

A COMPARISON OF THE EFFECTIVENESS OF EIGHT METHODS FOR THE REMOVAL OF ORGANIC MATTER FROM CLAY

A. D. VAN LANGEVELD, S. J. VAN DER GAAST, AND D. EISMA

Netherlands Institute for Sea Research, Texel

(Received 30 September 1977)

Abstract—Organic matter present in clayey sediments may act as a cement between the clay particles as well as a blocking agent for the swelling of clay minerals like montmorillonite.

Removal of the organic matter is important when a clay sample is to be characterized by X-ray powder diffraction, or when it is to be separated into the composing minerals on the basis of differences in density.

Eight different methods for the removal of organic matter from a North Sea clay sample have been studied. Of all methods tried bromine oxidation was found to be the most effective.

Key Words—Carbon disulfide, Hydrogen peroxide, Hypobromite, Montmorillonite, Organic.

EXPERIMENTAL METHODS

To study the effectiveness of various methods for the removal of organic matter from a North Sea clay sample, the carbon percentages and X-ray powder diffraction patterns were compared before and after removal of the organic matter.

Pretreatment of the clay

The pretreatment of the clay sample consisted of the removal of carbonate in a sodium acetate–acetic acid buffer (pH = 5), followed by extraction of free iron with sodium dithionite and sodium citrate following Holmgren (1967). This pretreatment is necessary, because carbonates and iron (as oxide and hydroxide) can act as a coating and as a cement. Moreover, organic carbon determinations cannot be made without such pretreatment. The fraction $<0.5 \mu$ of the pretreated sample was separated with a centrifuge and freeze-dried.

Methods for the removal of organic matter from clay

All sample treatments were carried out on 0.4 g of the homogenized, pretreated, fractionated, and freeze-dried sample. After the reactions all samples were thoroughly washed with distilled water and saturated with Ca ions before X-ray powder diffraction.

The following methods for the removal of organic matter were applied:

- 1) Oxidation by activated oxygen in a Tracerlab Low Temperature Asher type S.A. 33 during 16 hr. RF power 200 watts.
- 2) Oxidation in 200 ml 0.1% sodium permanganate in water (Dümmmler and Schroeder, 1965) during 2 hr at 40°C. After this the sample was washed with 1 N oxalic acid in water to remove manganese dioxide residues.
- 3) Oxidation by bromine (Mitchel and Smith, 1974).

The sample was treated during 2 hr at 40°C with a freshly prepared mixture of 150 ml 5% sodium carbonate and 50 ml of a saturated solution of bromine in water (pH \approx 7).

- 4) Oxidation by sodium hypobromite (Troell, 1976). The sample was treated for 2 hr at 25°C with a freshly prepared solution of 2.5 ml bromine in 100 ml 1 N NaOH in water; then another 100 ml of this solution was added, and 2 hr later the reaction was stopped. The reaction takes place at pH \approx 12, which implies that some clay minerals may be partly dissolved.
- 5) Extraction by a 1:1 mixture of 0.5 N NaOH in methanol and benzene (Farrington and Quinn, 1971), in which the sample was refluxed during 2 hr. After this, the sample was washed with ethanol.
- 6) A vigorous hydrogen peroxide oxidation. During 2 hr the sample was treated at 90°C in 100 ml of a 20% hydrogen peroxide solution.
- 7) A gentle hydrogen peroxide oxidation. During 24 hr the sample was treated at 25°C in 200 ml of a 5% hydrogen peroxide solution.
- 8) Triple extractions of 1 hr each at 25°C in 100 ml of a 1:1 mixture of carbon disulfide and ethanol (de Lange, 1976). After this the sample was washed with ethanol.

X-ray analysis

Of the pretreated samples about 40 mg was converted into a corresponding “Ca-clay” by washing the samples with a saturated CaCl₂ solution. These “Ca-clays” were oriented from a suspension on a slab of ceramic material by suction (Dümmmler and Schroeder, 1965). The 001 reflections of the samples were measured from $2\theta = 3^\circ$ – 16° under the following experimental conditions: 1) saturated with glycerol (“GLY”), 2) saturated with water (“H₂O”), 3) dried in air (65% relative humidity) (“ADR”), 4) at lowered pressure, 0.7 cm Hg (“0.7 Hg”), and 5) after heating the sample at 350°C during 0.5 hr (“350”). CoK _{α 1,2} radiation ($\lambda = 1.7902 \text{ \AA}$)

Table 1. X-ray diffraction and carbon content data of a clay sample before and after applying various methods for removal of organic matter.

		pre-treated	Low Temp. Asher	NaMnO ₄	Br ₂	NaBrO	NaOH in methanol/benzene	H ₂ O ₂ vigour.	H ₂ O ₂ gentle	CS ₂ in ethanol
I	H ₂ O ¹ 002/ ¹ 001	0,04	0,09	0,05	0,16	0,11	0,02	0,08	0,03	0,07
II	GLY ¹ 002/ ¹ 001	0,14	0,25	0,05	0,35	0,33	0,05	0,10	0,02	0,13
III	1 ₁₁₀ ¹	1,2	1,8	0,4	1,6	1,8	2,3	0,9	0,9	1,2
IV	d ₀₀₁ (Å), H ₂ O	14,41	14,37	14,25	18,65	18,52	14,66	14,35	14,25	14,58
V	d ₀₀₁ (Å), GLY	14,37	17,69	14,25	17,75	17,81	15,18	14,37	14,25	14,58
VI	d ₀₀₁ (Å), 0,7 Hg	12,83	14,10	12,77	11,75	11,99	12,99	12,59	13,26	12,83
VII	%C	6,1	1,8	4,3	1,8	1,8	4,2	1,6	5,0	5,4

saturated with water will swell until a d_{001} value of at most 18.9 Å is reached (Brown, 1961); only the samples treated with bromine and hypobromite show this.

Saturation of a clean montmorillonite with glycerol results in a d_{001} value of about 17.7 Å at most (Brown, 1961); only the samples treated in the low temperature asher, or with the bromine and hypobromite showed this. When the diffraction pattern of a clean montmorillonite is measured at lowered pressure (0.7 cm Hg), the d_{001} value will be about 11.40–11.90 Å, depending on the montmorillonite measured. Only the samples treated with bromine and hypobromite showed a decrease of this size.

As an illustration of the different nature of the samples, the diffraction patterns of the pretreated sample, and of the samples after the bromine, the hypobromite, the low temperature asher, and the vigorous hydrogen peroxide treatment, are shown in Figure 1.

According to the carbon percentages of the samples, the removal methods can be separated into two groups, one removing at most 30% of the carbon present in the pretreated sample, and a group removing about 70% of the carbon. The low temperature asher, the bromine, the hypobromite, and the vigorous hydrogen peroxide treatment remove about 70% each.

DISCUSSION

Remarkably, the X-ray analysis is a more sensitive method to check the cleanness of montmorillonite than the determination of carbon. The low temperature asher oxidation resulted in a montmorillonite sensitive only to saturation with glycerol and dehydration, while the so widely used vigorous hydrogen peroxide oxidation had nearly no positive effect on the montmorillonite blocked by organic material. The latter method, however, destroyed a considerable part of the montmorillonite, which is possibly enhanced by the presence of organic material (Douglas and Fiessinger, 1971). The results of the bromine and hypobromite

treatment were very similar, the only exception being the montmorillonite 001 peak for the sample saturated with water, which was more sharply defined after the bromine treatment than after the hypobromite treatment. This suggests a cleaner internal surface of the montmorillonite after bromine treatment.

The carbon percentage found after the bromine oxidation (1.8%), may in part be caused by carbonates adsorbed from the sodium carbonate solution. Carbonate removal with a sodium acetate–acetic acid buffer after the bromine oxidation lowered the carbon percentage to 1.2%. Because the carbon content of the original pretreated sample is 6.1%, even the most effective removal method left about 20% of the noncarbonate carbon in the sample.

CONCLUSION

Of all methods tried for the removal of organic matter from clay, bromine oxidation was the most effective. This result should be considered as somewhat preliminary because only one clay sample from one environment of deposition was tested.

ACKNOWLEDGMENTS

We are indebted to Mr. B. Verschuur for the drawings and to Mr. J. Kalf and Mrs. R. Gieles-Witte for carrying out organic matter analyses.

REFERENCES

- Brown, G. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals*: Mineral. Soc., London, 544 pp.
- de Lange, G. J. (1976) Röntgen diffractie aan kleimineralen van enkele Noordzee monsters: Internal Report N.I.O.Z., 1976-6, 25 pp.
- Douglas, A. L. and Fiessinger, F. (1971) Degradation of clay minerals by H₂O₂ treatments to oxidize organic matter: *Clays & Clay Minerals* **19**, 67–68.
- Dümmler, H. and Schroeder, D. (1965) Zur qualitativen und quantitativen röntgenographischen Bestimmung von Dreischicht-tonmineralen in Böden: *Z. Pflanzenernaehr. Dueng. Bodenk.* **109**, 35–47.

- Farrington, J. W. and Quinn, J. G. (1971) Comparison of sampling and extraction techniques for fatty acids in recent sediments: *Geochim. Cosmochim. Acta* **35**, 735-741.
- Holmgren, C. G. S. (1967) A rapid citrate-dithionite extractable iron procedure: *Soil Sci. Soc. Am. Proc.* **31**, 210-211.
- Mitchel, B. D. and Smith, B. F. L. (1974) The removal of organic matter from soil extracts by bromine oxidation: *J. Soil Sci.* **25**, 239-241.
- Troell, E. (1976) The use of sodium hypobromite for the oxidation of organic matter in the mechanical analysis of soils: *J. Agric. Sci. Cambz.* **21**, 476-483.

Резюме- Органическое вещество, присутствующее в глинистых отложениях может вести себя как цемент между глинистыми частицами и как блокирующий фактор для разбухания глинистых минералов подобных монтмориллону.

Удаление органического вещества важно, когда глинистый образец характеризуется порошковым методом рентгеноструктурного анализа или когда его необходимо разделить на составляющие минералы на основе различий в плотности.

Было изучено восемь различных методов удаления органического вещества из глинистых образцов с Северного моря. Было обнаружено, что все методы, использующие бромное окисление, являются наиболее эффективными.

Kurzreferat- Organisches Material in tonartigen Sedimenten kann sowohl als Bindemittel zwischen Tonteilchen, wie auch als Quellblockierungsmittel für Tonmineralien wie Montmorillonit wirken. Das Entfernen des organischen Materials ist wichtig, wenn eine Tonprobe durch Röntgenpulverdiagramme untersucht wird oder, wenn die Probe in die zugehörigen Mineralien getrennt werden soll, auf der Basis der unterschiedlichen Dichten. Acht verschiedene Methoden für die Entfernung von organischem Material von einer Nordseeprobe wurden untersucht. Von allen versuchten Methoden, Bromoxydation war die effektivste.

Résumé-La matière organique présente dans des sédiments argileux peut agir comme un ciment entre les particules d'argile, ainsi que comme un agent bloquant l'expansion de minéraux argileux comme la montmorillonite. Il est important que la matière organique soit retirée d'un échantillon d'argile quand ce dernier doit être caractérisé par diffraction aux rayons-X, ou quand il doit être divisé d'après les minéraux qui le composent sur la base de différences de densité. Huit méthodes différentes ont été étudiées pour retirer la matière organique d'un échantillon de la Mer du Nord. L'oxydation à la bromine était, de toutes les méthodes essayées, la plus efficace.