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Chemical and carbon isotopic evolution of hydrocarbons during prograde metamorphism from 100°C to 550°C: Case study in the Liassic black shale formation of Central Swiss Alps

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Abstract—Hydrocarbon distributions and stable isotope ratios of carbonates ($\delta^{13}C_{car}$, $\delta^{18}O_{car}$), kerogen ($\delta^{13}C_{ker}$), extractable organic matter ($\delta^{13}C_{EOM}$) and individual hydrocarbons of Liassic black shale samples from a prograde metamorphic sequence in the Swiss Alps were used to identify the major organic reactions with increasing metamorphic grade. The studied samples range from the diagenetic zone (<100°C) to amphibolite facies (~550°C). The samples within the diagenetic zones (<100 and 150°C) are characterized by the dominance of $C_{<20}$ *n*-alkanes, suggesting an origin related with marine and/or bacterial inputs. The metamorphic samples (200 to 550°C) have distributions significantly dominated by C_{12} and C_{13} *n*-alkanes, C_{14}, C_{16} and C_{18} *n*-alkylcyclopentanes and to a lesser extend C_{15}, C_{17} and C_{21} *n*-alkylcyclohexanes. The progressive ^{13}C-enrichment (up to 3.9‰) with metamorphism of the $C_{>17}$ *n*-alkanes suggests the occurrence of cracking reactions of high molecular weight compounds. The isotopically heavier (up to 5.6‰) $C_{<17}$ *n*-alkanes in metamorphic samples are likely originated by thermal degradation of long-chain homologous with preferential release of isotopically light C_1 and C_2 radicals. The dominance of specific even C-number *n*-alkylcyclopentanes suggests an origin related to direct cyclization mechanism (without decarboxylation step) of algal or bacterial fatty acids occurring in reducing aqueous metamorphic fluid conditions. The regular increase of the concentrations of *n*-alkylcycloalkanes vs. $C_{>13}$ *n*-alkanes with metamorphism suggests progressive thermal release of kerogen-linked fatty acid precursors and degradation of *n*-alkanes. Changes of the steroid and terpenoid distributions are clearly related to increasing metamorphic temperatures. The absence of 18α(H)-22,29,30-trisnorneohopane (Ts), the occurrence of 17β(H)-trisnorhopane, 17β(H), 21α(H)-hopanes in the C_{29} to C_{31} range and 5α(H),14α(H),17α(H)-20R C_{27}, C_{29} steranes in the low diagenetic samples (<100°C) are characteristic of immature bitumens. The higher thermal stress within the upper diagenetic zone (150°C) is marked by the presence of Ts, the disappearance of 17β(H)-trisnorhopane and thermodynamic equilibrium of the 22S/(22S + 22R) homohopane ratios. The increase of the $\alpha\alpha\alpha$-sterane 20S/(20S + 20R) and 20R $\beta\beta/(\beta\beta + \alpha\alpha)$ ratios (from 0.0 to 0.55 and from 0.0 to 0.40, respectively) in the upper diagenetic zone indicates the occurrence of isomerization reactions already at <150°C. However, the isomerization at C-20 (R → S) reaches thermodynamic equilibrium values already at the upper diagenesis (~150°C) whereas the epimerisation at C-14 and C-17 ($\alpha\alpha \rightarrow \beta\beta$) arrives to constant values in the lower anchizone (~200°C). The ratios Ts vs. 17α(H)-22,29,30-trisnorneohopane [(Ts/(Ts + Tm)] and 18α(H)-30-norneohopane (C_{29}Ts) vs. 17α(H),21β(H)-30-norhopane [C_{29}Ts/(C_{29}Ts + C_{29})] increase until the medium anchizone (200 to 250°C) from 0.0 to 0.96 and from 0.0 to 0.44, respectively. An opposite trend towards lower values is observed in the higher metamorphic samples.

The occurrence of specific hydrocarbons (e.g., *n*-alkylcyclopentanes, cadalene, hydrogenated aromatic compounds) in metamorphic samples points to kerogen degradation reactions most probably occurring in the presence of water and under reducing conditions. The changes of hydrocarbon distributions and carbon isotopic compositions of *n*-alkanes related to metamorphism suggest that the organic geochemistry may help to evaluate the lowest grades of prograde metamorphism. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

The thermal dependence of hydrocarbon distributions, molecular maturity parameters and *n*-alkanes stable carbon isotope composition has been studied in natural burial systems (e.g., Dzou et al., 1995; Farrimond et al., 1998; Norgate et al., 1999), igneous intrusions (Simoneit et al., 1981; Farrimond et al., 1999; Othman et al., 2001), and laboratory hydrous pyrolysis experiments (e.g., Lewan et al., 1986; Abbott et al., 1990). In thermally stressed systems, the evolution of hydrocarbon distributions has been observed to be mainly related to cracking reactions. Under hydrous pyrolysis conditions, water behaves as an external source of hydrogen, which facilitates organic matter cracking and inhibits cross-linking reactions (Lewan, 1997). The extent of the degradation reactions is mainly controlled by water availability and by the environmental chemical conditions which depend on the mineral assemblage (e.g., Seewald, 1994, 2001; Price and DeWitt, 2001). Further understanding into the relationship between environmental thermal conditions and organic matter transformations require the study of sedimentary sequences submitted to diverse degrees of thermal stress.

The Liassic black shale formation of the Central Swiss Alps

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is a unique sedimentary facies for this purpose. This formation was affected by prograde metamorphism ranging from low diagenesis at <100°C to amphibolite facies at 550°C. Previous work provided petrographic, mineralogical and geochemical information from this metamorphic sequence (e.g., Frey and Orville, 1974; Frey, 1978; Mullis, 1979; Frey et al., 1980; Hunziker et al., 1986; Sharp et al., 1995), which were used to constrain the metamorphic grades and fluid chemistry. A study of stable isotopes of carbonates ($\delta^{13}C_{car}$, $\delta^{18}O_{car}$) and total organic carbon ($\delta^{13}C_{TOC}$) from petrographically characterized samples (Hoefs and Frey, 1976) showed a systematic ^{13}C-enrichment in TOC (by up to 18.3‰ V-PDB) from samples undergoing temperatures above 300°C, and a trend to more ^{18}O-depleted values and uniform $\delta^{13}C_{car}$ values in carbonates from samples of increasing metamorphism. On the other hand, an organic molecular study of diverse thermally stressed geological environments, including samples from the studied metamorphic sequence, ore deposits and plutonic rocks concluded that the prevalence of metastable equilibrium over cracking reactions explains the persistence of high-molecular weight and oxygen-bearing lipids and the similarity of hydrocarbon distributions at elevated temperature (Price and DeWitt, 2001).

To gain further insight into the organic molecular and isotopic transformations under thermal stress, a geochemical study encompassing the molecular compositions of organic matter and carbon isotopic composition of carbonates, kerogen, *n*-alkanes, and aromatic hydrocarbons from a complete sampling set covering the metamorphic sequence of the Central Swiss Alps is reported in the present study. The new data set provides a unique opportunity for the characterization of the molecular transformations, e.g., cyclization, cracking, isomerization and degradation-generation, that have occurred during metamorphism of a uniform lithology.

2. GEOLOGIC SETTING, SAMPLE LOCATIONS, AND METAMORPHIC FLUID CONDITIONS

The metamorphic grades of the Liassic black shale formation range from the diagenetic zones in the Tafel Jura and those below the Molasse Basin, to amphibolite facies south of the Lukmanier Pass in the Swiss Alps (Fig. 1). The samples for this study were collected from 14 localities across the metamorphic sequence (Fig. 1 and Table 1) using well-known stratigraphic markers as the base of the Liassic or the quartzites in the Infraliassic (Trümpy, 1949; Frey, 1968; Von Wyss, 1986).

The metamorphic degree (Table 1) has been assessed by illite "crystallinity" (Frey, 1970, 1974, 1978; Frey et al., 1980; Rahn et al., 1995; Wang et al., 1996), index mineral assemblages (Frey and Orville, 1974; Frey, 1978; Livi et al., 1997), coal ranks (Frey et al., 1980), and fluid inclusions (Mullis, 1979; Frey et al., 1980). The mineralogical transformations define the following reaction isograds (Table 1, Fig. 1): pyrophyllite-in near the town of Glarus, stilpnomelane-in near the village of Nidfurn (Frey, 1978) and staurolite-in south of the Lukmanier Pass (Fox, 1975). Samples within the lower diagenetic zone with estimated temperature <100°C (Frey, 1970) were collected at the locality of Frick in the Tafel Jura (Fig. 1 and Table 1). The upper diagenetic zone samples come from a borehole in the Molasse Basin near Lindau, with present-day temperatures of 100 to 150°C (Rybach et al., 1980). The Glarus Alps localities range from lower anchizone in the north to medium epizone in the south. The boundaries between diagenesis/anchizone and anchizone/epizone determined by illite "crystallinity," correspond to estimated temperatures of ~200 and 300°C, respectively (Frey, 1986). Further to the south, the sampling localities in the Urseren Zone correspond to the low greenschist facies with estimated temperatures of ~450°C (Frey, 1978). In the Lukmanier area, the samples cover, from north to south, the transition from the greenschist near facies St. Maria Lake to the amphibolite facies near Brönich (Fig. 1). Close to the staurolite-in isograd (Niggli and Niggli, 1965; Fox, 1975), the rocks from the latter locality attain a peak metamorphism of ~550°C.

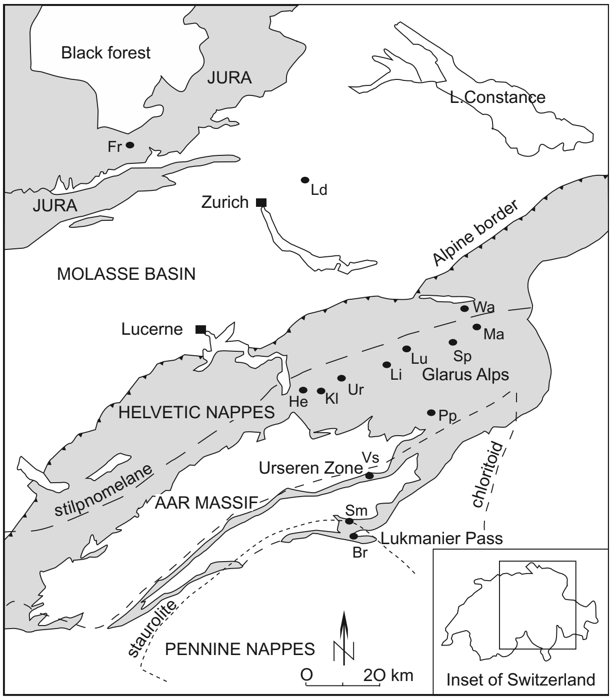

Fig. 1. Generalized geologic map of Central Swiss Alps showing the studied localities of the metamorphic sequence: Fr = Frick; Ld = Lindau; Wa = Walensee; Ma = Maschgenkamm; Sp = Spitzmeilen; Lu = Luchsingen; Li = Linthal; Ur = Urnerboden; Kl = Klausenpass; He = Heidmanegg; Pp = Panixier Pass; Vs. = Urseren Zone; Sm = St. Maria; Br = Brönisch.

The Liassic formation was originally composed of sandstones and arenaceous limestones intercalated with grey to black clay-rich marls, which have been transported in an alluvial fan from a SW extension of the Bohemian massif (Trümpy, 1949) and deposited in a shallow epicontinental sea in the northern European margin of the Tethys (e.g., Trümpy, 1960). Although the mean thickness varies considerably from 20 m in the Tafel Jura (Peters, 1964) up to 200 m in the Glarus Alps (Trümpy, 1949), this marine near-shore deposit can be considered isochemical (Frey, 1974). During the Alpine collision, the sediments in the Swiss Alps were mainly affected by a high-temperature low-pressure Eocene-Oligocene metamorphic event called the Lepontine phase. North of the Alpine border, the Liassic formation is covered by the Molasse Basin which is constituted by up to 5200 m of Oligocene-Miocene sediments.