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Thermoanalytical dehydroxylation of clays and combustion of organic compounds in a prograde metamorphic Liassic black shale formation, Central Swiss Alps

by *Günther Kahr*[1], *Martin Frey*[2] and *Fritz T. Madsen*[1]

Abstract

Thermoanalytical investigations (thermoanalysis combined with the analysis of the evolved gases) have been carried out on bituminous claystone samples from Switzerland with different diagenetic and metamorphic grades, ranging up to lower amphibolite facies. Mainly the course of water loss and the combustion of the organic compounds in flowing air were examined by thermoanalytical heating. The highest temperature of the structure water release from the samples was assigned to the dehydroxylation of the smectitic/illitic clays and muscovitic as well as paragonitic layer silicates, and is shown to be dependent on diagenetic and metamorphic grade. The highest temperature of combustion of the organic substance in the claystone samples is a good indication for the grade of diagenesis and metamorphism. The increase of the highest temperatures of dehydroxylation and combustion of the organic compounds shows a similar trend as the $\delta^{13}C$ isotopic ratio of the organic compounds with increasing degree of metamorphism.

Keywords: thermoanalysis, dehydroxylation, combustion, organic compounds, Alpine metamorphism, Central Alps, Switzerland.

Introduction

During the progressive metamorphism of claystones and marlstones, clay minerals are replaced by more stable sheet silicates, and the latter are finally replaced by anhydrous phases like feldspars and aluminum silicates. The loss of water taking place during these mineralogical changes may be studied by thermoanalytical methods. According to BRINDLEY and LEMAITRE (1987, p. 320), the following categories of principal thermal reactions are considered: 1. Low-temperature reactions below about 400 °C, involving the loss of molecular water from between layers of expandable clay minerals. 2. Intermediate-temperature reactions, mainly 400–750 °C, involving dehydroxylation and the formation of quasi-stable dehydroxylated phases. 3. High-temperature reactions, above 750 °C, involving recrystallization processes with the formation of new mineral phases. The present study is mainly concerned with dehydroxylation reactions, and these reactions have been discussed in detail by MACKENZIE (1970) and BRINDLEY and LEMAITRE (1987).

The organic material in sediments reacts very sensitively to increasing temperature, and the irreversible coalification process plays an important role in determining the grade of diagenesis and metamorphism. Chemically, this development is characterized by the relative increase of the solid carbon content and a decrease of volatile phases (e.g. TEICHMÜLLER, 1987).

In this study, thermoanalytic mass spectrometric investigations on pulverized bituminous claystone samples, ranging in grade from diagenesis to lower amphibolite facies, are presented. Thermal reactions are interpreted and quantified, and the course of water loss of hydrous minerals and the combustion of organic material are examined in detail. It will be shown that both the maximum dehydroxylation temperature and the maximum combustion temperature generally increase with increasing metamorphic grade.

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Methods

Thermoanalytical investigations were made in a system which is a combination of a Mettler thermobalance and a Balzers quadrupole mass spectrometer combined with a heated (150 °C) steel capillary. During thermal reactions in the thermobalance, evolved gases were sucked off with the flushing gas and part of it passed through the steel capillary and the variable leak (needle valve) in the quadrupole spectrometer. Selected masses of the gases were registered simultaneously (MÜLLER-VONMOOS et al., 1977). Samples of 100 mg weight were investigated with a heating

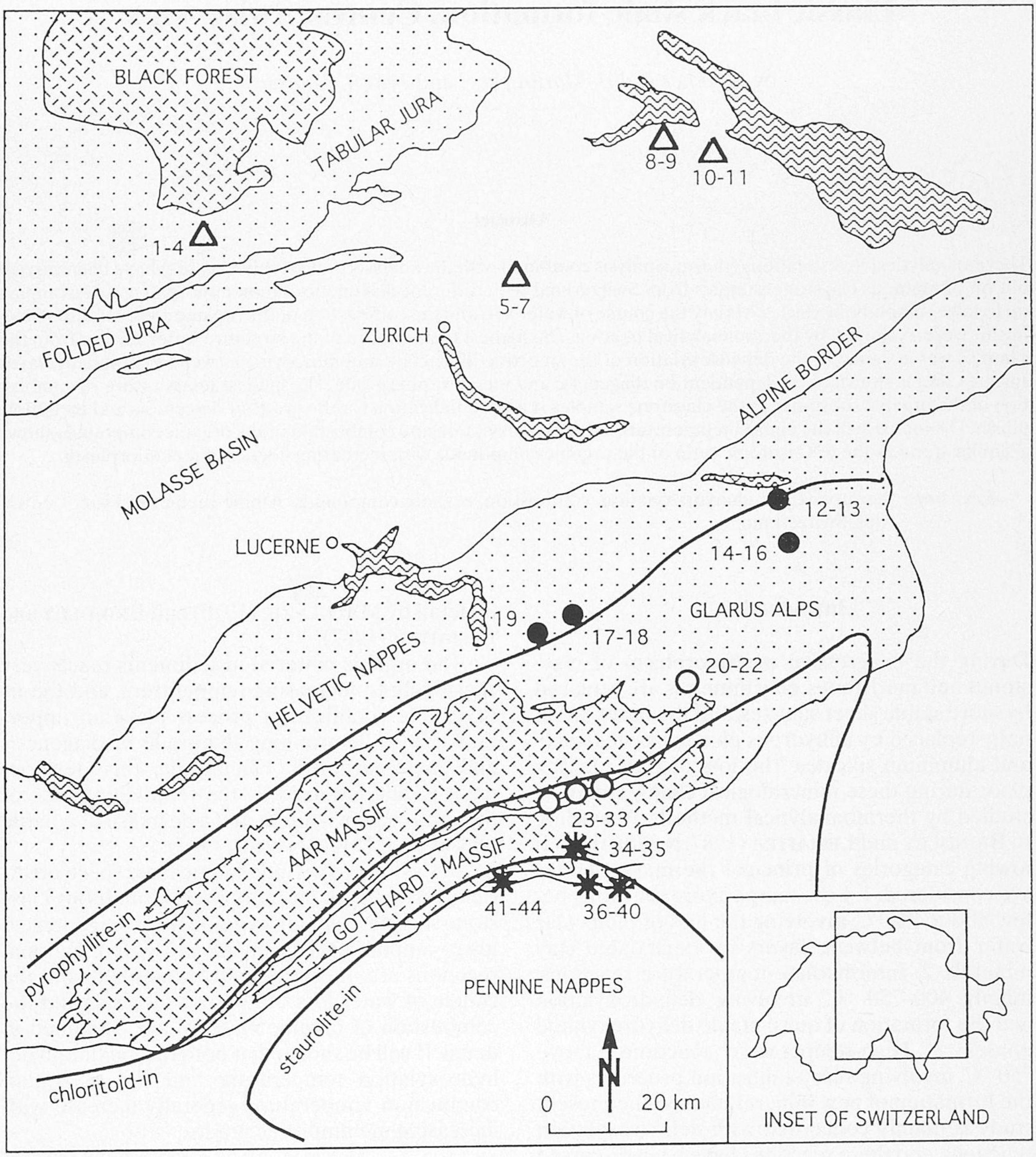

Fig. 1 Simplified geologic map of eastern Switzerland showing sample localities. Diagenetic and metamorphic grade at various sample localities are indicated by the following symbols: △ = diagenetic; ● = anchimetamorphic; ○ = lower greenschist facies; ✻ = upper greenschist and lower amphibolite facies.

Tab. 1 Sample locality, mineralogy and modal abundance of samples analyzed in this study. Data compiled from FREY (1969, 1970, 1978) and PETERS (1964). Mineral determinations were obtained by a combination of optical and X-ray methods.

No. Locality, sample	Illite and illite/smectite	Muscovite	Chlorite	Kaolinite	Pyrophyllite	Paragonite	Margarite	Chloritoid	Biotite	Clinozoisite	Staurolite	Garnet	Kyanite	Quartz	K-Feldspar	Plagioclase	Calcite	Dolomite
1 Frick F175	l		o	o										l	o	o	o	
2 Frick F173	l		o	o										l	o	o	l	o
3 Frick m24	l		o	o										l	o	o	l	
4 Frick m19.5	l		o	o										l	o	o	l	
5 Lindau L7	l		o	l										l	o	x	o	o
6 Lindau L5	l		o	o										l			l	
7 Lindau L2	l		o	o										l	o	x	l	
8 Berlingen B3	l		o	o										l	o		l	o
9 Berlingen B1	l		o	o										l				
10 Kreuzlingen K4	l		o	o										l				
11 Kreuzlingen K2	l		o	o										l		o		
12 Oberterzen MF582	l		l			o								l				
13 Oberterzen MF585	l		l			o								l			l	o
14 Guggenegg MF649		l	l			l								l			l	
15 Guggenegg MF651		l	o			o								l			l	o
16 Guggenegg MF659		l	l			l								l			o	
17 Urnerboden MF548		l	o											l			o	
18 Urnerboden MF555		l	l											l			l	o
19 Seelitalgraben MF539		l	o		o	o								l			l	l
20 Panixer Rotstock MF739		l	l			l								l				
21 Panixer Rotstock MF738		l	l			o								l				
22 Panixer Rotstock MF734		l	l											l				
23 Alp Tgom MF851		l	o			o	o	o						l				
24 Alp Tgom MF856		l	o			o		o						l				
26 Val Gierm MF81		l				l		o						l				
27 Val Gierm MF886		l	o			l								l			o	l
28 Val Gierm MF891		l	o			o								l			l	o
29 Val Gierm MF903		l					o	o						l				
31 Garvera MF922		l	o			o		l						l				
32 Garvera MF925		l				l		l						l				
33 Garvera MF932		l	l			o		o						l				
34 Lukmanierpass MF153		l	l				o		o	o				l				o
35 Lukmanierpass MF944		l	o				l		o	o				l		o	l	l
37 E Brönich MF1581		l	o			l			o	o	o	l	o	l		l		
38 Campra MF1600		o	o				o		l	o		o		l		l	o	
39 Campra MF1601		l	o				o		o	o	o	o	o	l		l	o	
40 Campra MF1606		l	o						o	o		o		l		l	o	
41 P. Camoghè MF1621		l	o						o	o		o		l		l	o	o
42 P. Camoghè MF1622		l	o				o		o	o		l		l		o	o	o
43 P. Camoghè MF1623		l							o		o	l	o	l				
44 Murinascia MF1634		l							o	o				l		l	l	o

l: > 10%, o: 1–10%, x: < 1%

rate of 10 °C per minute in streaming dry air (1.9 litre per hour) within a temperature range of 25–1000 °C. As reference material for the differential thermoanalysis (DTA), 50 mg of calcined kaoline was used. During the analytical heating, the combined equipment allows the parallel recording of thermogravimetry (TG), differential thermogravimetry (DTG), differential thermoanalysis (DTA), and the analysis of selected masses of evolved gases (MS-EGA). With dry air as a flush gas, O_2, N_2, H_2O, CO_2, and SO_2 will normally be observed with the mass spectrometer.

Material studied

A Liassic black-shale formation was followed from unmetamorphosed sediments into staurolite schists in order to determine the mineralogical changes with increasing regional Alpine metamorphism (Frey, 1978). Lithostratigraphic control is good at all metamorphic grades.

Unmetamorphic claystones and marlstones are found in the Jura mountains (samples 1–4, Fig. 1), and also in boreholes at 2–2.3 km depth below the Molasse Basin (samples 5–11). They consist of illite, irregular mixed-layer illite-smectite, chlorite, kaolinite, quartz, calcite, and dolomite, with accessory feldspars, pyrite and organic material. No mineralogical changes could be noted between the samples of the Tabular Jura, which were probably never buried more than 500 m, and those from the boreholes, where measured temperatures of around 100 °C were reached.

In shales and slates from the Glarus Alps (samples 12–22), pyrophyllite formed from kaolinite; paragonite formed from the mixed-layer illite-smectite with a possible interaction of a Na-rich pore solution. In addition, all samples contain illite-muscovite, chlorite, quartz, ± calcite, and ± dolomite with accessory pyrite and organic material (graphite d_3 after Landis, 1971). Feldspars are absent. The metamorphic grade of the Glarus Alps covers the anchizone and lower epizone, with temperature estimates ranging from about 200–250 °C in the north to about 300–350 °C in the south.

In phyllites of the Urseren Zone (samples 23–33), chloritoid formed from pyrophyllite + chlorite and margarite formed from pyrophyllite + calcite. The other main phases are muscovite, paragonite, chlorite, quartz, ± calcite, and ± dolomite with accessory pyrite and graphite (graphite d_{1A} after Landis, 1971). In the Urseren Zone the metamorphic grade reaches the lower greenschist facies with a temperature estimate of about 400 °C.

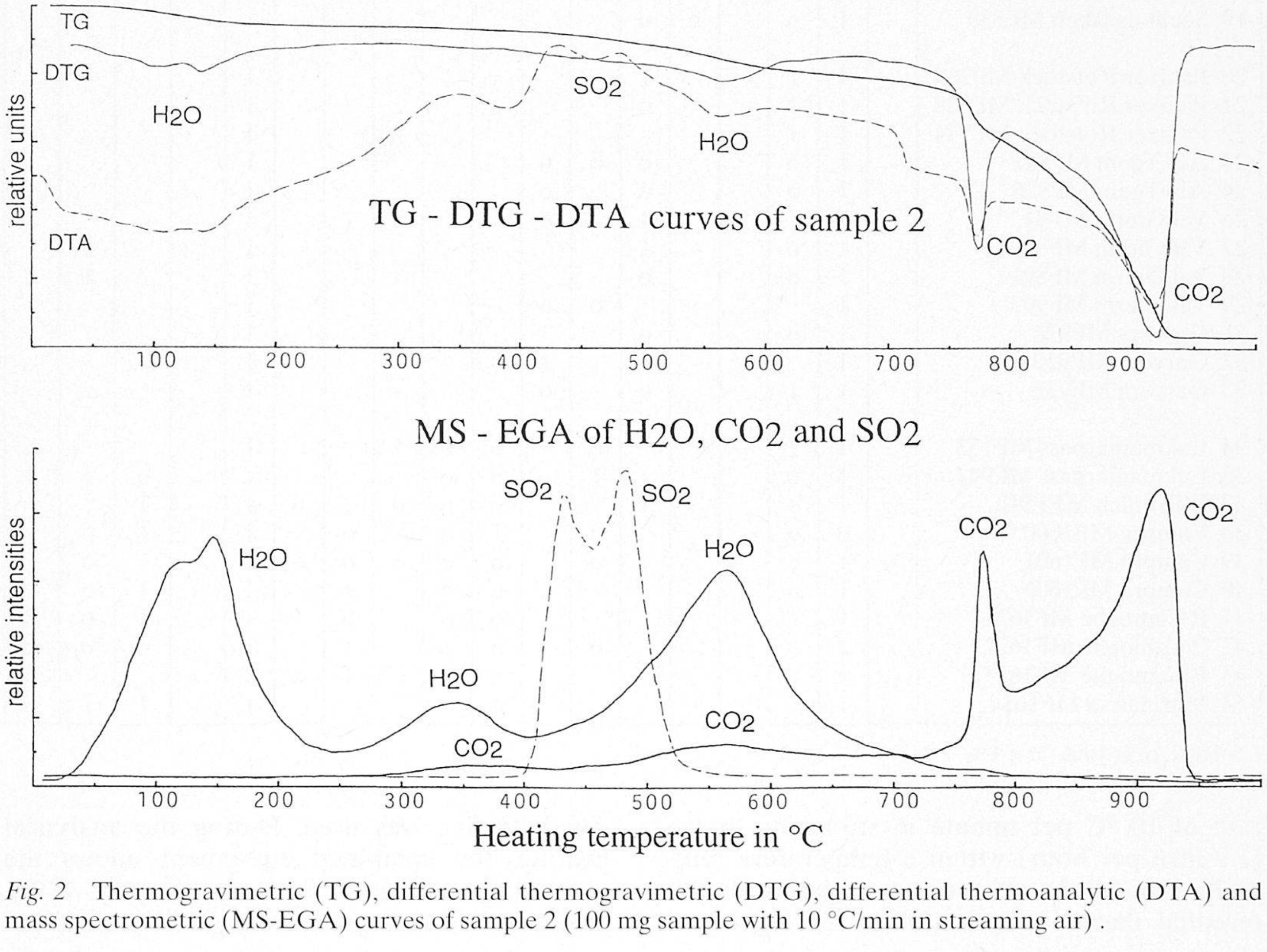

Fig. 2 Thermogravimetric (TG), differential thermogravimetric (DTG), differential thermoanalytic (DTA) and mass spectrometric (MS-EGA) curves of sample 2 (100 mg sample with 10 °C/min in streaming air).

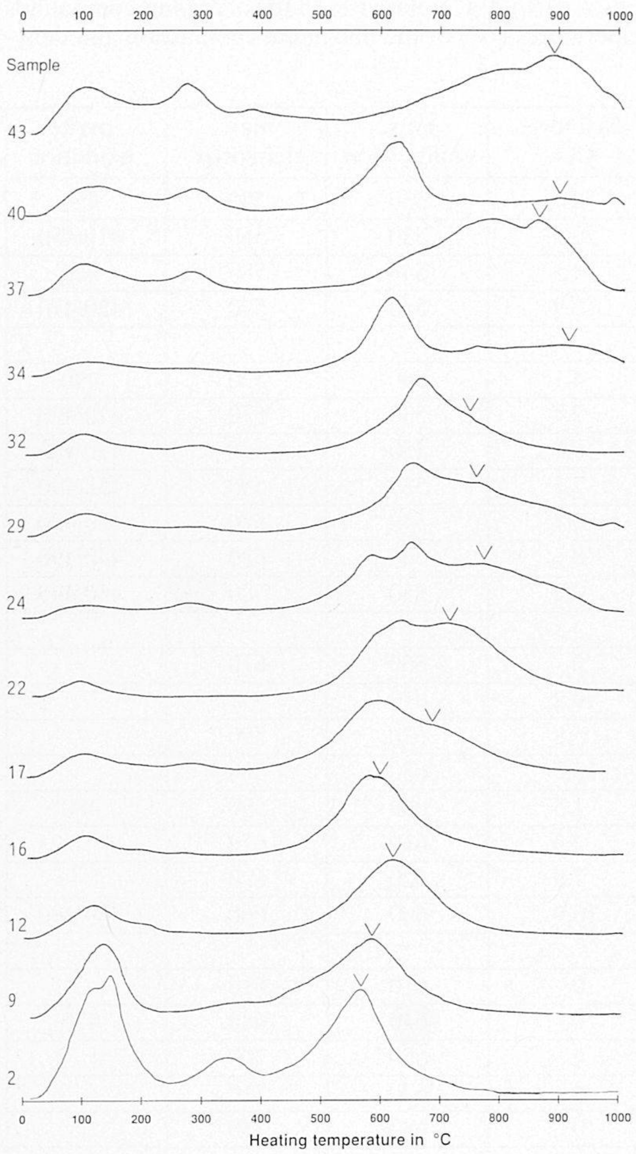

Fig. 3 Mass spectrometer curves of water (m/e = mass divided by charge = 18) during thermoanalytical heating of some selected samples. The V-sign indicates the maximum dehydroxylation temperature (see Tab. 2) which is based, at least in part, on the second endothermal maximum of DTA curves (not shown).

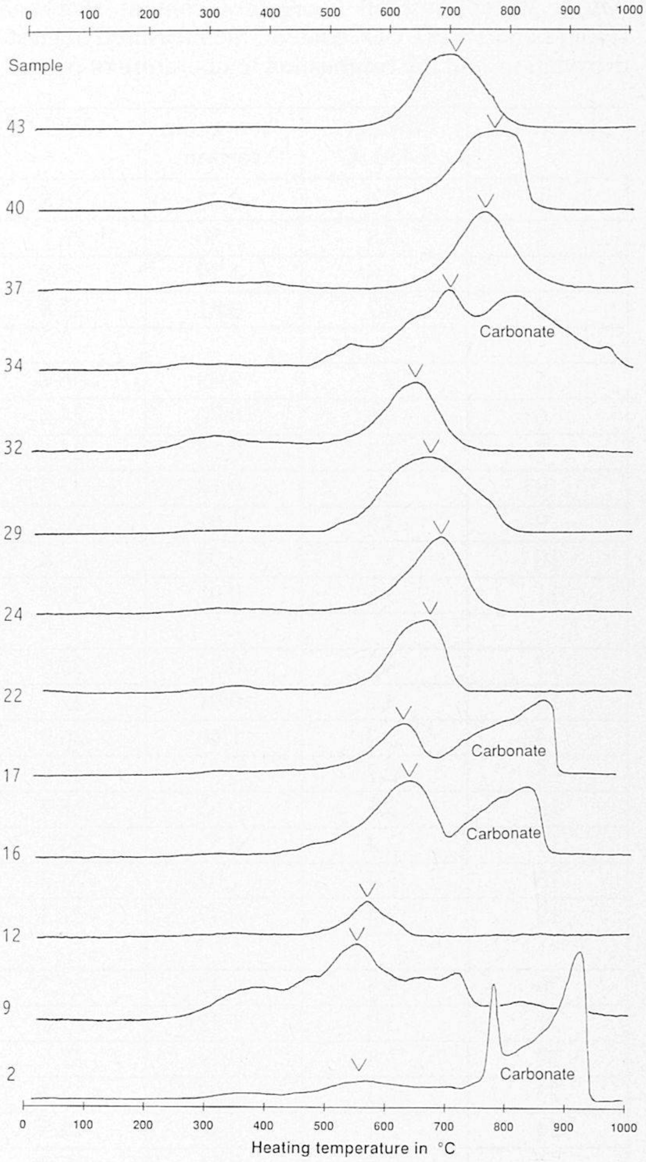

Fig. 4 Mass spectrometer curves of CO_2 (m/e = mass divided by charge = 44) during thermoanalytical heating of some selected samples. The V-sign indicates the maximum combustion temperature of organic material (see Tab. 2).

The higher-grade equivalents are well exposed in the Lukmanier and Val Piora areas along the southern border of the Gotthard Massif (samples 34–44). Major phases in marly schists at Lukmanierpass are muscovite, biotite, margarite, clinozoisite, plagioclase, quartz, calcite and dolomite. Chloritoid and paragonite are absent from marly bulk-compositions but still present in pelitic rocks. Accessory minerals include ilmenite, pyrrhotite, pyrite and graphite (graphite d_1 after LANDIS, 1971). In pelitic rocks of the Lukmanier area, FOX (1975) mapped four mineralogical zones, based on the first appearance of kyanite, staurolite, biotite and garnet in "maximum" assemblages, with increasing metamorphic grade. Samples 34–35 belong to zone 1 (chloritoid-chlorite-kyanite zone), while the remaining samples 36–44 come from zone 4 (biotite-staurolite-garnet-chlorite-kyanite zone). The metamorphic grade in the Lukmanier and Val Piora areas covers the transition zone from the greenschist to the amphibolite facies; temperature estimates range from 500 °C for the northern part to 550 °C for the southern part of the Lukmanier area (FOX, 1975; FREY, 1978).

Samples from this study are identical to those

Tab. 2 Water loss > 450 °C, organic C content (HOEFS and FREY, 1976), $\delta^{13}C$ (relative to PDB) of organic compounds (HOEFS and FREY), CO_2 content, the measured highest temperatures (°C) of the maximum combustion and dehydroxylation, and the combustion temperature of pyrite.

Sample no.	%water > 450 °C	% organic carbon	$\delta^{13}C$	% anorg. CO_2	max. combustion	max. dehydrox	pyrite oxidation
1	5.6	0.77	–28.8	2.1	530	580	450
2	3.8	2.86	–26	20.5	530	560	410/450
3	4.8	1.29	–25.8	4.5	540	580	420
4	4.7	0.81	–23.8	3.9	540	590	420/470
5	3	0.88	–26.7	4.1	560	570	490
6	3.5	0.70	–24.6	7.4	530	570	420/490
7	3.3	0.75	–24.5	6.7	550	580	430/490
8	2.2	0.18	–27.2	7.1	530	550	450/490
9	3.5	1.01	–24.8	0.3	540	570	450/480
10	3	0.99	–26.8	0	560	620	440/490
11	3.3	0.91	–25.9	0.2	550	580	450/490
12	3.2	0.28	–25.6	0	560	610	
13	3.2	0.91	–22	19.2	610	590	
14	3.7	1.40	–26.9	5.8	620	590	
15	2.7	0.51	–25.4	13.5	630	600	
16	3.6	0.65	–25.7	1.5	630	590	480
17	2.4	0.53	–24.8	2.4	610	670	
18	3.4	1.02	–24.3	7.9	620	690	
19	2.4	0.47	–27.3	16.9	600	660	450/480
20	3.3	1.47	–23.3	0	610	610	
21	3.9	1.32	–22.7	0	640	680	470
22	3.8	0.41	–22	0	650	700	
23	4.3	0.97	–17.2	0	670	710	
24	2.4	0.41	–16.5	0	680	750	
26	3.2	0.61	–17.5	0	660	680	510
27	2.8	0.66	–11	10.7	640	700	480
28	3.3	0.99	–12.5	11.3	nd	700	
29	3.9	0.76	–16.3	0	660	740	500
31	2.9	0.42	–18.9	0	650	760	
32	1.8	0.35	–18.1	0	640	740	
33	4	0.49	–16.5	0	650	700	490
34	1.5	0.20	–13.5	2.7	690	880	
35	1.3	0.42	–13.8	9.3	700	890	
37	1.8		–14.4	0	740	850	540
38	0.5		–12.6	1.9	760	890	
39	1.3	0.93	–10.5	1.3	740	920	
40	1.7		–15.6	0.3	760	890	
41	0.7	0.57	–10.7	4.2	nd	940	
42	0.5		–11.6	1.2	740	800	
43	0.5	1.60	–11.9	0	750	870	
44	0.7		–10.6	8	730	910	

nd: not determinable

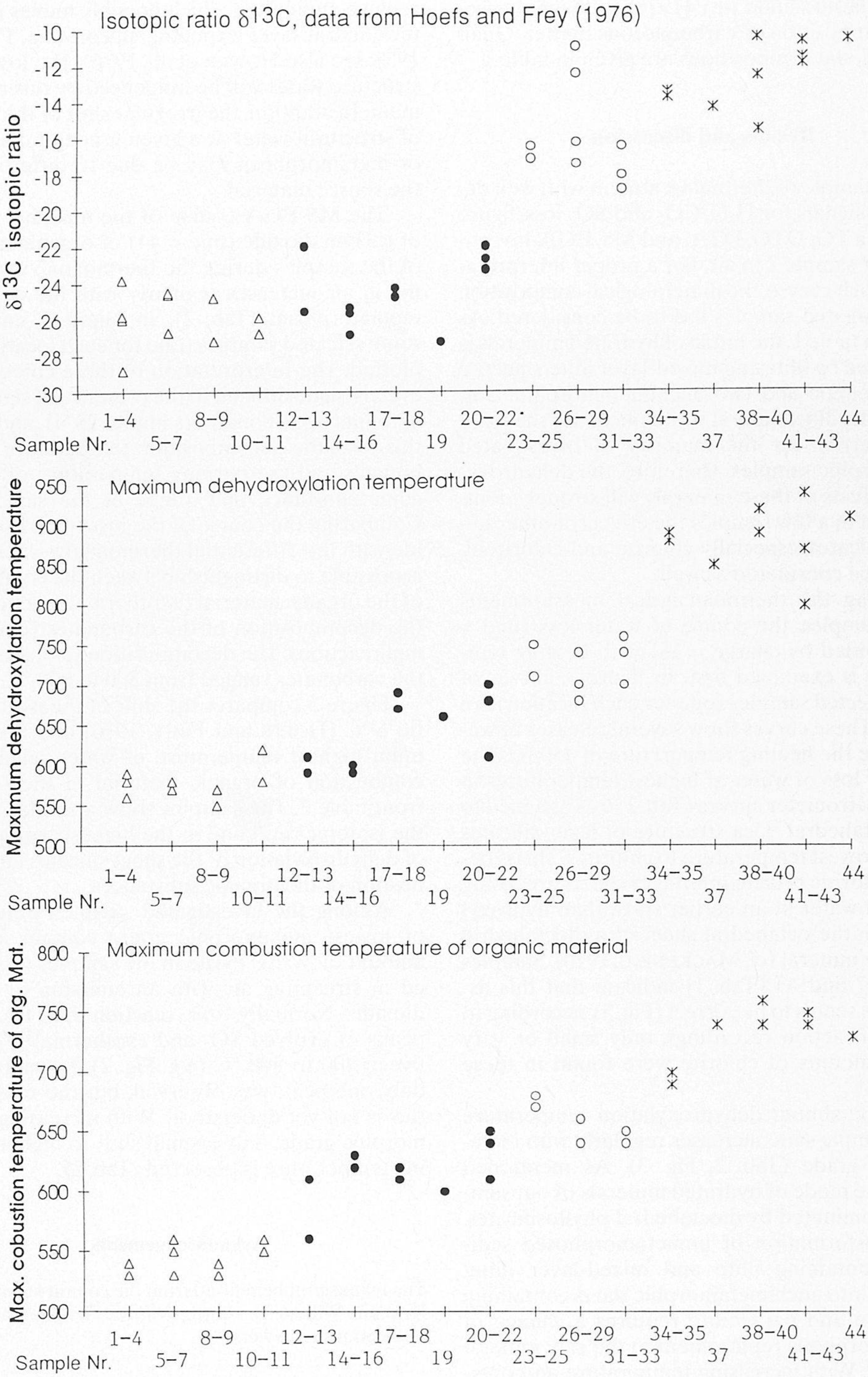

Fig. 5 Comparison between $\delta^{13}C$ (relative to PDB) and the maximum highest temperature of water loss of illitic clays and combustion of organic material. Samples are arranged according to increasing diagenetic/metamorphic grade.

used by HOEFS and FREY (1976) studying the isotopic composition of carbonaceous matter. Qualitative modal compositions are given in table 1.

Results and discussion

As an example of thermal treatment with well developed signals for H_2O, CO_2 and SO_2 loss, figure 2 shows a TG, DTG, DTA, and MS-EGA investigation of sample 2 in air. For a proper interpretation of such curves, the mineralogical composition of investigated samples has to be considered. As shown in table 1, the mode of hydrated minerals is dominated by illite and mixed-layer illite/smectite for diagenetic and two anchimetamorphic samples, whilst dioctahedral white micas are the main water carrier for the majority of investigated metamorphic samples. Therefore, the dehydroxylation effects of these minerals will strongly dominate, but in a few samples the effects of other hydrous silicates, especially chlorite and chloritoid, have to be considered as well.

Among the thermoanalytical measurements of the samples, the course of water loss (m/e = mass divided by charge = 18) with heating temperature is examined first. In figure 3, curves of some selected samples (one for each location) are plotted. These curves show several releases of water above the heating temperature of 450 °C. The maximal loss of water at highest temperatures in mass spectrometer curves (Tab. 2) was assigned to the dioctahedral mica structure of layer silicates and the lowest temperature to chlorites. This is because chloritic brucite interlayer sheets are losing hydroxyl water at an earlier stage than hydroxyl groups in the octahedral sheet of a dioctahedral mica like mineral (cf. MACKENZIE, 1970). Samples 29, 32, 37 and 43 (Tab. 1) indicate that this assumption seems to be correct (Fig. 3): according to X-ray diffraction recordings, only small or very minor amounts of chlorite were found in these samples.

The maximum dehydroxylation temperature of the sample suite increases regularly with metamorphic grade (Tab. 2, Fig. 3). As mentioned above, the mode of hydrated minerals of our samples is dominated by dioctahedral phyllosilicates. The transformation of unmetamorphosed sediments containing illite and mixed-layer illite/smectite into anchimetamorphic slates containing muscovite and paragonite requires a change of the isomorphous replacement in the clay mineral structure. With increasing temperature and pressure, iron and magnesium will move from exchangeable positions between the sheet silicate layers into the octahedral layer of the lattice and replace aluminium which possibly moves into the tetrahedral layer expelling silicon (e.g. POWERS, 1957; see also HOWER et al., 1976). The loss of the structure water will be influenced by this replacement. In addition, the irregular shift of the release of structural water at a given grade of diagenesis or metamorphism may be due to differences in the source material.

The MS-EGA course of the maximal release of carbon dioxide (m/e = 44) of organic material of the samples during the thermoanalytical heating in air increases regularly with the degree of metamorphism (Tab. 2). In figure 4, curves of some selected samples (one for each location) are plotted. The interpretation of these curves, however, is made difficult in the presence of significant amounts of carbonates (samples 28, 41, and 44). In this case, the decomposition temperature of carbonates and the burning temperature of the organic substance may range at the same level. Comparing the course of the loss of carbon dioxide with the differential thermoanalysis (DTA), it is possible to distinguish between the combustion of the organic material (exothermal reaction) and the decomposition of the carbonates (endothermal reaction). The decomposition temperature of the carbonates ranged from 800 to 900 °C.

Figure 5 compares the shift of the isotopic ratio $\delta^{13}C$ (HOEFS and FREY, 1976) and the maximum highest temperature of water release and combustion of organic material of the samples from table 2. The samples show a similar shift in the isotopic ratio and in the highest temperature of dehydroxylation of the sheet silicates and combustion of the organic substances.

Among the investigated samples, only those of lowest metamorphic grade contain a small amount of pyrite. Pyrite in the samples was roasted in streaming air with an emission of sulfurdioxide. Normally, this reaction has two main peaks of evolved SO_2 and exothermal DTA between 400 to 500 °C (e.g. Fig. 2). In many cases only one peak was observed, but the reason for this is not yet understood. With increasing metamorphic grade, only a small shift to higher roasting temperature is observed (Tab. 2).

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