A new, efficient, one-step method for the removal of organic matter from clay-containing sediments

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ABSTRACT: For the purpose of clay examination, a new one-step method for the removal of organic matter was developed using sodium peroxodisulphate combined with different buffers such as sodium hydrogen carbonate, disodium hydrogen phosphate and disodium tetraborate. From an early Cretaceous black shale from the Apennines with a high organic carbon content, the <2 μm clay fraction was separated and contained 10.9 wt% organic carbon. To prevent decomposition of the clay layers, the period of oxidation was short (25–60 min) and the pH was kept between 5 and 9.5. Up to 98% of carbon was removed by this method.

Unless the organic matter in claystone is removed, clay mineral properties like cation exchange capacity (CEC), water absorption or the mechanical behaviour are difficult to determine. Until now there has been no efficient way to remove the organic matter under pH conditions ranging from 5 to 10, during which clay minerals remain unaffected (Stumm, 1992; Huang & Keller, 1972). The organic compounds are generally strongly adsorbed on the surfaces, interlayers and edges of the clay minerals (e.g. Perez Rodriguez *et al.*, 1977; Keil *et al.*, 1994). Hence, the removal of these high molecular mass materials using classical methods is slow, ineffective or affects the pH-sensitive clay particles. The removal of carbon by hydrogen peroxide (e.g. Jackson, 1956), sodium hypochlorite (Anderson, 1961), oxygen in a plasma oven (e.g. Gluskoter, 1964; Taïeb, 1990) and enzymatic reaction (Keller, 1981) is usually ≪90%, depending on the type of organics. Therefore the treatment has to be repeated several times and even then not more than 93% of organic carbon is removed. The use of a plasma oven is effective, but very time consuming and only suitable for small quantities (ideal sample amount 30 mg; Taïeb, 1990).

The oxidative removal of organic matter with a solution of sodium peroxodisulphate activated by sulphuric acid has been described (Brunner, 1897; Bock, 1972; Gupta & Zanoni, 1974) but the yields are relatively low for clay-containing rocks or soils.

EXPERIMENTAL

Materials

Preliminary investigations were performed to test the optimal parameters for the oxidation of organic matter. For this purpose, an early Cretaceous, 'black shale' with low carbonate content from the Apennines ('Marne a Fucoidi' Formation) has been used as the starting material (total organic carbon, TOC, 17 wt%). Clay fractions (<2 μm) from this 'black shale' sample have been separated by sedimentation and the TOC content was determined to be 10.9 wt%. The maturity of the organic matter was determined by a pyrolysis T_{max} value of 427.0°C. The T_{max} is defined as a Rock-Eval pyrolysis thermal maturity parameter based on the temperature at which the maximum amount of organic compound, in mg HC/g TOC, is generated

from kerogen in a rock sample (e.g. Espitalié *et al.*, 1985), which corresponds to a vitrinite reflectance of 0.35 (analysis: R. Brown, NRG Newcastle). The <2 µm fraction, qualitatively determined by X-ray powder diffraction, and quantitatively by FTIR-spectroscopy, contained mainly quartz (24 ± 3 wt%), illite and mixed-layer illite-smectite (70 ± 7.5 wt%), chlorite (5 ± 3 wt%) and a small amount of pyrite (<1 wt%). The sample was free of any carbonate minerals.

The efficiency of the optimized oxidation method was tested on the <2 µm fraction of different types of organic carbon rich sediments (Table 1).

The oxidizing reagent was an aqueous solution of sodium peroxodisulphate, $Na_2S_2O_8$, (puriss. z.A. Merck) in combination with a buffer (all puriss. p.a. Fluka).
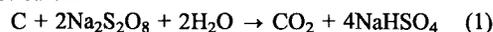
General procedure

A 200 mg sample of the organic clay fraction was dispersed in 70 ml of bidistilled water by ultrasonic treatment. Sodium peroxodisulphate and a molar amount of the buffer were added by stirring and diluted with water to a total volume of 150 ml. The mass ratio n = g $Na_2S_2O_8$/g clay was varied between $n = 1$ and $n = 50$. The pH was measured and the mixture was heated up to the reaction temperature. The pH was monitored using a pH-electrode and the colour of the organic clay suspension was taken as a sign of the reaction state. The reaction was stopped when no further bleaching was observed or when the pH dropped below 5. The mixture was cooled and centrifuged, the supernatant solution removed, and the clay washed several times with 70 ml of bidistilled water until it was dispersed completely. A few drops of a 10% calcium chloride solution were added to flocculate the clay and the washing procedure was repeated until total elimination of sulphate ions. The presence of sulphate in the removed supernatant solution was tested by addition of a few drops of 1 M barium chloride.
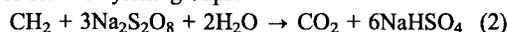
Traces of carbonate formed during the reaction were removed by addition of 50 ml 0.01 M hydrochloric acid to the clay sample dispersed in a volume of 50 ml water. After decomposition of carbonate, the sample was washed five times to reach neutral pH.

The theoretical amount of disodium peroxodisulphate required is:

for carbon:

$$C + 2Na_2S_2O_8 + 2H_2O \rightarrow CO_2 + 4NaHSO_4 \quad (1)$$

or for methylene groups:

$$CH_2 + 3Na_2S_2O_8 + 2H_2O \rightarrow CO_2 + 6NaHSO_4 \quad (2)$$

Two moles of disodium peroxodisulphate (molecular mass 238 g/mol) oxidize one mole

TABLE 1. Types and location of the organic carbon-rich samples used for testing the new method of removal of organic matter.

Sample	Type	Age	Location	Reference
1	Claystone ('Marne a Fucoidi' Formation)	Early Cretaceous	Gorgo a Cerbara (Italy)	Coccioni *et al.* (1987)
2	Lake Sediment organic-rich autumn lamination	Recent (1975)	Lake Baldegg (Switzerland)	Lotter, Sturm, Teranes & Wehrli (personal communication)
3	Organic matter-rich bentonite	Pannonian	Jelsovy Potok (Slovakia)	Kraus & Zuberec (1976)
4	Soil fine–loamy, mixed mesic Typic Eutrochrept	Recent	Dielsdorf (Switzerland)	Schmidhalter *et al.* (1994)
5	Claystone ('Opalinus Shale')	Middle Triassic	Holderbank (Switzerland)	Madsen & Nüesch (1990)
6	Marlstone ('Scaglia Variegata' Formation)	Early Cretaceous	Cismon (Italy)	Channell *et al.* (1979)

Sample 1 was adapted to optimize the oxidation procedure. To remove the organic matter, the <2 µm fraction of the decarbonated sample was used.

carbon (12) to carbon dioxide. Therefore, for a complete oxidation, a mass ratio of sodium peroxodisulphate/organic matter of 39.7 is needed. Hence, for CH_2 groups a mass ratio of sodium peroxodisulphate/organic matter of 51 is necessary. For an organic content of ~11%, an amount of 4.4–5.6 g sodium peroxodisulphate/1g organic clay should be sufficient to oxidize all of the organic matter. Partially oxidized functional groups such as COOH or COH, would require a smaller amount of oxidant. The optimal efficiency of the sodium peroxodisulphate in combination with a buffer was determined using different oxidant/sample mass ratios n (see Table 1). During the reaction, 2 moles acid/mol sodium peroxodisulphate were generated (eqn. 1). The mass ratios of buffer/oxidant were chosen to adjust the pH between 6 and 10.

(1) Sodium hydrogen carbonate, $NaHCO_3$; 1.1 g/g sodium peroxodisulphate (3 moles buffer/mol oxidant); (2) disodium hydrogen phosphate dodecahydrate, $Na_2HPO_4.12H_2O$; 4.0g/g sodium peroxodisulphate (2.66 moles/mol); (3) disodium tetraborate decahydrate, $Na_2B_4O_7.10H_2O$; 9.6g/g sodium peroxodisulphate (6 moles/mol).

Experiments with various mass ratios of oxidant/sample at a constant temperature of 80 ± 2°C were performed to determine any possible self-decomposition of the sodium peroxodisulphate. Furthermore, to prevent self-decomposition of the oxidant, a mixed solution of oxidant/buffer was added dropwise to the sample throughout the reaction time (Table 2).
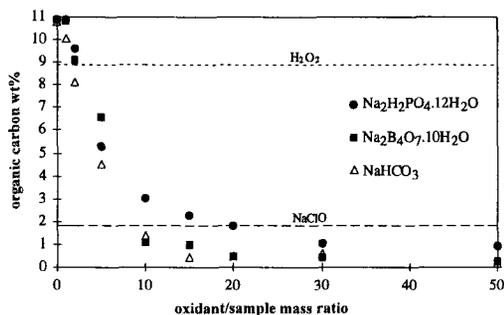

Fig. 1. Remaining organic carbon content of sample 1 after one oxidative step using buffered sodium peroxodisulphate solution as a function of the mass ratio $Na_2S_2O_8$/clay. Mass ratio buffer/$Na_2S_2O_8$: 1.1/1 for $NaHCO_3$; 4/1 for $Na_2HPO_4.12H_2O$; 9.6/1 for $Na_2B_4O_7.10H_2O$.

To check the role of the pH, oxidation at a low pH was carried out using di-sodium hydrogen phosphate as a buffer with $n = 30$. The starting pH of 3 was adjusted by adding a few drops of phosphoric acid. At the end of the reaction a dark organic film was still visible at the surface of the solution.

The TOC-content of the oxidized samples was measured with a Carlo Erba CNS Nitrogen Analyzer 1500 (reproducibility better than 0.1 wt% absolute value and minimum detectable value 0.01 wt%). Sulphanilic acid was used as a control standard and vanadium pentoxide as combustion catalyst.

X-ray powder diffraction was used to check relevant changes in the hk reflections of the crystalline phases after oxidation.

RESULTS AND DISCUSSION

The remaining organic carbon content after one oxidative run and the yield of the reaction for different mass ratios oxidant/sample and different buffers are shown in Table 3. The TOC data represent the mean value of three measurements.

Figure 1 compares the efficiency of the three different buffer systems at varying mass ratios of sodium peroxodisulphate/clay sample. The best results for all three buffers were obtained using a mass ratio for peroxodisulphate/clay of $n \geqslant 30$. The carbon content decreases strongly between the ratio 2 and 10. The use of sodium tetraborate and sodium hydrogen carbonate as buffer showed the best results. The former is less convenient because of its low solubility at room temperature. Using sodium tetraborate, the freshly oxidized sample has to be washed and centrifuged with hot water. Oxidation with hydrogen peroxide (H_2O_2) for several hours (Jackson, 1956) and also repeated oxidation-washing cycles (three times) with sodium hypochlorite (Anderson, 1961) were less effective.

Deactivation of the oxidant sodium peroxodisulphate by thermal decomposition is evidently not important because reactions at 80°C and 98°C give similar results (Table 2).

Figure 2 shows the pH evolution during the reaction period. With sodium hydrogen carbonate and disodium tetraborate decahydrate the pH remained alkaline. The final pH with sodium phosphate was lower than calculated. The reason has not been clarified.

As the pH is >5, the destruction of the silicate layer was at the detection limit. Analysis of the

TABLE 2. Oxidation systems used to remove the organic matter. The pH values at the beginning and end of the reaction are referred to in terms of oxidant/sample mass ratios, n.

Nr	$n =$ g $Na_2S_2O_8$/ g sample	Buffer	g buffer / g $Na_2S_2O_8$	pH: start/end	Reaction time/ temperature	Remarks
1a	1; 2; 3; 5; 10; 20; 30; 50	$NaHCO_3$	1.13	8.0/9.5	65 min/ 98°C	bleaching began after 5min; no further changes after 25 min.
1b	1; 2; 3; 5; 10; 20; 30; 50	$NaHCO_3$	1.13	8.2/8.8	120 min/ 80°C	bleaching began after 20 min; no further changes after 60 min; pale-greyish colour
1c	15; 30 slow addition of the oxidant/ buffer solution	$NaHCO_3$	1.13	8.1/9.2	30 min. 45 + 30 min/ 98°C	bleaching began after 10–15min; no further changes after 45–50 min; pale-greyish colour*.
2	1; 2; 3; 5; 10; 20; 30; 50	$Na_2HPO_4.12H_2O$	4	8.5/5.3	95 min/ 98°C	bleaching began after 10–15min; no further changes after 45–50 min; pale-greyish colour
3	1; 2; 3; 5; 10; 20; 30; 50	$Na_2B_4O_7.10H_2O$	9.6	9.3/8.5	90 min/ 98°C	bleaching began after 10–15min; no further changes after 45–50min; pale-reddish colour

* The mixed buffer/oxidant solution was added drop-wise to the sample solution during 45 min, and then stirred for 30 min at 98°C.

TABLE 3. Organic carbon (wt%) remaining after oxidation of sample 1 with $Na_2S_2O_8$ buffered with sodium hydrogen carbonate, disodium hydrogen phosphate and disodium tetraborate at different peroxodisulphate/sample mass ratios.

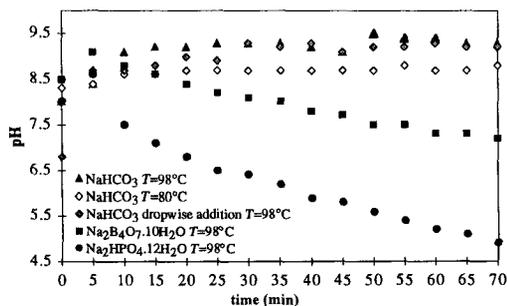| Nr	Buffer	Final carbon content							
		$n = 1$	$n = 2$	$n = 5$	$n = 10$	$n = 15$	$n = 20$	$n = 30$	$n = 50$
1a	$NaHCO_3$ $T = 98°C$	10.14 (7.0%)*	9.84 (9.7%)	2.98 (72.7%)	0.94 (91.4%)	0.97 (91.1%)	0.40 (96.3%)	0.34 (96.9%)	0.20 (98.1%)
1b	$NaHCO_3$ $T = 80°C$	9.98 (8.4%)	8.15 (25.2%)	4.63 (57.5%)	1.38 (87.3%)	0.99 (90.9%)	0.51 (95.3%)	0.48 (95.6%)	0.44 (96.0%)
1c	$NaHCO_3$ $T = 98°C$ slow addition of the oxidant over 45 min	–	–	–		– 0.45 (95.9%)	–	0.36 (96.7%)	–
2	$Na_2B_4O_7.10H_2O$ $T = 98°C$	10.85 (0.45%)	9.10 (16.5%)	6.60 (39.4%)	1.11 (89.8%)	1.01 (90.7%)	0.52 (95.2%)	0.43 (96.1%)	0.25 (97.6%)
3	$Na_2HPO_4.12H_2O$ $T = 98°C$	10.89 (0.1%)	9.61 (11.8%)	5.28 (51.6%)	3.03 (72.2%)	2.24 (79.4%)	1.80 (83.4%)	1.07 (90.2%)	0.96 (91.2%)

n = mass ratio $Na_2S_2O_8$/clay
* carbon removed

FIG. 2. pH value during oxidation ($n = 30$) of sample 1 in the presence of different buffers at 80°C and 98°C. The pH evolution is independent of the mass ratio oxidant/sample n.

supernatant solution by flame atomic absorption spectroscopy, showed a loss <3 mg Si and <2 mg Al from a 500 mg sample. The X-ray powder diffraction pattern was unchanged.

The sharp decrease in the organic carbon content at an oxidant/sample mass ratio of between 2 and 10 corresponds to the calculated theoretical ratio between 4.4 for high aromatic and 6.5 for aliphatic compounds. This also indicates that no significant decomposition of the oxidant occurs. However, an oxidant/sample ratio of $n \geqslant 30$ is necessary for removal of 98% organic carbon.

The buffer plays an important role because it determines the rate and the degree of the reaction (Table 1). We postulate two mechanisms. (a) The higher pH (unlike the chosen low pH conditions in earlier literature) increases the solubility of partially oxidized organics by deprotonating the carbonic acids. This is in agreement with our observation that oxidation at a low pH yields a black dusty film floating on the oxidation solution. Additionally, at

alkaline pH the clay remains dispersed and the coagulation by edge (positively charged)/ face (negatively charged) contacts can be avoided. (b) The buffers are edge-active substances, which are able to bond at the edges of clay minerals and consequently to displace the organic matter from these sites. In the system buffered with sodium hydrogen phosphate, the coagulation is prevented by the adsorption of phosphate at the edges of the clay (e.g. Lagaly, 1993). Both mechanisms provide better displacement of the organic compounds from the clay and improved access for the oxidant to the organic matter.

The results of the oxidation of the organic matter on different types of sediments using sodium hydrogen carbonate as buffer are listed in Table 4. The oxidation was performed at 98°C, over 60 min, using the oxidant/sample ratio $n = 40$.

The results confirm the effective removal of organic matter from different types of sediment.

CONCLUSIONS

By using a combination of sodium peroxodisulphate with a buffer such as sodium hydrogen carbonate, sodium tetraborate or sodium hydrogen phosphate, an efficient method was developed to remove the organic matter from clay-rich sedimentary rocks. This new oxidative procedure removes >98% of the total organic carbon in just one oxidation step. It allows a short reaction time under high pH conditions thereby avoiding attack of the clay edges. The reaction temperature only has a kinetic effect. Self-decomposition of the peroxide at higher temperatures is not important. The exact nature of the mechanism of organic matter removal using a buffered sodium peroxodisulphate solution and the influence of this oxidative treatment on the clay

TABLE 4. Remaining carbon content (wt%) after oxidation using an oxidant/sample ratio $n = 40$ and sodium hydrogen carbonate as buffer. Reaction time: 60 min; T, 98°C.

Sample	Initial carbon content	Final carbon content	Carbon removed
1	10.9	0.34	96.9
2	12.1	1.6	86.8
3	18.5	1.5	91.9
4	3.2	0.22	93.1
5	4.7	0.7	85.1
6	8.32	1.8	78.4

minerals properties are the subject of further investigations.

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