The utility of sediment pyrolysis

W.M. Sackett

Department of Marine Science, University of South Florida,
St. Petersburg, FL 33701, USA

Introduction

Most geochemical investigators who study some aspect of marine sediments realize, instinctively, that the simple air drying of samples results in a whole suite of inorganic and organic, chemical, physical and mineralogical changes in the sample. For an imaginary laboratory experiment consider what happens when an air-dried sample is gradually heated in a vacuum. First, from an inorganic point of view, free gases and water vapor, followed by adsorbed and occluded gases and water are lost as the temperature is raised. Next, more adsorbed water and water of crystallization are released at increasing temperatures, depending on the mineralogy and finally, beginning at about 300°C, various chemical reactions begin to occur at appreciable rates. At still higher temperatures, some minerals will begin to decompose, e.g. $CaCO_3 \rightarrow CaO + CO_2$ at about 850°C. For the organic matter associated with sediment, free, adsorbed and occluded gases behave in a similar way to the above. However, starting at temperatures of about 200°C, liquid and solid organic materials are gradually degraded to gaseous products and complex solid residues until at relatively high temperatures and long times in a closed system only simple compounds such as methane, carbon dioxide and amorphous carbon remain.

The basic question - Is it useful to collect and measure the amounts and isotopic compositions of various pyrolysis products?

Following sections give an inorganic and an organic example of the utility of the measurement of products resulting from the high temperature pyrolysis of sediment samples.

Methods

Briefly, accurately weighed sediment samples are evacuated while heating to about 400°C to eliminate most of the water [Fig. 1.1]. After this pretreatment, samples are sealed under a vacuum and then pyrolyzed at a prescribed temperature and time [Fig. 1.2]. The tubes are broken at ambient temperatures in a vacuum system and the product gases are processed for measurement of their amounts by manometry [Fig. 1.3] and/or other methods and stable isotope compositions of some components by isotope ratio mass spectrometry.

1.
SAMPLE IS SEALED UNDER VACUUM IN A GLASS TUBE

2.
SAMPLE TUBES ARE HEATED AT PRESCRIBED TEMPERATURES AND TIMES

3.
TUBES ARE BROKEN UNDER VACUUM, CH4 IS PUMPED INTO COMBUSTION TUBE WITH TOEPLER PUMP AND/OR CO2 IS CLEANED AND ITS PRESSURE MEASURED IN A CALIBRATED MANOMETER

FIG. 1. C–^{3}He–N ternary plot of the OKT and OGA gases. C and N are the total carbon ($CO_2 + CH_4$) and the total nitrogen ($2 \times N_2 + NH_4$), respectively. terrestrial examples are represented by White Island, N. Z. (Giggenbach, 1993).

Examples

Inorganic. Amorphous silica can be determined by a high temperature titration [HTT] with added calcium carbonate and manometric determination
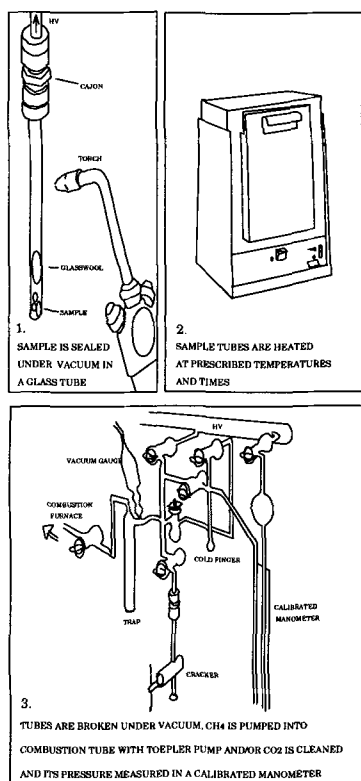
of the product CO_2 according to the following reaction: SiO_2 + $CaCO_3$ → $CaSiO_3$ [Wollastonite] + CO_2 The functionality of the reaction with regard to temperature, time, added $CaCO_3$, mineralogy and CO_2 partial pressure was described by Sackett and Lee [1992]. The standard procedure that was adopted was a one day pyrolysis at 600°C. Comparison of the HTT method with dissolution techniques gave only moderately good agreement. Additionaly, the $\delta^{18}O$ of the product CO_2 was shown to be a measure of the $\delta^{18}O$ of the water from which the silica was precipitated.

Organic. The thermal maturity of kerogen can be determined by the exhaustive pyrolysis [one hour at 700°C] of whole rock samples and measurement of the amounts and isotopic compositions of the pyrolysis-derived methane and total organic carbon in the rock sample [Sackett *et al*, 1993 and references therein]. Recent work showing the non-degradibility of methane at 700°C over a one hour period [the standard procedure] and the lack of carbon isotope exchange with carbon dioxide lends credibility to the pyrolysis-carbon isotope kerogen maturity method, Sackett [1994].

Conclusions

Sediment pyrolyses have been shown to be useful in determining the amount of amorphous silica in modern sediments and the thermal maturity of kerogen in ancient sediments.

Acknowledgements

References

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