Kaolinite Crystallization from an Amorphous Phase in Diagenetic Sandstones

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INTRODUCTION.

The occurrence of diagenetic kaolinite in sandstones has been described by different authors such as Nedkvitne and Bjorlykke (1992), Ehrenberg et al. (1993), Macaulay et al., (1993), Osborne et al. (1994), Beaufort et al., 1997, Arostegui et al. (2001) and Bauluz et al. (2008). Diagenetic kaolinite usually crystallized in two distinct sites: 1) forming aggregates of euhedral crystals within primary pores, and 2) constituting muscovite/kaolinite intergrowths.

In the first case, the kaolinites are euhedral and pseudohexagonal crystals with a range of sizes but usually up to 10μm diameter. The aggregates seem to expand into and fill pores in the rocks. The delicate, fragile shapes of these kaolinite aggregates or booklets suggest that they grew *in situ*. These booklets probably represent authigenic kaolinite formed in shallow burial conditions as a response to incipient diagenesis. Initially, they fill the primary porosity of the rock and, as diagenesis proceeds, the dissolution of previous phases such as K-feldspars and/or detrital kaolinite (Beafourt et al., 1997, Bauluz et al., 2008) increases, leading to progressive replacement by kaolinite. Beafourt et al. (1997) indicate that kaolinite did not crystallize in the alteration sites of detrital feldspars and that the dissolution of feldspars increases with increasing burial depths leading to progressive replacement of feldspars by secondary pores.

In relation with the second case, Arostegui et al. (2001) suggest that kaolinite grows between cleavage sheets of pre-existing mica. These authors indicate that the muscovite supplied a template suitable for the epitactic crystallization of diagenetic kaolinite.

In addition, Bauluz et al. (2008) describe the presence of these two types of diagenetic kaolinites in Lower Cretaceous sandstones and also an authigenic kaolinite-rich matrix with minor detrital kaolinite contributions.

In this study, we have investigated the formation of diagenetic kaolinite in sandstones to infer the possible presence of a precursor phase.

MATERIALS AND METHODS.

The samples were selected from set of sandstones previously characterized by Bauluz et al. (2008) by XRD, SEM and TEM techniques. They are medium to coarse sandstones that belong to the Utrillas formation (Albian in age, Lower Cretaceous) from the Iberian Range.

Fragments of sandstones were observed by SEM using secondary electron imaging. Sticky wax-backed thin sections were prepared with surfaces normal to bedding, and first examined by optical microscopy and SEM. Typical areas were removed for TEM observations via attached Cu washers, thinned in an ion mill and carbon coated. TEM data were obtained with a JEOL- 2000 FXII with an Oxford EDS detector. K-factors were determined by analysing albite, sodalite, biotite, muscovite, wollastonite, and benitoite standards. Analytical values displayed a margin of error of ~5-7%.

RESULTS AND DISCUSSION.

SEM images (Fig. 1a-b) show the typical appearance of kaolinite occurring as aggregates composed of pseudo-hexagonal plates 5-10 μm in diameter. These aggregates, up to 40μm thick along the c axis, seem to expand into and fill pores in the rocks. The kaolinite also constitutes (Fig. 1c) the rock matrix and it consists of euhedral and pseudo-hexagonal crystals. The distribution of these well crystallized kaolinites is not homogenous in the geological formation, since they were not detected in some of the sandstones. Altered-K feldspars grains were observed in most of the cases.

Low resolution TEM images (Fig. 2A) show kaolinite aggregates up to 2μm thick. The aggregates consist of single kaolinite crystals which sizes range from 25 to 35 nm (Fig. 2B).

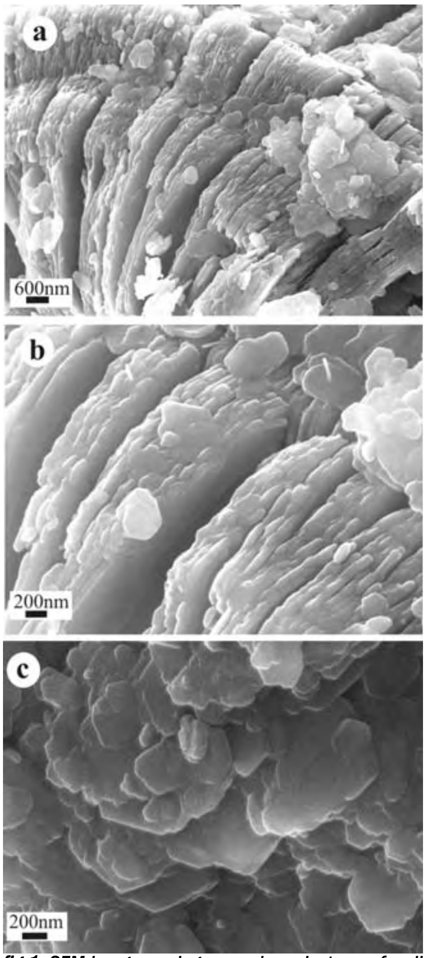

fig 1. SEM images, using secondary electron, of well crystallized kaolinites in sandstones.

palabras clave: Caolinita, Diagénesis, TEM. | *key words:* Kaolinite, Diagenesis, TEM.

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Those sandstones in which the SEM study does not show euhedral kaolinite display a typical texture shown in Figure 2C. The framework of the rocks, which mainly consists of quartz grains, is embedded on a continuous and homogenous matrix with no contrast in the TEM image. In some points the matrix does not produce selected area electron diffraction (SAED) patterns that indicate its amorphous nature. In other cases the SAED patterns consist only of poor defined rings typical of very poor crystalline phases.

The chemical composition of the matrix is variable. It always shows high Al and Si contents with minor and variable K and Fe. Some analyses resemble to K-feldspar composition but with low K, and other analyses resembles to kaolinite composition with minor Fe and K.

High resolution TEM images (Fig. 2D-E) allow to image nanometer kaolinites included in the amorphous phase. These kaolinites are pseudo-hexagonal to rounded plates and 25-30nm in diameter.

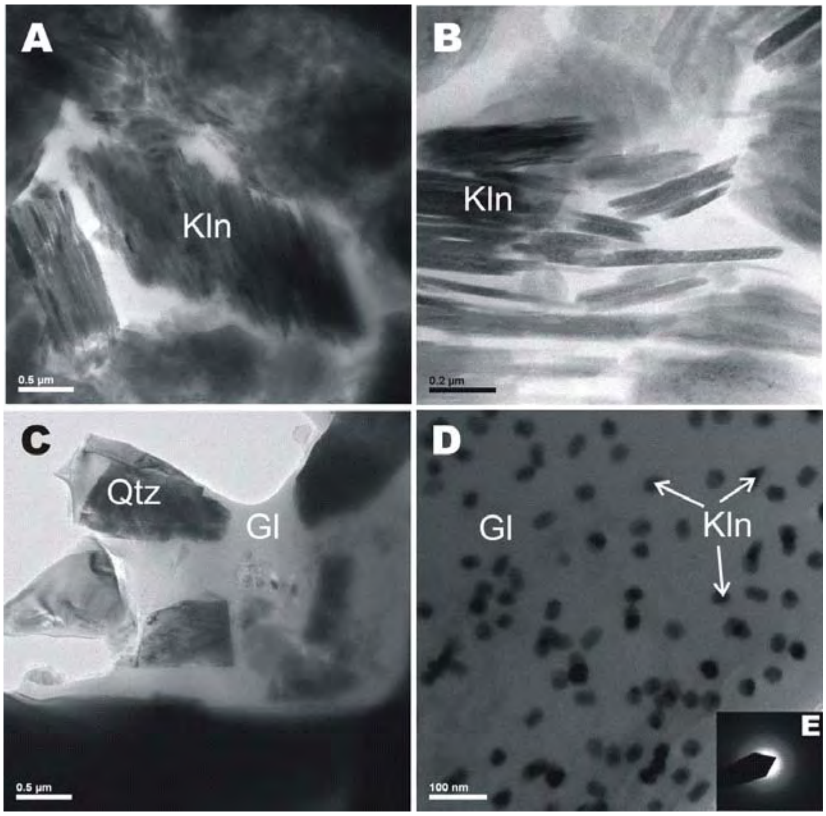

fig 2: TEM images of the sandstones: A: low TEM images showing kaolinite (Kln) aggregates, B: TEM images showing the kaolinite (Kln) crystals, C: Quartz grains (Qtz) imbedded in a homogenous glassy matrix (Gl), D) HRTEM image show nano kaolinite (Kln) particles in the homogenous glassy matrix (Gl), E: SAED of the glassy matrix.

DISCUSSION AND CONCLUSIONS.

The combination of SEM and TEM methods suggests the presence of an amorphous or poor crystalline phase with composition between kaolinite and K-feldspar in the studied sandstones. The composition of this amorphous phase suggests that its formation is a consequence of the K-feldspar alteration during the diagenesis. On the other hand, TEM images show the crystallization of kaolinite from this Al- and Si- rich phase.

The formation of an amorphous phase from the K-feldspar alteration has been already described in weathering conditions (Lei Chou & Wollast, 1984), however this is the first time that this process have been observed in diagenetic environments

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REFERENCES.

Arostegui, J., Irabien, M.J., Nieto, F., Sanguesa, J., Zuluaga, M.C. (2001): Microtextures and origin of the muscovite-kaolinite intergrowths in sandstones of the Utrillas Formation, Basque Cantabrian Basin, Spain. Clays and Clay Minerals, ***49***, *6, 529-539.*

Bauluz, B., Mayayo, M.J., Yuste, A., Gonzalez Lopez, J.M. (2008): Genesis of kaolinite from Albian sedimentary deposits of the Iberian Range (NE Spain): Analysis by XRD, SEM and TEM. Clay Min. in press.

Beaufort, D., Cassagnabere, A., Petit, S., Lanson, B., Berger, G., Lacharpagne, J.C., Johansen, H. (1997): Kaolinite-to-dickite reaction in sandstone reservoirs. Clay Min., ***33***, *297-316.*

Ehrenberg, S.N., Aagaard, P., Wilson, M.J., Fraser, A.R., Duthi D.M.L. (1993) Depth-dependent transformation of kaolinite to dickite in sandstones of the Norwegian continental shelf. Clay Minerals, ***28***, *325-352.*

Lei chou & Wollast, R. (1984): Study of weathering of albite at room temperature and pressure with a fluidized bed reactor. Geochim. Cosmochim. Acta, ***48***, *2205-2217.:*

MacAulay, G.E., Burley, S.D., Johnes, L.H. (1993) Silicate mineral authigenesis in the Hutton and NW Hutton fields: implications for sub-surface porosity development. 1377-1393. in: Petroleum Geology of Northwest Europe (J.R. Parker, ed.). The Geological Society London.

Nedkvitne, T. & Bjorlykke, K. (1992) Secondary porosity in the Brent Group (Middle Jurassic) Hulddra field, North Sea: Implication for predicting lateral continuity of sandstones? Journal Sedimentary Petrology, ***62***, *23-34.*

Osborne, M., Haszeldine, R.S., Fallick A.E. (1994) Variation in kaolinite morphology with growth temperature in isotopically mixed pore-fluids, Brent group, UK North Sea. *Clay Minerals,* ***29***, *591-608.*