Lithological control on the occurrence of chlorite in the diagenetic Wealden complex of the Bilbao anticlinorium (Basco-Cantabrian Basin, Northern Spain)

D. BARTIER, M. BUATIER, M. LOPEZ, J. L. POTDEVIN, H. CHAMLEY AND J. AROSTEGUI*

Sédimentologie et Géodynamique, CNRS-URA 719, Université de Lille 1, 59655 Villeneuve d’Ascq-Cedex, France, and *Departamento de Mineralogía y Petrología, Facultad de Ciencias, Universidad del País Vasco, 48080 Bilbao, Spain

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ABSTRACT: Sandstones and shales from the southern flank of the Bilbao anticline in the Gordexola and Orozko valleys, northwestern Spain, have been subjected to a detailed sedimentological, mineralogical and geochemical study. They are composed of proximal front-deltaic sandbars interbedded with silty-clayey sediments and correspond to a prograding sequence of a deltaic system. The clay mineral assemblages of doublets of sandstones and shales are composed mainly of illite, chlorite and illite-smectite mixed-layers R3 (ISII). The clay diagenesis consists of the transformation of smectite and IS mixed-layers to illite, the precipitation of Fe-rich chlorite in the pore spaces, and the alteration of micas to chlorite. According to petrographic, mineralogical and geochemical analyses, chlorite is more abundant in sandstones than in shales in both the <2 mm and coarser fractions. The relative abundance of chlorite increases in the sandstones located at the top of coarsening upward sandbars. Furthermore, chlorite formation occurs preferentially in the coarser grained sandstones previously cemented by ankerite. The geochemical and petrological investigations suggest that chlorite formed during burial diagenesis in a relatively closed system.

Knowledge of diagenesis in a siliciclastic environment has evolved over the last three or four decades in trying to understand and to predict sandstone reservoir quality. Diagenetic reactions of phyllosilicates in sandstones and interbedded shales have been studied by many authors, particularly with regard to the importance of temperature and burial depth (e.g. Jeans, 1984; Kantorowicz, 1984; Jahren & Aagaard, 1989) and their influences on porosity reduction (Boles & Francks, 1979; Bjurløykke et al., 1989). Factors governing mineralogical heterogeneities during diagenesis are commonly described in sedimentary basins: sedimentary facies and architecture, initial porosity variations, initial mineralogy and chemistry of sediments may control fluid flows and diagenetic reactions (Whitney & Northrop, 1987; Ruiz Cruz, 1994). Mass transport across the sandstone/shale boundaries can also create local diagenetic heterogeneity responsible for the formation of clay (Sullivan, 1988; Sullivan & McBride, 1991).

In this paper we consider the influence of lithology and initial chemistry of sediments on chlorite authigenesis in the strongly subsiding Basco-Cantabrian Basin (North Spain). Detailed sedimentological and petrographical analyses of two sections of Early Cretaceous sandstones and shales have been complemented by bulk rock geochemical and clay mineralogical investigations. The aim of this study is to document the mechanism of chloritization at the sedimentary sequence scale.

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GEOLOGICAL SETTING

The Basco-Cantabrian Basin represents the westernmost part of the Pyrenean domain. It is located between the massif of Cinco Villas to the East and the Asturian massif to the West (Fig. 1). The Lower Cretaceous to Middle Eocene deposits are related to the successive opening and closing of the Bay of Biscay (Choukroune et al., 1973). The sediment thickness increases from 2,000 m in the southern sector to 10,000 m in the northern and central sectors. During the early Cretaceous, an intense erosion in the steep hinterland induced the supply of terrigenous sediments (shales and sandstones) locally interrupted by carbonate deposition.

The Lower Cretaceous basin fill is commonly divided into three complexes: Wealden (Valanginian-Barremian), Urgonian (Aptian-Lower Albian), and Supra-Urgonian (Upper Albian-Lower Cenomanian) (Rat, 1983). The Wealden complex is composed of lacustrine clayey sediments passing into deltaic sandstones in the central sector and into fluvial deposits southward (in Arostegui, 1989). A fluvial-lacustrine system developed during the Berriasian-Barremian. Carbonate platform facies prevailed in the northern part of the basin, particularly during the deposition of the Urgonian complex (Arostegui et al., 1991). The Supra-Urgonian complex is represented by proximal platform facies in the southern part of the basin, replaced by deltaic facies in the central part and by turbiditic facies in the northern part (Arostegui et al., 1991).

SAMPLES AND METHODS

The studied area is located in the southern flank of the Bilbao anticlinorium. In this paper we focus on two representative sections of the Wealden complex characterized by similar sedimentary facies associations: the Orozko section located near the Cánuri-Alto village and the Gordexola section located near...
The mineralogy and texture of 81 sandstones, 43 shales and nine carbonates samples were examined in thin-section using an optical microscope and a scanning electron microscope (SEM) operating at 30 kV in back-scattered electron mode (Cambridge Stereoscan 240).

The clay fraction (<2 μm) of 133 samples was separated from the bulk rock by settling in a water column and oriented aggregates were mounted on glass slides following the procedure described in Holtzapffel (1985). Prior to separation, each sample was dispersed in deionized water, disaggregated, decarbonated with a HCl N/5 solution, and washed several times. Three X-ray diffraction (XRD) measurements were performed on the oriented mounts, air dried, glycolated and heated at 490 °C for 2 h. Slides were analysed using a Philips PW1710 X-ray diffractometer (Cu-Kα radiation). Clay minerals were identified by their characteristic basal reflections (Brown & Brindley, 1980) and compared with calculated patterns using the NEWMOD program (Reynolds, 1985). Semiquantitative determination of the major clay minerals was carried out using the intensity of the major XRD reflections with correcting factors (Holtzapffel, 1985).

Chemical analyses were obtained from selected powdered bulk samples (17 from the Orozko section, 21 from the Gordexola section). Samples were dried at 110 °C, melted in a mixture of lithium tetraborate, and introduced into a glycolated solvent. Major elements analyses were performed following the procedure described by Samuel et al. (1985) using an inductively-coupled plasma emission spectrometer (ARL 35000 C). The Na and K were determined by flame emission spectrometry. The major element oxides analysed include SiO2, Al2O3, MgO, CaO, Fe2O3, MnO, TiO2, BaO, P2O5, SrO, Na2O and K2O.

Mineral analyses were performed on polished thin-sections by using a Camebax SX electron
microprobe. Natural silicates and oxides were used as standards, the accelerating voltage being 15 kV, the counting time, 10 s, the current, 15 nA, and the spot size, 1 μm.

**LITHOFACIES DISTRIBUTION**

The Gordexola section is 10.5 m thick and displays four superimposed thickening and coarsening-upward sequences (Fig. 3) composed mainly of bioturbated shales and sandstones. The uppermost sandstone beds often display an erosional base and are channel shaped. Two representative facies associations were selected. The first corresponds to front-deltaic shales and rippled sandstone intercalations of middle to upper shoreface origin (Fig. 3A). The second one displays a 1.3 m thick front-deltaic sandbar from lower to upper shoreface (Fig. 3B).

The Orozko section is 10 m thick and comprises two sequences (Fig. 4): (1) offshore silty-clayey sediments with thin sandstone and carbonate beds; and (2) prograding shore-face sand lobes interbedded with offshore siltstones and mudstones. A detailed study was performed on a 2.3 m thick representative facies association of front-deltaic sandbar and associated sandstone-siltstone interbedding (Fig. 4A).

**RESULTS**

**Petrography**

The Orozko (WOR) and Gordexola (WGO) sections show three main lithologies: sandstone, siltstone and shale. Mineral components consist of quartz (60–80%), albite and orthoclase (1–15%), muscovite (5–10%), rock fragments (0–5%) and clay-rich matrix (1–10%). According to the quartz-feldspars-rock fragments petrographic classification of Pettijohn *et al.*, (1972), the sandstones are quartzarenitic to subarkosic. Quartz appears especially abundant in the coarse-grained sandstones (average grain size 0.5–0.6 mm). The abundance of muscovite, feldspar and clay matrix increases in the finer grained sandstones (average grain size 0.1–0.2 mm), siltstones and shales.

The cement chronology observed in Wealden sandstones is compared to observations of less buried Supra-Urgonian sandstones (not presented here). Both present similar lithology and cementation. However, Wealden sandstones show a dominant silica cementation with only carbonate cement residues whereas carbonate is the dominant cementation phase in the Supra-Urgonian sandstones. Carbonate cement occurs both as Fe-poor and Fe-rich phases, distinguished in thin-section by potassium ferricyanide and alizarin red-S stains. Three types of Fe-poor carbonate cement are observed, including two varieties of dolomite and calcite. The first type of dolomite is a minor phase occurring as fibrous rims around one side of the detrital muscovites. The second type of dolomite appears as sparry crystals which fill the primary porosity. Calcite is systematically observed in association with an Fe-rich carbonate determined as ankerite. Most thin-sections display the association of those three types of carbonate.

Two types of silification were observed, consisting of carbonate bioclast replacements and quartz overgrowths (Fig. 5A). Indented contacts between quartz grains clearly indicate that pressure-solution was an efficient mechanism. Carbonate bioclasts are replaced by chalcedony, microcrystalline quartz and mega quartz.

The petrographic investigations suggest that sparry dolomite cementation occurred during early diagenesis, and is followed by ankerite and calcite (Fig. 5C). Quartz is the last cement formed in the studied sandstones.

Clay minerals in the Wealden sandstones include an illitic matrix and a chlorite cement. The illite matrix occurs in the finer sandstones and is mixed with small quartz grains or small chlorite crystals. Diagenetic chlorite has been observed either as pore-space filling (Chlorite-1) (Fig. 5B) or as a replacement of detrital mica (Chlorite-2). Chlorite-1 is the dominant cement in the coarser sandstone beds located on top of coarsening up sandbars. Pore-filled chlorite-1 can be surrounded by quartz overgrowths. In some cases it also includes corroded detrital quartz. Relics of calcite and ankerite are present in the chlorite-1 cement (Fig. 5D). These observations suggest that the chlorite-1 cement is younger than calcite and ankerite cements but precedes quartz cement (Fig. 5E). On backscattered electron SEM images, authigenic chlorite-1 constitutes rosette-like and sometimes fan-shaped cluster fabrics. Individual rosettes are generally 1–5 μm in diameter but may reach 10–20 μm. Chlorite-muscovite (chlorite-2) stacks are commonly observed in these Wealden sandstones. Chlorite-2 crystals are located between expanded muscovite layers, and can also appear as
elongated bands through a muscovite crystal. Non-altered and altered muscovite display very similar elongated shapes deformed by compaction suggesting that chlorite-2 precipitated between mica layers but also partially replaced detrital muscovite (Fig. 5F).

At the scale of the sand bar body, a zonation of cements is observed in Wealden sandstones.

Fig. 3. Sedimentology and variations in clay mineralogy along the Gordexola Wealden section. A and B are the two sandbars selected for high resolution sedimentological and clay mineralogy studies.
Chlorite-1 cemented sandstones are present only at the top of sand bars whereas quartz cemented sandstones occur principally at the lower part of sand bars.

Clay mineralogy ($<2 \mu m$ fraction)

The $<2 \mu m$ fraction of both sandstones and shales contains illite, ordered (R3) mixed-layer illite-

Fig. 4. Sedimentology and variations in clay mineralogy along the Orozko Wealden section. Numbers correspond to the studied samples. A: selected detail interval for high resolution sedimentological and clay mineralogy studies.
Control on chlorite occurrence

Fig. 5. Petrographical data for the studied Wealden sandstones. A and B are optical micrographs of quartz overgrowth in sandstone WGO4 (A) and of chlorite-1 cementation in WOR12 (B); C and D are schematic representations of the carbonate cementation observed by optical microscopy on stained thin-sections: sparry dolomite cementation replaces ankerite and calcite (C), breakdown of ankerite in chlorite-1, some dolomite relics are still present (D); E and F are back-scattered electron micrographs of a chlorite-1 pore-filling surrounded by quartz in sandstone WGO19 (E) and a muscovite alteration into chlorite-2 in sandstone WOR28, chlorite-2 crystals are located between expanded muscovite layers (F). Qz: quartz; Ov: quartz overgrowth; Do: dolomite; An: ankerite; Cc: calcite; Chl: chlorite; M: muscovite.
smectite and chlorite. The XRD patterns shown in Fig. 6 correspond to the clay fraction of a chlorite-rich sandstone and of an illite-rich shale, respectively. The 002 and 004 reflections of chlorite located at 7.1 Å and 3.54 Å are more intense than the 001 and 003 reflections at 14.2 Å and 4.7 Å, suggesting the presence of an Fe-rich chlorite or chamosite (Brown & Brindley, 1980). Illite is characterized by the 001, 002 and 003 reflections located at 10.5 Å and 3.33 Å, respectively. The comparison of the XRD patterns of air-dried and glycolated samples with patterns calculated using the NEWMOD program (Reynolds, 1985) allowed the identification of an R3 illite-smectite (I-S) mixed-layer type clay. The R3 I-S mixed-layer clay displays diagnostic reflections at 14.88 Å in the air-dried sample which shifted to 11.65 Å after glycolation.

The relative abundance of clay minerals in the <2 µm fraction in Gordexola and Orozko sedimentary rocks give way to two major comments (Figs. 3 and 4): there is a greater abundance of chlorite in sandstones (8–70%) than in adjacent shales (0–30%); the abundance of chlorite increases with bed thickness and grain size in individual sandstone beds, as observed between 140–210 cm interval in the Gordexola section (Fig. 3B).

Fig. 6. Examples of XRD patterns of the <2 µm fraction from sandstone WOR10 and shale WOR11 from the Orozko section. A.D: air dried; G1: glycolated; H: heated at 490°C.
Microprobe analyses

Microprobe analyses have been performed on dolomite, ankerite and calcite yielding the following structural formulae: dolomite \((\text{Ca}_{0.98}\text{Fe}_{0.02}\text{Mg}_{0.96}\text{Mn}_{0.02})\)(CO\(_3\))\(_2\); ankerite: \((\text{Ca}_{1.08}\text{Fe}_{0.48}\text{Mg}_{0.38}\text{Mn}_{0.02})\)(CO\(_3\))\(_2\); calcite: \((\text{Ca}_{0.96}\text{Fe}_{0.01}\text{Mg}_{0.01}\text{Mn}_{0.01})\)(CO\(_3\)).

The illite matrix has been analysed in two types of sandstones, the first one corresponds to sandstones cemented by quartz (illite-1) and the second by chlorite (illite-2). The structural formulae of these two types of illite are: illite-1: \((\text{K}_{0.87}\text{Na}_{0.30}\text{Ca}_{0.30})(\text{Al}_{3.65}\text{Ti}_{0.05}\text{Fe}_{0.17}\text{Mg}_{0.14}\text{Mn}_{0.01})[[\text{Si}_{6.93}\text{Al}_{1.07}\text{O}_{20}]\text{OH}_4]\); illite-2: \((\text{K}_{1.52}\text{Na}_{0.24})(\text{Al}_{3.70}\text{Ti}_{0.05}\text{Fe}_{0.15}\text{Mg}_{0.14}\text{Ca}_{0.10})[[\text{Si}_{6.26}\text{Al}_{1.74}\text{O}_{20}]\text{OH}_4]\).

Both illites are less Fe-rich than the detrital muscovite and display differences in their K and Al contents. Illite-1 is depleted in K relative to illite-2, the higher K content of which coincides with an increase of the \([\text{Al}/\text{Si}]\)\(_{\text{IV}}\) ratio.

According to microprobe analyses of the chlorite cement, the structural formula of chlorite is: chlorite-1: \((\text{Mg}_{2.40}\text{Al}_{1.26}\text{Fe}_{0.42}\text{Mn}_{0.01})[[\text{Si}_{6.26}\text{Al}_{1.74}\text{O}_{20}]\text{OH}_4]\).

Chlorite formed by muscovite alteration has a very similar composition but contains more Al and less Fe than the chlorite cement. Its structural formula is: chlorite-2: \((\text{Mg}_{2.46}\text{Al}_{1.31}\text{Fe}_{0.92}\text{Mn}_{0.02})[[\text{Si}_{6.15}\text{Al}_{2.80}]\text{OH}_4]\).

Control on chlorite occurrence

Bulk-rock geochemistry

Chemical analyses of Orozko and Gordexola samples are given in Tables 1 and 2. The composition of shales is fairly homogeneous whereas sandstones display variations in their Al\(_2\)O\(_3\), K\(_2\)O and Fe\(_2\)O\(_3\) contents. The variations of major elements along Gordexola and Orozko sections are plotted in Fig. 7. Two groups of major elements can be distinguished. The first one includes Al\(_2\)O\(_3\), BaO, TiO\(_2\), K\(_2\)O and SrO or Na\(_2\)O, and the second one Fe\(_2\)O\(_3\) and MgO. In both sections, most shales are enriched in elements of the first group whereas sandstones contain more Fe\(_2\)O\(_3\) and MgO. The greater amounts of Fe\(_2\)O\(_3\) and MgO characterize the top of the sandstone bars. These differences are related to the mineralogical composition of the lithologies, i.e. their quartz and clay mineral contents.

The mineralogical differences, and particularly the chlorite and illite contents of the rocks, are expressed in a triangular diagram K\(_2\)O-Al\(_2\)O\(_3\)-(Fe\(_2\)O\(_3\)+MgO) (Fig. 8A). All analyses are distributed along a line defined by the chlorite and illite compositions. The greater abundance of chlorite in...
sandstones is established by these data, all sandstone data being located near the chlorite pole. The analyses plotted in a diagram of $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ (Fig. 8B) display a good correlation between these elements. The greater $\text{SiO}_2$ content of sandstones is attributed to the abundance of quartz, whereas the increase of $\text{Al}_2\text{O}_3$ in siltstones and shales reflects the abundance of clay minerals. An excellent correlation is also observed between $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ ($R^2 = 0.99$ for Gordexola analyses, and $R^2 = 0.96$ for Orozko analyses), and is attributed to the increase in illite in the smaller grain size sediments. In Fig. 8C, the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio vs. % chlorite in the <2 μm clay fraction is presented. The greater amount of chlorite in sandstones is correlated with greater $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. The large dispersion of sandstone plots is probably due to the presence or absence of a chlorite cement (see petrographic results), as well as to the abundance of chlorite in the coarser fractions. Notice that in the Herron (1988) classification, the sandstones which are plotted in the Fe-sand field correspond to chlorite-cemented sandstones (Fig. 8D).

These data establish the relationship existing between mineralogy and chemistry of the Wealden rocks. Sandstones contain more quartz and chlorite, whereas shales are enriched in aluminous components, especially illite.

**DISCUSSION**

**Chronology of cementations**

The chronology of cementation phases in sandstones is summarized in Fig. 9. The first cement corresponds to fibrous dolomite cement probably formed shortly after deposition (in Tucker, 1991). Three other generations of carbonate cement have been identified: a sparry dolomite and two generations of poikilotopic carbonates identified as ankerite and calcite. Ankerite and calcite cements

**TABLE 2. Major element oxides analyses (%) of bulk-rock samples of the Wealden Orozko (WOR) sections.**

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<th></th>
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<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>Mn₃O₄</th>
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<th>Na₂O</th>
<th>K₂O</th>
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commonly include dolomite relics confirming their early origin.

Quartz cementation postdates carbonate cements. Its formation could be related to: (1) a release of silica during kaolinization of feldspar (Bjørlykke, 1983); (2) pressure solution (Pettijohn et al., 1972); or (3) a release of silica during smectite illitization (Hower et al., 1976). In the present study, kaolinized feldspars are not observed and kaolinite is not detected by XRD. According to petrographic observations, pressure-solution processes are considered as having been active in the Wealden sandstones. However, some silicification could also have been induced by the transformation of smectite to illite (see below).

Chlorite cement (chlorite-1) is the dominant cement in the Wealden coarser-grained sandstone beds located at the top of coarsening up sandbars (Figs. 3, 4). Chlorite cementation is associated with ankerite and calcite relics. All observations suggest that the chlorite cement is younger than both ankerite and calcite cements (and obviously than dolomite), but preceded the quartz cementation.

**Clay minerals diagenesis**

Three main types of clay minerals have been distinguished in Wealden shales and sandstones: illite, illite-smectite mixed-layers and chlorite. Arostegui (1989), Arostegui et al. (1991), and

![Diagram showing variations in bulk-rock geochemistry and chlorite content.](image-url)
Nieto et al. (1996) studied the clay minerals distribution in shales from the Basco-Cantabrian Basin. They demonstrated that the smectite-to-illite transition takes place in the Lower Cretaceous sediments with increasing depth of burial, the most deeply buried sediment attaining the anchizone grade. Arostegui (1989) and Arostegui et al. (1991) have presented the distribution and the types of illite-smectite mixed-layers in Lower Cretaceous formations of the Basco-Cantabrian Basin, characterized by a south-to-north trend with dominant R1 (I-S) mixed-layer type in the southern part of the basin, and dominant R3 (ISII) in the central part. The XRD data of Wealden rocks are in agreement with this mineralogical distribution: the clay minerals of Gordexola and Orozko sections, which crop out in the central part of the basin, comprise R3 type illite-smectite mixed-layers. The very low abundance of R3 suggests that the Wealden series represents the last stage of the smectite-to-illite transition. In the Orozko section, some samples, e.g. WOR26 to WOR54, do not contain any I-S mixed-layers in the <2 μm clay fraction, suggesting that a higher diagenetic grade

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Fig. 8. Geochemical plots of Wealden rocks in the Gordexola and Orozko sections. Black squares: shales; triangles: silts; circles: sandstones. The average chemical composition of illite-2, detrital muscovite and chlorite are plotted in diagrams A and B (see text for comments). D: Plots of rock chemical analyses in the Herron (1988) classification.

Fig. 9. Relative chronology of the cementation phases in the Wealden sandstones.
has been reached in the central part of the basin than in the eastern external part.

In the sandstones, illite occurs mainly in the clay matrix, where microprobe analyses show two different chemical compositions: illite-1 in quartz and carbonate cemented sandstones, and illite-2 in chlorite cemented sandstones. Illite-2 contains more K and Al than illite-1. This different K and Al content can be explained by the presence of I-S mixed-layers containing illite particles in quartz and carbonate sandstones, whereas almost pure illite occurs in chlorite cemented sandstones. These data suggest that the smectite-to-illite transition is more advanced in chlorite cemented sandstones than in quartz and carbonate cemented sandstones.

According to Arostegui (1989) and Arostegui et al. (1991), chlorite is not very abundant in shales from the Basco-Cantabrian Basin. Nieto et al. (1996) have identified both authigenic and detrital chlorite crystals by YEM. According to these authors, the two types of chlorite can be distinguished from their chemistry, authigenic chlorite being more Fe-rich than detrital chlorite. This study, which focuses on Wealden shales and sandstones, demonstrates that chlorite is a significant clay mineral in the <2 μm fraction, particularly in the coarser-grained sandstones (up to 70%).

Chlorite cement is detected only in the Wealden complex, whereas it is absent in the less buried Supra-Urgonian complex (Bartier et al., 1996). Petrographical observations and microprobe data show that authigenic chlorite postdates ankerite and calcite and is Fe-rich. All observations therefore suggest that this chlorite differs in origin from chlorite formed during early diagenesis in the sandstones investigated in an offshore bar by Tillman & Almont (1979). In the studied sandstones, chlorite is clearly formed during burial. The presence of chlorite in the Wealden rocks supports the data of Arostegui et al. (1991) which suggests that these rocks have reached the anchizone grade. Chlorite formation could result from a smectite-to-chlorite transition. Such a process has been described by Dunoyer de Segonzac (1969) in the Douala basin, Cameroon, by Chang (1986) in the Brazilian offshore basin, and by Rinckenbach (1988) in the Mahakam delta, Kalimantan. However, the data obtained in this study on the Wealden rocks do not support such a mechanism: chlorite-smectite mixed-layers were not detected by XRD in sandstones and shales, and chlorite is less abundant in shales than in sandstones.

The diagenetic formation of chlorite in Wealden sandstones could have occurred by a reaction which involved carbonates representing the source of Mg and Fe, and a detrital assemblage of clay minerals and quartz forming the source of Al and Si. The formation of chlorite by a reaction involving the breakdown of carbonate has been described by Muffler & White (1969); dolomite, ankerite and kaolinite identified in siltstones and sandstones of the Salton Sea geothermal field (California) are replaced by chlorite and calcite at a depth extending from 1200 to 2300 ft. Hutcheon et al. (1980) proposed a similar reaction for Cretaceous sandstones of the Kootenay formation (Canada). These authors suggested that dolomite and illite reacted to form chlorite and calcite. More recently, Hillier (1993) also documented a chlorite authigenesis by reactions between a detrital dioctahedral clay assemblage and dolomite in lacustrine mudrocks from the Orcadian Basin (Northern Scotland). In all these studies, authigenic chlorite is a Mg-rich mineral. In the Wealden sandstones, the occurrence of Fe-rich chlorite can be explained by a reaction between ankerite as the source of Mg and Fe, and detrital dioctahedral clay (illite or muscovite type) as the source of Al and Si. These results confirm such a scenario proposed by Surdam et al. (1989) in a paper describing diagenetic pathways of sandstones and shale sequences.

A second type of chlorite observed in Wealden sandstones consists of chloritized mica. Its chemistry is very similar to that of chlorite formed in the pore-spaces of the sandstones. These data suggest that chlorite cementation and mica chloritization have the same diagenetic origin. Muscovite-chlorite stacks have been commonly described in mudstones that have undergone diagenesis and low-grade metamorphism. They are generally described as a product of the replacement of detrital biotite characterized by the following stages: (1) the detrital biotite is altered into chlorite through a layer-by-layer transformation; and (2) white mica progressively fills the chlorite cleavages (Li et al., 1994). Relics of biotite are generally observed in chlorite-mica stacks which are formed by this mechanism, as shown in slates from central Wales (Dimberline, 1986) and in many other sedimentary rocks (e.g. Al Dahan & Morad, 1986; Morad, 1990). Detrital biotite is absent in shales and sandstones from the investigated Wealden sections, muscovite being the only detrital mica identified. Non-altered and altered muscovite grains appear as
elongated crystals up to 200 µm. This morphology differs from the stocky chlorite-mica intergrowths described by Li et al. (1994). All these data suggest that chlorite-muscovite stacking in the Wealden sandstones results from a chloritization of detrital muscovite. This reaction implies the mobility of Si, Al, Fe, Mg and K, suggesting a dissolution-precipitation process. The characterization of the mechanism of the muscovite-chlorite transition needs further investigations.

**Lithological control**

Our investigations show that chlorite is more abundant in sandstones than in shales. However, there is no significant increase in the relative percentage of chlorite at each sandstone-shale boundary, which differs from the data obtained by Moncure et al. (1984) in the Pleasant Bayou well (Texas), and of Ruiz Cruz (1994) in deep water sandstones from southern Spain. The latter author deduced that diagenesis was controlled by the composition of detrital minerals, primary porosity, and permeability. She described fine-grained sandstones that are more frequently characterized by chlorite or illite cement than coarser quartz-arenite sandstones which are enriched in silica or carbonate. In Wealden sandstones of the Basco-Cantabrian Basin, chlorite cement is only observed in coarse-grained sandstones and particularly at the top of thickening and coarsening upward sandbars. The same correlation between the occurrence of chlorite and the coarsening of sandstones has been described by Spötl et al. (1994) in the Arkoma foreland basin, USA. These authors distinguished three types of chlorite (chlorite peloids, diffuse matrix and grain coatings), all of which appeared to have been formed during early stages of diagenesis. In the Wealden sandstones, chlorite is related to burial diagenesis. There is an excellent correlation between the relative percent of chlorite in the <2 µm fraction and the chemical composition of the bulk rock. The increase in chlorite is associated with an increase of Fe₂O₃ and MgO (see geochemical results). In the Supra-Urgonian complex greater Fe₂O₃ and MgO contents are also detected at the top of sandbars complex although chlorite is absent in the clay mineral fraction. The Supra-Urgonian sandstones with greater Fe₂O₃ and MgO percentages are mainly cemented by ankerite and remains of dolomite. These data suggest that chlorite formation is controlled mainly by the initial mineralogical composition and by the grain size of sandstones. During burial diagenesis, the ankerite dissolution was probably responsible for a release of Fe and Mg, which allowed the precipitation of Fe-rich chlorite in the pore space.

**CONCLUSIONS**

Mineralogical and geochemical investigations of Wealden sandstones-shales doublets in Orozko and Gordexola sections show that clay mineral assemblages are dominated by illite and chlorite, associated with minor R3-ordered illite-smectite mixed-layers. The origin of the neoformed illite can be related to a smectite-to-illite transition. The small relative abundance of I-S mixed-layers attests that the studied samples represent the latter stage of this transition. The main clay mineral difference between shales and sandstones is related to the chlorite abundance. Chlorite is more abundant in sandstones than in shales both in the <2 µm and coarser fractions (chlorite cemented sandstones). Moreover, chlorite abundance increases in the sandstones located at the top of coarsening upward sequences. Chlorite formation seems to be related to the primary occurrence of ankerite. During the burial diagenesis, the ankerite dissolution determined a release of Fe and Mg, which favoured the chlorite formation.

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Control on chlorite occurrence


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