# Depositional environment of the latest Gutenstein Formation (late Lower Anisian) from the Rabenkogel (Salzkammergut area, Austria), as deduced from hydrocarbon biomarker composition

By

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with 3 figures and 1 table

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## Abstract

The molecular composition of hydrocarbons of two samples of dolomitic mud- to wackestones from the upper part of the Gutenstein-Formation from the Rabenkogel (Salzkammergut area, Styria, Austria) provide information about the environmental conditions during their deposition. Based on conodonts, an early Anisian age of the samples is suggested. Phytoplankton and photosynthetic bacteria are considered as the major primary producers of the biomass accumulated within the immature, carbonate-rich rocks. Enhanced microbial activity in the depositional environment is considered, based on high contents of hopanoid biomarkers. The relative proportions of S/R isomers of the $\alpha\alpha\alpha$ $C_{29}$-steranes and the $\alpha\beta$ $C_{31}$-hopanes are consistent with a maturity of organic matter equivalent to vitrinite reflectance values of approximately 0.5% $R_o$. Conodont alteration index (CAI) values around 1.0 in samples from overlying strata are in agreement with these results. Organic matter from gymnosperms contributed to the biomass. The occurrence of aryl isoprenoids, derived from carotenoids specific for the photosynthetic green sulfur bacteria *Chlorobiaceae* and purple sulfur bacteria *Chromatiaceae*, indicates the presence of free $H_2S$ in the bottom water. The observed biomarker composition points to a high productivity, marine environment with limited water exchange and a stratified water column.

## 1. Introduction and geological setting

The Rabenkogel, located northeast of Bad Mitterndorf, has been considered by TOLLMANN (1960) as a part of the Hallstatt zone of the eastern Salzkammergut area (Austria). A complete early Middle Triassic sedimentary succession with the Gutenstein-Formation (Lower Anisian) on the base, followed by pelagic carbonates of the Lower Pelsonian, and the Steinalm Formation (Pelsonian) is exposed south and southwest of the 1534-m high Rabenkogel mountain (Fig. 1). The sedimentary sequence are composed of up to 200-m thick Gutenstein dolomite, exposed at the western flank of the Rabenkogel (TOLLMANN 1960), followed by a limestone-dolostone succession, partly with cherts, dated as early Pelsonian (SCHLAGINTWEIT et al. 2003). The base of this succession is dominated by coarse-grained dolostones of a total thickness of up to 250-m. The top of the sedimentary sequence is characterised by fine-grained, biomicritic limestones, separated from the dolostones by silizified horizons. The samples HR 66 and HR 68a, located below the silizified strata, are investigated by GC-MS on the molecular composition of hydrocarbons in order to obtain information about the depositional environment.

The age of the investigated sediments is late Lower Anisian, based on biostratigraphic information from conodont assemblages in samples overlying the sedimentary sequence, which indicate lower Pelsonian. The dark-gray to black carbonates investigated are followed by biomicritic limestones of unknown thickness (> 50 m) due to intense deformation. The biomicritic limestones are exposed at the eastern flank of the Rabenkogel, and have been mapped by TOLLMANN (1960) as Reifling limestone. Conodont assemblages from the base of these biomicritic limestones also provide a Lower Pelsonian age. Calcareous turbidites intercalated with the pelagic biomicrites are more frequent in the uppermost part of the succession. The top of the series is characterised by a massive limestone horizon (Steinalm limestone), exposed at the summit of the Rabenkogel mountain. The base of the Steinalm limestone is also dated as Lower Pelsonian based on conodont assemblages.

South of the Rabenkogel area (Fig. 1) the pelagic series are exposed with a thickness of up to 30 m, believed to represent the true thickness of this sedimentary succession between the dolostones at the base and the massive limestones at the top of the Rabenkogel.

## 2. Methods

Portions of the pulverized and homogenized samples were extracted for approximately 1 h using dichloromethane in a
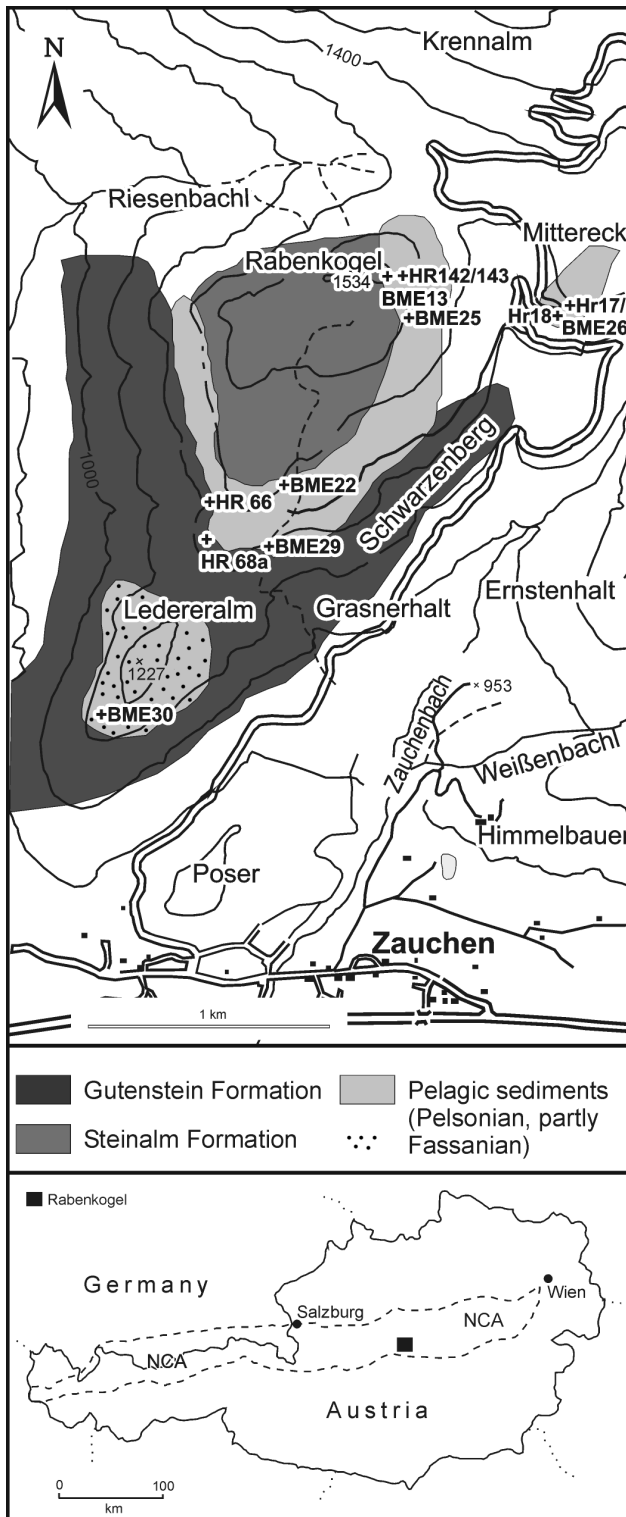
Fig. 1: Geological and topographic overview of the Rabenkogel area and location of the samples (after TOLLMANN 1986, and new mapping results).

Dionex ASE 200 accelerated solvent extractor at 75° C and 50 bar. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichloro-methane solution (80:1) and separated by centrifugation.

The fractions of the hexane-soluble organic matter were separated into NSO compounds, saturated hydrocarbons and aromatic hydrocarbons by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (RADKE et al. 1980).

The saturated and aromatic hydrocarbon fractions were analysed by a gas chromatograph equipped with a 25 m DB-1 fused silica capillary column (i.d. 0.25 mm) and coupled to a Finnigan MAT GCQ ion trap mass spectro-meter. The oven temperature was programmed from 70° to 300° C at a rate of 4° C min-1 followed by an isothermal period of 15 min. Helium was used as carrier gas. The mass spectrometer was operated in the EI (electron impact) mode and a scan rage from 50 to 650 daltons (0.7 s total scan time). Data were processed with a Finnigan data system. Identification of individual compounds was accomplished by retention time in the total ion current (TIC) chromatogram and by comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different com-pound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas from the gas chromatograms in relation to that of internal standards. The concen-trations were normalized to the to-tal soluble organic matter content.

## 3. Stratigraphy

The age determination of the samples investigated (HR 66, HR 68a) is based on conodont assemblages from overlying sedimentary series (Fig. 1) indicating Lower Pelsonian. By this we can reconstruct the whole sedi-mentary sequence with the carbonates of the Gutenstein Formation as early Anisian, follwed by pelagic influenced sediments of early late Anisian (lower Pelsonian) and on top the shallow water carbonates of the Steinalm Formation (Pelsonian) overlying by pelagic influenced carbonates of late Anisian (Illyrian) (see SCHLAGINTWEIT et al. 2003 for further information):

- Sample BME 13/1999: Gray, biomicritic limestone with recrystallized Radiolaria and filaments, partly laminated, with intercalated marly horizons. Age: Lower Pelsonian. Conodonts: *Gondolella* cf. *bulgarica* (BUDUROV & STEFANOV 1975). CAI = 1.0.
- Sample BME 22/1999: from overlying, gray, micritic limestones-marl succession. Age: Middle Triassic with *Gondolella*-multielement and *Gladigondolella*-multielement. CAI = 1.0.
- Sample BME 25/1999: Biomicrite with recrystallized Radiolaria and filaments. Age: Middle Triassic, most probable Anisian. Elements of *Gondolella* sp. CAI = 1.0.
- Sample BME 26/1999: Red, biomicritic limestone with recrystallized Radiolaria and filaments, partly laminated. Age: Lower Pelsonian. Conodonts: *Gon-dolella* cf. *bulgarica* (BUDUROV & STEFANOV 1975). CAI = 1.0.
- Sample BME 29/1999: in the neighbourhood and, based on field observations, directly overlying sample HR 70. Biomicrite with intercalated marl horizons. Age: Lowest Pelsonian. Conodonts: *Gondolella bulgarica*

(BUDUROV & STEFANOV 1975), *Nicoraella kockeli* (TATGE 1956) and *Nicoraella germanica* (TATGE 1956). CAI = 1.0.

- Sample BME 30/1999: from the south of Lederalm area. Biomicrite with marly horizons. Age: Fassanian. Conodonts: *Gladigondolella tethydis* (HUCKRIEDE 1958), *Gladigondolella tethydis-ME sensu* (KOZUR & MOSTLER 1972), *Gondolella pseudolonga* (KOVÁCS, KOZUR & MIETTO 1980), *Gondolella excelsa* (MOSHER 1968). CAI = 1.0.

- Sample HR 142: Biomicrite with recrystallized Radiolaria and filaments with intercalated marl horizons. Age: Middle Triassic, probably Anisian. Elements of *Gondolella* sp. CAI = 1.0.

- Sample HR 143: Biomicrite with recrystallized Radiolaria and filaments, partly laminated with marly horizons. Age: Lower Pelson. Conodonts: *Gondolella* cf. *bulgarica* (BUDUROV & STEFANOV 1975). CAI = 1.0.

- Sample HR 17: Red, biomicritic limestone with recrystallized Radiolaria and filaments, partly laminated. Age: Pelsonian. Conodonts: *Gondolella cf. bifurcata* (BUDUROV & STEFANOV 1972) and *Nicoraella kockeli* (TATGE 1956). CAI = 1.0.

- Sample HR 18: Gray, biomicritic limestone, overlying HR 17. Age: Illyrian. Conodonts: *Gladigondolella tethydis-ME sensu* (KOZUR & MOSTLER 1972), *Gondolella constricta* (MOSHER & CLARK 1965) – „cornuta"-type. CAI = 1.0.

# 4. Results and Discussion

## 4.1. Soluble organic matter yield

The yields of the soluble organic matter (SOM) are 861 µg/g rock for sample HR 68a and 1082 µg/g rock for sample HR 66. The relative proportions of hydrocarbons (saturated plus aromatic) are as high as 25% and 23% of the SOM, respectively, despite the low maturity of the organic matter (as discussed below). Aromatic hydrocarbons predominate over saturated hydrocarbons. The soluble organic matter is mainly composed of NSO compounds (about 60% of the SOM), which caused a red colour of the SOM.

## 4.2. *n*-Alkanes and isoprenoids

The gas chromatogram of the saturated hydrocarbon fraction of sample HR 68a is shown in Fig. 2a. The *n*-alkane distribution patterns are dominated by medium to long-chain *n*-alkanes without a marked odd over even predominance (CPI = 1.23 - 1.48; carbon preference index according to BRAY & EVANS 1961; Tab. 1) and maximum intensities in the $n$-$C_{22}$ and n-$C_{27}$ range (Fig. 2a). Equal relative proportions of mid-chain ($n$-$C_{21-25}$) and long-chain ($n$-$C_{27-31}$) *n*-alkanes relative to the sum of n-alkanes of about 35% are found (Tab.1). Long-chain lipids are known as biomarkers for higher terrestrial plants, as they are the main components of plant waxes (EGLINTON & HAMILTON 1967). The *n*-alkanes of low molecular weight (< $C_{20}$), which are predominantly found in

algae and microorganisms (CRANWELL 1977), are detected in lower amounts (~ 20 %) of the total *n*-alkane concentrations (Tab. 1). Considering the low maturity of the samples, the *n*-alkane distribution patterns are charactristic for organic matter of predominantly algal and/or microbial origin with minor contributions of land plants. This is indicated by the low carbon preference index and maximum intensities of *n*-alkanes in the mid-chain range (CRANWELL et al. 1987). Within the two samples investigated, the abundances of acyclic isoprenoids are high, norpristane, pristane and phytane are present in considerable quantities (Fig. 2a). The samples are characterized by high pristane / n-$C_{17}$ (1.92 and 3.35; Tab. 1) and high phytane / n-$C_{18}$ ratios (2.60 and 2.79; Tab. 1), indicating the low maturity of the organic matter (TEN HAVEN et al. 1987).

The pristane / phytane ratios are different in both samples (0.82 and 1.19, Tab. 1). According to DIDYK et al. (1978), low pristane / phytane ratios (< 1.0) indicate anaerobic conditions during sedimentation, and values above 1.0 were interpreted as reflecting dysaerobic environments. This would indicate slight differences in the redox conditions of the sedimentary environment during deposition and early diagenesis of samples HR 66 and HR 68a. However, pristane / phytane ratios are known to be affected by maturation (TISSOT & WELTE 1984) and by differences in the precursors for acyclic isoprenoids (i.e. bacterial origin; VOLKMAN & MAXWELL 1986, TEN HAVEN et al. 1987).
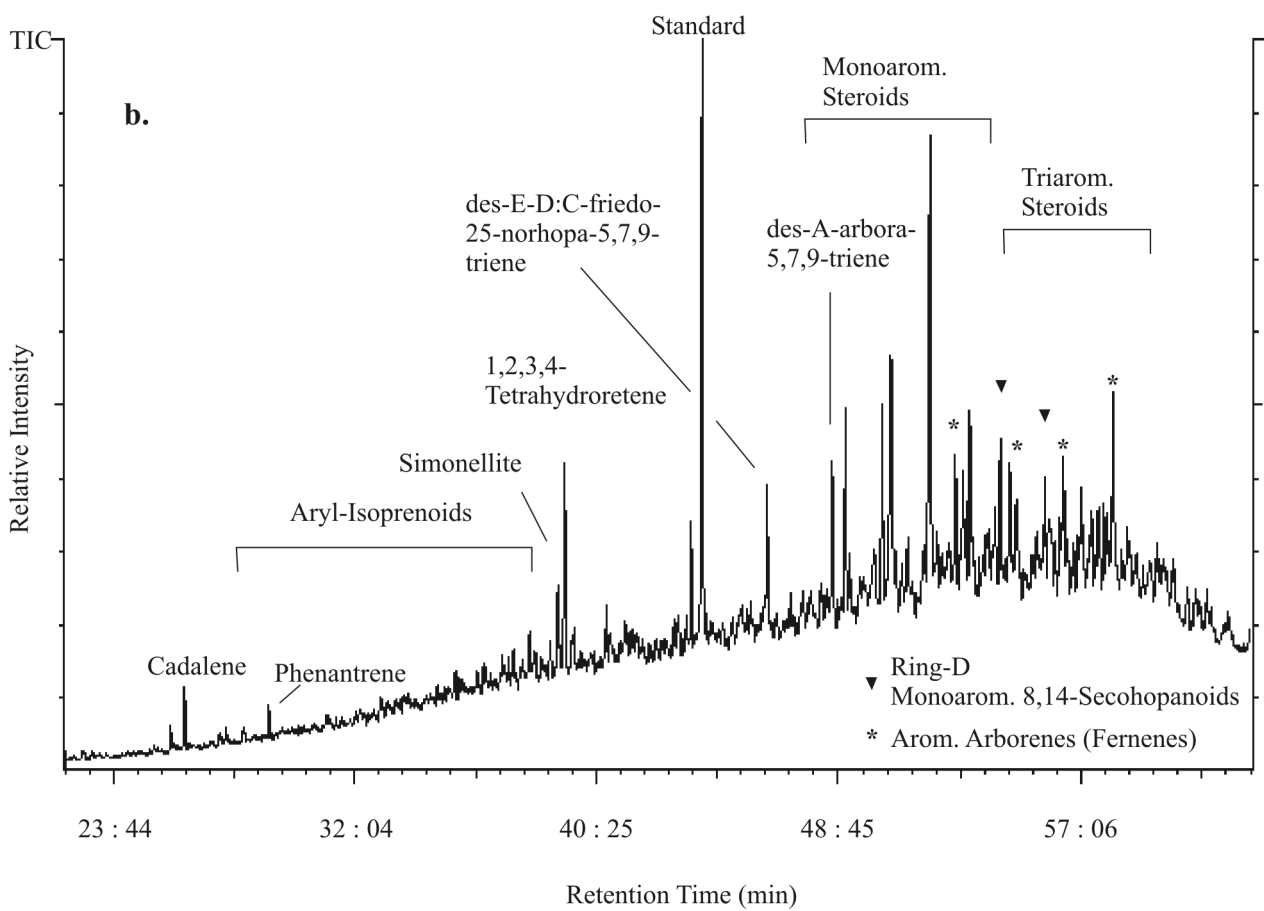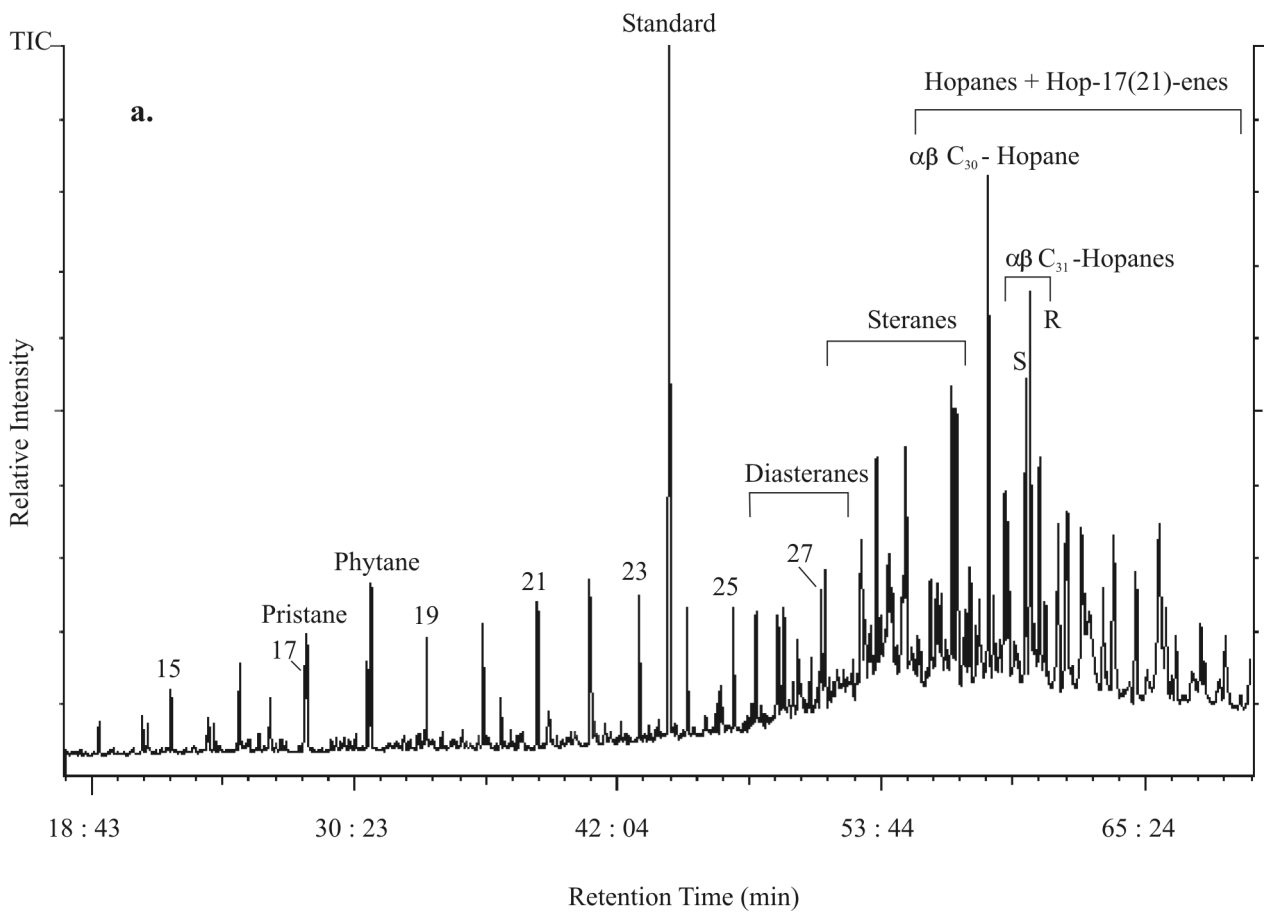
### 4.3. Steroids

In the saturated hydrocarbon fractions of the samples, steranes were detected in considerable quantities (Tab. 1; Fig. 2a). The $\alpha\alpha\alpha$ $C_{27}$-steranes and their $C_{29}$ homologues predominate over the $\alpha\beta\beta$ steranes. $C_{28}$-steranes are present in insufficient amounts for peak intergration. The corresponding diasteranes ($C_{27}$, $C_{29}$) were found in low quantities (Tab. 1). Comparable relative intensities of steranes are typically found in immature carbonate-rich rocks, and indicate the contribution of biomass from phytoplankton and photosynthetic bacteria, living in the photic zone of the water column, and probably land plants to the organic matter (VOLKMAN 1986).

The ratio of the (20S / 20S + 20R) isomers of the $\alpha\alpha\alpha$ $C_{29}$-steranes yield values of 0.21 and 0.23, respectively (Tab. 1). Using the diagram presented by MACKENZIE et al. (1982), the obtained ratios can be correlated to a vitrinite reflectance of approximately 0.5 % $R_o$.

In the aromatic hydrocarbon fractions (Fig. 2b), mono-aromonatic steroids predominate by far over the triaromatic steroids (Tab. 1). These compounds arise from the early

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Fig. 2: Gas chromatograms (TIC) of the saturated (a) and aromatic (b) hydrocarbon fractions from sample HR 68a. *n*-Alkanes are labeled according to their carbon numbers, specific compounds are identified in the GC traces. Standard = deuterated *n*-tetracosane in (a), 1,1´-binaphthyl in (b).

diagenetic transformation of sterols and subsequent aromatization from ring-C to ring-A (MACKENZIE et al. 1981). The low ratios of triaromatic versus the sum of mono- plus triaromatic steroids (Tab. 1) are consistent with the low maturity of the organic matter, as obtained from the proportions of R / S isomers of the $\alpha\alpha\alpha$ $C_{29}$-steranes.

## 4.4. Hopanoids

Hopanoids are the only constituents of the non-aromatic cyclic triterpenoids identified. The samples show similar hopanoid patterns, characterized by the occurrence of $\alpha\beta$-type hopanes from $C_{27}$ to $C_{35}$, the $C_{28}$-hopanes are absent. $\beta\alpha$ Hopanes from $C_{29}$ to $C_{31}$ are present in very low amounts. The predominant hopanoids are the $\alpha\beta$ $C_{30}$-hopane and the $\alpha\beta$ $C_{31}$-hopanes (Fig. 2a). The most probable biological precursors of the hopanes are 3-desoxyhopanes (OURISSON et al. 1979, ROHMER et al. 1992). These compounds have been identified in aerobic bacteria and fungi, as well as in kryptogames. The high contents of hopanes in the saturated hydrocarbon fractions (Tab. 1) indicate the importance of microbial biomass to the organic matter accumulated in the sediments. Minor constituents found in the same boiling point range as the $\alpha\beta$ hopanes are the hop-17(21)-enes (Fig. 2a). The presence of the $C_{30}$ to $C_{35}$ compounds is confirmed by their mass spectra. The distribution pattern of the hop-17(21)-enes is comparable to that of the $\alpha\beta$ hopanes, suggesting their early diagenetic origin through dehydrogenation reactions of bacteriohopantetrol.
The ratio of the (22S / 22S + 22R) isomers of the $\alpha\beta$ $C_{31}$-hopanes yield values of 0.45 and 0.47 (Tab. 1), distinctive from the equilibrium value of 0.6 (MACKENZIE et al. 1982). The results are in agreement with a maturity of the organic matter equivalent to vitrinite reflectance values of ~ 0.5 % $R_o$, as already proposed from the proportions of R/S isomers of the $\alpha\alpha\alpha$ $C_{29}$-steranes (MACKENZIE et al. 1982).

The m/z 365 mass fragments reveals the presence of regular ring-D monoaromatic 8,14 secohopanoids in the aromatic hydrocarbon fractions (HUSSLER et al. 1984). The presence of the $C_{29}$ and $C_{30}$ compounds (Fig. 2b) is confirmed by their mass spectra. These compounds are considered to have a bacterial source and occur in relatively high quantities within the soluble organic matter (SOM) of the samples (Tab. 1). A ring-B aromatized tetracyclic terpane, tentatively identified as des-E-D:C-friedo-25-norhopa-5,7,9-triene (HAUKE et al. 1993), was also detected in considerable amounts (Tab. 1; Fig. 2b). This compound was explained to originate possibly from hopenes via clay catalyzed rearrangement reactions yielding fernenes as intermediate products (HAUKE et al. 1993). However, this monoaromatic tetracyclic constituent of the SOM can also be traced back to arborene/fernene type precursor molecules (e.g. isoarborinol), as proposed by BORREGO et al. (1997).

## 4.5. Arborane/fernane derivatives

Beside the des-E-D:C-friedo-25-norhopa-5,7,9-triene, discussed above, specific compounds related to the arborane/fernane skeleton identified in the aromatic hydrocarbon fractions of the samples (Fig. 2b) are: des-A-arbora(ferna)-5,7,9-triene; 22,25,29,30-tetranorarbora(ferna)-5,7,9-triene; 24,25-dinorarbora(ferna)-5,7,9-triene; 24,25-dinorarbora(ferna)-1,3,5,7,9-pentaene; 25-norarbora(ferna)-5,7,9-triene (HAUKE et al. 1992a, b). The SOM-normalized concentrations of the arborane/fernane derivatives are high (Tab. 1). These compounds are controversially discussed with respect to their possible biological precursors (HAUKE et al. 1992b, 1995, VLIEX et al. 1994). Arborane-derivatives are derived from isoarborinol or arborinone during early diagenesis (JAFFE & HAUSMANN 1994). Isoarborinol, although present in various families of higher plants (OHMOTO et al. 1970; HEMMERS et al. 1989), it is a rather select compound. Geochemical and biosynthetic features have led to the proposal that fossilized isoarborinol (and other sedimentary arborane derivatives) might originate from as yet unknown aerobic bacteria (HAUKE et al. 1992b, JAFFE & HAUSMANN 1994). Carbon isotopic data, obtained by gas chromatography-isotope ratio mass spectrometry, comparable with the results from benzohopanes have been used to verify an bacterial origin of the arborane-derivatives (HAUKE et al. 1992b). A major ambiguity in assigning a arborane-derived structure to the biomarkers found in the GC traces arises from the fact that fernenols and fernenes, the latter abundant in contemporary ferns and probably their far-off ancestors (SHIOJIMA et al. 1993, VLIEX et al. 1994), may afford the enantiomeric structures which are indistinguishable by classical GC-MS analyses.

Exept the steroids and diterpenoids (discussed below), all prominent compounds of the aromatic hydrocarbon fractions are structurally related either to hopanoids or isoarborinol/fernenol and, in the present case, could be considered to be of bacterial origin.

## 4.6. Diterpenoids and sesquiterpenoids

The aromatic diterpenoids consist of compounds of the abietane-type (i.e. simonellite, 1,2,3,4-tetrahydroretene; Fig. 2b; PHILP 1985). Among the recent conifer families, abietane-type diterpenoids are widespread in species of Pinaceae, Podocarpaceae, Taxodiaceae, and Cupressaceae (OTTO et al. 1997). They are of little use for the taxonomical differentiation between conifer families (OTTO et al. 1997). However, the abundance of diterpenoids of the abietane-type (Tab. 1) argues for a contribution of gymnosperms to the biomass within the depositional environment. This conclusion is further supported by the presence of cadalene (Fig. 2b) in the aromatic hydrocarbon fractions. The biological precursors of cadalane-type sesquiterpenoids, cadinenes and cadinols (SIMONEIT et al. 1986), are commen constituents of the resins of the coniferales families Pinaceae, Taxodiaceae, Podocarpaceae, Cupressaceae and Araucariaceae (OTTO et al. 1997, and references therein).

## 4.7. Aryl-isoprenoids

The aromatic hydrocarbon composition of the samples is

| Compounds | Sample | |
|---|---|---|
| | **HR 66** | **HR 68a** |
| $n$-Alkanes | 2332 | 1831 |
| $n$-$C_{15-19}$ / $n$-Alkanes | 0.20 | 0.21 |
| $n$-$C_{21-25}$ / $n$-Alkanes | 0.34 | 0.35 |
| $n$-$C_{27-31}$ / $n$-Alkanes | 0.35 | 0.34 |
| CPI | 1.23 | 1.48 |
| | | |
| Pristane / Phytane | 1.19 | 0.82 |
| Pristane / $n$-$C_{17}$ | 3.35 | 1.92 |
| Phytane / $n$-$C_{18}$ | 2.60 | 2.79 |
| | | |
| Steranes | 2071 | 1838 |
| $C_{27}$-Diasteranes | 136 | 272 |
| $C_{27}$-Steranes | 583 | 920 |
| $C_{29}$-Steranes | 1351 | 647 |
| 20S/(20S+20R) $\alpha\alpha\alpha$ $C_{29}$-Steranes | 0.21 | 0.23 |
| | | |
| Hopanes | 8325 | 2243 |
| 22S/(22S+22R) $\alpha\beta$ $C_{31}$-Hopanes | 0.45 | 0.47 |
| Steranes / Hopanes | 0.25 | 0.82 |
| | | |
| Arom.Steroids | 1989 | 6540 |
| Monoarom. Steroids | 1514 | 5778 |
| Triarom. Steroids | 475 | 762 |
| Tri-/(Tri- + Mono-) arom. Steroids | 0.24 | 0.12 |
| | | |
| Arboran(Fernan)-Derivatives | 2653 | 1491 |
| des-E-D:C-friedo-25-norhopa -5,7,9-triene | 468 | 314 |
| Ring-D monoarom. 8,14- Secohopanoids | 1067 | 583 |
| | | |
| Aryl-Isoprenoids | 121 | 200 |
| Diterpenoids | 743 | 591 |

Tab. 1: Concentrations (µg/ g SOM) and their ratios of specific compounds in the saturated and aromatic hydrocarbon fractions

SOM = Soluble organic matter, CPI = Carbon preference index

further characterized by the occurrence of trimethyl-substituted aryl isoprenoids in the range from $C_{14}$ to $C_{22}$ (Fig. 2b). They have been found in very low amounts (Tab. 1). Aryl isoprenoids are thought to be derived from carotenoids specific for the photosynthetic green sulfur bacteria *Chlorobiaceae* and purple sulfur bacteria *Chromatiaceae* (Summons & Powell 1987). These organisms are phototrophic anaerobes and thus require both light and $H_2S$ for growth. In modern environments they appear in sulfate-containing water bodies which are sufficiently quiescent and organic-rich to enable sulfide production close to the photic zone (Summons 1993). Thermal and salinity stratification is usually involved, and euxinic conditions in the deep-water zone are required (Pfennig 1977). The occurrence of aryl isoprenoids within the samples indicates the establishment of euxinic conditions in the bottom water, an interpretation that is consistent with the observed low pristane / phytane and low steranes to hopanes ratios (Tab. 1). Comparable relationships were recently found within the Oligocene Schoeneck Formation in the Austrian Molasse Basin (Schulz et al. 2002), and have been interpreted as a result of organic matter accumulation within a silled basin.

## 5. Conclusions

The molecular composition of the hydrocarbons enables the characterization of the depositional enviroment of the investigated early Anisian dolomitic mud- to wackestones of late Gutenstein Formation (Fig. 3). $n$-Alkane distribution patterns and relative intensities of steranes are typical for organic matter of predominantly algal and/or microbial origin with minor contributions of land plants. Phytoplankton and photosynthetic bacteria are considered as the major primary producers of the biomass accumulated within the immature, carbonate-rich rocks. High contents of hopanoid biomarkers and constituents related to the arborane/fernane skeleton are considered to be of bacterial origin and indicate
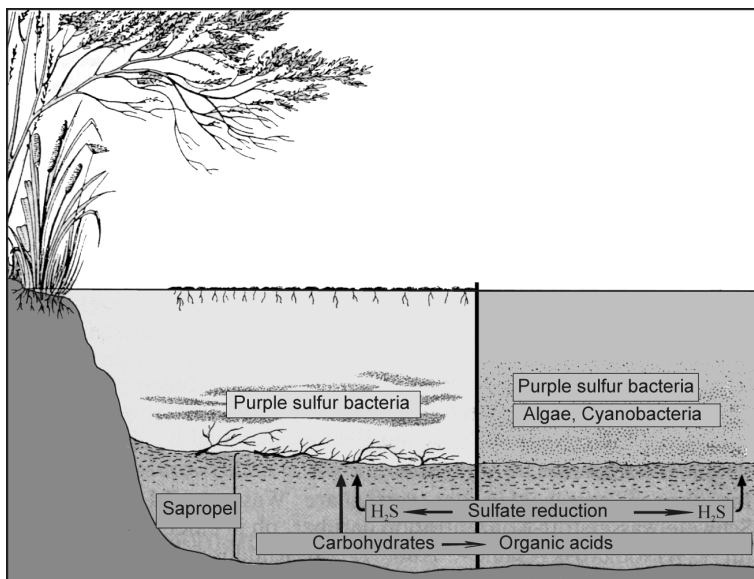
Fig. 3: Reconstruction of the depositional environment of the upper Gutenstein Fm. In the Rabenkogel area.

the enhanced microbial activity in the sedimentary environment. The relative proportions of S/R isomers of the $\alpha\alpha\alpha$ $C_{29}$-steranes and the $\alpha\beta$ $C_{31}$-hopanes are consistent with a maturity of organic matter equivalent to vitrinite reflectance values of approximately 0.5% $R_o$. This assessment is further confirmed by the predominance of monoaromatic over triaromatic steroids, and by a conodont alteration index (CAI) of 1.0 (means 50-90° C – see NÖTH 2001, KÖNIGSHOF 1992, and references therein) obtained from samples of overlying strata. The contribution of organic matter from gymnosperms is indicated by the occurrence of diterpenoids of the abietane-type and the aromatic sesquiterpenoid cadalene in the samples. The occurrence of aryl isoprenoids, derived from carotenoids specific for the photosynthetic green sulfur bacteria *Chlorobiaceae* and purple sulfur bacteria *Chromatiaceae*, indicates the establishment of euxinic conditions in the bottom water and the presence of free $H_2S$ within the water column. A high productivity, marine environment with limited water exchange and a stratified water column would be consistent with the observed biomarker composition (BECHTEL & PÜTTMANN 1997).

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