Article

Organic carbon and carbonate contents of black shales from the lower Cretaceous Paja Formation (Colombia) by loss on ignition and CHNS analysis: comparison of methods

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Abstract

Organic matter (and hence organic carbon) and calcium carbonate contents of soils and sediment can be estimated by simple loss on ignition (LOI) determinations, at temperatures ranging from 375 to 550℃ and 850-1000℃, respectively. Organic matter (OM) and carbonate contents of 24 carbonaceous black shale samples were determined by LOI and CHNS methods to compare these two techniques. Two LOI tests were carried out to determine the ignition times required at 550℃ and 1000℃ to ensure complete combustion of the OM and carbonate components. Results showed 4 to 6 hours of exposure at 550℃ were required to ignite the OM, and 3 hours further ignition at 1000℃ ensured decomposition of the carbonate. A complete set of sample were then ignited under these conditions, and the results compared with those from CHNS analysis. Although the results correlated well, LOI_{550} values (OM) were consistently greater than C_{org} by CHNS. Correction of the LOI data using a generic OM to C_{org} conversion factor commonly applied in the literature did not improve the results. A third experimental run with LOI determinations at 375℃, 550℃, and 1000℃ showed a strong correlation between LOI_{375} and C_{org} (CHNS), but relatively constant loss of weight (2-4 wt%) between 375℃ and 550℃ irrespective of C_{org} content. This suggests most of the weight loss below 375℃ was due to combustion of OM, whereas that between 375℃ and 550℃ was structural water lost from clays. Nevertheless, ignition at either 375℃ or 550℃ can give reasonable estimates of C_{org} ontent, provided calibration data for individual sample suites is available from an independent technique such as CHNS analysis. The results support proposals that use of generic OM to C_{org} onversion factors is inappropriate. Test of the viability of carbonate content determination was hampered by the non-calcareous nature of most of the samples. At low levels, neither LOI_{1000} nor CHNS seem to give good results. This is probably due to continued loss of structural water and other volatile phases, coupled with weight gains through oxidation of species such as Fe^{2+} and Mn^{2+}.

Key words: Black shales, LOI, CHNS, organic content, carbonate content.

Introduction

Loss on ignition method (LOI) is often used as a simple means of determining approximate organic carbon (C_{org}), organic matter (OM), and carbonate contents of soils, sediments and sedimentary rocks, particularly when they are calcareous and clay-poor (Ball, 1964; Dean, 1974; Sutherland, 1998). The method includes a first heating at 375 to 500-550℃ to ignite the OM, followed by a second ignition at 950-1000℃ to release carbon dioxide from carbonate minerals. Contents are derived from gravimetric data. However, many caveats surround the method. A number of authors (Sutherland, 1998; Heiri et al., 2001, among others) point out that losses of other compounds may also occur (e.g. volatile salts, structural water, inorganic carbon, pyrite), depending on the ignition temperature. Such losses can thus influence the accuracy of the C_{org} and carbonate determinations. Heiri et al. (2001) further noted that LOI is also influenced by heating time and sample size.

Chromatographic CHNS elemental analyses can also be used to accurately measure C_{tot}, C_{org} and carbonate contents, and to determine the composition of the organic matter (Minoru et al., 1999; Pimmel & Claypool, 2001; Sampei & Matsumoto, 2001). In this method samples are combusted in a reactor at 1000℃ in a temporarily enriched oxygen atmosphere. Temperature reaches 1800℃ during flash combustion. The reaction products are passed through a glass column packed with a tungsten trioxide and copper reducer to form CO_2, N_2, and SO_2. These products are then analyzed chromatographically, by calibration against an organic standard.

This paper examines the OM, C_{org} and carbonate contents of a suite of black shales from the Paja Formation of Colombia, as determined by both the LOI and CHNS methods. The primary purpose is to compare the results obtained by the two techniques, and determine if the LOI technique is appropriate for rocks of this type.

Geologic Setting

The Eastern Cordillera of Colombia is a NNE-SSW trending fold belt composed of Precambrian to Paleozoic basement covered by a thick sequence of Mesozoic to

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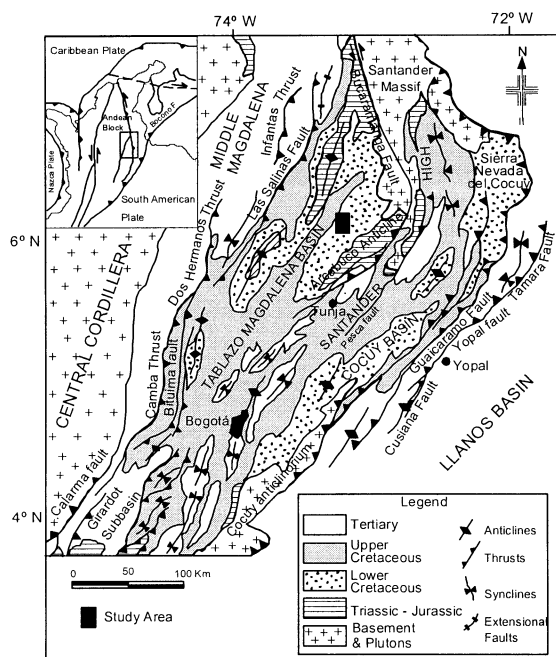
Fig. 1. Geology of the northern segment of the Eastern Cordillera and location of the study area (modified from Cooper et al., 1995).

Tertiary sedimentary rocks. The Eastern Cordillera formed during Miocene-Pliocene times by inversion of two Late Jurassic-Early Cretaceous basins, the Tablazo-Magdalena basin to the west and the Cocuy basin to the east. These former basins are separated by the Santander High, which is characterized by the occurrence of faults running parallel to the general trend of the cordillera itself (Colletta et al., 1990, Dengo & Covey, 1993, Cooper et al., 1995).

The study area is located in the Velez-Arcabuco anticlinorium in the western flank of the East Cordillera (Fig. 1). Micritic limestones of the Valanginian-lower Hauterivian Rosablanca Formation are conformably overlain by siliciclastic rocks of the Hauterivian-Aptian Paja Formation (Royero & Clavijo, 2000; and references therein). The present study focuses on surface samples of the Paja Formation. This sequence consists predominantly of organic-rich black shales, and minor intercalated silty, very fine-grained sandstones, massive organic-poor beige shales, and occasional massive organic-poor green mudstones. The black shales are generally massive, but occasionally show very thin lamination and foliation parallel to the overall orientation of the strata. These laminations usually consist of fine-grained quartz or other terrigenous detritus.

Methodology

Crushing

Samples for LOI determinations were chipped, washed in distilled water, and dried at 110°C for 24 h. They were then ground using a ROCKLABS (Model RC) ring mill equipped with a 100 g capacity tungsten carbide head. The method used followed that described in Roser et al. (1998). Chips showing any sign of oxidation, alteration or weathering were discarded. Maximum mill times were 30 seconds. Subsamples of the powders were stored in glass vials and held at 110°C for at least 24 hours prior to LOI determinations.

Powders for the CHNS analysis were prepared by manually crushing 10-20 g subsamples of the original hand specimens to <1 mm, followed by grinding in an automatic agate pestle and mortar for 10 minutes. The powdered samples were stored in glass vials and oven-dried at 70°C for 24 hours prior to analysis.

Loss on Ignition Determinations (LOI)

The parameters used to determine organic matter and carbonate contents by the loss on ignition method vary widely between studies. For determination of OM, ignition temperatures used vary between 375 and 550°C, with ignition times ranging between one and seventeen hours (Ball, 1964; Dean, 1974; Sutherland, 1998; Heiri et al., 2001; and references therein). For carbonate contents, temperatures used range between 850 and 1000°C, and times between 30 minutes and two hours. The method suggested by Heiri et al. (2001) for assessing organic matter and carbonate contents requires four hours of exposure at 550°C to ignite the organic matter, and two hours further ignition at 950°C to complete combustion of the carbonate component. We used the 550°C temperature for assessing organic matter following Heiri et al. (2001), but carried out the carbonate ignition at 1000°C rather than 950°C.

We first made two tests to determine reliable combustion times for each component. In the first test, five samples were selected at random and processed individually. After overnight oven drying at 110°C the samples were ignited at 550°C to determine OM content. Weights of the crucibles were taken every hour until the ninth hour, with the crucibles returned to the furnace after each weighing. Each hour-long ignition was timed from when the furnace regained 550°C. The samples were then ignited for a further 12 hours at 550°C, and the weights again measured. The furnace temperature was then raised to 1000°C. After constant temperature was reached, the samples were ignited for another two hours, cooled in a desiccator, and reweighed. The crucibles were then returned to the furnace for another three hours. Weights were remeasured every hour, as in the 550°C experiments.

In the second test, five duplicates of sample PES-31 varying in net weight from 2.7 to 3.4 g were ignited using the same conditions as above, to test the influence of sample size.

Following the above experiments, a complete set of 24 samples was ignited using optimal ignition times as determined from the trial samples. Percentage loss on

ignition at 550 and 1000℃ are given by the formulae:

$$\%LOI_{550} = \frac{(CS_{110} - CS_{550}) - (C - Ci)}{S_{110}} *100$$

$$\%LOI_{1000} = \frac{(CS_{550} - CS_{1000}) - (C - Ci)}{S_{110}} *100$$

where CS = weight of crucible + sample; C = crucible weight before ignition; Ci = crucible weight after ignition; S = sample weight (after Heiri *et al.*, 2001). LOI$_{550}$ thus corresponds approximately to the amount of OM in the sample, whereas the corresponding value at 1000℃ is related to the carbonate content.

Following the above, the CHNS analysis, and preliminary interpretation, we carried out a further experiment (test three) on a selected subset of samples. In this test, the samples were first ignited at 375℃ for 16 hours (after Ball, 1964; Dean, 1974), followed by six hours at 550℃, and three hours at 1000℃. Weight losses were determined at each step.

CHNS analysis

Total carbon (C$_{tot}$), organic carbon (C$_{org}$), H, N, and S contents of the suite of 24 samples were determined using a CHNS automatic elemental analyzer (FISSON, EA 1108). Total carbon contents were first determined, using powdered samples approximately 10 mg in weight. Accurately weighed samples were placed in tin foil capsules, which were crimp-sealed prior to analysis. Organic carbon contents were determined in a separate run. For these analyses 10 mg of rock powder were placed in Ag foil containers, and the samples treated by addition of 1 N

HCl to dissolve the carbonate fraction. If samples reacted strongly due to high carbonate content, HCl was added repeatedly until reaction ceased. The Ag capsules were then dried on a hot plate for 45 minutes at 110℃, and subsequently sealed. They were then placed within tin capsules, which were sealed in turn.

For both the C$_{tot}$ and C$_{org}$ analyses, products of the combustion were calibrated against BBOT standard [2.5-Bis-(5-tert.butyl-benzoxazo|-2-Y|-thiopen)]. The Eager 200 software was used to run the equipment, and to store and manipulate the data. Total carbon (C$_{tot}$) and organic carbon (C$_{org}$) contents were obtained directly from the equipment, whereas carbonate carbon (C$_{inorg}$) was calculated from the difference between C$_{tot}$ and C$_{org}$. The error inherent in this type of analysis is about ±3% relative.

Results

Loss on Ignition

Results for the first test show that weights of the two samples with lowest LOI (PES-9, PES-14) stabilized after only three hours hour of combustion at 550℃ (Fig. 2). No significant additional weight loss was observed after 12 hours further exposure at that temperature. In contrast, for samples PES-1, PES-25 and PES-35 weights did not stabilize until six hours had elapsed (Fig. 2). In the second test, weight losses converge after six hours of combustion at 550℃, and are identical after nine hours (Fig. 3). No significant weight loss was caused by a further 12 h exposure at 550℃. In both tests, constant weight was achieved in virtually all samples after six hours at 550℃. However, weight losses vary considerably with less than six hours combustion. This variability may be attributed to differences in OM content (test 1) and sample weight (test
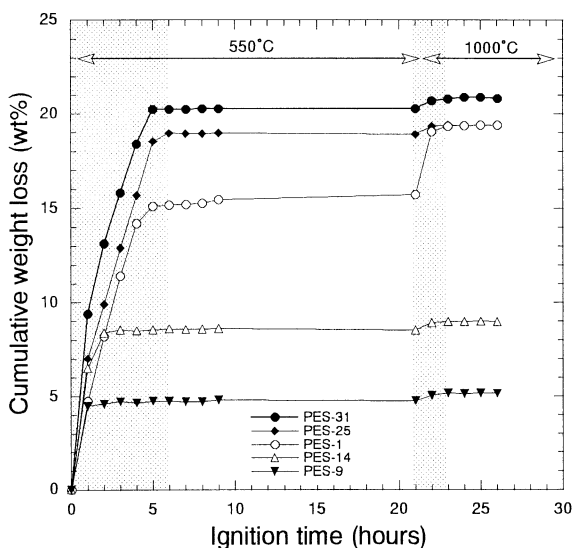

Fig. 2. Cumulative LOI (wt%) vs time for five black shale samples ignited at 550℃ (hours 1 to 21), and 1000℃ (hours 22 to 27).
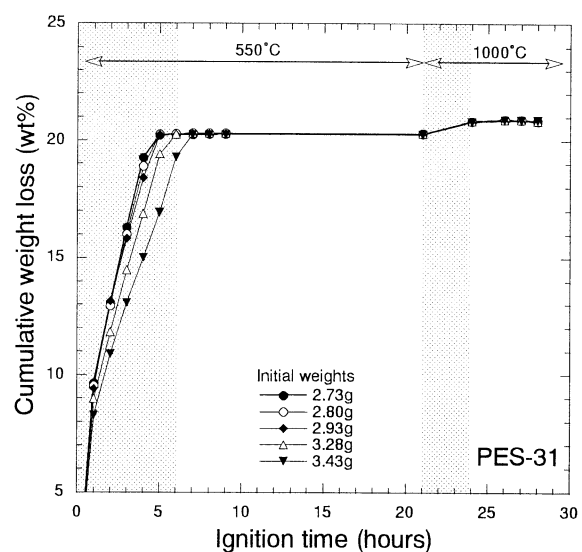

Fig. 3. Cumulative LOI vs time for five duplicates of a single shale sample (PES-31), with differing initial weights. Ignition at 550℃ (hours 1 to 21), and 1000℃ (hours 22 to 27) as in Fig. 2.

Table 1. Loss on ignition and CHNS analyses of black shales from the Paja Formation, Colombia.

| SaNr	Loss On Ignition (wt%)			CHNS Elemental Analyser (wt%)					
	Total	550°C	1000°C	Ctot	Corg	Cinorg	H	N	S
PES-1	19.08	11.24	7.83	11.75	11.40	0.35	0.40	0.26	0.19
PES-2	10.71	10.40	0.31	5.96	5.95	0.00	0.51	0.34	0.11
PES-3	22.96	21.95	1.02	16.50	16.50	0.00	0.86	0.76	0.40
PES-4	9.87	9.40	0.46	4.51	4.51	0.00	0.58	0.23	0.00
PES-5	41.73	11.02	30.71	21.88	13.69	8.19	0.39	0.27	1.45
PES-8	13.99	13.42	0.57	7.39	7.36	0.03	0.67	0.46	0.04
PES-9	5.07	4.66	0.41	1.19	1.13	0.06	0.46	0.21	0.00
PES-10	6.51	6.20	0.32	2.04	1.96	0.08	0.59	0.29	0.00
PES-11	4.87	4.47	0.40	1.03	0.89	0.14	0.53	0.21	0.00
PES-12	5.50	4.94	0.56	0.49	0.36	0.13	0.72	0.18	0.00
PES-14	8.85	8.48	0.37	4.56	4.27	0.29	0.61	0.20	0.00
PES-15	5.08	4.55	0.53	0.74	0.74	0.00	0.67	0.15	0.00
PES-16	5.08	4.35	0.73	0.38	0.25	0.13	0.76	0.04	0.00
PES-18	4.80	4.44	0.36	0.65	0.48	0.17	0.53	0.20	0.00
PES-20	4.76	3.96	0.79	0.24	0.13	0.11	0.68	0.02	0.00
PES-21	4.13	3.75	0.39	0.79	0.79	0.00	0.44	0.10	0.00
PES-23	8.05	7.49	0.56	0.84	0.66	0.18	1.00	0.32	0.00
PES-24	6.43	6.18	0.25	2.01	1.93	0.08	0.64	0.18	0.00
PES-25	19.21	18.03	1.18	13.48	13.11	0.37	0.89	0.63	0.34
PES-27	4.90	4.54	0.36	0.37	0.25	0.13	0.76	0.30	0.00
PES-28	3.99	3.67	0.32	0.17	0.03	0.14	0.59	0.06	0.00
PES-29	10.24	9.89	0.35	4.64	3.96	0.67	1.03	0.47	0.00
PES-30	6.63	5.89	0.75	0.20	0.09	0.11	1.01	0.19	0.00
PES-31	20.74	16.97	3.77	14.94	14.94	0.00	0.81	0.54	0.00

2). As could be expected, the larger the sample and the higher the organic content, the more time needed for combustion.

In both tests, increasing the temperature to 1000°C caused additional weight loss (Figs. 2 & 3). Most of the additional loss occurred within two hours at 1000°C, implying that carbonate ignition was largely complete. Weight loss after three hours further ignition was minimal, and a plateau was reached.

The above tests suggest that six hours ignition at 550°C was sufficient to burn off the OM, and three hours at 1000°C completed decomposition of the carbonate component. These times were adopted for the LOI determinations of the full suite of 24 samples; results show that LOI_{550} was >10 wt% in seven samples, with a maximum value of 21.95% (Table 1). Among those with LOI_{550} <10%, the majority yielded values in the range 4-6%. In contrast, LOI_{1000} values were generally much lower, with only samples PES-1, -5 and -31 having significant values (7.83, 30.71, and 3.77 wt%, respectively). These three samples also have the greatest CaO contents (5.89, 35.83 and 1.61 wt%; Campos, unpubl. data), suggesting the presence of some calcium carbonate. All other samples have low LOI_{1000} (0.25-1.01 wt%) and CaO (0.03-1.49 wt%; Campos, unpubl. data), suggesting their carbonate contents are minimal.

Results of the third test (sequential ignition at 375, 550 and 1000°C) showed that in half the samples the bulk of the cumulative weight loss at 550°C actually occurred after

ignition at 375°C (Fig. 4). In three samples the rate of loss was almost constant through to 550°C, and in one sample (PES-20), the greatest loss in weight occurred during ignition at 550°C. The only significant weight loss at 1000°C was recorded in the single highly calcareous sample (PES-5), as expected.
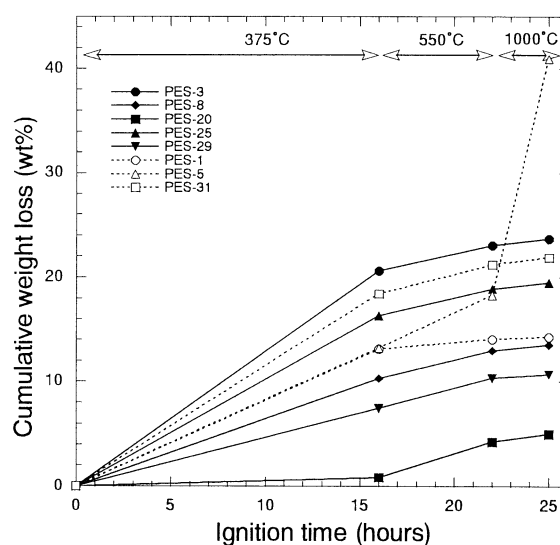
Fig. 4. Cumulative LOI vs time for eight black shale samples of equal weight (3.00±0.02 g) ignited at 375°C (hours 1 to 16), 550°C (hours 16-22) and 1000°C (hours 22 to 25). Solid symbols -carbonate-poor samples; open circles-carbonate-rich.
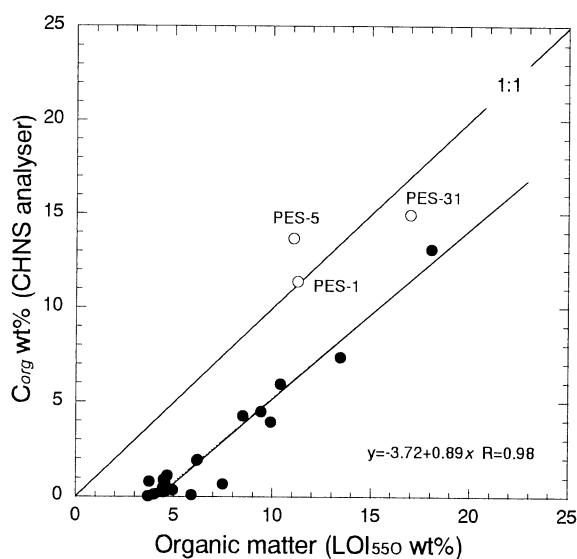
Fig. 5. Comparison of OM content based on LOI_{550} with C_{org} content determined by CHNS method. Open symbols (carbonate-rich samples) are excluded from the regression.
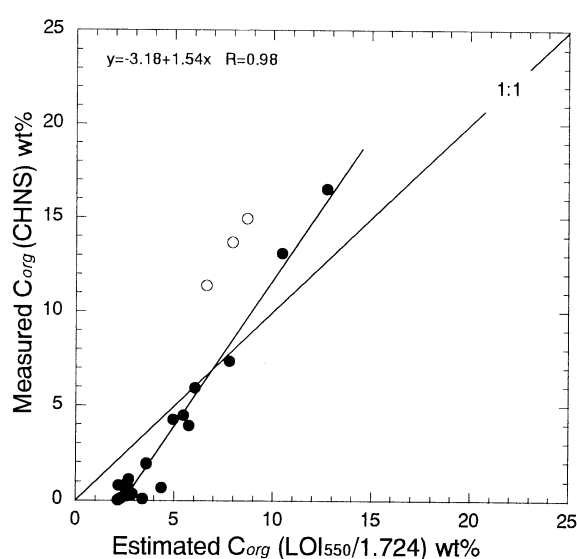
Fig. 6. Comparison of estimated C_{org} from LOI_{550} with measured C_{org} (CHNS analysis), using the generic OM to C_{org} conversion factor (1.724) commonly applied in the literature (Sutherland, 1998).

CHNS abundances

CHNS abundances in the suite of 24 samples show considerable variation. Organic carbon (C_{org}) contents range from 0.03 to 16.5 wt%, and the greatest C_{org} values are all associated with high LOI_{550} values. Although C_{inorg} varies from 0.00 to 8.19 wt% (Table 1), in only one sample (PES-5; 8.19 wt%) is it significant; all others are <0.67 wt%. Hydrogen (0.44-1.03 wt%) and nitrogen (0.02-0.76 wt%) were detected in all samples (Table 1). Nitrogen and C_{org} contents are moderately correlated ($R=0.77$); this correlation improves when three sample with both high C_{org} and LOI_{1000} (PES-1, -5, and 31) are omitted from the regression (R=0.89). However, no such relation exists between hydrogen and C_{org} ($R=0.26$). Sulphur was detected in only six samples, and with the exception of PES-5 (1.45 wt%), even in these samples abundances are low (0.04 -0.40 wt%). This suggests that sulphide minerals are not significant components of this suite.

Discussion

As expected from the LOI tests, ignition time and sample size seem to be the main factors influencing the results, especially the determinations at 550°C (Figs. 2 & 3). Samples must be ignited at 550°C for sufficient time to ensure total ignition of the OM component, and hence preclude any effects on the carbonate determinations at 1000°C (Heiri et al., 2001). This is particularly true for samples with high organic content. Heiri et al. (2001) suggested that four hours exposure at 550°C was sufficient to complete ignition of most OM, and that two hours of ignition at 950°C were sufficient to complete decomposition of carbonate. From our results, we found that six hours

exposure at 550°C are required to ensure complete weight loss due to combustion of the OM in samples weighing <3.3 g, and three hours further exposure at 1000°C guaranteed total loss of the carbonate fraction.

Comparison of LOI_{550} and C_{org} (CHNS analysis) shows that a strong linear correlation exists between OM content (LOI_{550}) and measured C_{org} when three samples (PES-1, -5 and -31) are excluded from the regression (Fig. 5). The compositions of these three samples differ from the others, as noted above. Although the observed correlation is strong, the intercept is non-zero. This situation is not unusual, as evident from the summary of regression models between C_{org} (dry combustion) and LOI given by Sutherland (1998); slopes may also vary significantly between suites. However, given the strength of the correlation, LOI_{550} values in this suite seem to be reasonable predictors of C_{org} using the equation derived.

Conventionally, C_{org} is estimated from loss on ignition data by dividing LOI_{550} by a conversion factor of 1.724, based on the assumptions that LOI_{550} is related to loss of OM, and that C_{org} comprises 58% of OM (Sutherland, 1998; and references therein). Applying this factor to the Paja samples produces overestimates at low values (<5% C_{org} by CHNS) and overestimates at higher values (Fig. 6). Sutherland (1998) highlighted the danger of assuming a fixed conversion ratio of 1.724 by summarizing an extensive body of literature data, and noted that factors actually ranged from 1 to as high as 16, depending on the nature of the OM. In his study of Hawaiian fluvial sediments, he found the factors ranges from 4.2 to 33.9. Conversion factors in given suites are approximated by the reciprocal of the slope of regressions between OM (LOI_{550}) and measured C_{org} (Sutherland, 1998), yielding a conversion
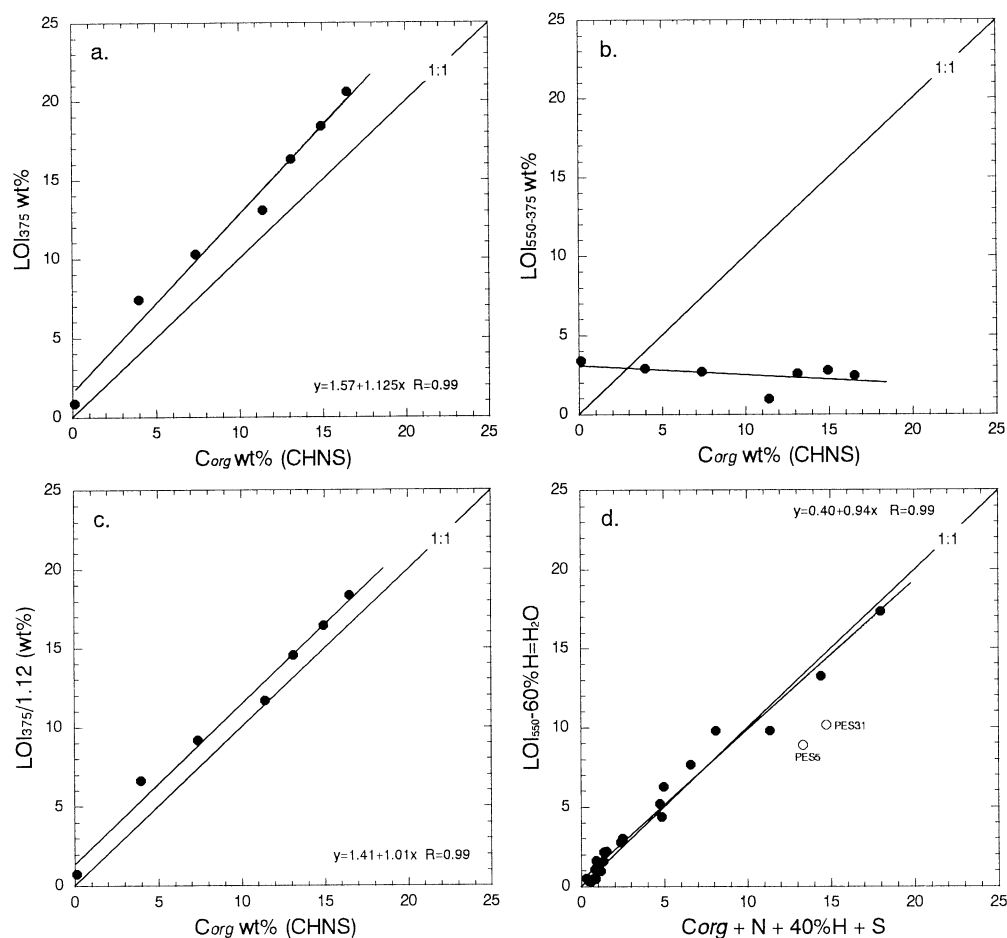
Fig. 7. Plots of (a) measured C_{org} (CHNS) vs weight loss after 16 h ignition at 375°C (LOI_{375}) in the samples from Fig. 4, excluding the highly calcareous sample PES-5; (b) Weight loss between 375°C and 550°C in the same samples compared to measured C_{org}; (c) estimated C_{org} ($LOI_{375}/1.12$) vs measured C_{org} (CHNS); (d) Modelled OM content from the LOI_{550} data in the entire sample suite, assuming 60% of measured hydrogen is lost as water, compared to measured $C_{org}+N+H_{residual}+S$ (CHNS). PES-5 and PES-31 were excluded from the regression.

factor of 1.12 in this case (Fig. 5). This supports Sutherland's contention that indiscriminant application of conversion factors can lead to serious errors in estimation of C_{org} from LOI data.

The non-zero intercept of the relation between OM (LOI_{550}) and measured C_{org} (Fig. 5) is most likely due to loss of water. Although temperatures of 500 to 550°C are used by many workers to estimate OM contents (e.g. Dean, 1974; Heiri *et al.*, 2001), loss of water from clay minerals at lower temperatures may be significant. Ball (1964) stated that most water loss from oven-dried clays occurs between 450 and 600°C, and cited work by Keeling (1962) that found prolonged ignition (16 h) at 375°C removed 90% of carbonaceous matter without affecting structural water in clays. Clay minerals are a significant component of the shales analyzed here. XRD analysis has shown the clay mineralogy consists of primarily of illite, chlorite, and smectite, with lesser montmorillonite and pyrophyllite in some samples (Campos, unpub*l.* data). The samples are also highly aluminous, with up to 27.3 wt% Al_2O_3 on a hydrous basis (Campos, unpubl. data), suggesting that the clays are a major component.

The results of the third test (successive ignitions at 375, 550 and 1000°C) also suggest loss of structural water from clay minerals during ignition between 375 and 550°C. A strong correlation exists between LOI_{375} and measured C_{org}, and the slope is near unity (Fig. 7a). In contrast, weight loss between 375 and 550°C ($LOI_{550-375}$) is more or less constant (2-4 wt%) irrespective of C_{org} content (Fig. 7b). This suggests that the bulk of the loss during prolonged ignition at 375°C is due to combustion of OM, and a more direct estimate of C_{org} can be obtained by ignition at the lower temperature. The correlation between LOI_{375} and C_{org} can be improved by applying the LOI_{550} OM to C_{org} conversion factor (1.12) derived from Fig. 5. A plot of the converted data shows the slope is virtually unity and the intercept is near zero (Fig. 7c).

The lack of correlation between hydrogen and C_{org} contents noted above also supports loss of water during ignition. Crude modelling gives some estimate of the amount of water that may have been lost. If an arbitrary 60% of the hydrogen in the CHNS analyses is recast as H_2O
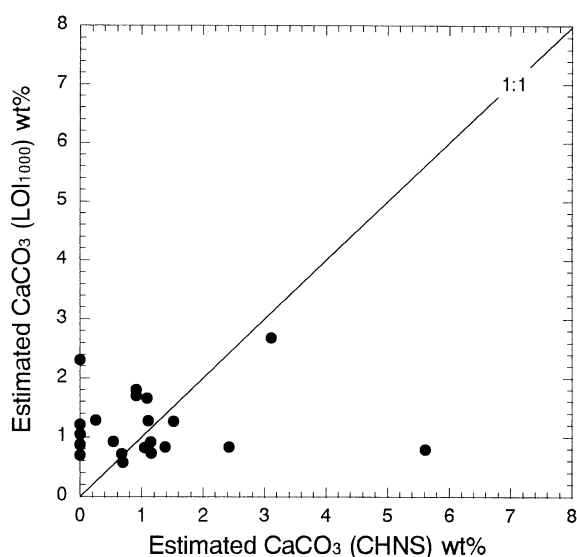
Fig. 8. Estimated CaCO₃ contents in carbonate-poor samples by LOI₁₀₀₀ and CHNS methods.

and deducted from LOI₅₅₀, and the residual H summed with C_{org}, N, and S to better reflect the composition of the organic matter, LOI₅₅₀ and CHNS results become comparable (Fig. 7d). In the entire sample suite, only PES-5 and PES-31 diverge from a 1:1 relationship to any extent. The latter sample has the highest H content (1.27 wt%) as well as high C_{org} (13.53 wt%), and a differing proportion of the hydrogen may have been lost.

The comparison of results at 375 and 550°C suggests that ignition at either temperature can provide an estimate of OM content and hence C_{org}, provided ignition is of sufficient duration to oxidize all organic matter. Structural water appears to be a significant component of the LOI₅₅₀ weight losses, but the strong correlation with CHNS C_{org} still allows reasonable estimates to be made. Although the results at 375°C give a more direct comparison, the longer ignition time required limits sample throughput. In either case, determination of C_{org} in representative samples by an independent method such as CHNS analysis is essential, so that calibration for individual suites can be made. This is necessary given the variation in conversion factors highlighted by Sutherland (1998). Generic conversion factors are clearly inappropriate.

Comparison of the LOI₁₀₀₀ and CHNS methods of determining carbonate contents was limited here by the range in carbonate contents of the suite analysed. Only three samples (PES-1, -5, -31) have significant LOI₁₀₀₀ values; they were also the only samples which effervesced during acid addition in the CHNS method. Results for PES-5, a highly calcareous shale, are good. Assuming all weight loss at 1000°C is CO_2, and all C_{inorg} is contained in calcite, calculated CaCO₃ contents are 69.84 wt% (LOI₁₀₀₀) and 68.29 wt% (CHNS). The results for PES-1 and PES-31 are very poor. PES-1 has an indicated CaCO₃ content of

17.81 wt% by the LOI₁₀₀₀ method, but only 2.94 wt% from recalculation of C_{inorg} from the CHNS analysis. Neither seems correct. Assuming all CaO in this sample (5.89 wt%, hydrous basis) is present as calcite, then maximum CaCO₃ content should be 10.5 wt.%. PES-31 returns an estimate of 8.56 wt% from LOI₁₀₀₀, but C_{inorg} was not detected in the CHNS analysis. The LOI₁₀₀₀ estimate is unrealistic, because the CaO content of this sample is only 1.61 wt%, (Campos, unpubl. data), equivalent to 2.87 wt% CaCO₃. The cause of the poor results for these two samples is unknown. Both samples had lower adjusted LOI₅₅₀ than expected (Fig. 5). They may contain a carbonaceous phase (e.g. graphite) that was not lost until the 1000°C ignition, or contain other hydrous phases that survived the lower temperature ignition. However, their whole-rock elemental compositions and XRD mineralogy (Campos, unpubl. data) are unexceptional.

Indicated CaCO₃ contents of the remaining samples by both methods are <6%, and most are less than 2% (Fig. 8). PES-14 and -29 have much greater CaCO₃ contents by CHNS than by the LOI method. Their low CaO contents (0.69 and 0.38 wt% respectively; Campos, unpubl. data) suggest that the CHNS data are incorrect, possibly due to dissolution of non-carbonate minerals by the acid addition used to determine C_{org}, and consequently C_{inorg}. Although some of the remaining samples yield comparable values by the two methods, a number have greater estimates from LOI₁₀₀₀. These include five samples in which C_{inorg} was not detected, but which have LOI₁₀₀₀ calcium carbonate values ranging from 0.6 to 2.25 wt%.

The poor estimates of carbonate contents by both methods at low contents may be partly due to loss of other volatiles between 550°C and 1000°C, as suggested by Heiri et al. (2001). This could include more tightly-bound structural water from hydrous silicate minerals other than clays. Other volatile species may include SO_2 from oxidation of sulphide minerals, and F and Cl. Moreover, at these temperatures, weight gain through oxidation of Fe^{2+} to Fe^{3+}, and of Mn^{2+} to higher oxidation states may also occur. The combination of these effects could obscure the results and contribute to the variability observed.

Conclusions

Simple loss on ignition procedure is a popular method for estimating OM and carbonate contents in sediments and soils. Tests of the method used by Heiri et al. (2001) and others suggest that the OM in Paja Formation black shales was lost after three to six hours heating at 550°C, and three further hours of ignition at 1000°C were sufficient to completely decompose the carbonate fraction. OM and estimated C_{org} concentrations determined by the LOI method were greater than those determined using a CHNS elemental analyzer, even when modified conversion factors were used as suggested by Sutherland (1998). Ignition tests at 375°C

give a better correlation between OM and C_{org}, and suggest that much of the weight loss between 375 and 550℃ is structural water from clays, which are an important component of the samples analysed. However, ignition at either temperature is viable, provided C_{org} data from an independent method such as CHNS analysis is available for calibration, and specific OM to C_{org} conversion factors can be derived for the sample suite concerned. The viability of estimating calcium carbonate contents from LOI_{1000} data could not be tested in our sample suite due to its generally carbonate-poor nature. Neither the ignition method nor CHNS analysis produced reliable results at the low levels of $CaCO_3$ present in most samples. Continued loss of volatile species and water from other hydrous phases may have contributed, and oxidation reactions causing weight gain may have also obscured the results.

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（要　旨）

N.O. Campos・B.P. Roser・三瓶良和，2002，コロンビア下部白亜系パジャ層黒色頁岩の有機炭素濃度と炭酸塩濃度の測定：イグニッションロス法分析結果のCHNS元素分析法による検討，島根大学地球資源環境学教室，21，9-16.

　　堆積岩や土壌の有機炭素濃度と炭酸塩炭素濃度は，一般に，簡便なイグニッションロス法(LOI法)を用いて，それぞれ 375–550℃と 850–1000℃下で加熱して求めることができる．本研究では，24 個の有機物に富んだ黒色頁岩試料を用いて，有機炭素濃度と炭酸塩炭素濃度を 2 つの方法(LOI法とCHNS元素分析法) で分析し，簡便なLOI法で得られる値の正確な意味について議論した．検討に先立ち，有機炭素濃度と炭酸塩炭素濃度を求めるLOI法の最適加熱時間を決めるため，550℃と 1000℃下で時間を変えて予備加熱実験を行った．その結果，有機炭素の燃焼には 550℃下で 4–6 時間(LOI$_{550}$)，炭酸塩の加熱には 1000℃下で 3 時間(LOI$_{1000}$)がそれぞれ必要であることが分かった．これらの条件下で黒色頁岩試料のLOI分析が行われCHNS元素分析結果と比較したところ，両者には強い相関関係が見られるものの，値には差が生じた．有機炭素濃度は，LOI$_{550}$ の方がCHNS元素分析値よりも一貫して高くなった．この理由については，LOI$_{550}$ では約 375℃ で有機物が燃焼し，375–550℃ 間でほぼ一定量(2–4 wt%)の粘土鉱物の構造水が放出されることが原因と推察された．従ってこれらを回帰計算で補正することにより，LOI$_{550}$ でも有機炭素濃度を正確に求めることができる．一方，炭酸塩炭素に関して，特に低濃度の場合にLOI$_{1000}$ とCHNS元素分析値はバラついて一致しなかった．その理由には，高温下でも粘土鉱物構造水の放出が継続していることや他の揮発性元素の逸散，また，Fe^{2+}やMn^{2+}が酸化して重量が変化することなどが示唆された．