of the stain. He adds that best results appear when divalent iodate cations such as Zn, Cd or Ca were simultaneously present with OsO_4. Nothing is found in the scientific literature to show whether these divalent cations are part of the dense black organometallic complex.

Our interpretation of the reducing process calls for complex cations, Os-Zn^{x+}, to oxidize double bonds from organic reducing substrates in the cells. It may be possible that Iodine is required for the development of the staining reduction, but this element is apparently removed from the preparations by subsequent washings of the histological procedure.

Conclusion. Structures stained by ZIO technique contain both Zn and Os. The distribution of both elements is similar and the ratio Zn/Os is constant.

By substitution of divalent cation such as Zn in the place of K in CHAMPY's, OsO_4-KI, staining fixative mixture, MAILLET affords a more constant staining technique where Os and Zn are associated and participate in the formation of some organometallic complex at the level of several histological and cytological structures, such as nervous peripheral structures[3,4].

Résumé. La sonde électronique de Castaing nous a permis de déceler la présence de zinc simultanément à celle de l'osmium au niveau des sites de réduction du fixateur-colorant histologique de CHAMPY-MAILLET. L'iode ne fait pas partie du complexe organométallique colorant.

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A Note on the Effect of Chemical Treatments in the Mineralogical Studies of Sediments

Several chemical treatments are commonly applied to natural sediment samples before their mineralogy is studied using X-ray and other analytical tools. The method often employed consists of treating the sediments with Na-citrate, Na-bicarbonate and Na-dithionite to remove metallic coatings, by reducing Fe and other metals to their soluble states, and then with H_2O_2 of breaking up the organics by oxidation[1]. Similar treatment has also been employed in the study of suspended sediments[2,3]. It is assumed during such treatment that the silicate minerals in the sediments are unaffected and that the separation of the sediments into non-detrital and detrital fractions is effective[1]. However, instances of the silicates being affected by such treatment are also known[4].

This note presents the result of Mössbauer effects on treated and untreated samples. The sediment sample, collected from the Atlantic Ocean off the mouth of the Amazon River, consists of equal amounts of kaolinite, illite and montmorillonite[2]. The source for γ-radiation in Mössbauer effect was Co^{57} in stainless steel. Metallic Fe was used as reference standard. The data obtained from the multichannel analyzer was computer fitted to obtain the velocity-absorption (intensity) spectra. The position, amplitude and width were allowed to vary independently in order to obtain the best fit.

Mössbauer effect was observed on both 'treated' and 'untreated' sediment. The sediment used has equal amounts of the 3 major clay minerals in ratios approximately the composition of world average suspended matter carried by rivers into the oceans[5]. Hence the single sediment employed is representative of all clay mineral suites delivered to world oceans at the present time.

The spectra from the Mössbauer effect are shown in the Figure and the data are presented in the Table. The upper and lower spectra in the Figure correspond to untreated and treated sediments respectively. From the computer calculated data shown in the Table, it is clear that chemical treatment affects the basic structure of the silicates, in addition to removing some of the Fe in coatings as reflected in changes in the intensity for

Fe^{+3} peaks. Peak A in the spectra represents the sum of 2 overlapping peaks identical with B and C (intensity of A = intensity of B + intensity of C). The spectra correspond to the presence of Fe^{+3} in hydroxide coatings, octahedral and tetrahedral lattice sites in clays and Fe^{+2} in octahedral sites in clays[2,6].

Treatments for removal of coatings are supposed to eliminate most of the Fe^{+3} from the sediments, since Fe in coatings far exceed Fe^{+3} in clay lattices, but there is only a very small change in the intensity of Fe^{+3} peaks after treatment; hence the treatment method also appears to be inefficient. Changes in the intensity of Fe^{+3} peaks have also been reported by other workers[6]. The enhanced intensity of Fe^{+2} peaks may be due to increase in Fe^{+2} relative to Fe^{+3} by removal of Fe^{+3}, as shown by the intensity ratios. Changes in various parameters observed for Fe^{+3} peak suggest the possible attack of chemicals on the octahedral Fe^{+3} in clays and also on octahedral Fe^{+2}[4].

Some of the Fe^{+2} in the octahedral sites could have been displaced by small changes in the lattice parameters after the chemical attack; Fe^{+3} in the octahedral sites could have been reduced during the treatment to Fe^{+2}, and become soluble, and thus removed from the silicates along with the Fe^{+3} in the coatings. In the sediment examined, kaolinite and illite fraction have probably no Fe^{+2} or Fe^{+3} in the lattices at all, but montmorillonite is likely to contain both Fe^{+3} and Fe^{+2} in the lattices as

[1] M. L. JACKSON, *Soil Chemical Analysis* (University of Wisconsin, Madison 1969).
[2] R. J. GIBBS, Bull. Geol. Soc. Am. *78*, 1203 (1967).
[3] J. W. PIERCE, D. D. NELSON and D. J. COLQUHOUN, *Shelf Sediment Transport* (Ed. D. J. P. SWIFT; Downden and Co., New York 1972), p. 281.
[4] N. H. GRANGAS, A. SIMOPOULOS, A. KOSHIKAS, N. J. YASSAGLOU and S. FILLIPAKIS, Clay Miner. Bull. *21*, 151 (1973).
[5] R. M. GARRELS and F. T. MACKENZIE, *Evolution of Sedimentary Rocks* (Norton and Co., New York 1971).
[6] E. C. WEAVER, J. M. WAMPLER and T. E. PECUIL, Science *156*, 504 (1967).
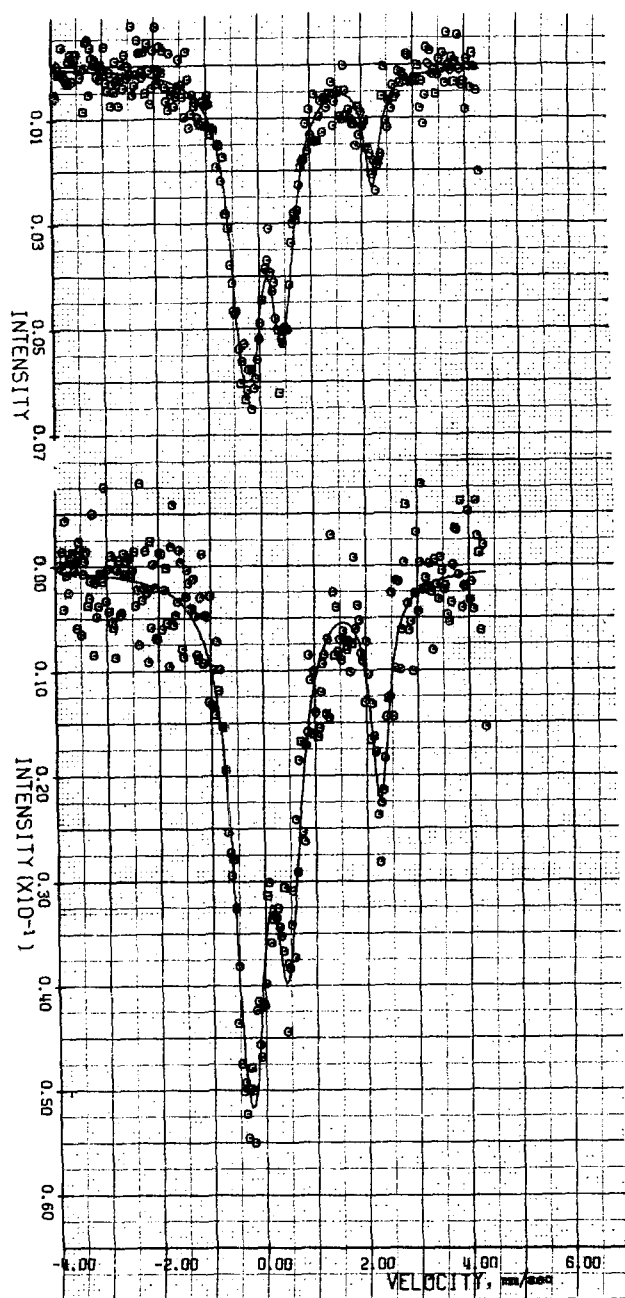
Mössbauer spectra for natural sediments. The top spectrum is before treatment and the lower one after treatment. Spectra taken at room temperature. Both spectra were taken under identical laboratory conditions. One of the peaks of quadruple doublet for Fe^{+2} is masked by the highly prominent Fe^{+3} peak near the centre of the figure.

Mössbauer spectra-data	Untreated sample [a]	Treated sample [a]
Total counts	1.094×10^5	1.093×10^5
Peak A	$- 0.352 \pm 0.009$	$- 0.400 \pm 0.013$
Peak B	$+ 0.434 \pm 0.007$	$+ 0.437 \pm 0.011$
Intensity Fe^{+3}	0.0457 ± 0.001	0.033 ± 0.001
Isomer shift, Fe^{+3}	$+ 0.041 \pm 0.001$	$+ 0.018 \pm 0.001$
Quadrupole splitting, Fe^{+3}	0.786 ± 0.001	0.837 ± 0.001
Width	0.561 ± 0.018	0.626 ± 0.027
Peak AB [b]	$- 0.109 \pm 0.016$	$- 0.186 \pm 0.018$
Peak C	$+ 2.195 \pm 0.018$	$+ 2.246 \pm 0.014$
Intensity Fe^{+2}	0.021 ± 0.001	0.021 ± 0.001
Isomer shift, Fe^{+2}	$+ 1.043 \pm 0.010$	$+ 1.050 \pm 0.010$
Quadrupole splitting, Fe^{+2}	2.304 ± 0.012	2.500 ± 0.012
Width	0.352 ± 0.035	0.436 ± 0.036
Intensity Fe^{+2}/intensity Fe^{+3}	0.470	0.620

[a] All values, except intensity and counts, are expressed as mm/sec. Isomer shift and quadrupole splitting values have been calculated from peak positions. [b] Peak AB is overlapped between A and B: hence not plotted by computer.

well as in the exchange sites. Since it is not possible to separate the individual clay minerals from the mixture physically, it is difficult to assign specific changes to any particular clay minerals. In view of the known properties of illite and kaolinite, it is most likely that any structural changes in clay minerals due to chemical treatment are probably in the montmorillonite fraction.

From the comparison of spectra for untreated and treated clay mixtures, it appears that the usefulness of chemical pretreatment for mineralogical studies needs to be re-evaluated.

Résumé. A l'aide de l'effet Mössbauer, il a été observé que les méthodes conventionnelles pour enlever les incrustations affectent les silicates quand elles sont appliquées aux sédiments avant leur examen minéralogique.

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Quantitative Separation of Titanium from Numerous Metal Ions by Thin Layer Chromatography

Thin layer chromatography has been extensively used for the separation of organic substances. The use of this technique for the separation of inorganic ions has not been investigated in detail. Seiler and Seiler[1] had applied thin layer chromatography for the separation of cations. Earlier studies in these laboratories have shown that mixed solvent systems are very useful for the qualitative separation of inorganic ions. However, quantitative aspect of the separations is still lacking. It was therefore considered worthwhile to use mixed solvent systems for a

[1] H. Seiler and M. Seiler, Helv. chim. Acta *43*, 1939 (1960).