Clays and Clay Minerals, Vol. 44, No. 3, 429–436, 1996.

XRD IDENTIFICATION OF TWO COEXISTING MIXED LAYER EXPANDABLE MINERALS IN SEDIMENTARY ROCKS

Key Words—Diagenesis, Expandable interstratified minerals, X-ray diffraction.

The co-existence of two smectite minerals from a diagenetic series has not often been reported by clay mineralogists. The generalized use of smectite/illite mixed mineral series as indicators of diagenesis (Whitney and Velde 1993) relies on the correct identification of the mixed layer minerals present. We have found that at times, there can be two expanding mineral series present in large quantity within the clay fraction from the same sedimentary rocks. This situation can lead to uncertainty of mineral identifications unless precautions are taken. This short note is intended to alert clay mineralogists of this possibility.

EXPERIMENTAL METHOD

Clay mineral fractions of the <2 μm fraction of clay-rich, handpicked deep well drilling cuttings were prepared by settling ultrasonically dispersed samples within water overnight. Flocculation of the clay fraction was affected by adding a drop of 1 M $SrCl_2$ solution, which both flocculated and affected cation exchange of the smectite fraction of the sample. It is assumed that the normal hydration state from air-dried samples is 15.2 Å. The reasons for this assumption are that the most common smectite layer for I/S minerals is low charge montmorillonite (Velde and Brusewitz 1986), which stably hydrates under most room conditions to a two water layer structure when Sr is the exchange ion. We have tested this hypothesis for different samples and always found a 15.2 Å spacing for disordered mixed layer minerals.

The flocculated concentrate was sedimented onto a glass slide and X-rayed using an INEL 120 curved position sensitive detector. The resulting digitized spectra were smoothed using a data smoothing routine (7 point step) and the background subtraction was effected in order to obtain the diffraction maxima (Lanson 1990). Decomposition of the treated spectra was accomplished using the DecompXR program (Lanson 1991). As found for previous clay mineral studies (Lanson and Velde 1992), four major bands were identified by decomposition from the air dried spectra. Two bands near 10 Å were attributed to the illite fraction, one fine grained (If) and the other with greater than about 20 diffracting continuity (Ic) layers. Two other bands were attributed to expanding minerals, one is called an I/S (illite/smectite) mineral and the other S (smectite of undetermined type). Glycolation gave a four band spectrum with a 17.7 to 17.2 Å band, two illite bands (10.6 and 10.0 Å), and a band near 9.5 to 9.2 Å. Heating to 200 °C produced a three band spectrum of 13.9 Å, and the two illite bands, If and Ic. These relations are shown in Figure 1 for two samples from different points from the drill hole series.

Samples Studied and Observations on XRD Spectra

The series of samples treated are from a well from the Angola offshore area (courtesy of Elf Aquitaine, France. Walgenwitz et al. 1990). The age-depth relations of the sediments (sedimentation curve) of the well are shown in Figure 2. Figure 3a shows a sequence of air dried spectra for the well and 3b glycolated samples. It is evident that decomposition methods are necessary to find the diffraction maxima as shown in Figure 4 for two samples from different depths. The results expressed as band position or basal spacing and width at half height (WHH) for the different samples studied for the well after decomposition of the spectra are shown in Figure 5. It is evident that the positions of the illite peaks are only slightly changed. However, the width of the band at slightly greater than 10.0 Å becomes more narrow with depth indicating a general increase of crystallite site as depth increases and diagenesis proceeds. The position of the I/S band changes from near 13 Å to less than 11 Å regularly with depth. However there seems to be no systematic change for the I/S band width, but a very slight change to more narrow bands at the greatest depth is apparent. The band designated as simply smectite, for want of a better determination, has a position of 15.8 Å evolving to slightly less than 14 Å with a depth from the 2300 m depth. The width of this smectite band is from 2.2 to 1.7 °2Θ using CoKα radiation. At greater depths, the band position shifts rapidly to near 12 Å. No distinct, sharp 14 Å peak was observed for these samples, which would indicate the presence of chlorite. Band width of this smectite phase seems to increase with depth.

Investigation of the 1.50 to 1.54 Å region showed peaks near 1.52 and 1.50 Å. This indicates illite, I/S and kaolinite structures near 1.50 Å as shown in Figure 6. The band component observed near 1.52 Å is considered to represent the smectite phase.

DISCUSSION

If one simply looks at the raw, air-dried spectra (Figure 1), there is a large well defined peak maximum at or near 15 Å, a sharp mica peak and a strong kaolinite peak. The 15 Å peak flattens and broadens somewhat

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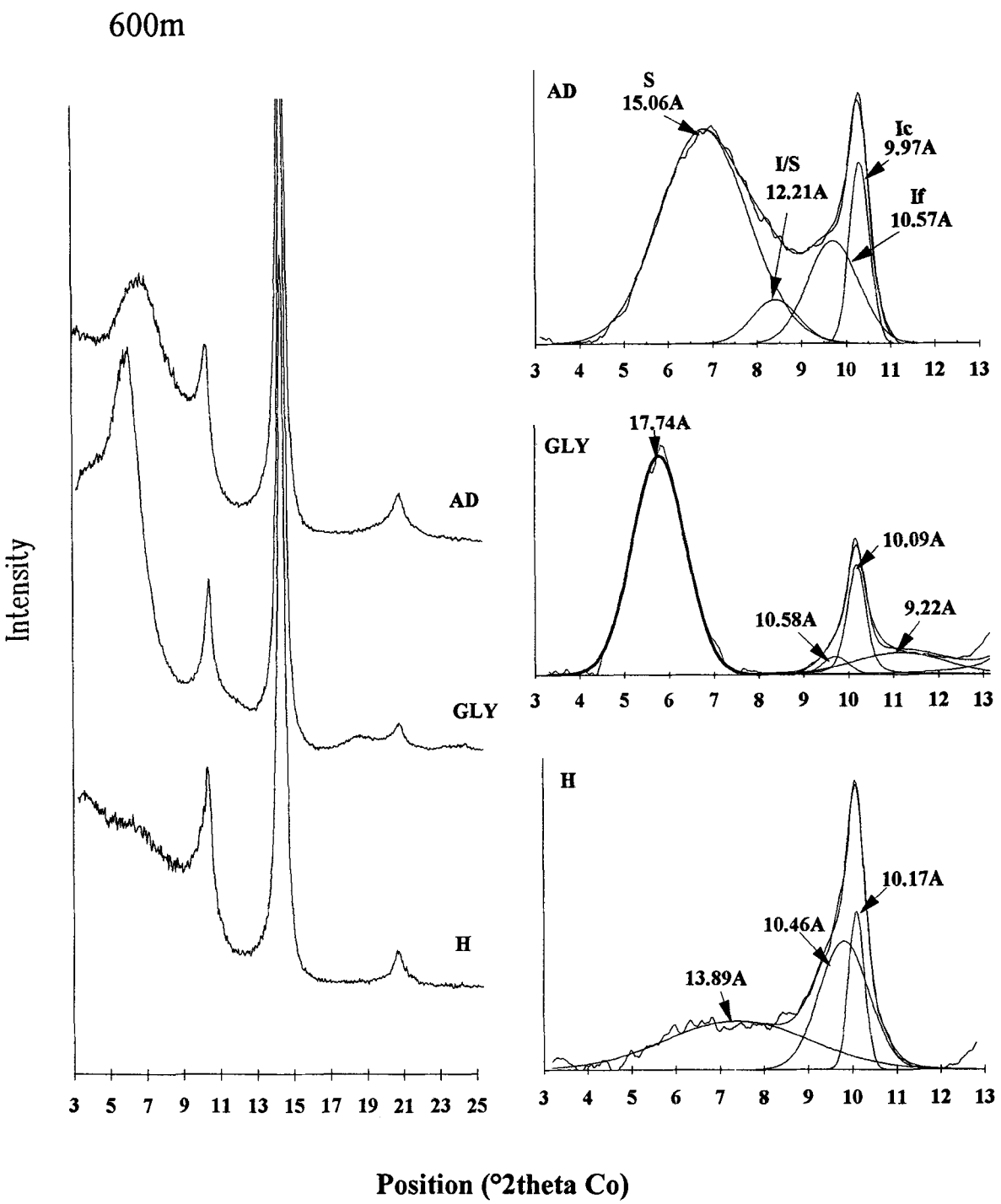


Figure 1 a–b. X-ray diffractograms (Co radiation) of two samples from the Angola well depths of 600 and 2300 m. Air dried (AD), glycolated (GLY) and samples heated (H) to 200 °C. Decomposition of the mica-smectite (001) bands is shown.

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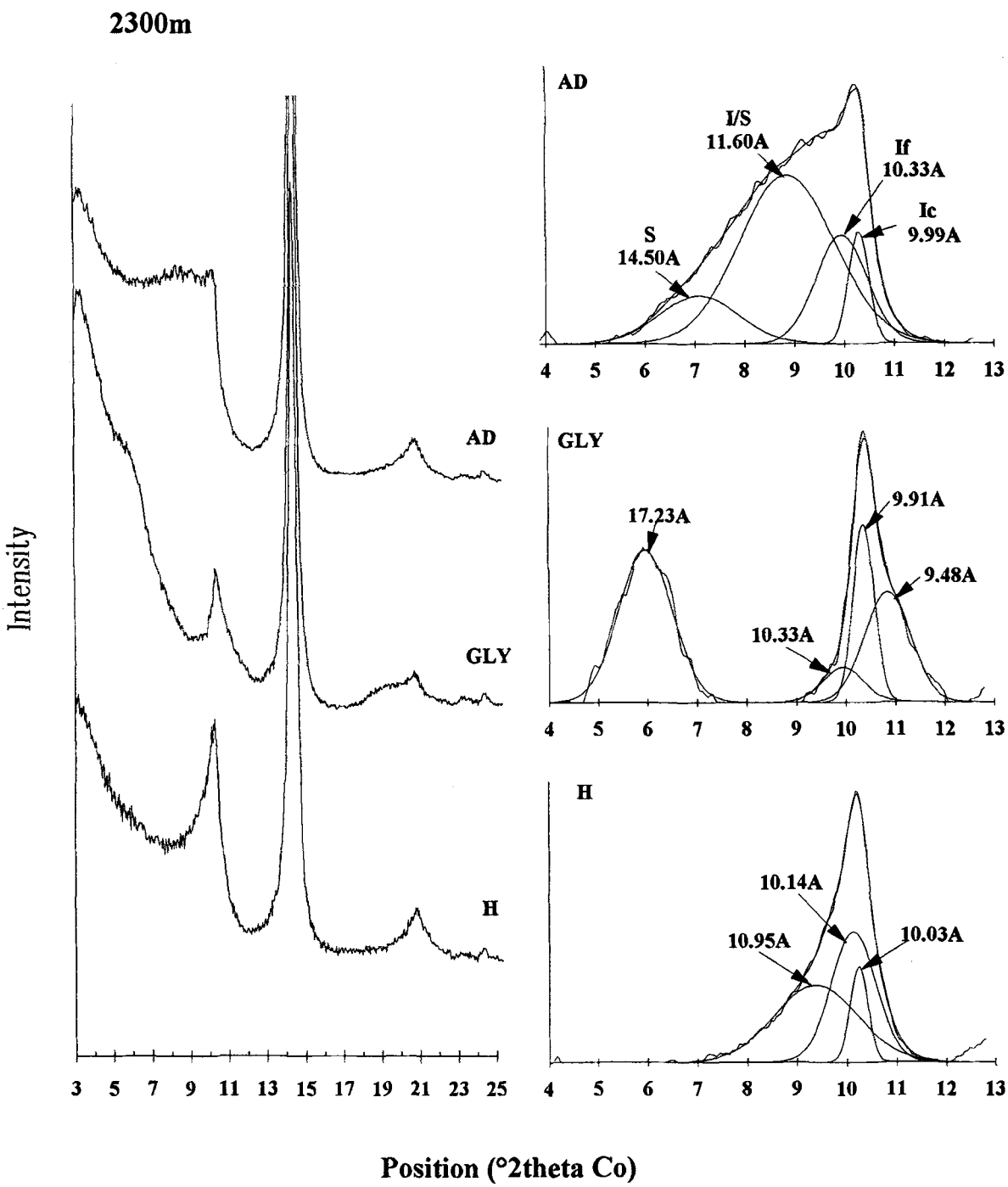


Figure 1. Continued.

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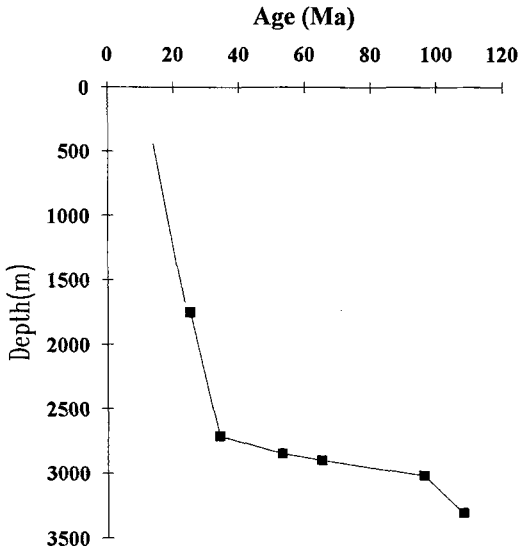


Figure 2. Sedimentation history in the well studied shown as a function of depth and age of the sediments.

with depth. Using these observations there seems to be little change in the mineralogy with depth except at the 2000 m level. Common interpretation would suggest that there is no change in clay mineralogy. Yet the burial depth of the samples has reached over 3 km after a burial history of 110 M.y. For the Texas Gulf coast, these burial conditions would have affected most of the diagenesis of the smectite to illite transformation (Velde and Vasseur 1992). It seems reasonable to expect that the smectite has largely transformed to illite from the mixed layer mineral series. This is in fact the observation made when decomposition methods are employed. One sees I/S bands decreasing in position for the air-dried state with depth, accompanied by the typical two band structure of illite, one describing the evolution of small grain size and the other the well crystallized micaceous material (Lanson and Velde 1992). Thus it appears that the I/S series does evolve from a normal manner for the Angola samples studied.

Looking at the complex bands and the decomposition results, it is evident that it is critical to use the same and correct number of bands during decomposition routines. The choice of the number of bands to use to determine the mineral assemblage was guided by past experience and demonstration from diagenetic shale series. Initially, Lanson and Besson (1990) have demonstrated the use and validity of the decomposition method comparing it to calculated spectra. The use of two bands to describe the micaceous material was demonstrated by Lanson and Velde (1992). These authors also indicated the decomposition method that should be employed and they described the evolution of the bands to be used to describe the I/S minerals present. Band width and position deduced for the Angola series I/S minerals are concordant with results from other series of sedimentary rocks from different basins. For the samples studied, by subtraction (decomposition), one must use another band to describe the spectra completely and hence use a band that seems to correspond to a smectitic material. This band dominates for the shallow material.

This smectite shows a band position change with depth, from 15.8 to 13.9 Å that suggests a change in composition or structure with depth and hence the probability of a mixed layered mineral. As we could find no evidence of a trioctahedral mineral from the assemblage [(060) spacings all near 1.50 Å] we used the Reynolds NEWMOD program (Reynolds 1985) to calculate spectra for possible dioctahedral expanding minerals. As we believe we have identified an I/S phase (R = 1), we postulate a smectite of another composition than the smectite with an I/S interlayer. We believe that a logical possibility is a dioctahedral smectite-dioctahedral chlorite interlayered mineral with a very high proportion of smectite. During the simulations of disordered interlayered dioctahedral smectite-chlorite, one obtains a spectrum with a very intense (001)/(001) peak near 15 Å and very low intensity peaks for the other reflections. This corresponds to our spectra where the only "new" peaks encountered were those in the 15 Å region. The simulations are based upon a 15.2–14.2 Å spacing interlayer series. For the Angola minerals, the initial band position seems to be near 15.8 Å, suggesting a smectite with a higher basal spacing in the hydrated state. Also the width of the band at half height from the glycollated state (Figure 1) is rather large, 1.5 °2Θ, whereas the normal bentonitic and diagenetically formed smectites have a width of much less than one degree. It seems plausible to identify the highly expanding mineral tentatively as a smectite-rich dioctahedral smectite-chlorite. Trioctahedral minerals would give more intense bands for the higher order reflection regions near 4.5 and 3.5 Å than those observed here and a diffraction peak near 1.54 Å, which was not observed with sufficient intensity from our samples to attribute it to the presence of a specific phase.

Nevertheless, no definitive identity specific to this mineral (that is, trioctahedral or other type) can be made because it is intimately mixed with two or three other clay mineral phases. The change in band position to near 12 Å at greater depth might lead one to think of an illite/chlorite mineral but no clear trioctahedral character of the more expandable mineral was evident at any stage of its evolution.

The presence of a large and intense kaolinite band from the XRD diagrams of clay fractions indicates a generally aluminous bulk composition. This is compatible with the supposed aluminous smectite/dioctahedral chlorite mineral. One can imagine that the chemical reason for this phase would be lack of alkali (K) ions available to form an illite/smectite mineral. When these ions

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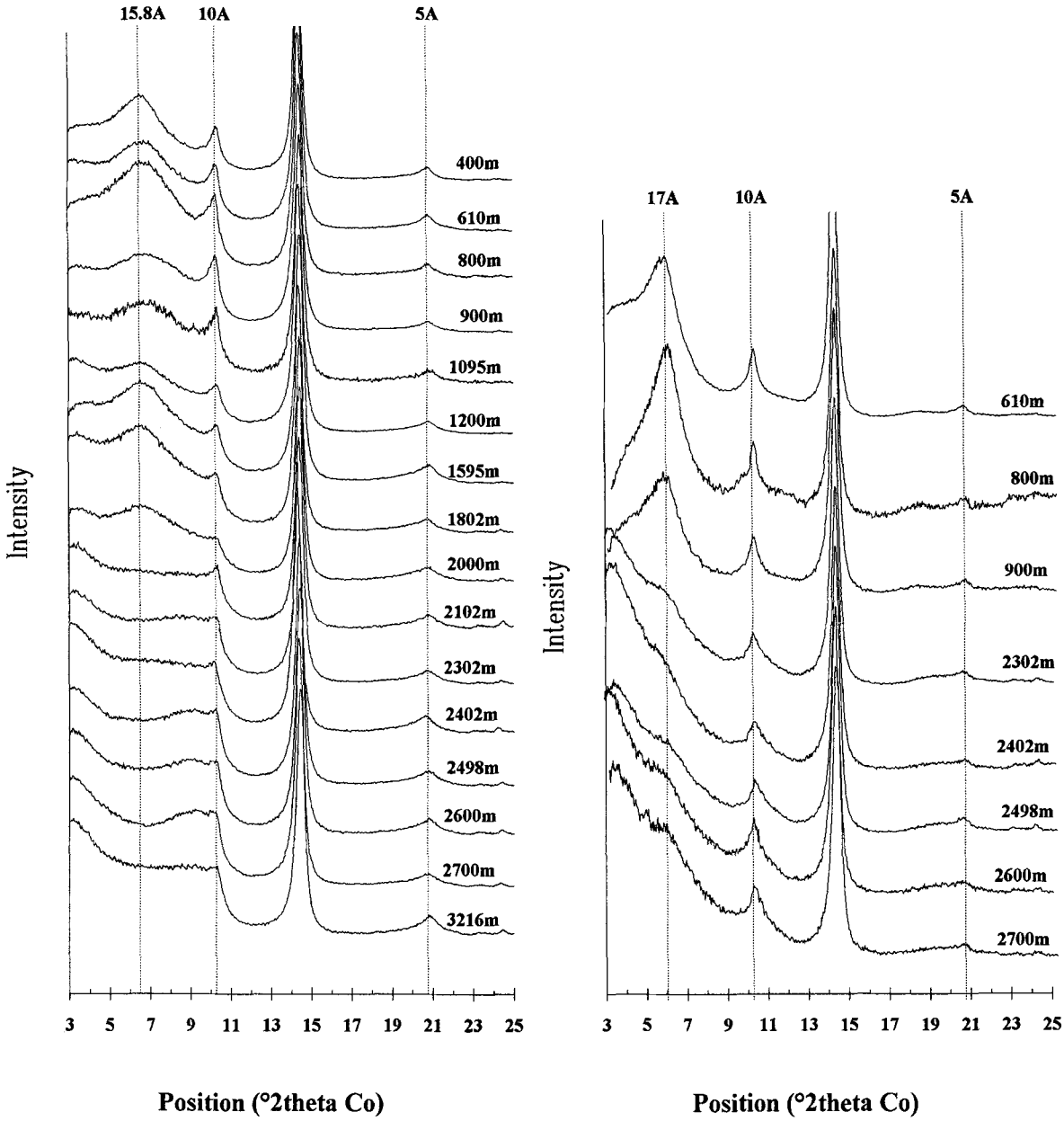


Figure 3a. Raw XRD patterns in air-dried state show the evolution of the spectra with depth in the well studied. Note the continued, very intense peak for kaolinite at 14.5 degrees. Figure 3b. Glycolated samples.

are available in sufficient quantity, perhaps the conversion of the aluminous phase to illite can occur and leave an assemblage without significant ferromagnesian trioctahedral chlorite. Within the global mineral assemblage of the Angola sample, there is a large quantity of detrital muscovite. Perhaps this material is of a sufficiently large grain size to be only slowly dissolved, releasing K at depths greater than other, more normal diagenetic argillaceous sedimentary series.

We have encountered similar minerals within sedimentary series from the southern North Sea area of the Norwegian and Dutch sectors. However, there are reports of deep wells where the smectitic clay minerals do not appear to change expandability with depth (Huggett 1992) and perhaps these also contain the mysterious expanding phase. In any event, it is a problem that should be considered when a series that has obviously experienced burial diagenesis conditions shows no apparent clay mineral evolution for the expanding phases.

The closest mineral to the proposed interlayered type is tosudite, a regularly interstratified dioctahedral

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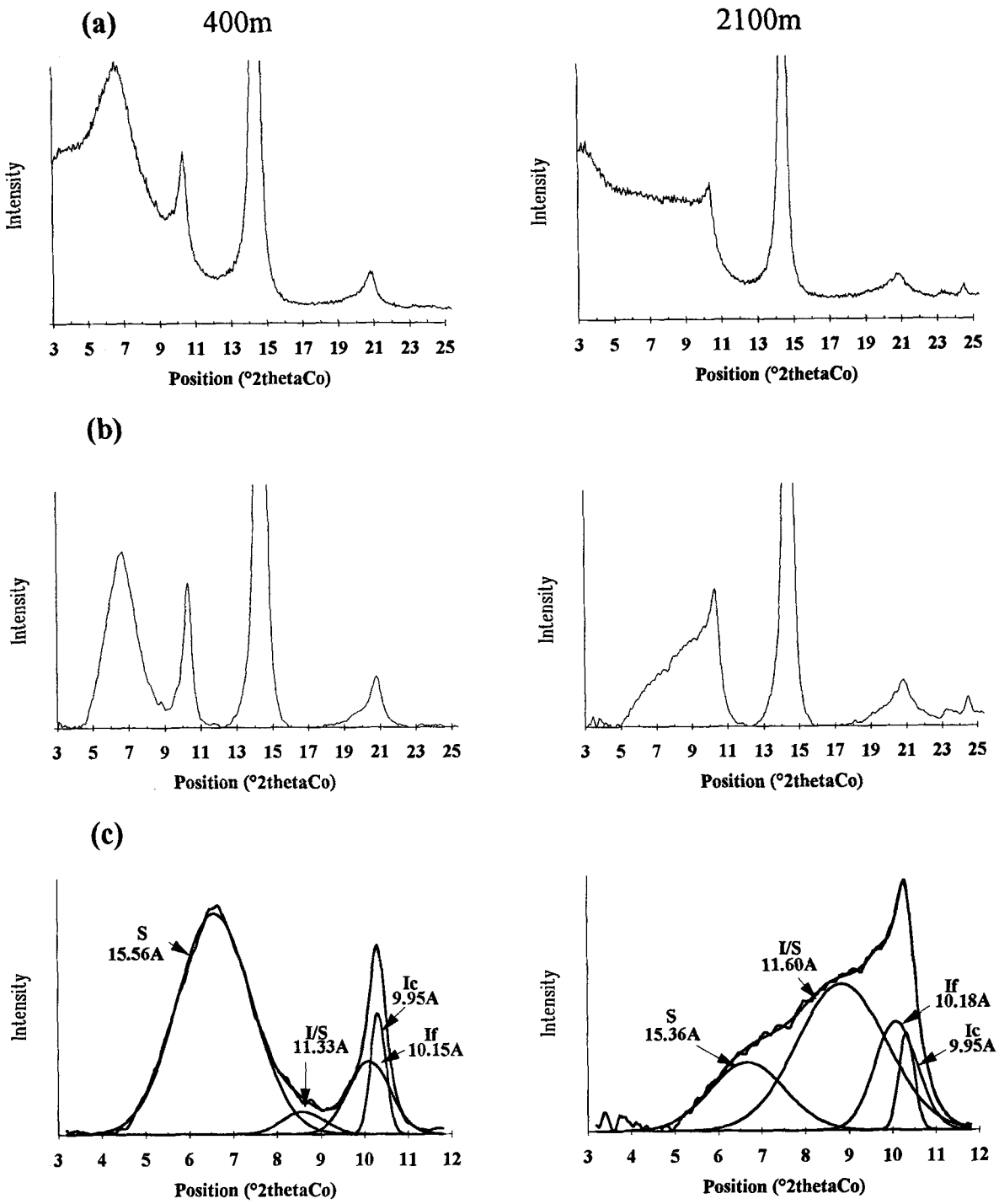


Figure 4. XRD and decomposition spectra for two samples from different depths in their raw: a) smoothed and background subtracted form; b) and decomposition results for samples at three depths showing the specific evolution of the two smectite phases, illite/smectite (I/S) and smectite (S) assumed to be aluminous and dioctahedral in nature, a smectite-chlorite mineral. The band If indicates the fine-grained illite fractions and Ic indicates the coarse-grained illite fractions.

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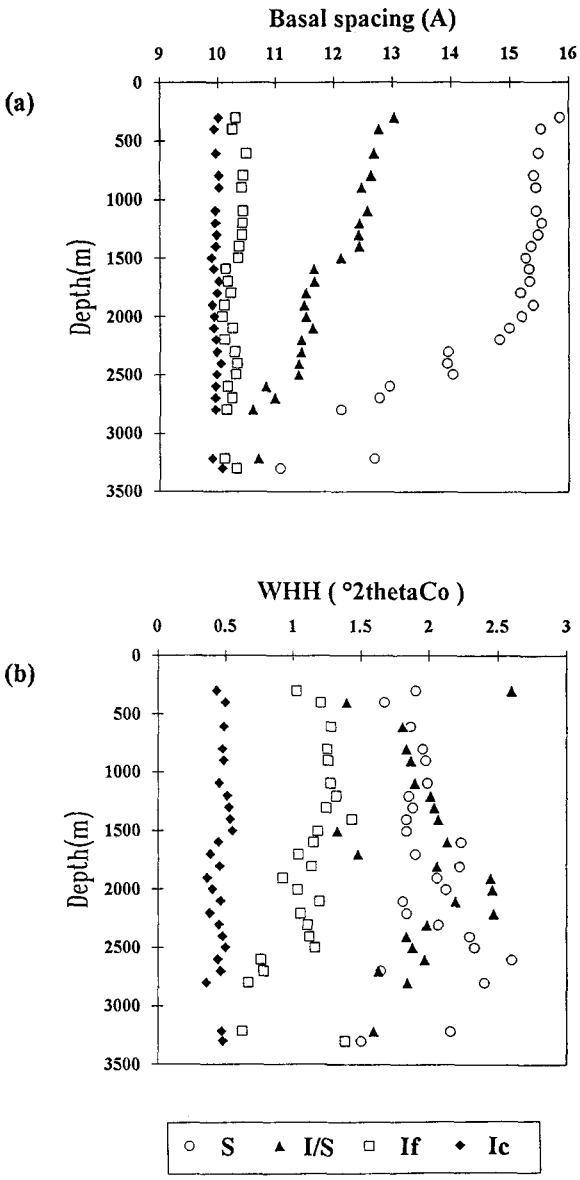


Figure 5. Plot of decomposition band position and band width at half height (WHH), for the identified phases after decomposition as a function of depth in the well. circles = smectite band, triangles = I/S band, squares = If fine-grained illite, and diamonds = Ic coarse-grained illite.

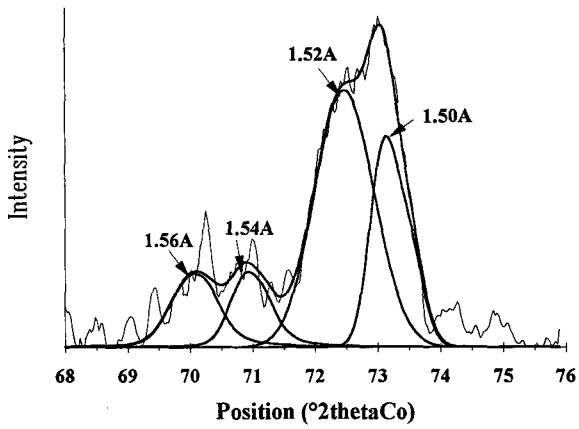


Figure 6. Decomposed spectra of the (060) region for a smectite-rich sample. Two dioctahedral band positions are apparent, one at 1.50 and the other at 1.52 Å.

chlorite/smectite mineral of 50% chlorite. In most cases the smectite component of tosudoite seems to be 15.2 Å or less (Bailey et al. 1982) but occasionally (Ichikawa and Shimoda 1976), one can deduce a larger spacing smectite layer (15.7 Å) if the chlorite component is 14.2 Å in a low Li specimen. A possible low temperature occurrence for dioctahedral smectite/chlorite minerals can be considered by Garvie (1992) who has found tosudite in a diagenetic context.

CONCLUSIONS

The existence of two expandable mixed layer minerals that evolve at different rates (under burial conditions) can lead to very special interpretations when considered to be a single-phase I/S assemblage. The persistence of a highly expandable mineral at depth for a series suggests the presence of a new phase. The smectite band will be larger (>2 °2Θ) than normal. Such a possibility is important to consider when interpreting the thermal history of sediments from a diagenetic context.

ACKNOWLEDGMENTS

We would like to thank Elf Aquitaine for the samples and their help to interpret the geological context.

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(Received 7 February 1995; accepted 30 August 1995; Ms. 2618)

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