

CLAYS and CLAY MINERALS

at a glance

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USE OF LONG-SPACING ALCOHOLS AND ALKANES FOR CALIBRATION OF LONG SPACINGS FROM LAYER SILICATES, PARTICULARLY CLAY MINERALS

G. W. Brindley and Hsien Ming Wan

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Lattice spacings of layer silicates, particularly clay minerals, may exceed 20 Å. The errors in measuring lattice spacings increase rapidly for spacings greater than about 10 Å, and diffraction angles 2θ less than about 10° . Long-chain organic compounds, such as normal alcohols, C_{14} - C_{20} , and normal alkanes (paraffins), C_{26} - C_{30} , provide useful calibrations for lattice spacings in the range 10-50 Å. The basal spacings of the calibrating substances are determined from their higher order reflections in the angular range where reflections from quartz and silicon are used as standards.

Fourier transform calculations, and chemical and physico-chemical analyses indicate that both the ratio of the amounts of non-hydrated clays (illite) to hydrated clays and the K_2O content of clays increase with burial depth; cation exchange capacity and surface area decrease with burial depth.

Based upon a classification scheme, which was devised by combining criteria and data derived from the studies of Weaver (1961a), Kubler (1966), Burst (1969) and Dunoyer de Seconzac (1970), the upper and middle parts of the formation (upper 3250 ft) fall within the middle stage of diagenesis whereas the lower part (1000 ft) is allocated to the beginning of late diagenesis. In terms of Burst's (1969) work, the upper 3250 ft are transitional between the stability and dehydration zones indicating that, prior to uplift, hydrocarbons may have been in the process of migration. The lower 1000 ft of the formation are in the restricted dehydration zone, indicating that hydrocarbon migration should have been completed.

DIAGENESIS OF CLAY MINERALS FROM LOWER CRETACEOUS SHALES OF NORTH EASTERN BRITISH COLUMBIA

A. E. Foscolos and H. Kodama

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Clay minerals from shale outcrops of the Lower Cretaceous Buckingham Formation (4250 ft thick) were investigated in order to assess their degree of diagenesis and their oil-generating potential. Crystallinity index, sharpness ratio, per cent of illite which is the 2M polymorph and presence of discrete minerals have been studied in the whole clay fraction, while the very fine clay fraction has been subjected to X-ray diffraction, differential thermal, thermogravimetric, differential thermogravimetric, infrared spectroscopy, surface area and chemical analyses. With information derived from these studies and from published data, a classification scheme was devised which relates variation of clay mineralogy to diagenetic stages and burial depth.

Data on the $<2\ \mu\text{m}$ size fraction show that the crystallinity index decreases while the sharpness ratio and per cent of illite which is the 2M polymorph increase with burial depth. Results on the $<0.08\ \mu\text{m}$ fraction reveal that a three-component interstratified clay mineral exists. In addition,

COMPARATIVE STUDIES ON EXTRACTION OF SEDIMENT INTERSTITIAL WATERS: DISCUSSION AND COMMENT ON THE CURRENT STATE OF INTERSTITIAL WATER STUDIES

F. T. Manheim

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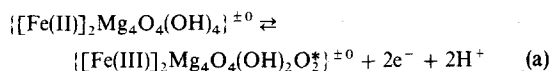
The implication by Murthy and Ferrell (1972) that interstitial water studies are in a confused state is criticized on the basis that the authors have not drawn on a considerable body of data, especially Soviet studies since the 1950's, and results of the Deep Sea Drilling Project. Pressure filtration systems for extracting interstitial waters are currently the methods of choice for marine studies and have achieved substantial reliability and reproducibility. Although gaps and problems remain, many aspects of interstitial composition of marine sediments have been clarified; these include the substantial constancy of composition of interstitial waters in deep sea pelagic deposits, depletion of interstitial cations owing to authigenic mineral formation in more rapidly accumulated (especially terrigenous) sediments, and special phenomena in sediments overlying salt deposits.

IRON OXIDATION AND REDUCTION
EFFECTS ON STRUCTURAL HYDROXYL
AND LAYER CHARGE IN
AQUEOUS SUSPENSIONS OF
MICAEOUS VERMICULITES

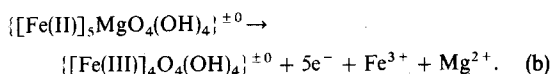
J. A. Veith and M. L. Jackson

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Four $\text{Na}_2\text{S}_2\text{O}_4$ -reduced Na-vermiculites, each with some trioctahedral mica interstratified, were oxidized with H_2O_2 at pH 6.5 and again reduced with $\text{Na}_2\text{S}_2\text{O}_4$ in suspensions at pH 7.5–8.0. The layer charge ($\text{CEC} + \text{K}^+$), measured at pH 6.50, did not change significantly when octahedral Fe were oxidized ($7.92 \text{ mmole } 100 \text{ g}^{-1}$) or reduced ($6.71 \text{ mmole } 100 \text{ g}^{-1}$). Electroneutrality was maintained within the octahedral sheet when Fe was oxidized or reduced. When Fe(II) was oxidized, electroneutrality was maintained by deprotonation of octahedral OH^- groups.



and by ejection of (dissolution of structural) octahedral metallic cations,



When Fe(III) was reduced, electroneutrality was maintained by reprotonation of the deprotonated sites (O^* , equation a). Reaction (b) was not reversible. Thus, reversibility of the reaction, $\text{Fe(II)} \rightleftharpoons \text{Fe(III)}$, within the octahedral sheet decreased with increasing amount of ejected metallic cations. The amount of Fe(III) and Mg^{2+} ejected per Fe(II) oxidized was related to the degree of vermiculitization, being greatest with Na-degraded biotite [0.03 Fe^{3+} and 0.11 Mg^{2+} per Fe(II) oxidized] and lowest (nearly zero) with South African vermiculite. The number of deprotonated (O^*) and reversible sites increased from 0.69 per Fe(II) oxidized with the K-depleted biotite to approximately 1.0 with South African vermiculite. The weathering increment was small since, of the total amount of Fe + Mg, less than 1.3 per cent was ejected from any of the 4 vermiculitic materials. When biotite was K-depleted, about 20 m-equiv of layer charge per 100 g (300°C basis) was lost, while 51 mmole of Fe(II) per 100 g was oxidized in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ and 82 mmoles in its absence in the aqueous suspensions. Since sequential reduction–oxidation–reduction treatments of K-depleted biotite and mica-containing vermiculites did not cause significant changes in layer charge ($r^2 = 0.04$), the layer charge changes were concluded to be entirely independent of the oxidation or reduction of Fe in these minerals.

EFFECT OF OXIDATION AND REDUCTION ON
POTASSIUM EXCHANGE OF BIOTITE

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The selectivity of K over Ca of Amelia biotite increased sharply upon oxidation by H_2O_2 at pH 6.0. This increase in K selectivity was only partially reversible upon reduction by $\text{Na}_2\text{S}_2\text{O}_4$. Oxidation by H_2O_2 of the Ca-form of this biotite resulted in a loss of no more than 2.8 and 0.4 per cent of the total Fe and Al, respectively, and caused a small and perhaps insignificant decrease in layer charge. Although 95 per cent of the structural Fe^{2+} of the Ca-form of this biotite was oxidized by H_2O_2 , only 17 per cent was reduced again by four treatments with $\text{Na}_2\text{S}_2\text{O}_4$.

The evidence indicates that under the conditions of this experiment the loss of protons from structural hydroxyls was the dominant mechanism by which electroneutrality in the biotite was maintained during oxidation of structural Fe^{2+} . Because this mechanism increases the bond strength interlayer K, it explains the increased K selectivity of biotite upon H_2O_2 oxidation. The relatively small reduction by $\text{Na}_2\text{S}_2\text{O}_4$ of structural Fe^{3+} to Fe^{2+} , which implies an equally small reprotonation of structural hydroxyls, explains the incomplete reversibility of K selectivity by $\text{Na}_2\text{S}_2\text{O}_4$ treatment.

SWELLING OF MONTMORILLONITE IN POLAR
ORGANIC LIQUIDS

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The crystalline and osmotic swelling of Na-, Cs-, Mg- and Ca-montmorillonite has been measured in dimethyl sulphoxide and in formamide, *N*-methyl formamide, dimethyl formamide, *N*-methyl acetamide and dimethyl acetamide. These liquids have similar dipole moments but their relative permittivities vary appreciably from values less than water to values greater than water.

Na-montmorillonite exhibits osmotic swelling (diffuse double layer development $-d(001) \gg 19 \text{ \AA}$) in formamide and *N*-methyl formamide and Cs gives osmotic swelling behavior in formamide. Cs-montmorillonite in the crystalline swelling region gives spacings greater than those found for water with all liquids. Mg- and Ca-montmorillonite did not give spacings greater than 19 Å in any of the liquids studied.

The swelling behavior of montmorillonite is affected by relative permittivity but for liquids with a similar relative permittivity methyl substitution in the molecule may prevent the development of diffuse double layers on the particle surfaces.