Diagenesis and shear rheology of a Recent-Pleistocene volcanogenic sequence, Mexican Basin. Implications to swelling and stability

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ABSTRACT

Low-grade diagenesis in the Recent-Pleistocene volcanogenic sequence of the Mexican Basin formed, in the gravel and sand strata, kaolinite, smectite and interstratified kaolinite/smectite, intimately associated with fine ash containing volcanic glass, opal-C, plagioclase, K-feldspar and pyroxene, in an environment of high permeability, high hydraulic conductivity and acid fluids. In the mud, transformation was total to 1H₂O- and 2H₂O-smectite, in an environment of low permeability, low hydraulic conductivity, and alkaline fluids. At depth, kaolinite transforms to smectite via interstratified kaolinite/smectite. The clay minerals are the continuous phase within the sequence. A suspension prepared with 15.45 wt. % clay separated from the <2 µm fraction of 26 m deep sediment in the gravel strata, containing kaolinite, smectite and interstratified minerals, shows non-Newtonian viscoelastic behavior, shear rate <0.02 s⁻¹, shear stress <1.5 Pa, strain <0.8, instantaneous viscosity 190 Pas at a stress of 1.03 Pa, low-energy particle association. A suspension prepared with 14.02 wt. % of clay separated from 60 m deep sediment, containing smectite and low kaolinite, shows viscoelastic behavior, shear rate <0.004 s⁻¹, shear stress 2-10 Pa, strain <0.2, instantaneous viscosity 3800 Pa s at a stress of 5.91 Pa, high-energy face-to-face particle association. The 60 m clay, subjected to a deformation stress vibrating at 1 hertz, within the viscoelastic range, develops cinematic viscosity <0.8 Pa s, in-phase shear modulus higher than the out-of-phase shear modulus. When vibration is raised to 5 hertz the cinematic viscosity is <4 Pa s, the out-of-phase shear modulus is higher than the in-phase one, more energy is dissipated than stored. Differences between the clay minerals from the 26 and 60 m deep sediments sustain that differences on the abundance, type and distribution of clay minerals, and consequently in the fine fraction, result in a non-uniform differential behavior of the sediments across the sedimentary sequence.

Keywords: rheology, Recent, volcanogenics, diagenesis, clay sediments, Mexican Basin

RESUMEN

Diagenesis de bajo grado en la secuencia volcanogénica del Reciente-Pleistoceno de la Cuenca de México formó, en los estratos de grava y arena, caolinita, esmectita e interestratificados caolinita/esmectita, íntimamente asociados con ceniza fina conteniendo vidrio volcánico, plagioclasa, feldespato potásico, ópalo-C y piroxena, bajo condiciones de alta permeabilidad, alta conductividad hidráulica, y fluidos ácidos. En los estratos de lodo, la transformación fue total a 1H₂O- y 2H₂O-smectite, en un ambiente de baja permeabilidad, baja conductividad hidráulica, y fluidos alcalinos. A profundidad, la caolinita se transforma a esmectita vía interestratificados caolinita/esmectita. Los minerales arcillosos son la fase continua en la secuencia. Una suspensión preparada con 15.45 % en peso de arcilla separada de la fracción <2 µm de sedimento de 26 m de profundidad, conteniendo caolinita, esmectita e interestratificados, presenta comportamiento no-Newtoniano viscoelástico, tasa de cizalla <0.02 s⁻¹, esfuerzo de cizalla <1.5 Pa, deformación < 0.8, viscosidad instantánea 190 Pa s a una tensión de 1.03 Pa, y asociación de baja energía entre partículas. Una suspensión prepa-
INTRODUCTION

Swelling and mechanical instability are common in sedimentary basins. They are particularly significant to soil mechanics and civil engineering problems and to oil reservoirs where if uncontrolled may cause significant damage. They are closely dependent on the clay mineralogy of the sediments. In old basins, the clay minerals usually are trioctahedral smectite, Mg-rich chlorite, interstratified chlorite/smectite and corrensite. Diagenesis of smectite to chlorite depicts the trend towards diminishing swelling and increasing stability (Kubler, 1973; Kopp and Fallis, 1974; Furbish, 1975; Almon et al., 1976; Hutcheon et al., 1980; April, 1981; Pevear and Whitney, 1982; Ahn and Peacor, 1985; Chang et al., 1986; Meunier et al., 1988; Roberson, 1989; Shau et al., 1990; Hillier and Velde, 1991; Inoue and Utada, 1991; Hillier, 1993; Huggert and Shaw, 1993; Scotchman, 1993; Rae et al., 1993; Jiang and Peacor, 1994; Jiang et al., 1994; Schiffman and Staudigel, 1995; Bettison-Varga and Mackinnon, 1997; Barrenechea et al., 2000).

In young basins, diagenesis has not been so completely documented although the transformation of volcanicogenic sediments to smectite is known. Associated with smectite may occur 7 Å-layer minerals loosely referred to as 7 Å serpentinite-like mineral or 7 Å-clay, Fe-chlorite, kaolinite, berthierine and odinite (Karpova, 1969; Hutcheon et al., 1980; Odin, 1985; Odin et al., 1988; Jiang et al., 1994). Diagenesis to chlorite is assumed but similarities of the X-ray diffraction patterns and differences in chemical compositions (Bailey and Brown, 1982; Brindley, 1982; Bailey, 1988a, 1988b) question the nature of the 7 Å-layer mineral and its role. Ordinarily, dioctahedral clay minerals predominate in mechanically unstable young sedimentary basins whereas trioctahedral minerals are common in older basins. It may be presumed that diagenesis in young basins could be more complex than the accepted direct transformation to smectite and that the distribution and composition of minerals could vary through the sedimentary sequence.

Clay minerals can form in sedimentary sequences a continuous phase of variable composition and content that may modify physical and chemical parameters like permeability, flow or adsorption. They behave different under static and dynamic conditions. Changes in the clay mineralogy will modify the behavior of the sediments. If so, knowledge on the relations between clay minerals, diagenesis and physical and chemical characteristics would contribute to explain the behavior of the sediments. The behavior of the clay minerals can be interpreted through their rheology, which is solely attributed to the interaction between clay particles, allowing assessment of the behavior of the fine fraction of the sediments and the influence of diagenesis.

The present paper study the shear rheology of the clay fraction of the Recent to Pleistocene volcanicogenic sediments of the Mexican Basin and its correlation with the mineralogy, diagenesis and behavior of the fine-size fraction of the sediments.

GEOGRAPHIC AND GEOLOGIC SETTING

The Mexican Basin extends between the 19°00' and 20°15' N latitude and 98°15' and 99°33' W longitude, covering an area of 7,160 km² in central Mexico (Figure 1). The geology of the Basin has been documented by various authors (Mooser, 1956a, 1956b; López-Ramos, 1979; Gasca and Reyes, 1977; Sistema Hidráulico del Distrito Federal, 1994). The Basin was formed in the middle Tertiary when active volcanism developed thick sequences of basaltic andesite, andesite, dacite and latite. Volcanic activity decreased towards the end of the Miocene. In the Pliocene, high rainfall created the abrupt relief of the middle and upper Tertiary volcanic complexes and resulted in extensive fluvial deposits intercalated with strata of silstone, lava flows and tuffs (Tarango Formation). During the Pleistocene the climate was humid and cold and large portions of the Tarango Formation were destroyed. The area was covered with thick layers of basalt and pumice until
intense lava effusions closed the drainage at the south end of the Basin. This was followed by an intense deposition of air and water transported ash that settled in the low areas (Tacubaya Formation). The Formation is characterized by intercalated strata of pyroclastic sands and ashes that in the lacustrine environment were transformed into the high swelling clays common to the basin. Overlying the Tacubaya Formation are the lacustrine sediments of the Becerra Formation. A simplified stratigraphic column of the Mexican Basin shows a layered sequence of silt, mud, sand and gravel randomly distributed (Figure 2).

The thickness of the mud strata varies. Southeast of the basin (areas of Xochimilco and Chalco) and northeast (Texcoco) is about 100 m thick whereas to the northwest (Atcapotzalco) ranges from 60 to 100 m. The mud retains large amounts of water forming gels that liquefy easily, are mechanically unstable, highly compressible, of fine particle size and substantial swelling (Marsal and Mazari, 1962).

METHODOLOGY

The sediments studied were sampled from more than 20 drillholes extended over the Basin down to depths of 324 m. Two holes, located in the north (Charcos) and south (Tezongo) areas of the basin and represented by 155 samples each, were selected to describe the mineralogy and diagenesis in the basin. Of

![Figure 1: Geologic map of the Mexican Basin.](image1)

![Figure 2: Schematic stratigraphic column of the Mexican Basin.](image2)
these, two samples representative of the clay minerals assemblies recognized in the basin were selected to illustrate the rheology of the fine-size fraction of the sediments. The sediments are black to brown mudstones with variable contents of sand and ash and coarse ash with volcanoclastic gravel-size fragments, lapilli, sand and ash. The average properties of the mudstones had been described as water content 400 wt. %, liquid limit 1-70, plastic limit 30-80, cation exchange capacity 70 meq/100 g, deformation modulus 10.60 k/cm² when containing 50-600 wt. % water and compressive modulus 2-8 kg/cm² (Marsal and Mazzari, 1962).

The samples for analysis were prepared by screening coarse ash and gravel, dispersing in deionized water, gravity settling of fine silt and sand and centrifugation to separate the <2 µm fraction. The high swelling and jellying of the clay made practically impossible the complete separation of the fine-size non-clay minerals even after dilution, prolonged settling and centrifugation. The mineralogy of the fine-size fraction was studied by X-ray diffraction (XRD) of suspended material deposited drop-wise on glass slides, air-dried and glycolated, using a D5000 Siemens diffractometer, CuKα radiation, scanning at 1° 2θ/min from 5° to 65° 2θ and at 0.5° 2θ/min from 2 to 45° 2θ. Experimental patterns of the mixed-layer minerals were compared with those calculated from NEWMOD (Reynolds and Reynolds, 1996). Smectite and vermiculite were differentiated by saturation with Mg and glycerol. Kaolinite was identified by its 001, 002 and 003 reflections that were not displaced by glycol and by the absence of the 14 Å chlorite peak. Volcanic glass was recognized optically and by a broad diffraction peak extending between 10-14° 2θ.

The shear rheology studies were done on the <2 µm fractions repeatedly centrifuged to separate the fine-size non-clay minerals. The two samples selected are: (1) 26 m deep, in the upper coarse ash strata, and (2) 60 m deep, in the same strata. The rheology measurements were done in a Bohlin Controlled Stress Rheometer (Bohlin Instruments Ltd., England) using a stationary cup and rotating cylinder assembly at a constant temperature of 25°C, vibrating frequencies from 0 to 10 hertz. Measurements included yield stress to evaluate the flow curve, behavior and viscoelastic range changing the stress linearly with time, and oscillatory tests to assess the shear dynamic response by varying the stress linearly with time at distinct frequencies.

RESULTS AND DISCUSSION

The clay mineralogy and diagenesis of the sediments of the Mexican Basin will be briefly reviewed for their significance to the rheology and behavior of the sediments. In the depositional sequence of coarse ash, gravel, sand and mud of the basin, clay minerals and fine-size ash occur intimately associated in variable proportions in all the strata. The clay minerals vary between 5-90 wt. % of the sediment. They are the continuous phase within the depositional sequence; the behavior of the sediments will depend on the abundance, mineralogy, diagenesis and continuity of the clay phase and on its effects on the physical and chemical parameters of the sediments.

In the northern area (Charcos) of the basin, coarse ash overlies the mudstone. At a depth of 18 m (Figure 3) the clay minerals are kaolinite, 2H₂O-smectite and interstratified kaolinite/smectite occur with fine-grained plagioclase, opal-C and K-feldspar. P, kaolinite; S, smectite; PS, kaolinite/smectite; CR, cristobalite; Pg, plagioclase; KF, K-feldspar.

![Figure 3. X-ray diffraction patterns of sediment 18 m deep: (A), <2 µm, air-dried; (B), glycolated; (C), <0.5 µm, air-dried; (D), glycolated. Kaolinite, 2H₂O-smectite and interstratified kaolinite/smectite occur with fine-grained plagioclase, opal-C and K-feldspar. P, kaolinite; S, smectite; PS, kaolinite/smectite; CR, cristobalite; Pg, plagioclase; KF, K-feldspar.](image)
basin (Tezongo), the mineralogical sequence is reversed. Mudstone essentially formed by $2H_2O$-smectite overlies the coarse ash. At 60 m, $2H_2O$-smectite still prevails; at 68 m, the coarse ash contains about equal parts of $2H_2O$-smectite and kaolinite and minor fine-grained plagioclase. From 108-286 m smectite is absent and kaolinite occurs with interstratified kaolinite/smectite mixed-layers. In the coarse ash strata occur kaolinite and smectite intimately associated with volcanic glass and, in the mud, smectite is the single clay component.

At 18 m in the upper strata, through a process of silicification, sapropelic, organic acids removed $Si^{4+}$ from the ash components, enriched the fluid phase in electrolytes and crystallized kaolinite. Volcanic glass was transformed to smectite and to silicified smectite. Silicic acid developed opal-C. With increasing depth, permeability and flow were gradually reduced, alkalinity increased, and smectite became progressively abundant by further transformation of volcanic glass and from kaolinite transformed via kaolinite/smectite mixed-layers. The smectite is dioctahedral, with an average content of 3.67-4.00 $^{18}Si$ atoms per half-cell, octahedral 1.83-1.96 $^{vi}Al^{3+}$ and 2.01-2.27 Mg$^{2+}$. The adsorbed cations vary between 0.2-0.9 afu, that correspond with layer charges within the range of montmorillonite and vermiculite in the zone where there is no difference in the stability of the layers (Mering and Pedro, 1969; Suquet et al., 1975, 1977; Güven, 1988; Suquet and Pezerat, 1987, 1988).

Kaolinite was formed in the upper strata where hydraulic conductivity and permeability were at their maximum. At depth, higher alkalinity of fluids, lower permeability and flow viscous to stagnant were more favorable to the formation of smectite. Environments of high permeability that prevent retention of fluids are prone to diagenesis to kaolinite (Hower et al., 1976; April, 1981) whereas low permeability and stagnant fluids favor the formation of smectite.

The two samples selected for the rheology studies represent the two clay assemblages predominant in the

Figure 4. X-ray diffraction patterns of sediment 86 m deep: (A), <2 $\mu$m fraction, air-dried; (B), glycolated; (C), <0.5 $\mu$m, air-dried. Kaolinite, $1H_2O$- and $2H_2O$-smectite, interstratified kaolinite/smectite and glass occur with fine-grained plagioclase and opal-C. Abbreviations as in Figure 3.

Figure 5. X-ray diffraction patterns of sediment 262 m deep: (A), <2 $\mu$m, air-dried; (B), glycolated; (C), <0.5 $\mu$m, air-dried; (D), glycolated. $1H_2O$- and $2H_2O$-smectite, interstratified kaolinite/smectite, kaolinite, fine-grained plagioclase, K-feldspar and opal-C. Abbreviations as in Figure 3.
upper strata. One sample is 26 m in depth, contains kaolinite, 2H₂O-smectite, interstratified kaolinite/smectite, and volcanic ash, fine-grain plagioclase and opal-C. Another sample is 60 m depth, contains smectite, interstratified kaolinite/smectite, kaolinite and fine-grain plagioclase, opal-C and volcanic glass. The former sample contains more kaolinite and less smectite than the latter one.

Jellified suspensions of the 26 m clay fraction, containing 15.45 wt % solids, and of the 60 m clay fraction containing 14.02 wt % solids show non-Newtonian behavior (Einrich, 1956). The flow curves (Figures 6A and 7A) do not indicate the constant rate of shear/shear stress ratio or constant viscosity (Figures 6B and 7B) that typifies Newtonian behavior. The behavior is pseudoplastic, confirmed by the convex variation of the

Figure 6. Flow curves of the 26 m clay. The behavior is non-Newtonian viscoelastic. A: rate of shear and shear stress; instant viscosity (B) and strain (C) with rate of shear; D: shear stress with time; E: strain with shear stress; creep compliance (F), elastic creep compliance (G); and shear relaxation (H) with time.
Figure 7. Flow curves of the 60 m clay. The behavior is non-Newtonian viscoelastic. (A): rate of shear and shear stress; instant viscosity (B), and strain (C) with rate of shear; D: shear stress with time; E: strain with shear stress; creep compliance (F), elastic creep compliance (G) and shear relaxation (H) with time.

shear rate to the shear stress (Figures 6A and 7A), viscosity (Figures 6B and 7B), the non-linear exponential variation of the strain with the shear rate (Figures 6C and 7C) and with the shear stress (Figures 6E and 7E). The suspensions are thixotropic, of reversible gel-sol transformation and viscosity decreasing on shear but building upon rest.

The behavior of the suspensions changes from elastic to viscous or from thickening to thinning at shear stresses respectively of 1.03 Pa (Figure 6A) and 5.91 Pa (Figure 7A). The 26 m clay generates lower shear stresses at shearing rates <0.02 s\(^{-1}\) (Figure 6A), viscosity <195 Pa s (Figure 6B) and strain <0.90 (Figure 6C). The 60 m clay produces shear stresses below 10 Pa at low rates of shear <0.006 s\(^{-1}\) (Figure 7A) and strain <0.2 (Figure 7C) and higher viscosities <3800 Pa s (Figure
The shear creep compliance or shear strain/stress ratio (Figures 6F and 7F) is approximately linear within a short span of time, with the total elastic recovery of 0.15 Pa$^{-1}$ for the 26 m clay and 0.008 Pa$^{-1}$ for the 60 m clay. The creep compliance and the elastic part of the creep compliance ($J(t)-t/\eta$) show minimal deviation from zero within a period of time (Figures 6G and 7G). These extended plateaus and the stress relaxation modulus $G(t)$ or reciprocal of the creep (Figures 6H and 7H) further confirm the viscoelastic behavior.

Increments in the shear rate increase the stress and the instantaneous viscosity elastically to a maximum after which decreases rapidly for the 26 m clay and at a slower pace for the 60 m clay, in viscous behavior. The elastic behavior and rising viscosity are associated with particle orientation under the deformation force; the viscous behavior implies reduction in viscosity while shear rate and strain increase. Differences between the two samples confirm the gradation or differential behavior that may exist between them. While the upper levels of the strata may be fluidized viscously, the lower ones may be raising their viscosity elastically. Prevailing elastic behavior and high viscosity would tend to prevent flow through the pores and channels of the sediment. When the behavior changes to viscous and viscosity decreases, flow will proceed. Distinct flow patterns will set through the sediments.

Viscoelastic bodies exhibit linear viscoelastic behavior within a short span of time in which the stress-strain ratio, though a function of time, is independent of the stress, allowing the measurement of the stress-strain ratio under a time-dependent loading pattern. When the viscoelastic body is subjected to a deformation force varying linearly with time at small frequencies, the mechanical energy is partly stored in the body and partly is dissipated as heat. The behavior of the body is specified by the ratios of the stress-in-phase and the stress out-of-phase respectively to the strain. The dynamic response is valued as the shear dynamic storage modulus $G'$ (in-phase component of the stress/strain ratio), the shear dynamic loss modulus $G''$ (out-of-phase component of the stress/strain ratio), and the complex dynamic modulus $G^*$ ($G^*=G'+jG''$). $G'$ corresponds with the energy stored by the system and $G''$ with the energy loss in the form of heat. The cinematic viscosity $\eta^*$ is the ratio between the absolute modulus $|G^*|$ ($|G^*|=\sqrt{(G'^2+G''^2)}$) and the frequency of vibration ($\omega$). The phase angle between the two vector components of the stress is $\psi$ and $\tan \psi$ represents the loss tangent (Figures 8 and 9).

The 60 m clay suspension, under a stress augmented linearly with time while the frequency of vibra-

![Figure 8](image-url)

Figure 8. Shear dynamic response of the 60 m clay subjected to a linearly modulated shearing stress at 1 Hz frequency, showing the change relative to the strain of (A), shear storage $G'$, shear loss $G''$ and total shear modulus $G$; (B), cinematic viscosity; (C), phase angle; (D), stress.
tion remained constant at 1 hertz -sufficiently small to assure linear viscoelastic behavior-, required high strains to develop stresses <20 Pa (Figure 8D), shear modulus <5 Pa (Figure 8A) and cinematic viscosities <0.8 Pa s (Figure 8B). At the higher frequency of vibration of 5 hertz, the same suspension required lower strains <0.4 to develop higher stresses <80 Pa (Figure 9D), shear modulus <120 Pa (Figure 9A) and cinematic viscosities <4.0 Pa s (Figure 9B). Vibrations of lower frequency result in shear storage dynamic modulus G’ higher than the shear dynamic loss modulus G” or they preferentially store energy whereas at higher frequency more energy is dissipated as heat than is stored. The dynamic response of the clay minerals and of the fine fraction of the sediment changes with the frequency of the applied vibration; high frequencies store less energy, dissipate more heat and raise the cinematic viscosity.

Differences in the mineralogy of the fine fraction, formed essentially by the clay minerals, result, at 26 m where kaolinite, interstratified kaolinite/smectite and smectite predominate, in stresses nearly four times weaker to develop instantaneous viscosities 20 times lower than those produced at 60 m where smectite prevails. Considering that the rheology measures the interaction among clay particles, which at the end depends on their structure, replacement and surface, particles at 26 m associate in a low-energy edge-to-edge or edge-to-face manner, whereas at 60 m clay particles associate in two distinct face-to-face forms of much higher energy, thinner fluid films and smaller distances between particles. A direct dependence between the clay minerals and the behavior of the fine <0.5 µm continuous fraction is maintained.

The dynamic response of the clay fraction is sensitive to the vibration frequency of applied stresses. For the same clay mineralogy, 2H₂O-smectite at 60 m, changes in the frequency result in major differences in the stored and dissipated energies. Large frequencies dissipate more heat, and store less energy. The more energy is dissipated, the higher is the temperature and its effect on the physical and chemical behavior of the fine fraction of the sediments.

CONCLUSIONS

Clay minerals form in the sediments a continuous phase that changes in abundance, type and distribution of clay minerals across the depositional sequence. Large differences in the interaction among clay particles sustain that their behavior and that of the fine-size sediments is non-uniform, differential, across the sequence.

Figure 9. Shear dynamic response of Sample 1 subjected to a linearly modulated shearing stress at 5 Hz frequency, showing the change relative to the strain of (A): shear storage G’, shear loss G” and total shear modulus G; (B): cinematic viscosity; (C): phase angle; (D): stress.
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