ABSENCE OF CLAY DIAGENESIS IN CRETACEOUS-TERTIARY MARINE SHALES, CAMPOS BASIN, BRAZIL

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Abstract—In Upper Cretaceous-Tertiary marine shales (Campos Formation) from the Campos basin, Brazil, mixed-layer illite/smectite (I/S) has remained randomly interstratified to depths of 3500 m and to temperatures as high as 100°C, in contrast to the typical pattern of shale diagenesis in, for example, the Gulf Coast area. X-ray powder diffraction analysis of the bulk shale and several size fractions from samples from one well in the Brazilian basin and from one in the Gulf Coast region were carried out to assess the factors that might have controlled the lack of illitization in the Campos Formation shales.

In samples from the Gulf Coast well, the clay minerals are I/S (montmorillonite-type), discrete illite, chlorite, and minor kaolinite. In contrast, the clay minerals in samples from the Campos basin well are kaolinite, clay-size biotite, and I/S (nontronite-type). Kaolinite is abundant in this well, and the variation of its abundance with depth seems to reflect variations in sea-level stands. The original composition of the I/S (nontronite-type) was probably the main factor controlling the lack of illitization in the shales of the Campos Formation.

Key Words—Diagenesis, Illite, Interstratified, Nontronite, Shale, Smectite, X-ray powder diffraction.

INTRODUCTION

The transformation of smectite to mixed-layer illite/smectite (I/S) in response to increasing temperature has been widely reported in thick sequences of pelitic sediments (Burst, 1959, 1969; Perry and Hower, 1970; Foscolos and Kodama, 1974; Hower *et al.,* 1976). The reaction also seems to be related in time to the formation of overpressured zones (Burst, 1969; Plumley, 1980) that may influence petroleum migration (Powers, 1967; Burst, 1969; Perry and Hower, 1972). In addition, hydrated clays undergoing burial diagenesis may catalyze the breakdown of organic matter into liquid and gaseous hydrocarbons (Johns, 1982).

The main factors that control the reaction are: (1) temperature (Perry and Hower, 1970, 1972); (2) the length of time that the shale has been subjected to elevated burial temperatures (McCubbin and Patton, 1981); (3) the presence of detrital components that can provide K^+ and Al^{3+} to drive the reaction (Hower *et al.,* 1976); (4) pore-fluid chemistry (Ca^{2+} and Mg^{2+} were shown experimentally by Blatter (1974) to slow the reaction); and (5) the starting composition of the smectite (Foster and Custard, 1982).

The relative importance of these factors to the reaction of smectite is not completely known. In Lower Cretaceous shales from sedimentary basins in northern Brazil, Chang (1983) reported not only the progressive illitization of smectite, but also the chloritization of trioctahedral smectite (saponite) in response to increasing burial depth. In the Campos basin, however, Cretaceous and Tertiary marine shales of the Campos For-

mation appear to have undergone only limited illitization (Anjos, 1984).

The objective of the present study was to investigate why the illitization reaction has been so limited in shales of the Campos Formation. For this purpose, one representative well was selected for a detailed mineralogical analysis. For comparison, a well from the Texas Gulf Coast, where extensive illitization has occurred, was also studied.

LOCATION AND GEOLOGIC SETTINGS

The Campos basin underlies the continental shelf of the state of Rio de Janeiro in southeastern Brazil. The basin is bounded on the north by the Victória arch and on the south by the Cabo Frio high (Figure 1). The basin is the most promising petroleum province of Brazil. The Campos basin is a typical passive, continental-margin basin of the Atlantic type (Ponte and Asmus, 1978).

The sedimentary fill of the basin has been divided into four major lithostratigraphic units (the Lagoa Feia, Macaé, Campos, and Emborê Formations), which represent the main stages of tectonic evolution of the basin (Figure 2) and the formation of the South Atlantic Ocean (Ponte and Asmus, 1978). The Lagoa Feia Formation consists of continental clastic and volcanic rocks from the rift-valley stage overlain by evaporites of the proto-oceanic gulf stage. The Macaé Formation represents the beginning of the open-marine stage sedimentation and consists of shelf carbonates. The Campos Formation consists of deep-water shales and
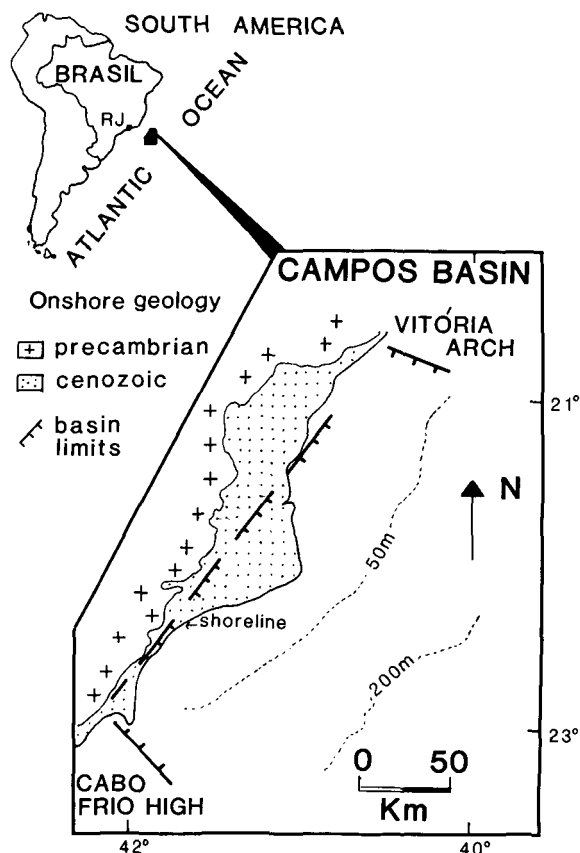
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Figure 1. Location map and structural framework of the Campos basin, Brazil. Dashed lines = water depth.

intercalated sandstone turbidites, whereas the Emborê Formation consists of proximal fluvial deltaic sandstones. Both thermal and isostatic subsidence prevailed during the evolution of the basin. The Campos Formation was deposited primarily during isostatic subsidence.

SAMPLES AND METHODS

Samples

Drill cuttings were selected under a binocular microscope and gently washed with distilled water to remove drilling mud.

Gulf Coast well. The Gulf Coast well was located off the Texas shore. The samples cover the stratigraphic interval from Oligocene to Upper Miocene. They comprise the Anahuac and Frio formations; and the boundary between them occurs at about 2680-m depth. The maximum depth of about 5000 m corresponds to borehole temperatures as high as 137°C. The samples consisted mainly of light-grey, green-brown shales. In the shallow samples, red-brown shales were also present.

Campos well. Samples from the Campos well covered the stratigraphic interval from Coniacian (Upper Cre-

taceous) to Upper Miocene. The maximum depth was about 3500 m; the maximum borehole temperature was 100°C. The samples consisted of micaceous, organic-rich, dark-grey to brown silty shales.

Analytical methods

Ten grams of shale chips were ultrasonically disaggregated in distilled water. From this suspension, the following size fractions were obtained by centrifugation: <2, 2–10, >10, <0.1, <0.2, and <0.3 μm. The procedure used was a modification of that of Hower *et al.* (1976) and was described by Anjos (1984). Some samples were treated chemically (Jackson, 1974) to eliminate carbonates and organic matter and thus increase the yield of very fine (<0.2 μm) material. The procedure, however, yielded no substantial increase in the amount of this material.

X-ray powder diffraction (XRD) analyses of all samples were made using either a Philips-Norelco diffractometer or a Siemens D-500 diffractometer (CuKα radiation), the latter equipped with a graphite monochromator, at a scanning rate of 1° or 2°2θ/min. Whole rock samples were ground with mortar and pestle and then in a SPEX ball mill for 10–15 min, side packed in aluminum sample holder, and X-rayed from 2° to 65°2θ. Semiquantitative estimates of the minerals in the shale were obtained following the method described by Hoffman (1976).

XRD patterns of randomly oriented mounts of the clay fraction were obtained between 58° and 65°2θ to define the 060 peak position of the clays. These were the only analyses performed on the Siemens D-500 diffractometer. Slides of oriented samples of each of the size fractions obtained were prepared by suction onto ceramic tiles, suction onto Millipore filters, or sedimentation onto glass slides, depending on the amount of material and type of equipment available. Samples were solvated by ethylene glycol by applying drops of ethylene glycol onto the ceramic tiles or by placing the glass slides in an ethylene glycol atmosphere for at least 30 hr. The <2-μm samples were also treated by heating them at 550°C for 30 min, Mg- and K-saturation, and K-saturation plus glycolation. The samples were saturated following the methods of Jackson (1974).

Semiquantitative estimates of the amount of different clay minerals present were made by measuring the heights on patterns obtained on air-dried samples. The amount of illite/smectite (I/S) was estimated from the 15-Å peak, illite from the 10-Å peak, and kaolinite + chlorite from the 7-Å peak. The distinction between chlorite and kaolinite was only qualitative.

The identification of the type of ordering and the amounts of each component of the I/S was obtained by comparing the XRD patterns of glycolated samples with computer-calculated diffraction profiles, following Reynolds and Hower (1970). The percentage of
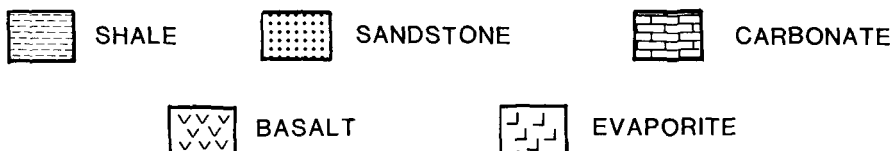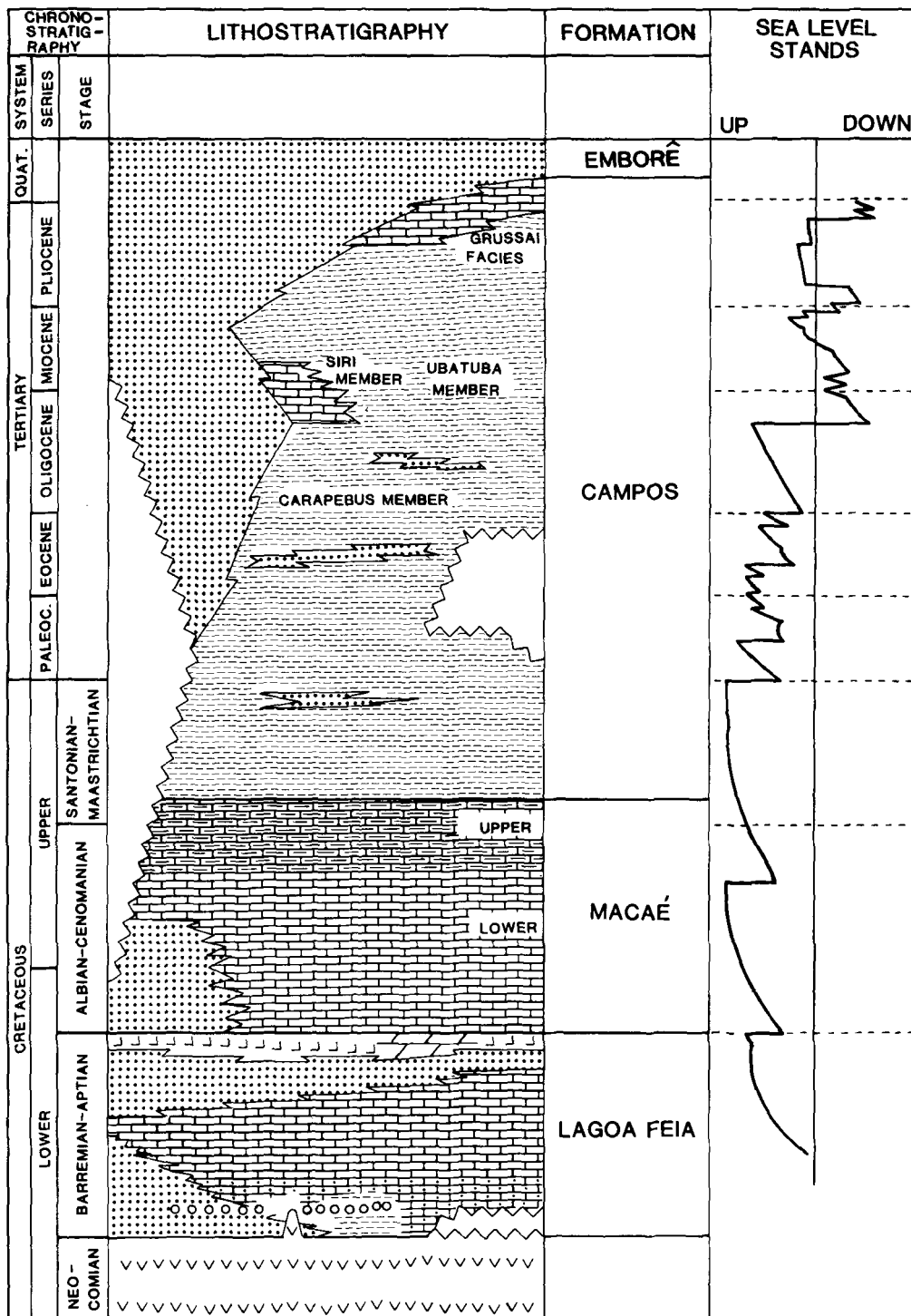
Figure 2. Geologic column of the Campos basin. Curve at right represents global eustatic variation of sea level; from Vail *et al.* (1977).
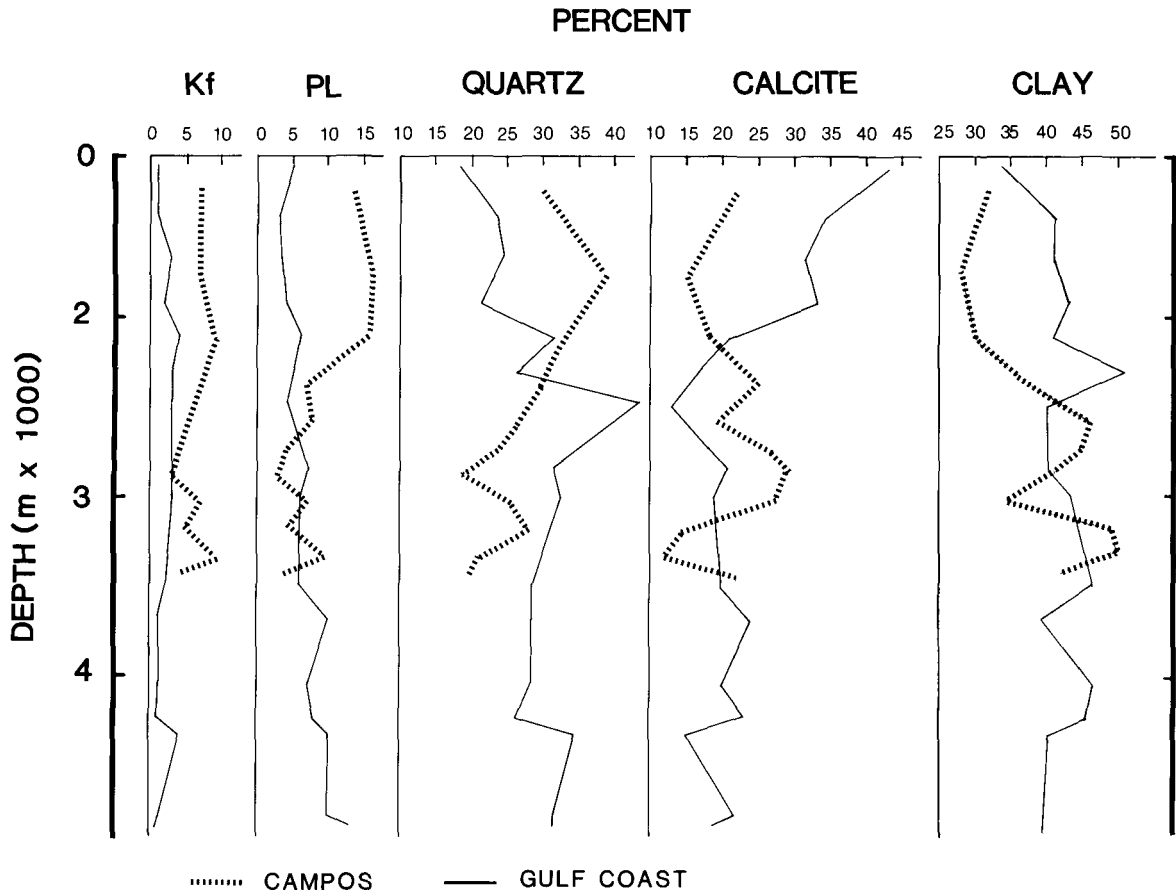
Figure 3.   Semiquantitative abundances of clay and non-clay minerals with depth for Campos basin and Gulf Coast wells. Q = quartz; Kf = K-feldspar; Pl = plagioclase; clay represents total phyllosilicate. Values obtained according to Hoffman (1976).

illite in randomly interstratified I/S was determined by the saddle/peak ratio at 17 Å. The $(002)_{10}/(003)_{17}$ reflection was also used if the peak resolution was satisfactory. For regularly interstratified I/S, the position of the $(005)_{27}/(002)_{10}$ reflection was used.

RESULTS

Whole-rock mineralogy

The whole-rock mineralogy of the Campos and Gulf Coast shales (Figure 3) consists of quartz, calcite, plagioclase, K-feldspar, and clay minerals and rare traces of pyrite. The mineralogy of the Gulf Coast well is more consistent than that of the Brazilian well, suggesting that the composition of the sediments in the Gulf was nearly constant through time.

In the Gulf Coast well, the total clay and K-feldspar contents vary little with depth, whereas plagioclase increases. Calcite is abundant in the shallower samples, but decreases markedly with depth to 2600 m. The calcite content of deeper samples is nearly constant. The total clay content of samples from the Campos

well varies with depth. K-feldspar, plagioclase, and quartz decrease down to 3000 m; calcite increases slightly with depth.

Mineralogy of size fractions

The mineralogical difference among the different size fractions within a given sample from the Campos and Gulf Coast wells (Figure 4) shows that quartz, calcite, and feldspar are concentrated in the coarse fractions (>2 μm). Feldspar concentrated in the >10-μm fraction, whereas calcite seems to predominate in the 2–10-μm fraction. In the <2-μm fraction, clay minerals predominate and feldspar is absent. Minor quartz and calcite are also locally present. In the very fine fractions (<0.3, <0.2, and <0.1 μm), only clay minerals are present. In the Gulf Coast well I/S is the dominant clay mineral present plus minor amounts of chlorite and/ or kaolinite and discrete illite. On the other hand, in the Campos well kaolinite and mica, rather than I/S, are the major clay minerals even in the fine fractions. In the Gulf Coast well, I/S is the chief clay mineral in
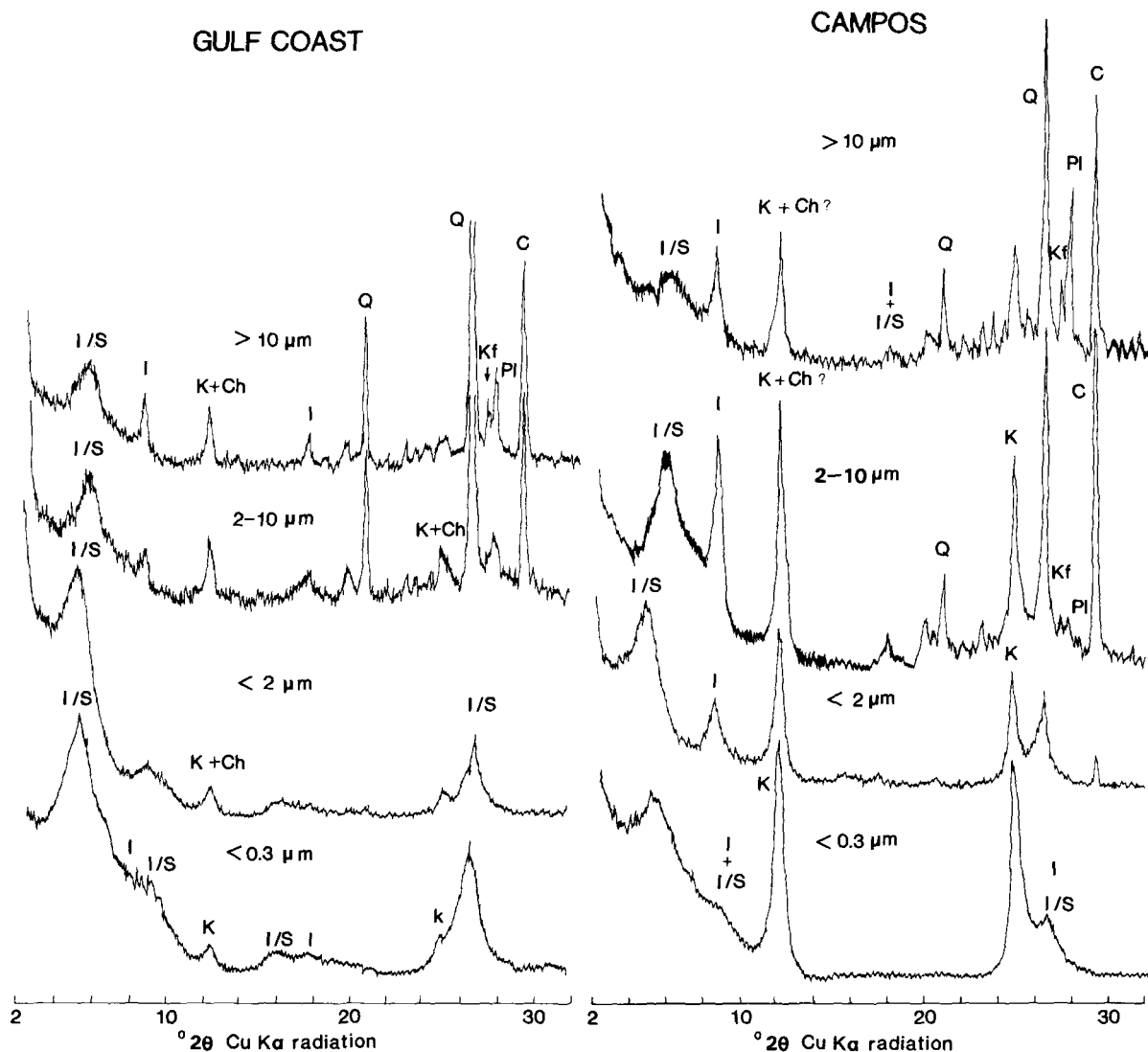
Figure 4. X-ray powder diffraction patterns of oriented aggregates of different size fractions: (A) sample from the Campos well (2600 m) and (B) sample from the Gulf Coast well (2600 m). Coarse fractions are untreated. The <2- and <0.3-μm fractions were solvated with ethylene glycol. Q = quartz, C = calcite, Kf = K-feldspar, Pl = plagioclase, I/S = illite/smectite, I = illite, K = kaolinite, and Ch = chlorite. Note the weak 002 reflection of illite in all size fractions in the Campos well.

all fractions, whereas in the Campos well, kaolinite and mica are present in significant amounts in all fractions. Chemical analysis that could have led to full identification of the I/S was not possible because the I/S could not be isolated from the other clays. In all size fractions of the Campos samples, the 10-Å mineral yielded a weak 002 (5 Å) reflection, typical of biotite, glauconite, or phlogopite. In the Gulf Coast samples, the relative intensities of the basal reflections suggest a muscovite-type mica.

<2-μm fraction. Semiquantitative estimates of each clay mineral as a function of depth for both wells are shown in Figure 5. In the Gulf Coast well, the clay minerals are I/S, discrete illite, and chlorite. Kaolinite, if present, occurs in very small amounts. In this figure, chlorite is combined with kaolinite, but chlorite is by far the more abundant of the two, particularly in the deeper samples. Discrete illite occurs throughout the well, and no systematic change with depth was observed; however, in samples that contain ordered I/S, discrete illite was difficult to distinguish from I/S. The predominant clay mineral in all samples is I/S.

The I/S is randomly interstratified (R=0) in samples from 1250 to 3000 m in the Gulf Coast well and ordered (R=1 and R>1) below 3700 m. A sequence of XRD patterns of glycolated samples in order of increasing depth (Figure 6) shows the change in ordering
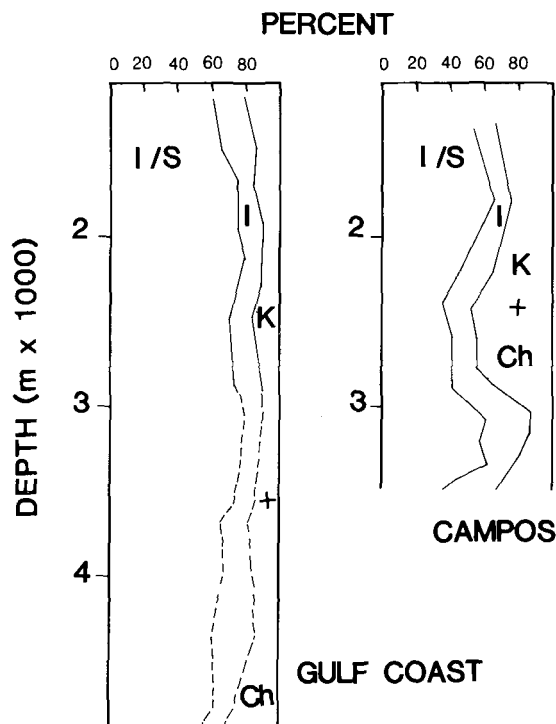
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Figure 5. Semiquantitative estimates of clay minerals present in the <2-μm fraction in Gulf and Campos wells obtained by measuring peak height. Dashed line signifies that the limits are inferred, because the illite/smectite (I/S) is ordered and the same peaks could not be used as for upper samples. I/S = illite/smectite; I = illite; K = kaolinite; Ch = chlorite.

of the I/S. The 17-Å peak indicates random interlayering (R=0) in the first two samples, whereas the 13.2- and 12.8-Å peaks of the next two samples represent ordered interlayering (R=1), and the 12.3-Å peak of the last sample indicates some long-range ordering (R>1). The percentage of illite in the I/S ranges from 42% in the shallowest sample to 80% below 4056 m (Figure 7).

In the Campos basin well, the clay minerals present are abundant kaolinite, mica, and I/S and in some samples, small amounts of chlorite (Figure 5). The kaolinite content shows no systematic increase or decrease with increasing depth, and seems to be related to time of deposition.

The 10-Å mineral present in about the same concentration throughout the well cannot be called illite (dioctahedral mica), because the 5-Å reflection is too weak for a true illite. The presence of biotite flakes observed with the binocular microscope, the abundance of the micaceous mineral in larger size fractions, and an 060 peak of 1.54 Å lead to the conclusion that the 10-Å mineral is chiefly biotite.

In the Campos samples, the I/S in all samples is randomly interstratified. Only a slight increase in the

percentage of illite layers was noted with increasing depth, from about 35% to 50% (Figures 6 and 7).

The behavior of the Campos I/S with different treatments (Figure 8) typically shows that the low-angle peak for the air-dried material is at 14.7 Å, expanding to 17 Å on glycolation. The peak collapses to 10 Å on heating. K-saturation followed by glycolation yielded a 17-Å peak. A comparison of this peak with the 17-Å peak of the non-K-saturated glycolated material shows an increase in the intensity of the background, suggesting a more illitic composition, perhaps due to the presence of some vermiculite-like layers. The increase in background can also be an artifact of the K-saturation treatment, which can produce mixed-layered structures in homoionic K-smectite (Čičel and Machajdik, 1981). The difference in peak positions between the air-dried version and the Mg-saturated material indicates that the I/S contains mainly divalent cations in the interlayer position.

The I/S in the Campos shales shows a very weak 002/003 reflection. A computer-simulated pattern of a dioctahedral I/S containing large amounts of Fe is similar to the pattern of the Campos clays (Figure 6, bottom). Trioctahedral smectites also yield low 002/003 intensities, but the 060 spacing at 1.504 Å indicates that the I/S is dioctahedral (Figure 9A). A comparison of the experimental XRD pattern with the computer-simulated pattern suggests that the I/S in the Campos basin is an Fe-rich dioctahedral I/S.

Figure 9A shows that both dioctahedral and trioctahedral minerals are present in the <2-μm fraction of the Campos shales. The trioctahedral reflection at 1.54 Å represents trioctahedral mica plus quartz whose presence is confirmed by the peak at 1.817 Å, which in pure quartz has twice the intensity of the peak near 1.54 Å. The dioctahedral peak at 1.496 Å represents the kaolinite; the I/S peak is at a greater d-value. The 1.496-Å peak is not clearly resolved, but the shoulder on the low-angle side indicates that a dioctahedral species other than kaolinite is present. The position of the 060 peak of the I/S is greatly influenced by the kaolinite reflection. The actual peak position is probably located at a spacing higher than that noted for the Gulf Coast samples (1.50 Å) because of the increased Fe content which causes the peak to migrate to a higher d-value.

DISCUSSION

The non-clay minerals of the Campos and Gulf Coast shales are similar, although their amounts and trends with depth are different (Figure 4). In the Campos shales, the upward increase of quartz above 3000 m correlates with a seaward-stepping deltaic sequence and sea-level fall, as shown in Figure 2. The increase in quartz is probably related to source or coastal proximity in the shallowing upward sequence. The variation of quartz
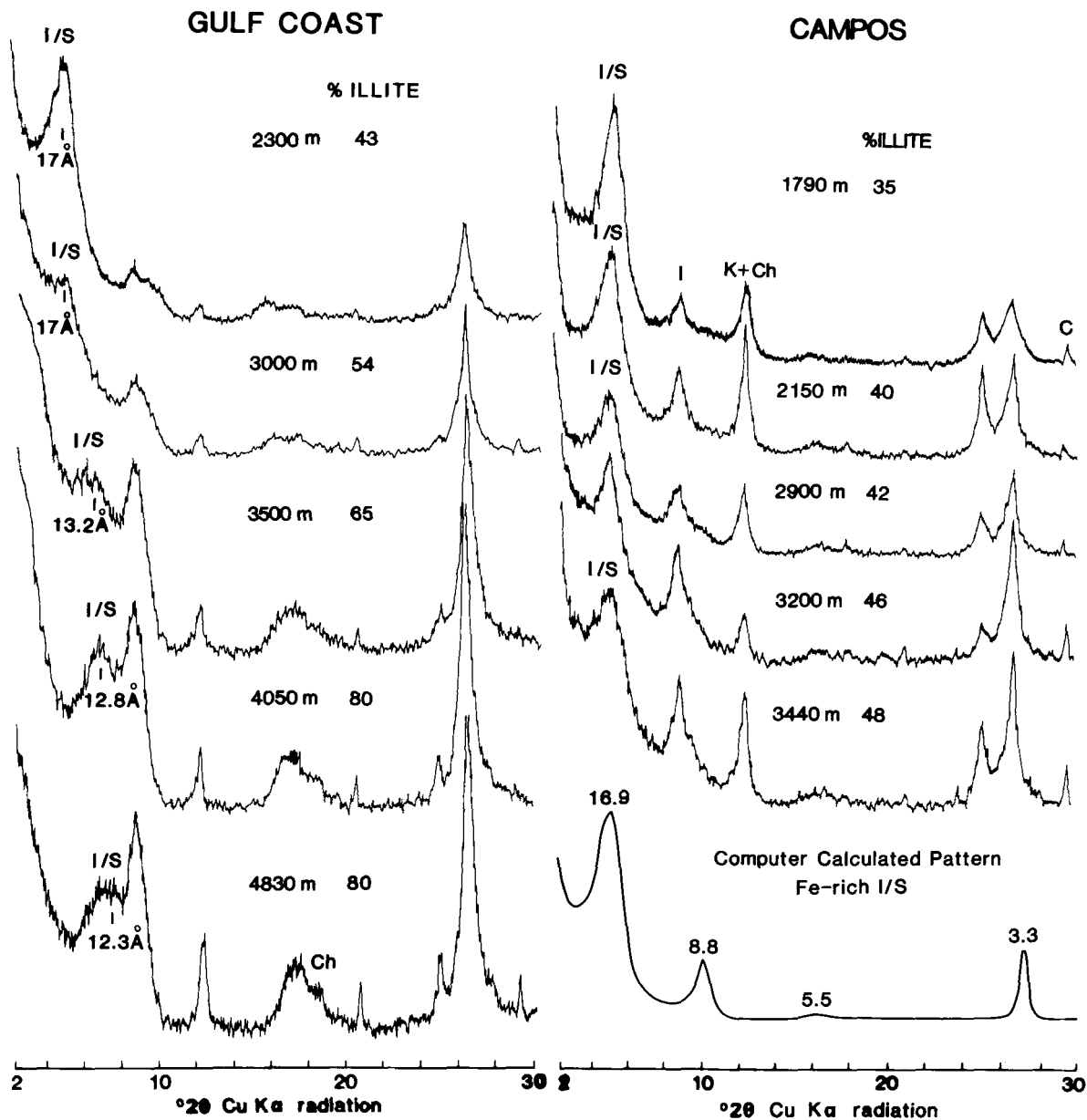
Figure 6. X-ray powder diffraction patterns of glycolated samples of the <2-μm fractions from the Campos and Gulf Coast wells. The computer-simulated pattern of an Fe-rich dioctahedral I/S was produced by the MODDP program (a Fortran program written by R. C. Reynolds, Dartmouth College, Hanover, New Hampshire). The parameters used were: di-mica smectite, Si = 3.7; ethylene glycol = 16.9; K = 0.8; C = 0.4; XCC = 0.4; CCC = 0.4; powder, N = 7, 13, 1 in a gaussian-like distribution.

content also affects the trends of the other components. The total clay content of the Campos shales varies with depth, which reflects the change in kaolinite content. More kaolinite was deposited during periods of falling sea level and less was deposited at high sea-level stands. The sample at 2600 m (containing a large amount of kaolinite) corresponds to the Oligocene, which was a period of low sea-level stand. At this time, large can-

yons were cut in the basin and turbidite sandstones were deposited. The quartz and kaolinite trends indicate that the detrital mineralogy is still strongly represented in the Campos well. These conclusions agree with Weaver (1961), who noted that a change from low to high kaolinite content represents a change from a relatively more open to a more nearshore marine condition.
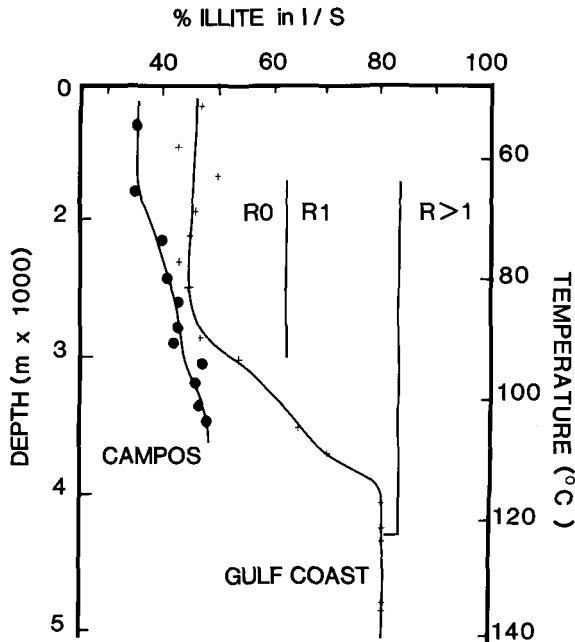
Figure 7. Proportion of illite in the illite/smectite (I/S) in the <2-μm fraction as a function of temperature (bottom-hole temperature) for the Campos and Gulf Coast wells. The values correspond to geothermal gradients of about 23°C/1000 m and a surface temperature of 25°C.

Figure 8. Behavior of a representative sample from the Campos well (3000 m) under different treatments. Values are in Ångstroms.

A plot of the percentage of I/S in shales of different ages and their degree of ordering (Figure 10) indicates that I/S becomes ordered at different temperatures as a function of age. The I/S from well 1 (Pleistocene), well 2 (Pliocene), and wells 3 and 4 (Oligocene) become ordered at 150°, 130°, and 100°C, respectively. These data suggest that the conversion of smectite to illite is in part time controlled, i.e., the older the rock, the lower the temperatures required for the ordering of the I/S. The Gulf Coast I/S analyzed in the present study follows the trend of these other wells, i.e., the age of the shales is consistent with I/S ordering at about 100°C. The oldest Campos shales, however, do not follow such a trend. The I/S in the Campos well, at a given depth and temperature, is always richer in smectite than that in the Gulf Coast well. At about 3400 m and 100° C, the I/S in the latter is ordered having about 65% illite layers, whereas in the Campos well at this same depth and temperature, the I/S is randomly interstratified.

A kinetic interpretation requires that the older Campos clays have reacted more than their Gulf Coast equivalents. Temperature, age, and geothermal gradient (similar to the Gulf Coast area) should have resulted in more complete illitization of the Campos I/S than has been observed. Other factors may have inhibited the reaction. K^+ is a crucial component in the illitization reaction. K-feldspars and/or micas are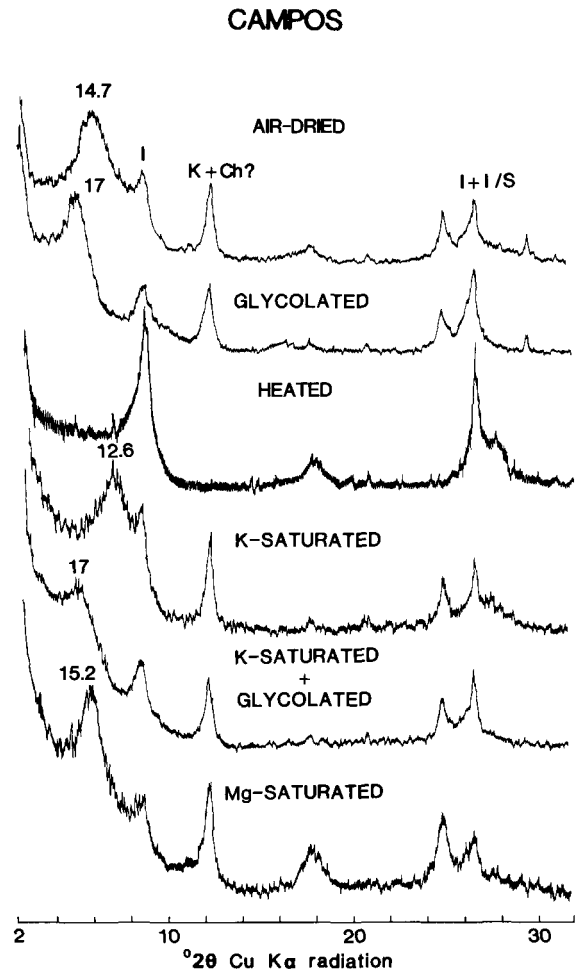 thought to be the sources of K^+ for the reaction. In the Campos shales, K-feldspar is even more abundant than in the Gulf Coast shales (Figure 4). The pore-fluid chemistry may also have affected the illite reaction. In shales, however, the pore-fluid chemistry is largely controlled by the chemistry of the solid phases, which is similar in the Campos and Gulf Coast shales (Figure 4). Therefore, availability of K^+ and pore-fluid chemistry were not the controlling factors for the low reactivity of the Campos I/S. The main difference between the shales from the two areas studied is their clay mineralogy, namely the composition of the I/S, the type of mica present, and the presence or absence of kaolinite. On the basis of the XRD data, the I/S in the Campos shales is an Fe-rich dioctahedral mineral, different from the aluminous smectite in the Gulf Coast (Hower et al., 1976).

The charge-building mechanism is crucial to the formation of mixed-layer clays. Experimental work, comparing the reactivity of di- and trioctahedral smectites
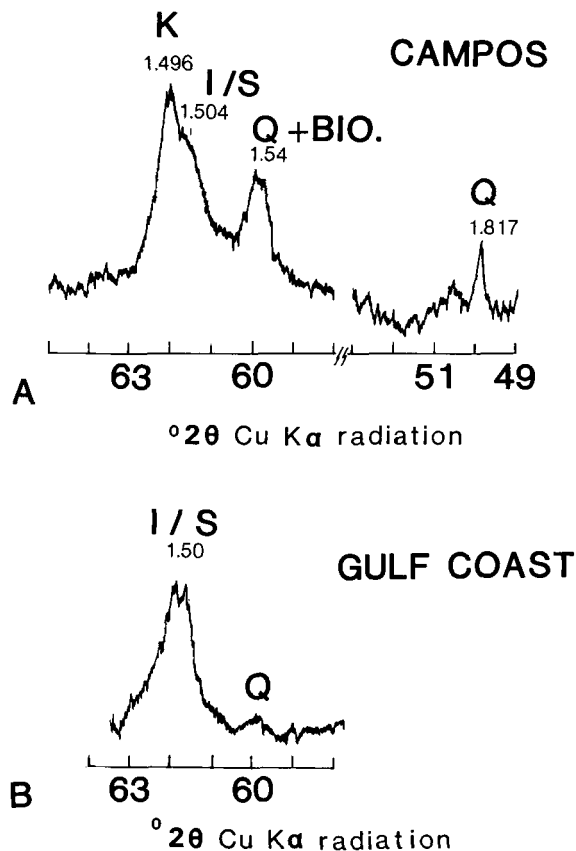
Figure 9. 060 reflections for (A) Campos sample at 2600 m (<2 μm). (B) Gulf Coast sample at 2850 m (<0.3 μm). K = kaolinite; I/S = illite/smectite; Q = quartz; BIO = biotite.

Figure 10. Proportion of illite in illite/smectite (I/S) in the <2-μm fraction as a function of temperature (bottom-hole temperature) in the clay fraction of shales from: (1) Salton Sea area, from Jennings and Thompson (1986); (2) well C, Gulf Coast area, from Perry and Hower (1972); (3) well E, Gulf Coast area, from Perry and Hower (1972); (4) well CWRU-6, Gulf Coast area, from Hower et al. (1976). Dashed lines to the right show type of ordering for different wells at different temperatures. The Campos and Gulf Coast wells of this study are also shown.

with increasing temperature, has attributed the high reactivity of dioctahedral smectites to their charge building options, as opposed to those of their triocta-hedral counterparts (Eberl et al., 1978). Foster and Custard (1982) pointed out that in montmorillonite having predominantly octahedral substitution, the il-litization reaction proceeds more rapidly than in bei-dellite, which has substitution mainly in the tetrahedral site. The response of an Fe-rich dioctahedral smectite to increasing temperature has not yet been experimen-tally demonstrated; but the fact that the I/S in the Campos shales is not a montmorillonite type may (partly) explain why the illitization was retarded. Hence, temperature and age in Campos and Gulf Coast areas cannot be used as comparative parameters, because these areas were and are mineralogically different.

The Gulf Coast I/S probably came from Cretaceous and Tertiary rocks from the western interior of the United States, where at that time silicic volcanism pro-vided ash to a marine environment which altered to montmorillonites and random I/S (Nadeau and Reyn-olds, 1981). In the Campos basin, silicic volcanism was absent. The detrital minerals came mainly from the
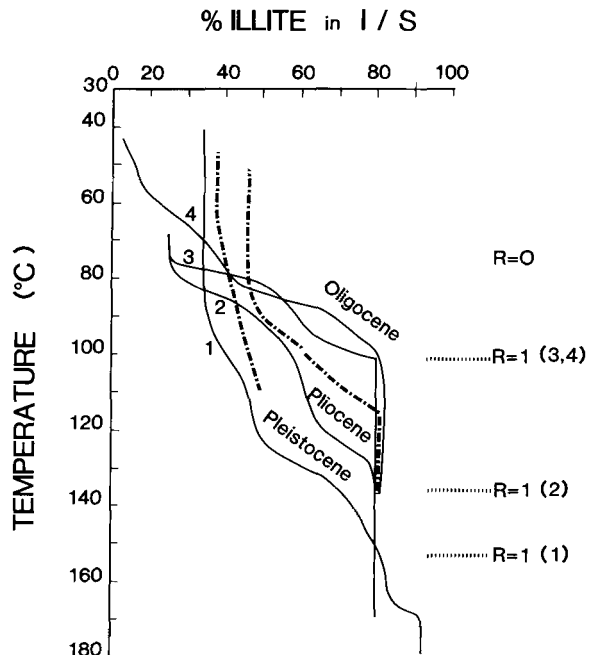
weathering of the hinterland Precambrian Shield where the predominant rocks are gneisses, charnockites, and granulitic rocks (Guazelli and Carvalho, 1981). Thus, I/S in the Campos samples could represent an authi-genic marine nontronite; however, the following con-siderations indicate that the I/S in the Campos shales is detrital rather than authigenic: (1) In the Campos basin, I/S and other clays occur in all parts of the basin and are present in more than 2000 m of shale. (2) The clay mineralogy of sediments being deposited on the continental shelf of the Rio de Janeiro province con-sists of kaolinite, smectite, and illite (da Rocha et al., 1975). This clay mineralogy, similar to the Campos shales, was considered by da Rocha et al. (1975) to represent the weathering product of Precambrian coastal rocks under a temperate climate with high rain fall. (3) The abundance of kaolinite indicates continental weathering contribution.

The occurrence of Fe-rich smectite in sedimentary rocks is somewhat restricted. Sherman et al. (1962) reported nontronite and nontronite-like minerals in a variety of climates, but mainly as the alteration product of mafic rocks. They also pointed out that the smectites

in humid tropical areas tend to be enriched in Fe. In the Campos basin, basalts associated with rifting occur deep in the section and probably did not provide a continuous supply of sediments throughout the deposition of the Campos Formation. Apparently, the I/S in the Campos Formation represents the weathering product of felsic rocks influenced by climatic conditions that favored a high concentration of Fe. Nevertheless, biotite is not stable in the weathering site. More specific studies on source areas and provenance of the Campos Formation shales, however, are needed.

Geologic implications

In the two wells studied, the pressure changes with depth can be followed by the drilling mud weight. In the Gulf Coast well the drilling mud weight increased abruptly from 10 to 14 pounds per gallon at about 3000 m, about the same depth at which the I/S became ordered. In the Campos well, on the other hand, the mud weight increased only slightly with increasing depth. These data emphasize the possible role of the illitization reaction in the formation of pore-fluid overpressuring, which in turn may act as the fluid drive mechanism that allows migration of hydrocarbons from shale sources to reservoir rocks.

Johns (1982) showed that the catalytic activity of smectite is enhanced with increasing Fe content; nontronite and Fe-montmorillonite produced the lowest activation energies for the decarboxylation reaction. Although in the Campos Formation the I/S did not appear to contribute to an increase in pressure that could have enhanced petroleum migration, the I/S has a composition that might have favored petroleum generation.

The clay mineralogy of the Campos Formation shales is a response to the tectonic setting of the area (no silicic volcanism) and climate. Thus, in areas with similar tectonic and climatic conditions (e.g., western African basins), an equivalent shale sequence may have a similar mineralogy, and illitization reactions will probably be retarded. The retardation of the illitization reaction in the Miocene of the Niger delta reported by Bruce (1984) corroborates such an inference.

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