FORCES BETWEEN SUSPENDED BENTONITE PARTICLES
PART II—CALCIUM BENTONITE[1]

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ABSTRACT

In a previous paper (van Olphen, 1956) data were presented for the rheological and sedimentation behavior of sodium bentonite suspensions in water. From these data particle interaction energies were derived. Analogous data have been collected for calcium bentonite suspensions. It was observed that more clay is required to obtain a gel or a certain sediment volume with calcium bentonite than with sodium bentonite. This result can be quantitatively interpreted on the basis of a larger average particle thickness in the calcium bentonite suspensions. It is furthermore concluded that the interparticle forces are of the same order in both calcium and sodium bentonite suspensions.

INTRODUCTION

In a previous paper (van Olphen, 1956) rheological and sedimentation studies on sodium bentonite suspensions were presented. When a sodium bentonite suspension is converted into a calcium bentonite suspension a strikingly different suspension is obtained. The calcium bentonite suspension is less transparent and settles more rapidly than the sodium bentonite suspension. This difference would indicate a larger average particle size in the calcium bentonite suspensions. Since the suspensions are made from the same parent material it seems unlikely that the larger particle size is a matter of larger diameter of the plates, and, as a matter of fact, electron micrographs show the same average plate sizes for the particles of the two suspensions. Therefore, the calcium bentonite particles are apparently thicker than the sodium bentonite particles. This is actually shown by relative viscosity determinations (to be discussed later) from which a larger thickness-to-diameter ratio for the calcium bentonite particles can be calculated. The presence of divalent calcium ions in the flat double layer causes a higher degree of parallel association (or flocculation) of the unit layers than monovalent sodium ions. This association is what might be expected from the electrical double-layer theory.

A consequence of the larger particle thickness of the calcium bentonite is that it takes more weight of clay to obtain the number of clay particles required to build the scaffolding structure of a gel or a sediment.

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The question can be raised, therefore, whether differences in the rheological and sedimentation behavior of sodium and calcium bentonite suspensions can be explained solely on the basis of increased particle thickness, or, whether also differences in particle interaction energies enter the picture.

A series of experiments, completely analogous to those reported for sodium bentonite suspensions, were carried out to answer this question.

PREPARATION OF SYSTEMS

Raw Wyoming bentonite was suspended in water, and all matter larger than 2μ equivalent spherical radius was removed by sedimentation and decantation. This parent material is comparable to that from which the sodium bentonite suspension marked T was formerly prepared. In the preparation of pure calcium bentonite suspension the same procedure of resin column conversion and supercentrifuge washing was used as for sodium bentonite, except, of course, that now the resin was used in the calcium form.

Portions of different clay concentrations were obtained by ultracentrifugation of the dilute suspension. Portions containing different $CaCl_2$ concentrations were also made up, with the final clay concentration kept constant.

RHEOLOGICAL OBSERVATIONS

Concentrated Suspensions

Modified Stormer viscometer.—In Fig. 1 the viscometer data are plotted for some of the suspensions. Deviations from Bingham behavior are observed at slightly higher rates of shear than in the case of sodium bentonite : 125–150 sec^{-1} instead of about 100 sec^{-1}.

In Figs. 2 and 3 the Bingham yield stress and the differential viscosity are plotted at the left versus the clay concentration, and at the right versus the amount of $CaCl_2$ added at a constant clay concentration of 12.18 percent by weight.

Figure 4 shows that the clay concentration dependence of the Bingham yield stress τ_B can be fitted in the form

$$\tau_B = k . (c - c_m)^2,$$

by choosing a proper value of c_m, where c is the weight concentration of the clay, and k and c_m are constants, the values of which are tabulated in the figure. The value of c_m appears to be practically equal to the clay concentration required to obtain a detectable yield stress of 5 dynes/cm^2 as found from the extrapolation of the $\tau_B - c$ curve in Figs. 2 and 3. An analogous relation was found previously for the sodium bentonite suspensions.

Shear propagation.—In Fig. 5 the pulse arrival times in the shear propagation apparatus are plotted versus the traveling distance of the shear wave for several clay concentrations. The computed modulus of elasticity is

reported in the figure for each concentration, the slightly varying density of the suspensions being neglected.

The increase of the modulus of elasticity with clay concentration is represented in Fig. 6, in which the modulus of elasticity μ is plotted versus
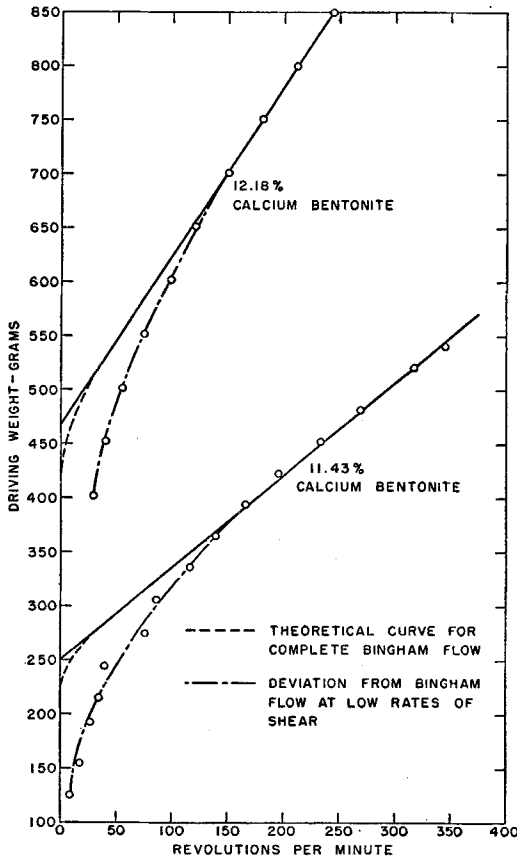

FIGURE 1.—Bingham flow curves obtained with the modified Stormer viscometer.

$(c - c_m)$ on a double logarithmic scale. It can be seen from the figure that the following relation holds:

$$\mu = k' . (c - c_m)^{5.7}.$$

The pure calcium bentonite suspensions seemed to be nonthixotropic: they did not display any change of arrival time with time elapsed after stirring. However, those suspensions to which small amounts of $CaCl_2$ were added
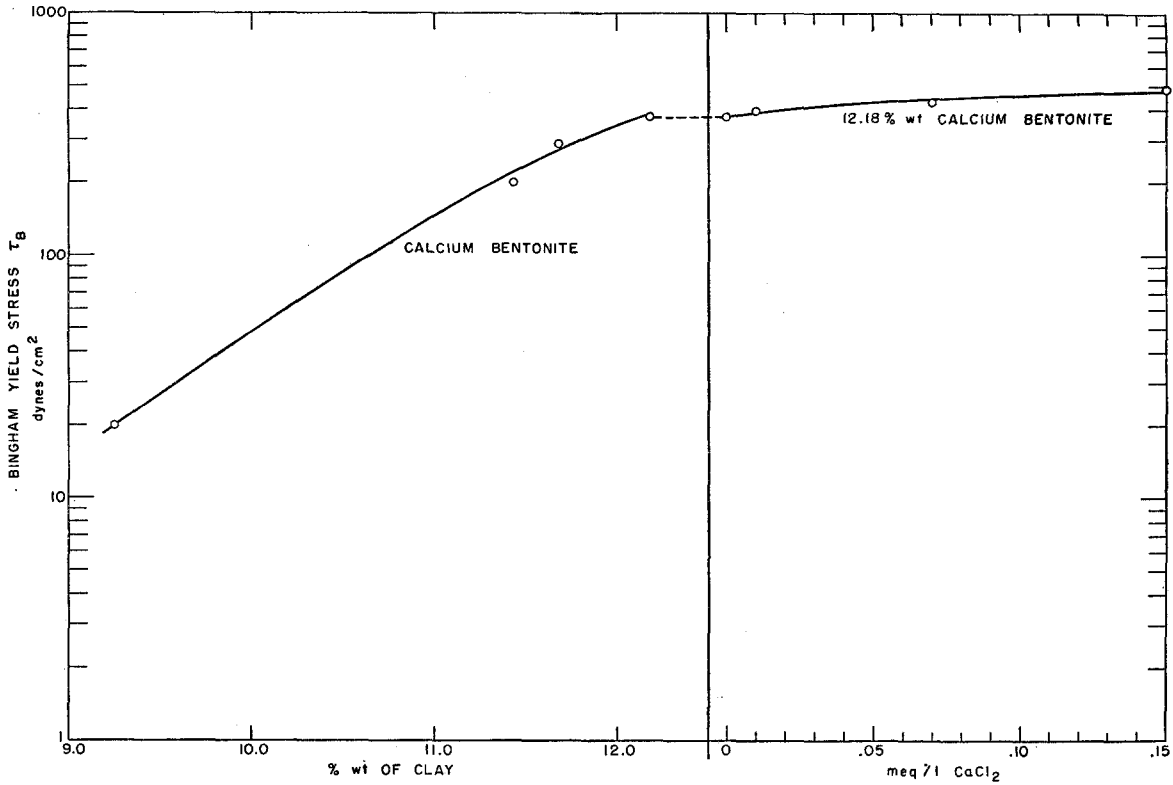
FIGURE 2.—Bingham yield stress as a function of clay concentration and amount of $CaCl_2$ added.
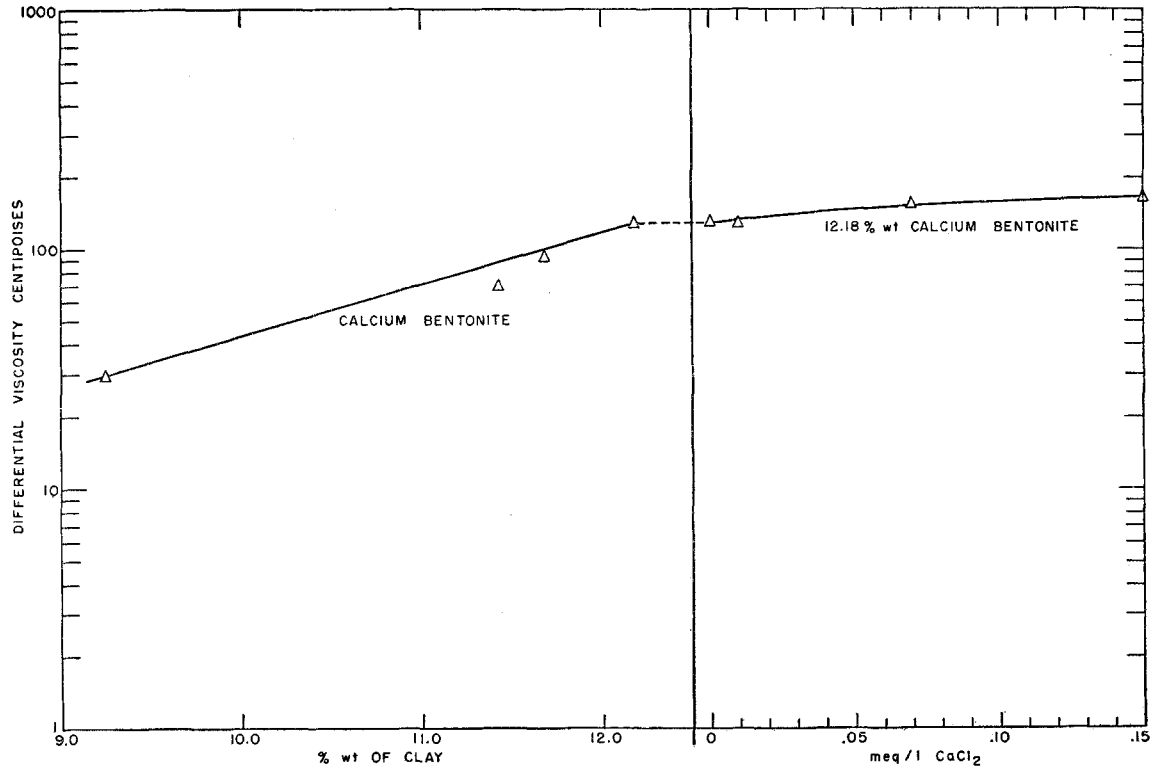
FIGURE 3.—Differential viscosity as a function of clay concentration and amount of CaCl₂ added.
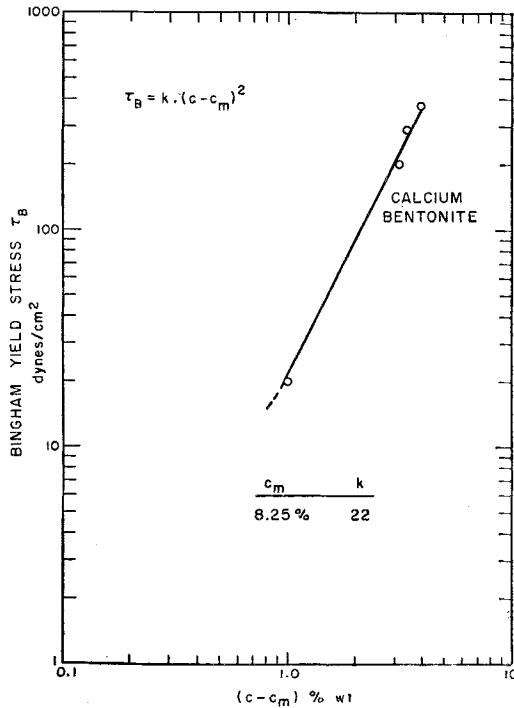
FIGURE 4.—Bingham yield stress as a function of $(c - c_m)$.

were setting slowly after previous stirring. This is shown by the increase of arrival time of the shear wave with setting time as tabulated below:

TABLE 1.—DEPENDENCE OF THE MODULUS OF ELASTICITY μ ON SETTING TIME t ($\mu = kt^a$) FOR 8.34 PERCENT BY WEIGHT CALCIUM BENTONITE SUSPENSIONS IN THE PRESENCE OF VARIOUS AMOUNTS OF $CaCl_2$

Amount of $CaCl_2$ Added (meq/l)	Relation of μ and t
0.5	$\mu = 530$, $a = 0.118$
1.0	$\mu = 1850$, $a = 0.144$
2.0	$\mu = 1810$, $a = 0.230$

Dilute Suspensions

Ostwald capillary viscometer.—In Fig. 7 relative viscosity data for dilute calcium bentonite suspensions are plotted versus the clay concentration and, to the right, versus the $CaCl_2$ concentration at a constant clay concentration

of 0.25 percent by weight. For comparison the relative viscosity-clay concentration curve for the sodium bentonite suspension T is included in the figure.
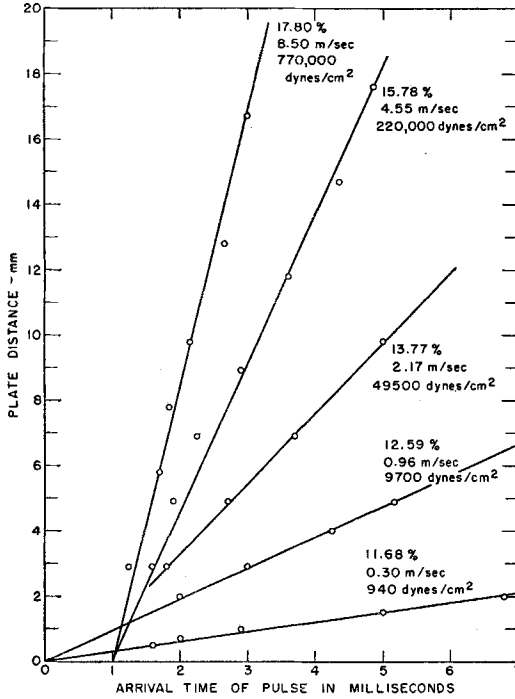

FIGURE 5.—Arrival time of pulse at different plate separations for 5 different concentrations of calcium bentonite suspensions.

Sediment volume in the ultracentrifuge.—The sediment volumes of calcium bentonite suspensions appear to be much smaller than those of sodium bentonite suspensions. The following data were obtained after 1080 min. of centrifuging at 15,000 r.p.m. (average 22,000 g) :

	Sed. Volume	Clay Conc. of Sed.
Pure sodium bentonite suspension T	6.75 ml/g clay	14.8% by weight
Pure calcium bentonite suspension	1.70 ml/g clay	59 % by weight

Only little change in calcium bentonite sediment volume was observed on addition of $CaCl_2$ after 45 min. spinning at 18,000 r.p.m.

DISCUSSION OF RESULTS

Effect of Electrolyte Addition on the Rheological and Sedimentation Behavior

It may be recalled that the addition of NaCl to sodium bentonite suspensions causes some peculiar changes in the rheological and sedimentation behavior of these suspensions. The pure suspensions made nonthixotropic gels, whereas salt addition resulted in thixotropic gels. At small salt concentrations—a few meq/liter—the yield stress of the suspensions became smaller than that of the pure suspensions, but further addition of salt caused the normal increase of yield stress due to flocculation. Analogous changes were observed in the sediment volumes on salt addition.
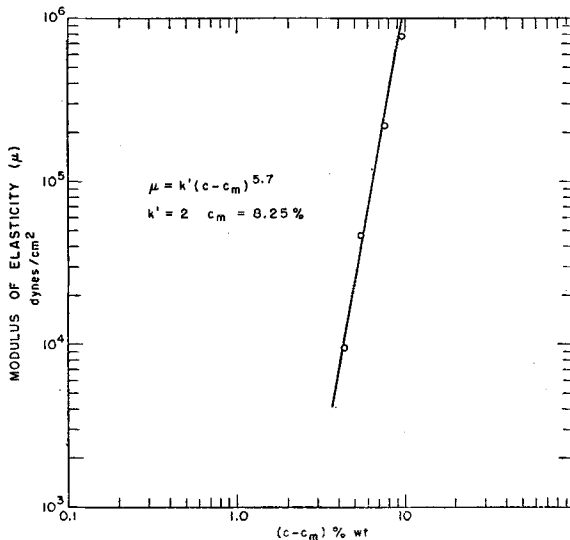

FIGURE 6.—Modulus of elasticity of calcium bentonite suspensions as a function of $(c - c_m)$.

In the study of the effect of electrolyte on calcium bentonite suspensions, NaCl was replaced by $CaCl_2$ in order to avoid any complications due to ion exchange. Because of the stronger flocculating action of the divalent calcium ions, lower concentrations of $CaCl_2$ were studied. Nevertheless, contrary to the effect of NaCl on sodium bentonite, no indication of an initial yield stress reduction or sediment volume reduction was found on addition of small amounts—as low as 0.01 meq/liter—of $CaCl_2$ to calcium bentonite suspensions. However, the pure gels and the $CaCl_2$-flocculated gels did show the same difference in character as in the case of sodium bentonite : The pure gels were nonthixotropic, the electrolyte-containing gels thixotropic. Therefore, the same explanation for this difference in character may be put forward :
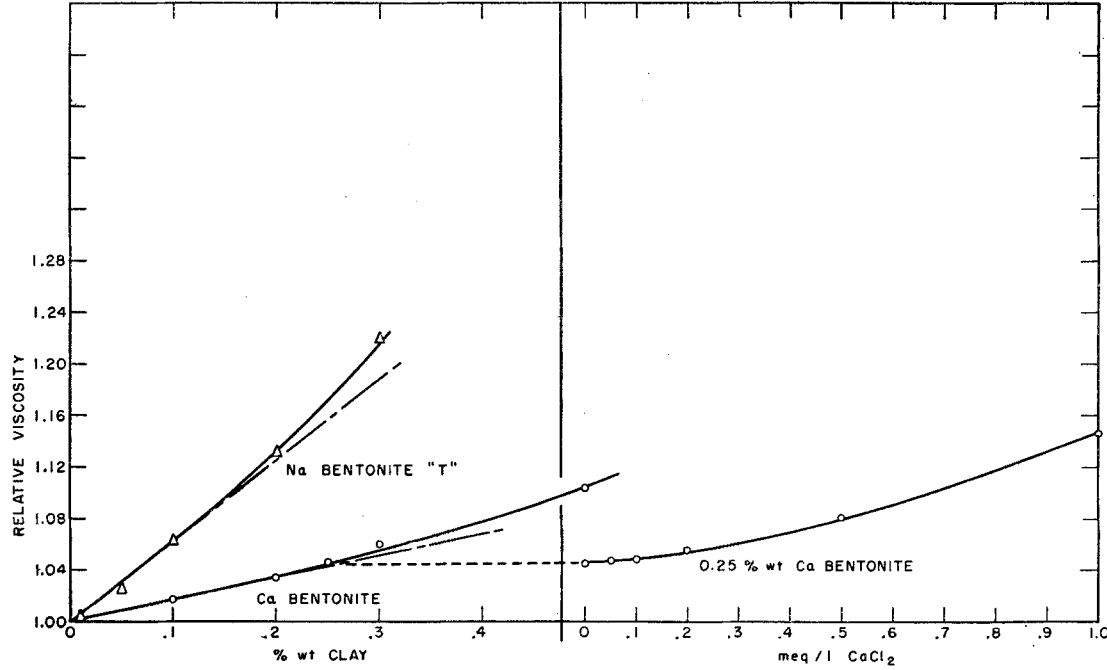
FIGURE 7.—Relative viscosity of dilute calcium bentonite suspensions as a function of clay concentration and the amount of $CaCl_2$ added.

The pure gels result from positive edge-negative flat surface linking by Coulomb forces, the electrolyte-containing gels result from van der Waals attraction becoming predominant when the energy barrier due to the double-layer repulsion is reduced.

Rheology and Particle Linking Forces in Calcium Bentonite Gels

Gel development.—According to the Peterlin–Burgers equation, at a given concentration of the suspended particles, the diameter-to-thickness ratio for large plates is proportional to the relative viscosity of the suspension minus 1. From the data in Fig. 7 it is seen that for sodium bentonite this ratio is about 3.8 times that for calcium bentonite. Assuming equal diameters for the plates of the two ion forms made from the same parent material, it follows that the calcium bentonite particles are 3.8 times as thick as the sodium bentonite particles.

If the interparticle forces in the two gels are about the same, one would expect that for the formation of a gel with a barely detectable Bingham yield stress the concentration of calcium bentonite would need to be about 3.8 times the concentration of sodium bentonite. From the c_m values for both gels, expressed as grams of clay in 100 ml of suspension, it appears that $8.71 : 2.54 = 3.4$ times as much calcium bentonite as sodium bentonite is required for first detectable Bingham yield stress development. This is in reasonable agreement with expectation.

Also the sediment volumes per gram of clay in the two ion forms should show this ratio. The sediment volumes in the ultracentrifuge after identical conditions of spinning were found to be in the ratio $6.75 : 1.7 = 4$, which is indeed close to the expected ratio of 3.8. Apparently, therefore, the first-order differences in rheological and sedimentation behavior of sodium and calcium bentonite can be explained by the differences in degree of layer association in the two ion forms.

The linking forces in the calcium bentonite gels, then, seemingly, are not too different from those in the sodium bentonite gels. It may be recalled that the value of the linking forces is actually estimated from the consideration that the shear life of a link and its thermal life are of the same order at the rate of shear where deviation from Bingham behavior begins. It is true that this occurs at a somewhat higher rate of shear for calcium bentonite than for sodium bentonite. Also, referring to the computation for sodium bentonite and the meaning of the symbols in the previous paper, the value of ν may have to be taken a little smaller for the heavier calcium bentonite particles, probably a factor $\sqrt{3.8}$ smaller. However, these corrections do not lead to more than about 10 percent smaller estimates for the linking force. Also for the calcium bentonite gels a value $p = 6$ is found rather than $p = 10$, as can be shown by substituting the yield stress and differential viscosity values for the calcium bentonite suspensions in the calculations.

It may also be remarked that the calcium bentonite gels show a slightly different elasticity behavior—in particular, the modulus of elasticity appears

to increase more rapidly with the corrected concentration, the exponent being 5.7 instead of 3, as was found for sodium bentonite.

All this, however, is of secondary importance when compared with the pronounced first-order effects which can be readily explained from the increased thickness of the calcium bentonite particle.

Note : Clay concentrations in this paper as well as in the previous one are expressed in percent by weight, which means grams of clay in 100 g of suspensions. They were determined by weighing a portion of the gels and suspensions, evaporating the water at 105°C, and weighing the clay residue.

In the interpretation of rheological data, concentrations should be known in terms of grams of clay in 100 ml of suspension or gel. For a density of the dry clay of 2.70, the concentration in grams per 100 ml can be calculated from the weight percent concentration *c* by multiplying by the factor

$$\frac{100}{100 - 0.64c}$$

This factor is significant for only the higher gel concentrations.

REFERENCE

van Olphen, H. (1956) Forces between suspended bentonite particles, in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Coun. pub. 456, pp. 204–224.