si. Based on TEM observations of shale and bentonites, Bell (1986) describes a SST processes in which smectite layers are replaced laterally by illite layers. In a high-resolution TEM (HRTEM) study of shales, Bauluz et al., (2000) report lateral transition from R1 I/S to illite and from R1 I/S to R3 I/S (e.g. in Figure 3). These replacements of individual layers probably occur via fluids at reaction interfaces, in contrast to solid-sate reactions, *sensu strictu*.

Other investigators have proposed that smectite illitization can follow a continuous transformation of smectite layers to illite (Hower et al., 1976, Hower, 1981, Inoue et al., 1990, Lindgreen et al., 1991, Drits et al., 1997). In comparison, Amouric and Olives (1991) by means
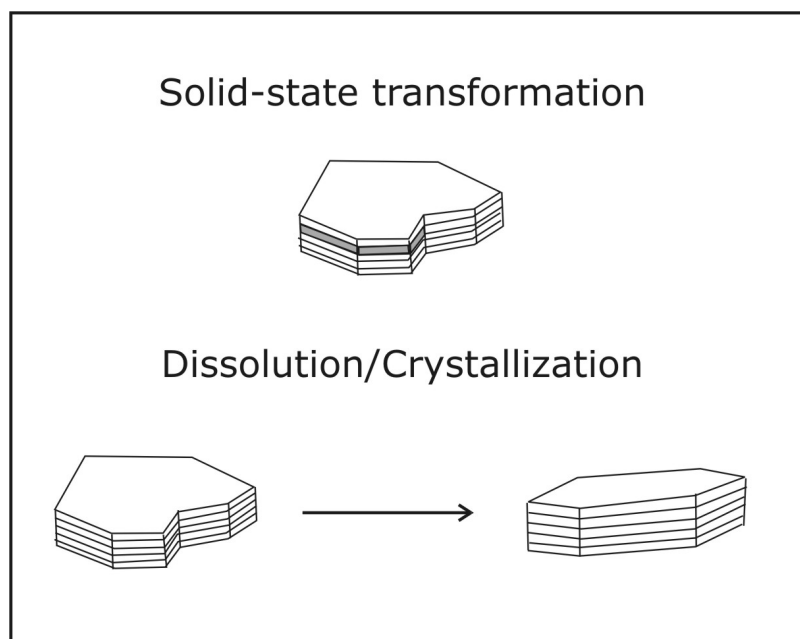

FIGURE 2. *Scheme of different mechanism for mineral reactions: solid-state transformation and dissolution/crystallization. Modified from Altaner and Ylagan (1997).*
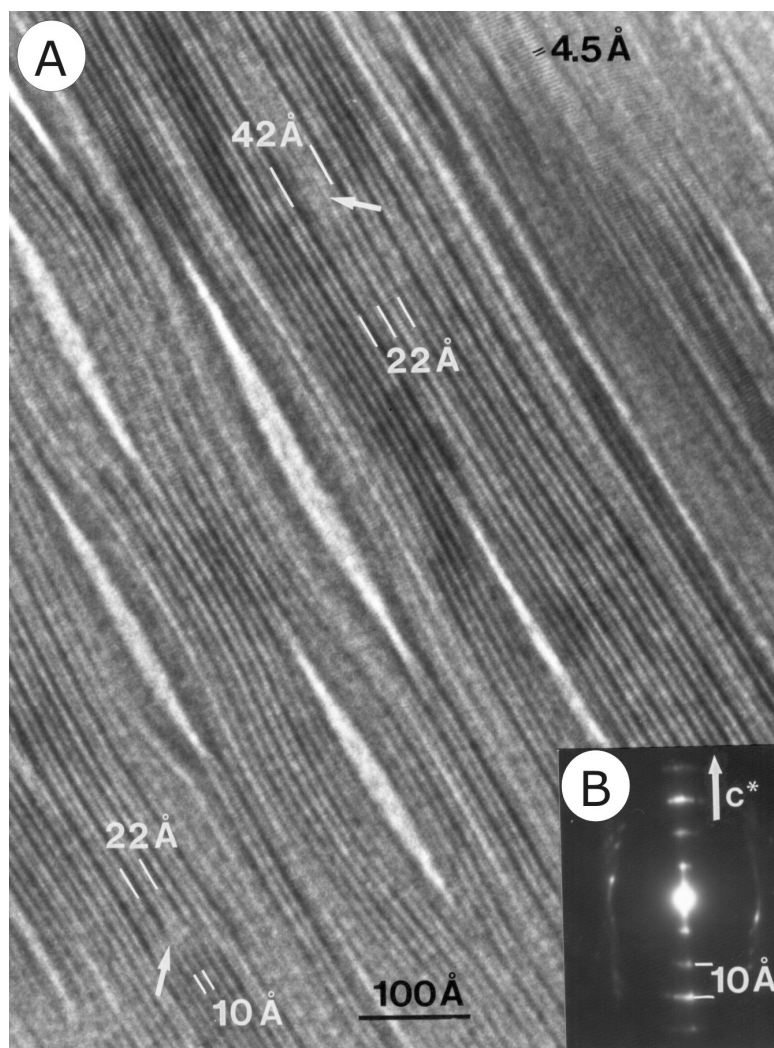
FIGURE 3. *TEM image of a shale of diagenesis grade. Lattice-fringe image (A) showing lateral transition from R1 I/S (22Å) to illite (10Å) and from R1 I/S (22Å) to R3 I/S (42Å). B: SAED pattern displaying high orders of 00l reflections with $d_{(001)}$ of 10 Å. Modified from Bauluz et al. (2000).*

Other investigators have proposed that smectite illitization can follow a continuous transformation of smectite layers to illite (Hower et al., 1976, Hower, 1981, Inoue et al., 1990, Lindgreen et al., 1991, Drits et al., 1997). In comparison, Amouric and Olives (1991) by means of the HRTEM describe the coexistence of both processes in the same sample; the formation of I/S by SST evidenced by the transition of smectite layer into illite layer and the growth of illite by DC.

DC mechanisms involve complete dissolution of the previous mineral followed by nucleation and growth of the new mineral. During dissolution, the structural memory of the parent is lost. Indications of a DC mechanism are changes in polytype and loss of morphological characteristics of the parent. Several DC models for smectite illitization have developed from mineralogical and TEM studies of I/S (Nadeau et al., 1984, 1985, Yau et al., 1987, Inoue et al., 1987, Eberl and Srodon, 1988, Drits et al., 1996). Pollastro (1985) concludes that smectitic I/S dissolves and reprecipitates as both illitic I/S and discrete illite, resulting in a decreasing abundance of I/S as illitization proceeds. According to Inoue et al. (1987), anhedral smectite crystallites (10-A thick) become unstable, dissolve and recrystallize forming thin (20-A thick) euhedral illite laths, some of which in turn dissolve and grow into larger (≥40A thick) euhedral illite laths and hexagons. To

describe illitization in Gulf Coast shale, Ahn and Peacor (1986) present a mechanism intermediate to the SST and DC models in which smectite dissolves and illite crystallizes from an aqueous fluid in the same space as the parent smectite (Figure 4).

Dong et al. (1997) studied by HRTEM a prograde shale sequence of the Gulf Coast and a set of bentonites, which have been previously characterized by XRD. The TEM data demonstrate that the continuous aspect of such trends is due to changes in proportions of three discrete phases, not in the proportions within single sequences of layers of individual packets. They are smectite, R1 I/S (50% illite) and illite. The chemical composition of R1 I/S (0.7- 0.8 K p.f.u. for 4 tetrahedral positions) indicates that this phase is not an average of those of smectite and illite, which is consistent with the uniqueness of the R1 I/S structure. This was also suggested by Jiang et al. (1990) and Ramsom and Helgeson (1993). In order to explain the structure of I/S phases, two competing models exist: model A which considers such interstratified clays as a stacking of layers identical to endmember illite and smectite layers, implying discrete and independently formed units (fundamental particles, e.g. Nadeau et al., 1984), and model B which shows the clays as composed of crystallites with a unique structure that maintains coherency over much greater distances, in line with local charge balance about interlayers (Altaner et al., 1988). Stixrude and Peacor (2002), on the basis of first-principles quantum mechanical calculation, find that the total energy of the second model is lower than that of the previous model and that this energy difference can be traced to structural distortions in the first model due to local charge imbalance. Such results favor dissolution and neocrystallization processes because the differences in Al–Si ordering between R1 I/S (rectorite) and illite or smectite are incompatible with transformations by means of solid-state diffusion of Al and Si at the low transformation temperatures observed in Nature. This is also supported by many TEM studies (Nieto et al., 1996, Dong et al., 1997, Tillick et al., 2001, Yan et al., 2001, Bauluz et al., 2002) (e.g. in Figure 5). The observation of the study by Dong et al. (1997) and the above cited references imply a sequence of discrete steps in which assemblages of higher free energies are replaced by others with lower energies. Such changes must be by dissolution and precipitation; the scale and atomic-level mechanisms may appear to be very different, however, as they depend on reaction kinetics and path. More recent papers which combine XRD and TEM data also support DC mechanism for illitization process (Inoue et al., 2004, 2005, Murakami et al., 2005, Arostegui et al., 2006).
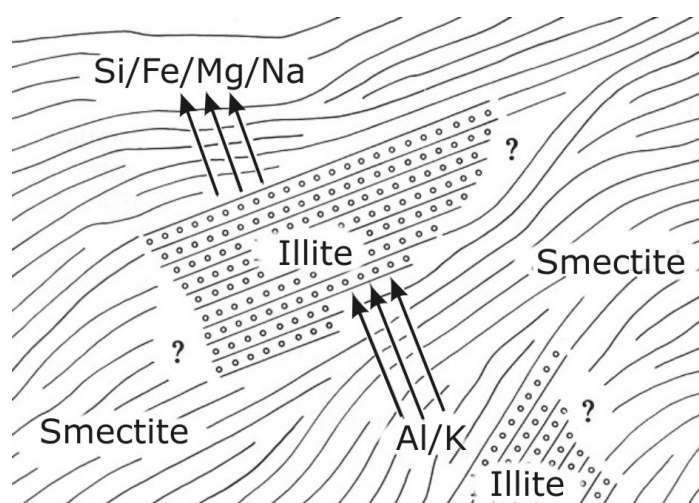

FIGURE 4. *Interpretation of the direct transformation of smectite to illite in Gulf Coast argillaceous sediments, from HRTEM observations. Modified from Ahn and Peacor (1986).*

Illitization process in prograde shale sequences vs. alteration hydrothermal systems

The factors which usually control the illitization process (temperature, fluid composition, time, fluid/rock ratio, composition of precursor phases) may have different influence in each geological environment. In hydrothermal systems, the time can be ignored because the formation generally took place over geologically short period of time, probably during a single event, in contrast to burial diagenesis. The fluid composition and the fluid/rock ratio in hydrothermal environments are also critical factors. In such systems the temperature in which the clays crystallize depend on the fluid temperature, however, the temperature during diagenesis of shales is mainly controlled by the burial and, therefore, by the geothermal gradient.

Characterization of illitization sequences in hydrothermal systems (Tillick et al., 2001; Yan et al., 2001, Bauluz et al., 2002, Inoue et al., 2005, Murakami et al., 2005) have displayed that all the dioctahedral phyllosilicates form by dissolution of volcanic phases and neocrystallization directly from fluids. In some hydrothermal alterations, it is possible to visualize the dissolution of previous phases and crystallization of dioctahedral clays both at angstrom and nanometer scale (e.g. in Figures 5 and 6).
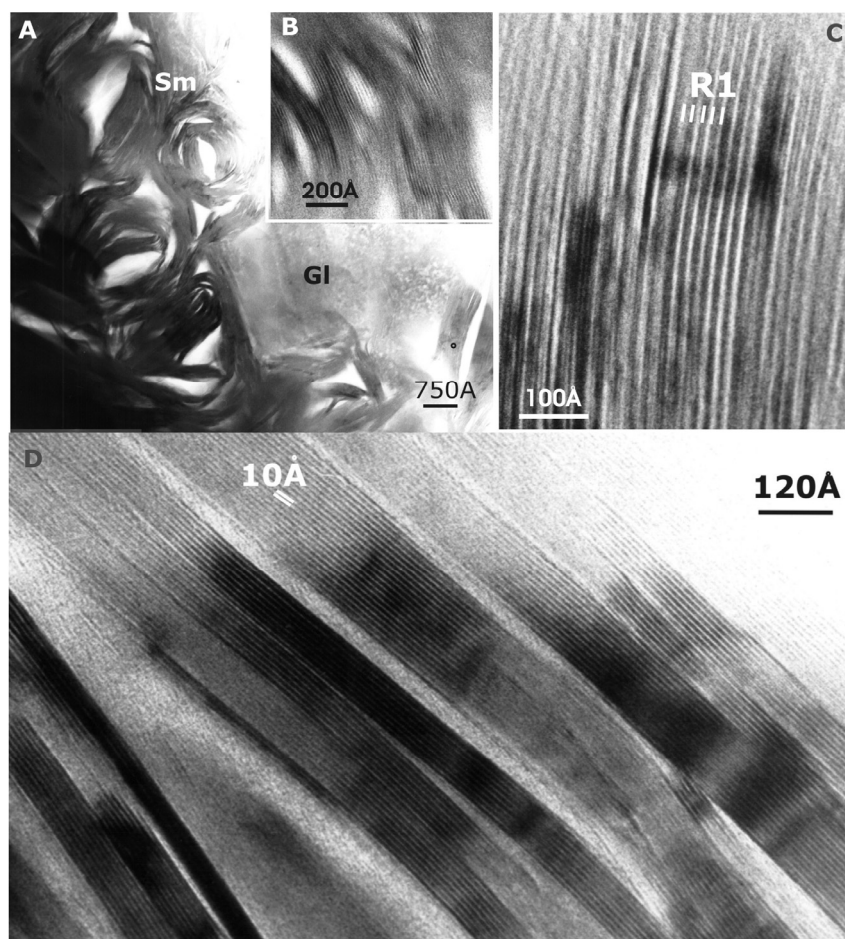

FIGURE 5. *TEM images of the illitization sequence in a hydrothermal alteration. A: Low-magnification images showing the typical curved lens-shaped morphology of smectite (Sm) surrounding relatively featureless amorphous cores (Gl). B) HRTEM of smectite displaying wavy and discontinuous lattice fringes of smectite, with spacings from 10 to 13 Å. C) Lattice-fringe images showing typical area rich in R1 I/S phases (21-22-Å periodicity). D) Lattice-fringe image of illite crystals. These areas consist of 10-15-nm thick, parallel and subparallel packets with relatively well-defined boundaries. The image shows defect-free lattice fringes with constant 10-Å spacings. Modified from Bauluz et al. (2002).*
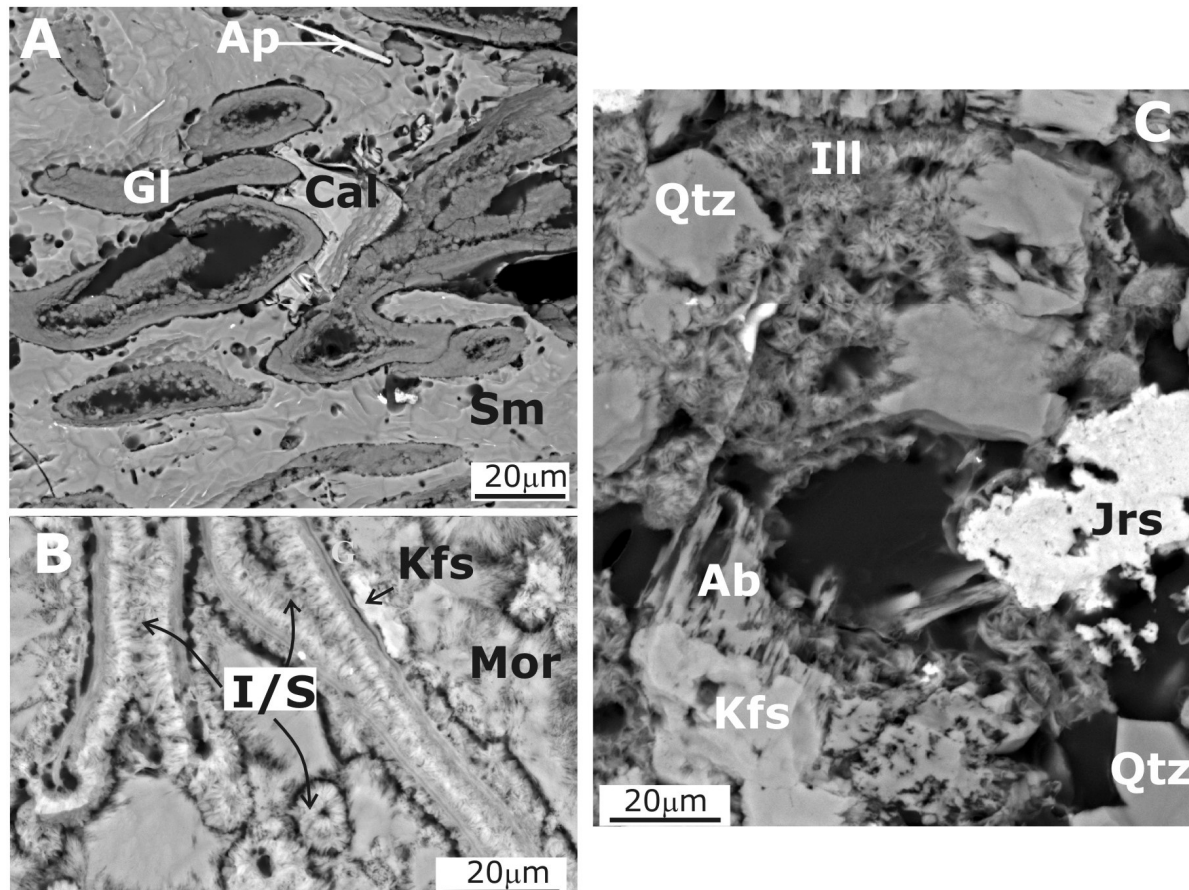
FIGURE 6. *Back-scattered images (scanning electron microscopy) of samples with different grade of hydrothermal alteration. A: obsidian clasts (Gl) partially replaced by smectite imbedded in a smectite-like matrix (Sm), adjacent to authigenic calcite (Cal) and apatite (Ap). B: pumice pseudomorphs replaced by I/S phases and hairy mordenite filling pores (Mor) and K feldspar (Kfs). C. Illite (Ill) filling pores and replacing corroded albite feldspar (Ab) adjacent to authigenic quartz (Qtz), K feldspar (Kfs) and Jarosite (Jrs). Modified from Bauluz et al. (2002).*

However, the shale systems do not display evident dissolution/crystallization processes and it is necessary a carefully characterization by XRD and HRTEM to determine the illitization mechanism. The episodic alteration in hydrothermal materials produces a sequence of clay minerals identical to those of prograde diagenesis of pelitic sediments and the clay sequence is similar to those described by Dong et al. (1997). They suggest that all clay minerals are inferred to have formed simultaneously by crystallization from fluids rather than trough a series of sequential transformation reactions from precursor smectite. In contrast, the studies focused on shales, as previously explained, have reflected some disagreement among the proposed illitization mechanisms (SST, layer-by-layer transformation, DC).

Conclusions

The smectite-to-illite transition has been identified and characterized in different geological environments and it has been intensively studied in prograde shales and hydrothermal systems. Despite all the investigation characterizing the transition, there are some unresolved aspects such as the types of intermediate I/S mixed layers and the illitization mechanisms. Evidences supporting both gradual replacement of smectite by I/S and I/S by illite and dissolution and crystallization of the clays are found in the bibliography. However, the recent

papers combining XRD and TEM techniques and quantum mechanical calculation show new data which favor dissolution and crystallization processes. The described differences among sequences if they exist may be due to thermodynamic considerations controlled by factors such as temperature, fluid composition and fluid/rock ratio. Future research to characterize the illitization process must be done in different geological settings being essential to obtain much more data to compare XRD and TEM results. The rate of the smectite-to-illite reaction may be very different in different rock types, thus, more work is needed on sequences which involve a variety of coexisting rock types. These new studies also could help to determine whether a third component in the mixed-layer phases exists or not.

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