on the left hand and middle scale, respectively, and reading the true angle from the right hand scale.

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ANOMALOUS BEHAVIOR OF MONTMORILLONITE CLAYS IN CLERICI SOLUTION

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Clerici solution (thallium formate-malonate mixture) is a very useful medium for separating minerals because of the high specific gravities attainable and the ease with which specific gravities may be changed by dilution or concentration. Occasionally reactions occur between mineral and solution which may prove troublesome or even be useful.

Holzner, working with stilpnomelane[1] and stilpnochloran,[2] later shown by Gruner[3] to be nontronite, demonstrated a base exchange reaction in which thallium replaced the alkalies, and in the case of stilpnochloran, the calcium and part of the water as well. The treated mineral contained up to about 13% thallium oxide. The specific gravity of stilpnomelane was raised from 2.823 to 3.068, and of stilpnochloran from 2.523 to 3.111. Behavior was normal in acetylene tetrabromide-benzol solution.

During some recent work in this laboratory, differences were noted in the behavior toward Clerici solution of kaolinite on the one hand, and of montmorillonite and its zinc-bearing variety, sauconite, on the other. Ninety-two per cent of the kaolite sample floated at a specific gravity of 2.70 while 97% and 87%, respectively, of the montmorillonite and sauconite samples sank at 3.55 specific gravity. Semiquantitative spectrographic analyses of the washed samples showed that the montmorillonites had taken up appreciable amounts of thallium (Table 1). Both montmorillonite and sauconite floated in methylene iodide at specific gravity

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[1] Holzner, J., Beiträge zur Kenntnis der varistischen Gesteins und Mineralprovinz in Lahn-Dillgebiet.-2. Über den Stilpnomelane von Grube Theodor (Lahngebiet) und einem beim Trennen mit Clerici-lösung auftretenden Basenaustausch: *Neues Jahrbuch für Min. Geol. u. Pal., Beilage Band*, **66**, Abt. A, pp. 213–225 (1933).

[2] Holzner, J., Neue Daten über den Stilpnochloran von Gobitschau (Mähren), zugleich Bericht über eine ungewöhnliche Umtauschreaktion: *Centralblatt für Min., Geol. u. Pal.*, Abt. **A**, pp. 250–256 (1934).

[3] Gruner, John W., The structural relationship of nontronites and montmorillonite: *Am. Mineral.*, **20**, 475–483 (1935).

3.25. *X*-ray diffraction patterns of the kaolinite fractions were normal, but the montmorillonite and sauconite fractions showed the 14.72 Å dimension either increased beyond the scope of the camera or too diffuse to be observed, while montmorillonite showed the 4.5 Å line greatly weakened and the 3.04 Å line missing entirely.

TABLE 1. THALLIUM CONTENT OF WASHED SPECIFIC GRAVITY FRACTIONS—PERCENT

	>3.55	<3.55	<2.70
Montmorillonite	15.0	3.4	
Sauconite[a]	6.2	2.9	
Kaolinite	0.9	0.7	1.0

[a] Quantitative analysis showed the zinc content of the >3.55 and <3.55 fractions to be 17.1% and 8.8%, respectively.

Up to this point, the behavior of montmorillonite parallels that described by Holzner. In a further experiment montmorillonite first separated in Clerici solution at specific gravity 3.33 showed over 99% greater than 3.33 specific gravity.* This same sample after washing and drying was centrifuged in methylene iodide, when over 99% of it separated in the less than 3.25 specific gravity fraction. It appears that the thallium taken up by base exchange, as shown by Holzner, and which will survive ordinary washing with water, produces a moderate permanent increase in specific gravity, but a much larger, temporary, increase in specific gravity occurs *while the montmorillonite is in contact with the Clerici solution.* This property may prove useful as a separation technique.

APPLICATION TO MIXTURES

A 50-50 mixture of montmorillonite and kaolinite was taken, ground together in a mortar, screened through 200 mesh, put through a homogenizer with Clerici solution at 3.55 specific gravity and centrifuged. The mixture split, 51.42% greater than 3.55, and 48.58% less than 3.55 specific gravity. *X*-ray patterns showed only montmorillonite in the >3.55 fraction and only kaolinite in the <3.55 fraction. The method might well be applied to natural mixtures of active and inactive clays as a separation and diagnostic technique. Care should be taken not to use too high a specific gravity. In a Clerici solution of specific gravity 3.75

* The sample loading was so light, 2 gms. in about 60 ml. of Cleric solution, that the adsorption by the clay of thallium salts must have a negligible effect on the specific gravity of the solution. 60 ml. of solution contains about 185 grams of thallium salts.

only 39% of a pure montmorillonite sample separated in the heavy fraction.

Discussion

The known behavior of montmorillonite in adsorbing water and organic materials into the interlayer position offers a probable explanation of the above phenomena. It seems possible that the thallium salts are more strongly attracted to the interlayer position than the solvent water, thereby raising the specific gravity of the swollen clay above that of the solution. That methylene iodide is also taken into the interlayer position seems quite probable but, since it is a pure compound the specific gravity of the clay could not be increased to a greater value than that of the liquid.

Method of Carrying Out the Separations

A brief description of the method of centrifuging fine materials in heavy liquids may be useful. The sample, crushed through 200 mesh or finer, is mixed with the heavy liquid, sometimes with the aid of a "homogenizer" to insure dispersion. Separations are carried out in Lusteroid plastic tubes. Twenty to thirty minutes may be required at 3500 r.p.m. or approximately 1500 times gravity.

After centrifuging, each tube is pinched together at the center with a laboratory clamp. Provided the tube is not too cold, this may be done without leakage. The "float" fraction may then be poured off and the top of the tube washed out. The pinch clamp is released, the tube squeezed back into shape with a vise, and the "sink" fraction removed. Tubes which have been pinched cannot be used again, but the facility with which heavy and light fractions may be separated is well worth the few cents which the tubes cost.

Acknowledgments

The montmorillonite and kaolinite samples used in this study were two of the clay mineral standards (Polkville, Miss., No. 19 and Bath, S. C., McNamee No. 1 Mine, respectively), of The American Petroleum Institute and were furnished this laboratory through the courtesy of Professor Paul F. Kerr. The sauconite sample, designated "Stadiger vein," was collected at Friedensville, Pa., by Dr. Thomas L. Hurst.

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