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ORIGINAL PAPER

An overview on source rocks and the petroleum system of the central Upper Rhine Graben

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Abstract The petroleum system of the Upper Rhine Graben (URG) comprises multiple reservoir rocks and four major oil families, which are represented by four distinct source rock intervals. Based on geochemical analyses of new oil samples and as a review of chemical parameter of former oil fields, numerous new oil–source rock correlations were obtained. The asymmetric graben resulted in complex migration pathways with several mixed oils as well as migration from source rocks into significantly older stratigraphic units. Oldest oils originated from Liassic black shales with the Posidonia Shale as main source rock (oil family C). Bituminous shales of the Arietenkalk-Fm. (Lias α) show also significant source rock potential representing the second major source rock interval of the Liassic sequence. Within the Tertiary sequence several source rock intervals occur. Early Tertiary coaly shales generated high wax oils that accumulated in several Tertiary as well as Mesozoic reservoirs (oil family B). The Rupelian Fish Shale acted as important source rock, especially in the northern URG (oil family D). Furthermore, early mature oils from the evaporitic-salinar Corbicula- and Lower Hydrobienschichten occur especially in the area of the Heidelberg-Mannheim-Graben (oil family A). An overview on potential source rocks in the URG is presented including the first detailed geochemical source rock characterization of Middle Eocene sediments (equivalents to the Bouxwiller-Fm.). At the base of this formation a partly very prominent sapropelic coal layer or coaly shale occurs. TOC values of 20–32 % (cuttings) and Hydrogen Index (HI) values up to 640–760 mg HC/g TOC indicate an extraordinary high source rock potential, but a highly variable lateral distribution in terms of thickness and source rock facies is also supposed. First bulk kinetic data of the sapropelic Middle Eocene coal and a coaly layer of the 'Lymnäenmergel' are presented and indicate oil-prone organic matter characterized by low activation energies. These sediments are considered as most important source rocks of numerous high wax oils (oil family B) in addition to the coaly source rocks from the (Lower) Pechelbronn-Schichten (Late Eocene). Migration pathways are significantly influenced by the early graben evolution. A major erosion period occurred during the latest Cretaceous. The uplift center was located in the northern URG area, resulting in SSE dipping Mesozoic strata in the central URG. During Middle Eocene times a second uplift center in the Eifel area resulted in SW-NE-directed shore lines in the central URG and contemporaneous south-southeastern depocenters during marine transgression from the south. This structural setting resulted in a major NNW-NW-directed and topography-driven migration pattern for expelled Liassic oil in the fractured Mesozoic subcrop below sealing Dogger α clays and basal Tertiary marls.

Keywords Petroleum system · Upper Rhine Graben · Oil families · Source rocks · Migration · Lias · Posidonia Shale

Introduction

The Upper Rhine Graben (URG) is the oldest known oil province in Western Europe where the exploitation of tar

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sands at Pechelbronn (Alsace, France) started on a small scale in 1498. Recently, the discovery of the Römerberg oil field has sparked new interest in oil exploration in this rather mature basin (Dill et al. 2008; Gawenda 2011).

The early period of hydrocarbon exploration in the URG focused on Paleogene and Neogene (in the following named 'Tertiary') reservoirs, particularly those associated with oil shows at or near to the surface. In Baden-Württemberg, the Posidonia Shale (Lias ε) was mined for smoldering prior to the start of modern hydrocarbon exploration in 1934 (Wirth 1962). At Pechelbronn more than 5500 wells were drilled until 1964 (Levi 1962; Sittler 1985). However, the first major hydrocarbon (oil) discovery next to Pechelbronn was made at Landau in 1955 (Wirth 1962). In this context, the URG has been a target for geological studies for a long time, resulting in a wealth of published data with numerous studies addressing the structural development and geothermal potential of the URG, as well as the petroleum system, source rock investigations, oil–oil and oil–source rock correlations, e.g., Schad (1962a), Welte (1979), Gamintchi (1979), Hollerbach (1980a), Sittler (1985), Rückheim (1989), Hillebrand and Leythaeuser (1992) and Bruss (2000).

The recent discovery of the Römerberg oil field with the new Buntsandstein play has, however, encouraged new research due to the need to redefine many aspects of the petroleum system of the URG, since the presence of producible oil at this structural and stratigraphic setting unit was completely unexpected. Particularly, an existing classification into four oil families (Bruss 2000) needed to be verified and known source-reservoir pairs had to be reviewed and updated after the Römerberg discovery. In this context, source rock and oil samples were analyzed and compared to published data, aiming on reviewing and summarizing geochemical data to achieve a comprehensive characterization of the petroleum system. The analysis and review of potential source rocks, the composition and origin of oils, the charging mechanism as well as timing of oil expulsion became necessary in order to understand the nature of the Römerberg discovery. The complex structural events including periods of subsidence and uplift, which led to the present-day structure of the URG, are expected to have had a key influence on the geographic distribution of source rocks, their maturation history and migration pathways. Therefore, an integrated understanding of the basin development of the URG is required, in order to quantitatively understand the generation and migration of hydrocarbons as well as trapping mechanisms.

Geological setting

Tectonic and sedimentary evolution

The Upper Rhine Graben (URG) is a NNE–SSW trending about 300-km-long, 35- to 40-km-wide continental rift formed over a preexisting Hercynian shear zone during Middle Eocene, which forms the central section of the European Cenozoic Rift System (Fig. 1; Ziegler 1992; Ziegler and Dèzes 2007; Grimm et al. 2011).

Graben formation commenced during Eocene times in the foreland of the Alps and Pyrenees in response to the build-up of north-directed collision-related intraplate stresses (Dèzes et al. 2004; Ziegler and Dèzes 2007). Before the formation of the URG, the Mesozoic succession was affected by a significant erosional period during late Cretaceous times, resulting in a SE-directed dip of the underlying Jurassic, Triassic, Permian and partly Carboniferous deposits (Schumacher 2002; Geyer and Gwinner 2011).

The basal Eocene graben fill is characterized by weathering products and clayey-carbonatic layers (Fig. 2; Eisbacher and Fielitz 2010). Above, marly-bituminous clays, coals and freshwater limestones ('Planorbenkalke'—Bouxwiller-Fm.) were deposited in shallow lakes under humid and warm climatic conditions during 45–37 Ma (10–60 m thick). During the Late Eocene, a major acceleration of subsidence and synrift sedimentation started and marine ingressions from southern directions entered the central URG (Fig. 2 deposition of the 'Grüne Mergel,' formerly termed 'Lymnäenmergel'; Grimm et al. 2011).

The main passive-rifting period occurred during the Oligocene due to regional WNW-ESE extension of the lithosphere. In this period, three Rupelian transgressions flooded the whole basin and marine environments were established extending even across the graben margins and resulting in the deposition of clayey organic-rich marls, for example the 'Fish Shale' (Hochberg-Subfm.—part of the 'Froidefontaine-subgroup', so-called Gray Beds; Grimm et al. 2011). After this main rifting period, a new northern depocentre, the so-called Heidelberg-Mannheim-Graben (Fig. 1), was established by transtensive sinistral shear movements in the late Oligocene to Miocene (starting at about 25 Ma). Concurrently, the southern parts of the URG were gradually uplifted and late Oligocene sediments were extensively eroded during Middle Miocene uplift (Villemin et al. 1986; Schumacher 2002).

Petroleum system URG

The hydrocarbon system of the URG comprises multiple source rocks and reservoir units. Most reservoirs have been discovered through drilling of conventional 3-way dip closures located on the up-thrown side of tilted fault blocks. Additionally, stratigraphic traps occur especially within the Tertiary sequence. Productive reservoirs are known to occur nearly in every porous or fractured stratigraphic unit in the Tertiary graben fill as well as in the underlying Mesozoic subcrop. As shown in Fig. 2, a large number of known

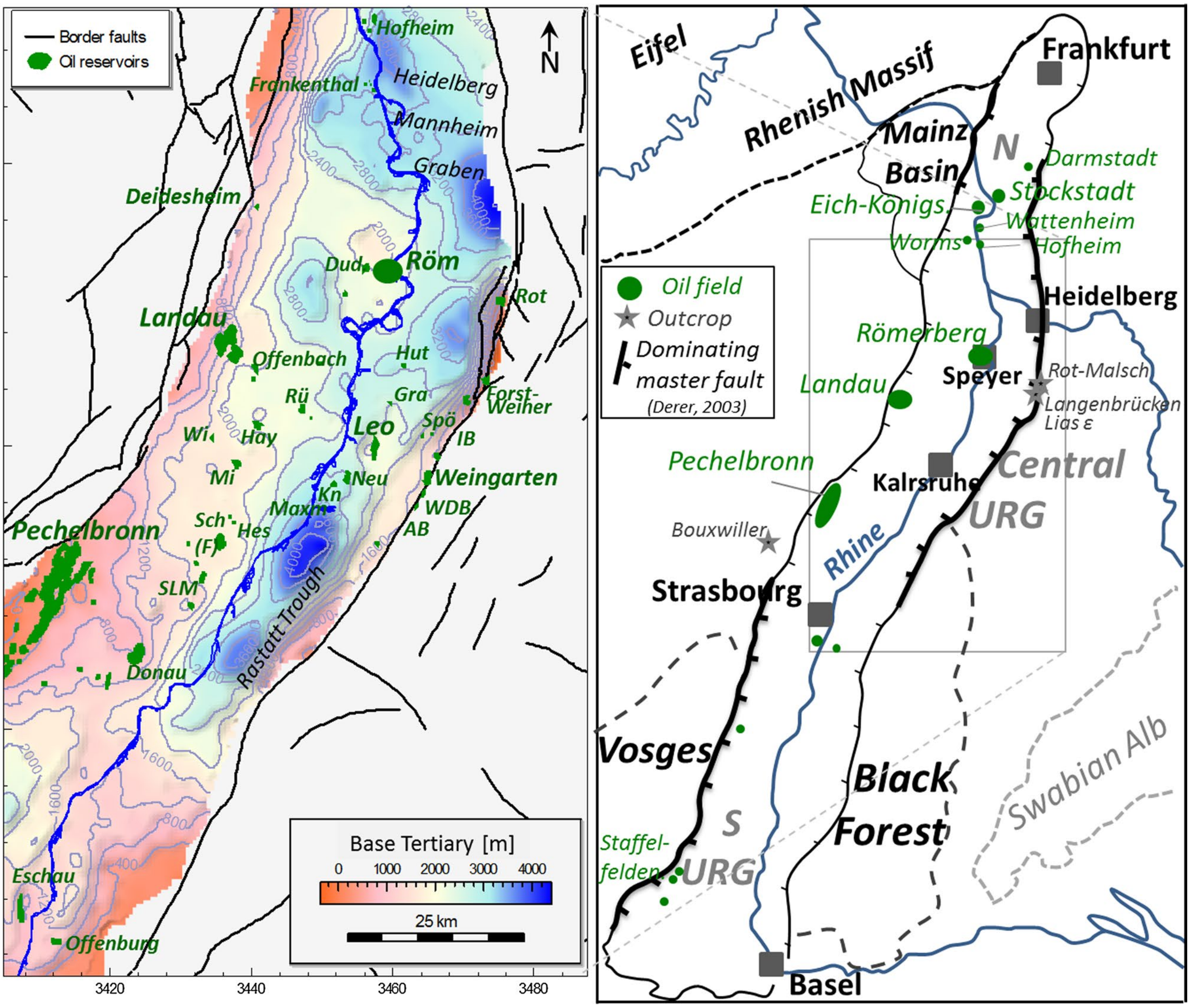

Fig. 1 Overview map of the geologic setting and close-up of the study area in central Upper Rhine Graben (*grey rectangle*; structural map from Sokol and Nitsch 2013). The study area focuses on the area between the Offenburg oil field as southernmost point and the oil fields Hofheim, Stockstadt and Eich-Königsgarten in the northern URG. For abbreviations, see Table 4

producing reservoirs occur throughout nearly the entire Tertiary stratigraphic column (reservoirs in more than 10 different Tertiary stratigraphic units). The Pechelbronn-Schichten (abbreviated PBS) represent the most important Tertiary reservoirs, e.g., producing at Pechelbronn, Landau, Stockstadt and Eich-Königsgarten. However, most of the clastic Tertiary reservoirs are of limited lateral and vertical extent (Straub 1962; Dill et al. 2008). Sands in the Froidefontaine-subgroup (Meletta-Schichten, Cyrenenmergel) and Niederrödern-Fm. ('Bunte Niederrödern-Schichten'—abbreviated BNS) are often discontinuous and of minor thickness (e.g., Mauthe et al. 1993).

The occurrence of oil reservoirs is usually restricted to those formations that occur beneath efficient seals typically formed by major transgressive events. This includes reservoirs in the Upper PBS beneath the Foraminiferenmergel/Fish Shale (Froidefontaine-subgroup) seal or the BNS reservoirs beneath the Cerithium-Schichten seal (Worms-subgroup).

The producing Mesozoic reservoirs include Buntsandstein matrix and fractured reservoirs, fractured Muschelkalk limestones, Keuper sandstones and fractured carbonates, heterogeneous Dogger oolites as well as Oxfordian reservoirs in the southern URG. The Jurassic Dogger oolite only forms a reservoir in the southern and eastern graben area (e.g., Eschau, Offenburg, Schaeffersheim). Partly, oil shows within Rotliegend sandstones underlying basal Tertiary layers have been reported from single wells in the northern URG, e.g., at Stockstadt (Boigk 1981). Most previous oil discoveries were made in shallow fields situated at

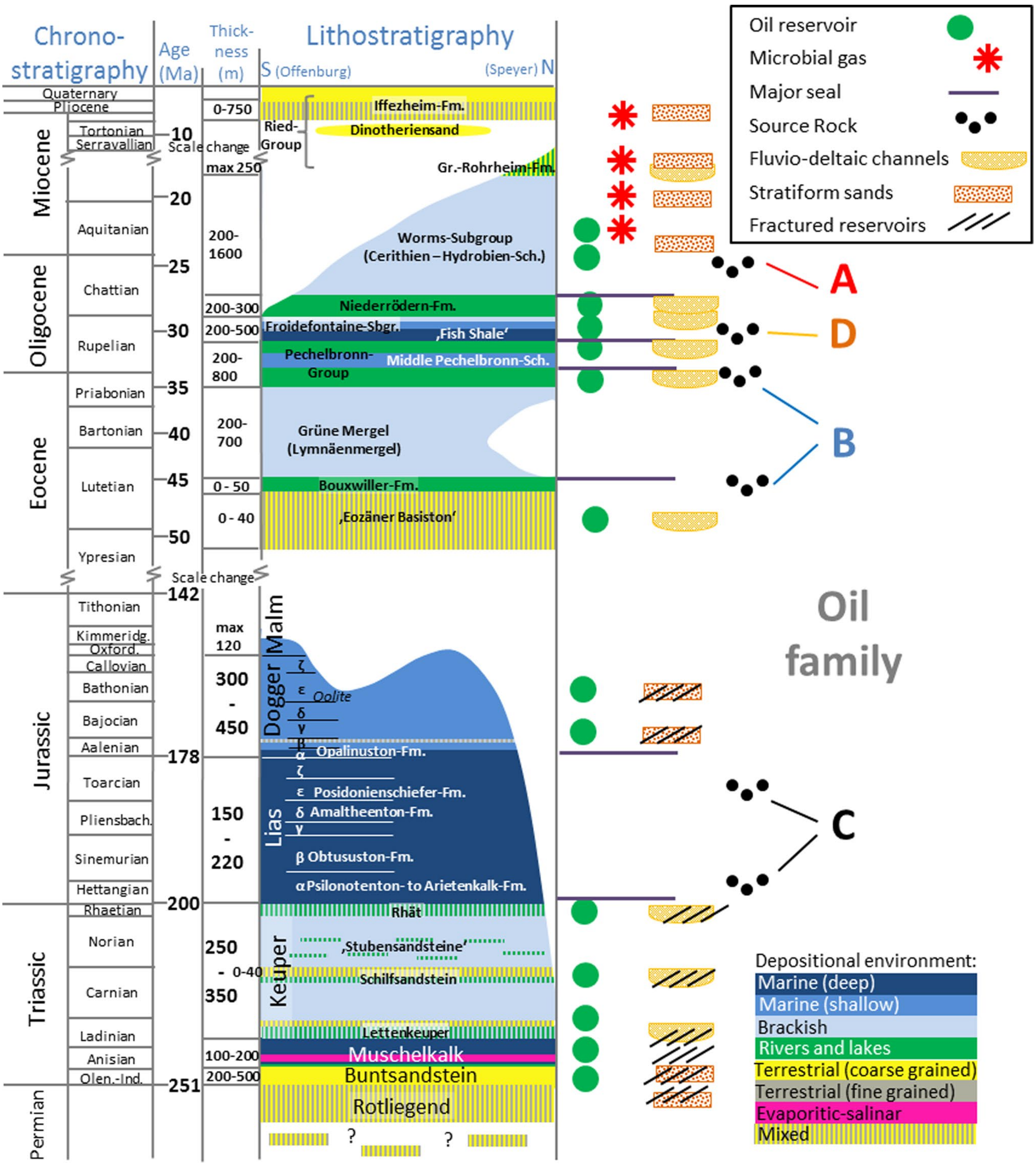

Fig. 2 Stratigraphic column of the central URG including petroleum system elements (reservoirs, source rocks, oil families) and indications of the depositional environment. Selected important groups, formations and subdivisions are displayed. Tertiary stratigraphic column modified after Grimm et al. (2011)

the western and eastern rim of the URG, typically located on the first rift shoulder. In most cases several reservoir levels occur within an oil field. As an example, at the Landau field a total of 10 producing stratigraphic units are known (Schad 1962b). There, oil is produced from fractured Muschelkalk limestones, Keuper sandstones, the 'Tertiary Basal Sand', in addition to numerous reservoirs in the Tertiary sequence (PBS, BNS, etc.).

Furthermore, 14 gas fields occur mostly in Miocene sandstone and dolomite reservoirs in the northern URG and with probable microbial ('biogenic') origin (Dill et al. 2008). Partly, in these Chattian to Burdigalian sequences very minor oil production occurred, especially from a few reservoirs in the so-called Corbicula-Schichten (now Mittlere Cerithienschichten—Grimm et al. 2011) and Hydrobienschichten.

Oil families were distinguished by Bruss (2000), who investigated 26 oils from diverse oil fields in the central to northern URG. Potential source rocks were examined concerning maturity, chemical and isotope characteristics and were compared to the oil families. Bruss (2000) identified four major oil families (A, B, C and D; Table 1) in addition to mixed oil groups and four main petroleum systems (source-reservoir pairs) in the URG—in stratigraphic order: *Oil family C* (*oils from marine-anoxic source rocks*): Posidonia Shale (Lias ε) source rock—Keuper sandstones plus Dogger and PBS reservoirs occurring in the entire graben area south of Heidelberg; *Oil family B* (*high wax oils*): (Lower) PBS source rocks—sandstones in the PBS; *Oil family D* (*oils from marine-suboxic source rocks*): Fish Shale/Foraminiferenmergel (formerly named 'Septarienton')—'Gray Beds', BNS and Upper PBS sandstones. New analyses of oil family D showed that the Fish Shale is the major source rock and the underlying Foraminiferenmergel and overlying Meletta-Schichten have only very subordinate source rock potential (Böcker and Littke 2014). *Oil family A* (*oils from evaporitic-salinar source rocks*): Corbicula-Schichten/Lower Hydrobienschichten—Upper Hydrobienschichten reservoirs (limited to the northern-central part of the URG).

Samples and methods

Tertiary and Mesozoic source rock as well as oil samples were gathered from wells in the central URG (listed in Tables 2, 3, 4) and analyzed by geochemical methods. Core samples and cuttings were analyzed for source rock investigations. Because oil samples of most fields from the thirties and fifties to sixties of the last century do not exist anymore, it was not possible to achieve detailed geochemical data for oil–source rock correlations. Hence, bulk oil parameters such as API gravity, sulfur and paraffin content or setting point were used to accomplish a potential correlation to an oil family.

For source rock samples, modern stratigraphic nomenclature was used, e.g., Tertiary units after Grimm et al. (2011) and Deutsche Stratigraphische Kommission (2012). For the Jurassic units the Greek letters (Lias α-ζ) used by Quenstedt have been abandoned (Bloos et al. 2005), although the new formation names are following Quenstedts subunits (Geyer and Gwinner 2011). However, the old terms are well known among petroleum geologists and used in most well reports and studies. Consequently, the Greek letters were used in this study.

Total organic carbon (TOC) and total inorganic carbon (TIC) were measured using a LECO RC-412 carbon analyzer via IR absorption in a two-stage measurement process (TOC from 350 °C to 520 °C; TIC from 520 °C to 1050 °C), without prior removal of carbonate by acid treatment. Total sulfur (TS) was measured using a Leco S 200 sulfur analyzer. Rock–Eval pyrolysis was performed using 120 mg (if TOC < 2 %), 100 mg (TOC 2–8 %), 50 mg (TOC 8–20 %), 20 mg (TOC > 20 %) of powdered rock. Samples were gradually heated in the helium stream of a DELSI INC Rock–Eval VI instrument according to guidelines by Espitalié et al. (1985) and Lafargue et al. (1998).

For microscopic analyses, core and cutting samples were embedded in a mixture of epoxy resin and hardener, and a section oriented perpendicular to the bedding plane or rock grains was polished. Microscopic measurements were performed in incident light. Random vitrinite reflectance (VR_r) was measured using a Zeiss Axio Imager microscope. An yttrium–aluminum–garnet mineral standard (YAG; 0.889 %) was used for calibration. Details of the analytical procedure are described in Littke et al. (2012).

Bulk kinetic parameters were determined at Helmholtz-Zentrum Potsdam (GFZ). Two coaly samples, one of the basal part of the Middle Eocene (Equivalents to the Bouxwiller-Fm.) and the other from the top part of the 'Lymnäenmergel,' were analyzed by way of programmed temperature open system pyrolysis at four linear heating rates (0.7, 2.0, 5.0 and 15 °K/min) using a Source Rock Analyzer (Humble Instruments & Services Inc.). The pyrolysis products were detected via flame ionization detector (FID) in a constant He flow (50 ml/min). The Kinetics 2000 software was used to determine the discrete activation energy distribution with a single frequency factor (Burnham et al. 1987).

For gas chromatography (GC) and gas chromatography-mass spectrometry (GC–MS) analysis, hydrocarbons present in the rock samples (10 g) were extracted ultrasonically with dichloromethane (DCM; 40 ml) and n-hexane (40 ml) subsequently (Wang et al. 2006, Sachse et al. 2011). The extract was fractionated depending on polarity into subfractions of non-aromatic hydrocarbons (5 ml pentane), aromatic hydrocarbons (5 ml pentane/DCM, 4:6) and heterocompounds (5 ml MeOH) employing a silica gel chromatographic column. GC analyses were performed utilizing a Fisons Instrument GC 8000 series equipped with a split/splitless injector and FID. Hydrogen was used as carrier gas with a gas velocity of 40 cm/s. A Zebron ZB-1 HT Inferno fused silica column (30 m; 0.25 mm i.d. film thickness 0.25 µm, Phenomenex) was used. Conditions

Table 1 Overview chart of the petroleum system Upper Rhine Graben in stratigraphic order

Oil family	Source rock	Main reservoirs	Main occurrence	Fluids
A	Corbicula- and Lower Hydrobienschichten	(Upper) Hydrobienschichten	Northern URG, Heidelberg-Mannheim-Graben	Early mature oil
D	Fish Shale (minor additional potential from the Foraminiferenmergel and Meletta-Sch.)	Upper Pechelbronn-Sch., ‘Gray Beds,’ BNS sandstones	Central and northern URG	Oil
B	Coals and coaly shales of the Lower Pechelbronn-Sch., and Upper and Middle Eocene layers	Pechelbronn-Sch., (fractured) Pre-Tertiary reservoirs	Western-central and northern URG	Oil
C	Liassic Black Shales with the Posidonia Shale and Lias α bituminous shales as excellent source rocks	BNS, ‘Gray Beds‘, Pechelbronn-Sch., Dogger sandstones, Keuper, (fractured) Muschelkalk, Buntsandstein	URG south of Heidelberg	Oil, wet gas

Modified after Bruss (2000)

were: injection volume 1 µl, 270 °C injector temperature, split–splitless injection, splitless time 60 s. Oven temperature program was 80 °C for 3 min isothermal, then programmed at 5 °C/min to 300 °C. GC–MS analyses were performed on a Finnigan MAT 95 spectrometer coupled to a HP 5890 chromatograph. A 30 m × 0.25 i.d. × 0.25 µm film Zebron-ZB1 fused silica column was used with He as carrier gas at 35 cm/s. Oven temperature was programmed from 80 (held for 3 min) to 300 °C at 3 °C/min. The spectrometer operated in low-resolution EI + mode with 70 eV (source temperature 200 °C) scanning from *m/z* 35 to 700 with a scan rate of 1 decade/s and an interscan time of 0.1 s.

Results: source rock characterization

The identification of source rocks is of key interest to understand the distribution of oil and gas in the URG. Several source rock investigations have been performed focusing especially on Tertiary source rocks, e.g., Welte (1979) and Rückheim (1989). Compiled results of source rock studies are displayed in Fig. 3 and allow the identification and determination of major source rocks intervals by TOC values. Source rocks in this sense are defined as rocks which generate and release enough hydrocarbons to form an accumulation of oil or gas. The minimum TOC required to generate and expel commercial quantities of oil from an immature source rock is about 1.5 % (Hunt 1996). Gas and condensate appear to be expelled down to at least 0.5 % TOC. An approximate minimum initial Hydrogen Index (HI) of >200 mg HC/g TOC is considered as threshold for a potential expulsion of oil, and below <200 mg HC/g TOC all generated oil is retained by sorption (Pepper and Corvi 1995).

The Posidonia Shale is the sequence with the highest mean TOC value (Lias ε in Fig. 3). Detailed geochemical investigations of the Posidonia Shale from the nearby Swabian Jura determined a mean value of 8 % in the black shale facies (750 samples; Röhl et al. 2001; compare Song et al. (2015) for Posidonia Shale from different locations and Rullkötter et al. (1988) for Posidonia Shale at different maturity levels). However, mean values from Fig. 3 have to be used with caution; e.g., the Posidonia Shale mean value of 8 % is representative for an about 15-m-thick unit. The values for the Fish Shale are valid for a roughly 10-m-thick interval with about 4.5–5 % TOC analyzed in the outcrop Unterfeld in Rauenberg (Grimm et al. 2002; Micklich and Hildebrandt 2005). In contrast, the Lower PBS show a varying thickness between 50 and 330 m in the central and northern URG (Grimm et al. 2011). Typically, only relatively thin coals and coaly shales within these layers show significant source rock potential represented by higher TOC values.

Table 2 Overview on source rock parameters for selected samples

Well (location)	Sample no.	Type	Strat. unit	Depth (m MD)	TOC (%)	TIC (%)	TS (%)	$CaCO_3$ (%)	Rock–Eval			
									HI	OI	PI	T_{max}
Frankenthal 10	14/1262	Core	Cyrenenmergel	2660.4	0.6	3.5		29				
	14/1263		Meletta Beds	2944.9	0.4	4.8		40				
	14/1264		Upper PBS	3154.15	0.2	0.2		2				
	14/1265		Lower PBS	3174.6	0.3	2.3		19				
	14/1266		Lower PBS	3242.5	0.3	0.2		2				
	14/1267		Lower PBS	3331.9	0.3	0.2		2				
Rülzheim 1	14/1268	Core	Cyrenenmergel/Meletta-Sch.	1532.9	0.5	4.0		33				
	14/1269		Up. Pechelbronn.Sch.	1685.8	0.4	0.9		7				
	14/1270		Up. Pechelbronn.Sch.	1759.5	0.5	3.8		31				
	14/1271		Lower Pechelbronn-Sch.	1865.5	0.9	0.2		2				
	14/1272		Lymnäenmergel	1975.5	0.6	0.5		4				
	14/1273		Lymnäenmergel	2035.3	1.1	2.6		21				
	14/1274		Lymnäenmergel	2082.9	1.1	3.5		29				
	14/1276		Up. Keuper (Rhätsandstein)	2282.7	0.5	0.0		0				
Well X11-SE	13/1455	Cuttings	Lymnäenmergel (coaly)	2210	8.3	2.8		24	436	37	0.10	440
Well X16-E	13/1537	Cuttings	Lymnäenmergel	1724	0.9	2.6		22				
	13/1538		Lymnäenmergel (coaly)	1726	2.0	2.2		19	175	65	0.04	440
	13/1539		Lymnäenmergel	1728	0.6	2.9		24				
Well X21-N	13/1127	Cuttings	Lower Pechlebronn-Sch.	2155	1.7	1.4		12				
	13/1129		Lymnäenmergel	2205	0.9	1.7		14				
	14/004		Middle Eocene (coaly)	2210	5.3	0.6		5	400	29	0.15	441
	14/005		Basal Clay	2215	1.3	0.4		3				
Well X25-N	13/1521	Cuttings	Middle Eocene	2360	2.2	2.5		21	396	69	0.10	441
	13/1522		Middle Eocene (coaly)	2365	31.9	2.5	1.7	21	642	19	0.08	442
	13/1523		Middle Eocene (coaly)	2370	20.4	2.7		22	762	29	0.05	443
	13/1524		Middle Eocene (coaly)	2375	5.3	2.2	1.6	18	432	27	0.07	448
Well X26-N	13/1529	Cuttings	Middle Eocene	2265	0.9	0.3		2				
	13/1528		Middle Eocene	2260	1.4	0.6		5				
Well X27-N	13/1533	Cuttings	Middle Eocene (coaly)	2450	3.0	3.7		31	277	48	0.15	437
Well X28-N	14/996	Cuttings	Middle Eocene (coaly)	2500	3.2	2.0		17	374	47	0.12	441
	14/997		Middle Eocene (coaly)	2505	7.4	1.0	1.6	9	358	21	0.12	441
	14/998		Middle Eocene (coaly)	2510	4.7	0.7	1.5	6	338	30	0.11	439
X42-S	14/1180	Core	Dogger α	675.7	1.0	0.4		3				

Table 2 continued

Well (location)	Sample no.	Type	Strat. unit	Depth (m MD)	TOC (%)	TIC (%)	TS (%)	$CaCO_3$ (%)	Rock–Eval			
									HI	OI	PI	T_{max}
Well X45-S	14/1172	Core	Upper Pechelbronn-Sch.	312	2.1	2.2		18	67	72	0.10	418
	14/1173		Dogger β	745.45	1.0	2.8		23				
	14/1174		(uppermost) Dogger α	770.4	1.3	0.3		2				
	14/1175		Dogger α	851	1.4	0.3		2	201	86	0.04	439
	14/1179		Lettenkeuper	1152.55	2.5	0.3		3	153	61	0.13	440
	15/064		Lias α	981.75	5.1	0.9		8				
	15/065		Lias α	984.7	1.0	1.3		11				
	15/066		Keuper (Rhät)	988.7	0.5	0.2		2				
Well X60-S	14/318	Core residue	Lettenkeuper	758.15	0.6	6.7		56				
Well X61-S	14/332	Cuttings	Lymnäenmergel	1280	0.6	3.6		30				
Well X71	14/886	Core	Lymnäenmergel	2096.8	0.6	2.0		17	58	189	0.25	–
	14/887	Core	Lettenkeuper	2198.5	0.5	0.4		3	114	220	0.22	441
Well X111	14/369	Core residues	Lymnäenmergel	2191.2	3.1	0.2		2	38	49	(0.32)	430
	14/375	Core	Lymnäenmergel	2191.2	2.0	0.3		3	165	62	0.10	446
	14/407		Lymnäenmergel	2197.8	1.1	0.2		2	164	94	0.10	445
	14/408		Lymnäenmergel	2197.8	0.6	0.2		2				
	14/888		Lymnäenmergel	2197.8	2.3	0.4		3	204	62	0.13	444
	14/889		Lymnäenmergel	2197.8	13.2	2.6	1.6	21	367	21	0.09	444
	14/409		Lettenkeuper	2325	0.8	3.2		26	257	150	0.08	450
	14/890		Lettenkeuper	2332.9	0.8	0.2		2	107	167	0.15	445
	14/373	Core residue	Lettenkeuper	2340.4	0.5	0.2		2				
	14/410	Core	Lettenkeuper	2347.9	0.5	2.5		21				
	14/891		Lettenkeuper	2347.9	0.6	2.5		21	209	226	0.11	440
	14/374	Core residue	Lettenkeuper/Ob. MK	2347.9	0.6	0.8		6	193	186	(0.32)	–

Depth in meters measured depth. For Fish Shale and Liassic samples, see Böcker and Littke (2014, 2015)

TOC total organic carbon, *TIC* total inorganic carbon, *TS* total sulfur, *HI* Hydrogen Index in mg HC/g TOC, *OI* oxygen index in mg CO_2/g TOC, *PI* production index, *PBS* Pechelbronn-Schichten

T_{max} in °C

Table 3 Results of geochemical analyses of selected oil samples and source rock extracts as an addition to geochemical data for oil families (A, B, C, D) from Bruss (2000)

Well/location	Abbreviation	Sample no.	Type	Stratigraphic unit	Depth (m)	Oil family	Gas chromatography				GC/MS	
							Pr/Phy	Pr/nC_{17}	Phy/nC_{18}	nC_{17}/nC_{27}	Oleanane/C_{30} Hop	HBI C_{25}
Pechelbronn-Sondage 2962 (1927) Surbourg	Pech.2962	14/1204	Produced oil	Upper Pechelbronn-Schichten		C	1.6	0.5	0.5	14.9	–	–
Pechelbronn tar pit	Pech.tar	14/1205	Oil from tar pit (RW 3412251; HW 5420891)			C	1.7	1.0	0.9	13.2	–	–
Well X110		14/893	Produced oil	(Oligocene)		C	1.6	0.6	0.5	7.7	–	–
Weingarten N1	WeN1	11/412	Produced oil	Rhätsand	1015	C	1.5	0.9	0.7	3.1	–	–
Weingarten Deutag 204	WeD204	11/413	Produced oil	Meletta-Sch./ Cyren.M.	435	C	1.6	0.5	0.4	5.9	–	–
Leopoldshafen 1a	Leo 1a	11/410	Produced oil	Bunte Nied-erödern Sch.	855	CD	1.8	0.5	0.3	4.3	b.d.l.	b.d.l.
Leopold-shafen 7	Leo 7	11/411	Produced oil	Meletta-Schichten	1250	CD	1.8	0.5	0.3	5.0	b.d.l.	b.d.l.
Well X25-N		13/1522	Extract (Cuttings)	Base Middle Eocene	2365		3.2	0.7	0.3	2.6		–
Well X25-N		13/1523	Extract (Cuttings)	Base Middle Eocene	2370		2.9	0.5	0.2	3.5	0.06	–
Well X111		14/889	Extract (Core)	Top Grüne Mergel	2200		6.8	0.7	0.1	3.8		–

Pr pristane, *Phy* phytane, *HBI* highly branched isoprenoid, *b.d.l. Below detection limit*

Table 4 Overview of oil and gas fields in the URG and their corresponding source rock

Country	Field–well			Type	Reservoir	Production (2014; LBEG data)			Oil family		Reference oil–SR correlation/ Geochemical data without oil–SR correlation
	Field	Well	Abbreviation			Oil produced [1000 t]	Oil-ass. Gas produced [1000 Vm^3]	(Mean) GOR	This study	Existing oil–SR correlation	
GER	Aurora-Baden	Aurora-Baden 2	AB (B), AB (G)				Not specified	'<5'		C	Bruss (2000)/ Gamintchi (1979)
	Darmstadt	Darmstadt 2a	Dar2a	Oil	Hydrobiensch.		Not specified		A		/LBEG
	Deidesheim	Deidesheim 2	Dei	Oil	Meletta-Sch.	0.4	Not specified	'<5'		B	Bruss (2000)
	Dudenhofen	Dudenhofen 104	Dud	Oil	Ob. Hydrobiensch.		Not specified	'<5'		A	Bruss (2000)
	Eich-Königsgarten		'Echo'-'Tangosierra'	Oil	PBS	1374.9	30,596	19	D (B) (partly B)	Rupelian Clays + Mid. PBS	Rückheim (1989)/ LBEG (1952)
		Eich 17		Oil	PBS				B		/LBEG (1959)
	Frankenthal	Frankenthal 3	Fra	Oil	Ob. Hydrobiensch.		Not specified			A	Bruss (2000)
	Forst-Weiher			Oil		95.9	Not specified	'<5'		Lias (C)	Welte et al. (1975)
		ITAG-Baden 1a	IB1a	Oil	Dogger Beta					C	Bruss (2000)
		ITAG-Baden 1b	IB1b	Oil	Lettenkeuper					C	Bruss (2000)
	Graben	Graben 1	Gra	Oil	Cyrenenmergel	7.6	Not specified	15–30 (LBEG)		D	Bruss (2000)
	Hagenbach		Hag	Ass. gas	BNS		Not specified				/Boigk (1981)
	Hayna		Hay	Oil/ass. gas (Wh: 86 %)	BNS, Cyrenen Mergel	2.1	Not specified	'Very high' (LBEG)	(B)		/LBEG (1960)
	Hessbach	Hessbach 1	Hes (B), Hes (G)	Oil	Upper PBS		Not specified			BC	Bruss (2000)/ Gamintchi (1979)
	Hofheim		Hof, 'Uniform'	Oil	Upper PBS	12.5	Not specified	30–45 (LBEG)		Rupelian Clays + Mid. PBS	Rückheim (1989)
	Huttenheim	Huttenheim 1	Hut	Oil	Cyrenenmergel	5.4	Not specified	'<5'		D	Bruss (2000)

Table 4 continued

Country	Field–well			Type	Reservoir	Production (2014; LBEG data)			Oil family		Reference oil–SR correlation/Geochemical data without oil–SR correlation
	Field	Well	Abbreviation			Oil produced [1000 t]	Oil-ass. Gas produced [1000 Vm^3]	(Mean) GOR	This study	Existing oil–SR correlation	
	Knielingen	Knielingen 3	Kn (B); Kn (G)	Oil	Cyrenen-mergel	10.0	4460	383 (100–1000; LBEG)		D	Bruss (2000)/Gamintchi (1979)
	Landau	Landau 173	La173	Oil	Upper PBS	4499.7	17258	3		BCD	Bruss (2000)
		Landau 104	La104	Oil	Eoz. Basissand					BC	Bruss (2000)
	Leopoldshafen	Leopoldshafen 2, 3, and others	Leo2, Leo3, and others	Oil	Cyr.M.; Mel. Sch. BNS	187.6	12113	56	CD	CD	Bruss (2000)/Gamintchi (1979)
	Maximiliansau	Maximiliansau 2	Maxm2	Oil		1.9	496	227	B	'Tertiary'	Richard (1994)
	Minfeld	Minfeld 1	Mi1	Oil	Lower PBS	32.9	Not specified	15–60 (LBEG)		B	Bruss (2000)
		Minfeld 9	Mi9	Oil	Cyrenen-mergel					B	Bruss (2000)
	Neureut	Neureut 5	Neu5	Oil	Cyrenen-mergel	9.4	Not specified	60–150 (LBEG)		CD	Bruss (2000)
		Neureut 3	Neu3	Oil sample	Lower Hydrobiensch./Corbicula-Schichten				A		/Gamintchi (1979)
GER	Offenbach	Offenbach 1	Off.ba1	Oil	Cyrenen-mergel	32.9	316	13		D	Bruss (2000)
	Offenburg		Off.bu	Oil	Hauptrogen-stein	9.2	303	29		Lias (C)	Durst (1991), Richard (1994)
	Rot	Rot4, Rot6	Rot4, Rot6	Oil	Lettenkeuper	61.2	Not specified	'<5'		CD	Bruss (2000)
	Römerberg		Röm	Oil	Buntsandstein, MK, Keuper	813.4	6895	7			e.g., Böcker et al. (2014) and references therein
	Rülzheim	Rülzheim 2	Rü2	Oil	BNS	41.0	14309	301		D	Bruss (2000)
		Rülzheim 1	Rü1	Oil	Meletta-Sch.				B		/Gamintchi (1979)

Table 4 continued

Country	Field–well			Type	Reservoir	Production (2014; LBEG data)			Oil family		Reference oil–SR correlation/Geochemical data without oil–SR correlation
	Field	Well	Abbreviation			Oil produced [1000 t]	Oil-ass. Gas produced [1000 Vm^3]	(Mean) GOR	This study	Existing oil–SR correlation	
	Scheibenhardt	Scheibenhardt 2	Sch2	Oil	Lower PBS	Not specified	Not specified			B	Bruss (2000)
	Spöck		Spö	Ass. gas	Rhätsandstein	Not specified	Not specified				/Boigk (1981)
	Stockstadt	Stockstadt 135		Oil	Hydrobiensch.	960.0	15158	14	A		/LBEG (1960)
			Sto	Oil	PBS ('oberes Lager')				D (B)	Rupelian Clays + Stockstadt 5 oil shale	Hillebrand and Leythaeuser (1992)
				Oil	PBS ('unteres Lager')				D (B), B		
	Wattenheim		Wat, 'Foxtrott 1'	Oil	Pechelbronn-Sch.	26.0	785	26	D	Rupelian Clays + Mid. PBS	Rückheim (1989)
	Weingarten/Werrabronn	Wiag-Deutag 204	WD204	Oil	Meletta-Sch.	77.0	Not specified	'<5'	C		
		Weingarten N1	We1	Oil	Rhätsandstein				C	C	Bruss (2000)
	WIAG-Deutag-Baden	WIAG-Deutag-Baden 2	WDB2	Oil	Meletta-Sch.	Not specified	Not specified			C	Bruss (2000)
	Winden	Winden 1	Wi	Oil	Lower PBS	4.3	270	54		BC	Bruss (2000)/LBEG (1979)
	Wolfskehlen		Wol4	Oil	Hydrobiensch.	Not specified			A		/LBEG (1952)
	Worms		'Alpha 4'	Residual oil	Hydrobiensch.	0.7	Not specified		A		/Rückheim (1989)
FR	Eschau		Esc	Oil	Dogger	81.3	Not specified	10		'Jurassic'—Lias (C)	Richard (1994)
	Pechelbronn	Sondage 2692	P.S6, P.tar, P.mine, P.2962, etc.	Produced and mined oil	PBS, Mesozoic	3303.7	Not specified	'<5'	C	Lias (C)	Gerling et al. (1988); Blümel et al. (1989); Richard (1994); Bruss (2000);/Gamintchi (1979)
	Schaffhosue			Dry gas (>98 % C1)	Gray Beds'	–	Not specified				/Sittler (1985)

Table 4 continued

Country	Field–well			Type	Reservoir	Production (2014; LBEG data)			Oil family		Reference oil–SR correlation/ Geochemical data without oil–SR correlation
	Field	Well	Abbreviation			Oil produced [1000 t]	Oil-ass. Gas produced [1000 Vm^3]	(Mean) GOR	This study	Existing oil–SR correlation	
	Scheibenhard (F)		,SCB4'; Sch (F)	Oil		356.7	Not specified		B	'Tertiary—Sannoisian'	Richard (1994)/Blumenröder (1958)
	Schelmenberg	Schelmenberg 1	SLM1-Stampian	Oil		55.7	Not specified		B	'Tertiary—Sannoisian'	Richard (1994)
		Schelmenberg 1	SLM1-Sannois.	Oil						'Jurassic'—Lias (C)	Richard (1994)
	Schäffersheim			Wet gas (78 % C1)	Dogger		Not specified				/Sittler (1985)
	Staffelfelden		Sta	Oil	Dogger oolite	55.5	Not specified		C		/Tschopp (1952)

GOR values of oil fields and wetness ratios (Wh) of reservoired gas. Oil and gas production data are taken from LBEG (1952–2015). For all oil fields without available oil gravity data an oil gravity of 0.86 t/m^3 were used for the GOR calculation

Pre-Jurassic source rocks

In the Triassic sequence no significant source rock occurs (Lutz and Cleintuar 1999). Oldest possible source rocks are Carboniferous trough deposits, which have not been drilled and analyzed in the central URG area so far.

From the lower Rotliegend, minor coal seams are known in the surrounding area (e.g., in the Black Forest area; Boigk 1981), as well as local black pelites from Lower Rotliegend sediments in the Mainz Basin (e.g., Schwarz et al. 2011). These black pelites and coals are suggested to have minor gas generation potential and are taken into account as possible source of minor gas shows in a number of Buntsandstein wells, e.g., at Eschau 1 (Lutz and Cleintuar 1999).

In the Middle Muschelkalk subgroup (Karlstadt-Fm.—'Upper Orbicularismergel') partly bituminous marls, limestones and dolomites of about 10 m thickness are described in Baden-Württemberg (Schad 1962a; Eisbacher and Fielitz 2010; Geyer et al. 2011:157). Source rock potential for these units has not yet been verified by geochemical investigations.

In the Keuper section, only the Erfurt-Fm. (Lettenkeuper) is assumed to have minor gas generation potential due to thin coaly layers interbedded. These layers are partly described as bituminous (Schad 1962a). Only few geochemical investigations are available indicating only minor gas generation potential by TOC values of typically <1–2 %, partly 6–8 %, with hydrogen lean type III kerogens (cf. Welte 1979).

Jurassic source rocks

The Lias α and in particular the Posidonia Shale (Lias ε) are well-known oil shales and bituminous marls with good to excellent source rock potential in the URG area (Schad 1962a; Bruss 2000). Several authors identified the Lias ε as the major source rock of several reservoirs in the URG (designated as oil family C—Bruss 2000). The Lias ε can be classified as excellent oil-prone source rock characterized by marine type II kerogen with high TOC contents of 8 % on average and high Hydrogen Index values of 581 mg HC/g TOC on average (170 samples from the Swabian Jura; Röhl et al. 2001). Source rock quality data from the central URG compiled in Fig. 4 illustrate its extraordinary high potential to generate hydrocarbons. From the URG similar TOC and Rock–Eval values are known (Böcker and Littke 2015).

Published TOC and Rock–Eval data of the marine Lias α black shales in the URG area exist only to a very limited extent, e.g., from well Scheibenhardt 2 (Welte 1979), Mingolsheim 1968 (Quan et al. 2008) and local outcrops (Böcker and Littke 2015). The marine Lias α shales and

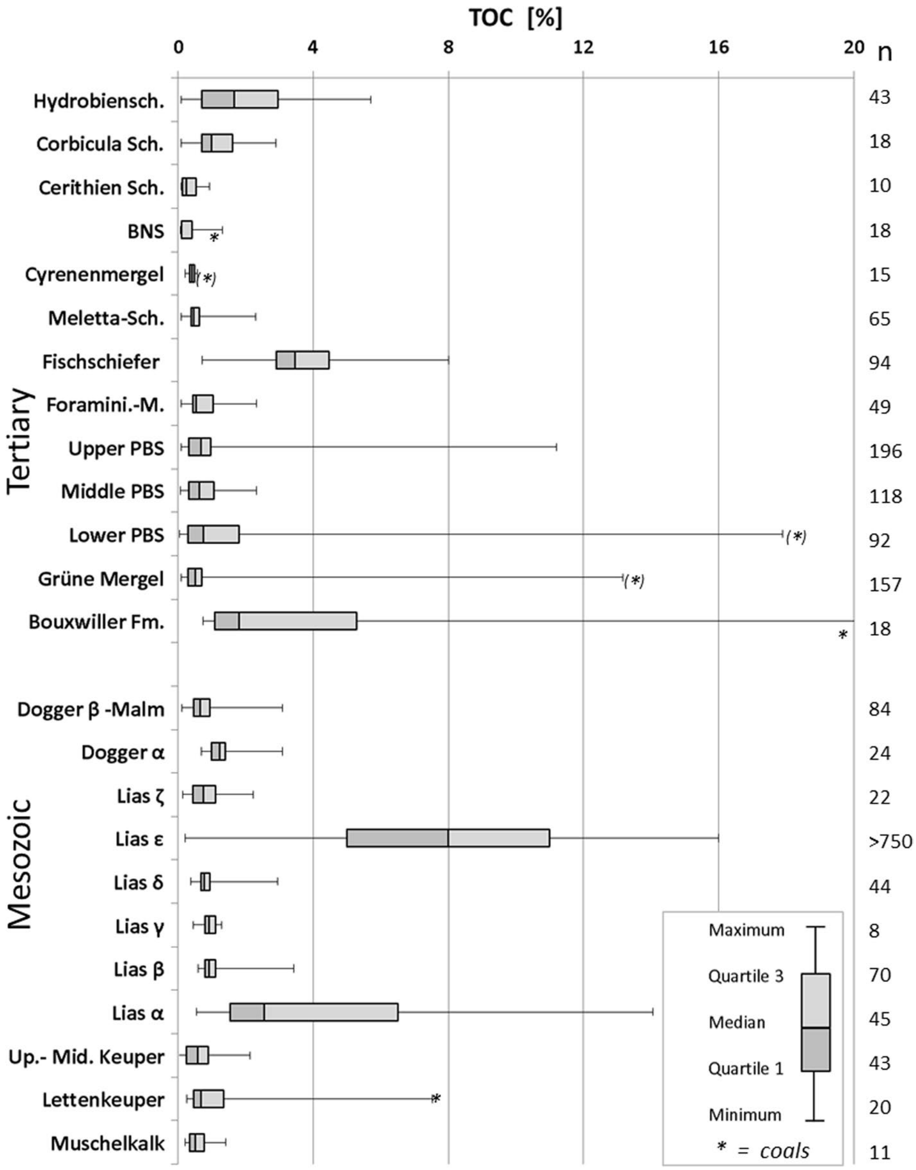

Fig. 3 Total organic carbon (TOC) values of compiled studies in the central URG with minimum, maximum, quartile 1, 2, 3 values, and number of measurements (*n*). Layers with known coal layers after Grimm et al. (2011) are marked with * or (*) for 'partly coaly.' PBS: Pechelbronn-Schichten, BNS: Bunte Niederrödern-Schichten. For the Lias ε also reference data from the adjacent Swabian Alb were used. Data are from Welte 1979; Radke et al. 1991; Bruss 2000; Röhl et al. 2001; Frimmel 2003; Böcker and Littke 2014, 2015; and references therein. *Remark*: The values display TOC measurements of outcrops, cores and cuttings in order to identify main source rock intervals by TOC values. Thus, the results will be biased to organic carbon-rich intervals and not represent the entire stratigraphic unit. Exceptions are the Lias ε and Fish Shale, which reveal oil shale character from base to top

marls are supposed to show significant additional source rock potential, indicated by high TOC values up to 14 % (Fig. 5). However, varying TOC contents and irregular HI values of 100–350 and only rarely >600 mg HC/g TOC suggest rather a heterogeneous mixed oil to gas prone type II–III kerogen (Fig. 4). Furthermore, minor source rock potential is suggested for single samples of the Lias β by HI values >400 mg HC/g TOC and TOC of 2 %. However, its hydrocarbon generation potential is significantly lower as compared to Lias ε and Lias α.

Thickness of the Lias ε is typically in the order of 10–35 m in the central URG. Maximum values of >35 m are reached in the Langenbrücken area thinning in western and southern direction to 10–15 m (Fig. 1). Petroleum expulsion efficiencies (PEE) for the Lias ε are extraordinarily high with ca. 86 % at VR_r of 0.9 and >96 % of the generated hydrocarbons to be expelled at the end of the oil window (Rullkötter 1988; Eseme 2006).

The Dogger α (Opalinuston-Fm.) is partly considered to have source rock potential in the URG (Welte 1979), but oils originating from Dogger α claystones are not known in the URG. In general, the Dogger α contains minor to moderate quantities of OM, i.e., typically the TOC content is <3 % and the HI value does not exceed 300 mg HC/g TOC (Figs. 3, 4b; Geyer and Gwinner 2011). Thus, the Dogger α has only a minor source rock potential, which is significantly lower compared to the Lias ε and α black shales. Upper Dogger and Lower Malm stratigraphic units do not have a significant source rock potential and are typically characterized by TOC values <1 %.

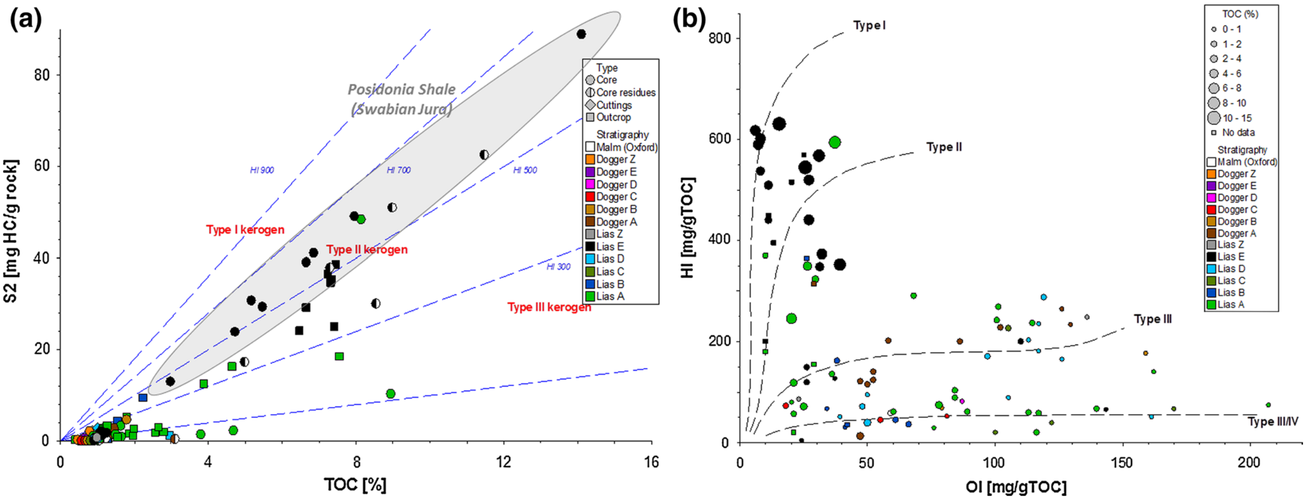

Fig. 4 Source rock characterization by **a** TOC versus S2 values and **b** HI versus OI values for Liassic and Dogger samples. High mature samples from the end of the oil window are not considered for these plots. A typical range for Posidonia Shale values from the Swabian Jura outcrops is outlined (Röhl et al. 2001; Frimmel 2003—HI ca. 581 mg HC/g TOC on average). Own data (shown in Table 2) is compared to published data including data from Radke et al. (1991), Bruss (2000), Böcker and Littke (2015) and internal reports

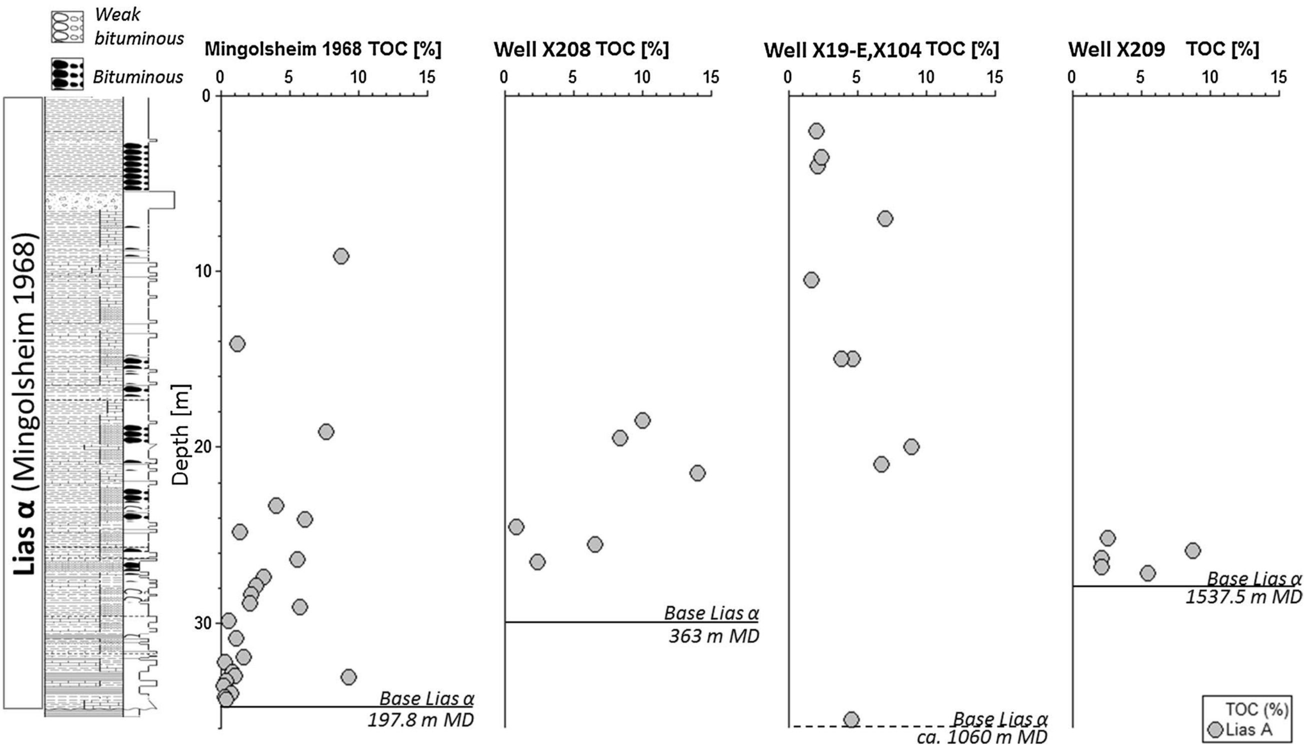

Fig. 5 Lias α TOC profiles (core samples)—bituminous zones are marked for the Mingolsheim 1968 profile (core description from Hettich 1974)

Tertiary source rocks

Early Tertiary source rocks

The early Tertiary sequence from the 'Eozäner Basiston' ('Eocene Basal Clay') up to the base of the Rupelian clays comprises several coaly layers in the Middle and Upper Eocene successions (Bouxwiller-Fm. and 'Lymnäenmergel') and Lower and Upper Pechelbronn-Schichten (PBS). These layers are potential source rocks for the occurring 'high wax oils' of oil family B (oils from Minfeld, Scheibenhardt 2 and Deidesheim; Bruss 2000). 'High

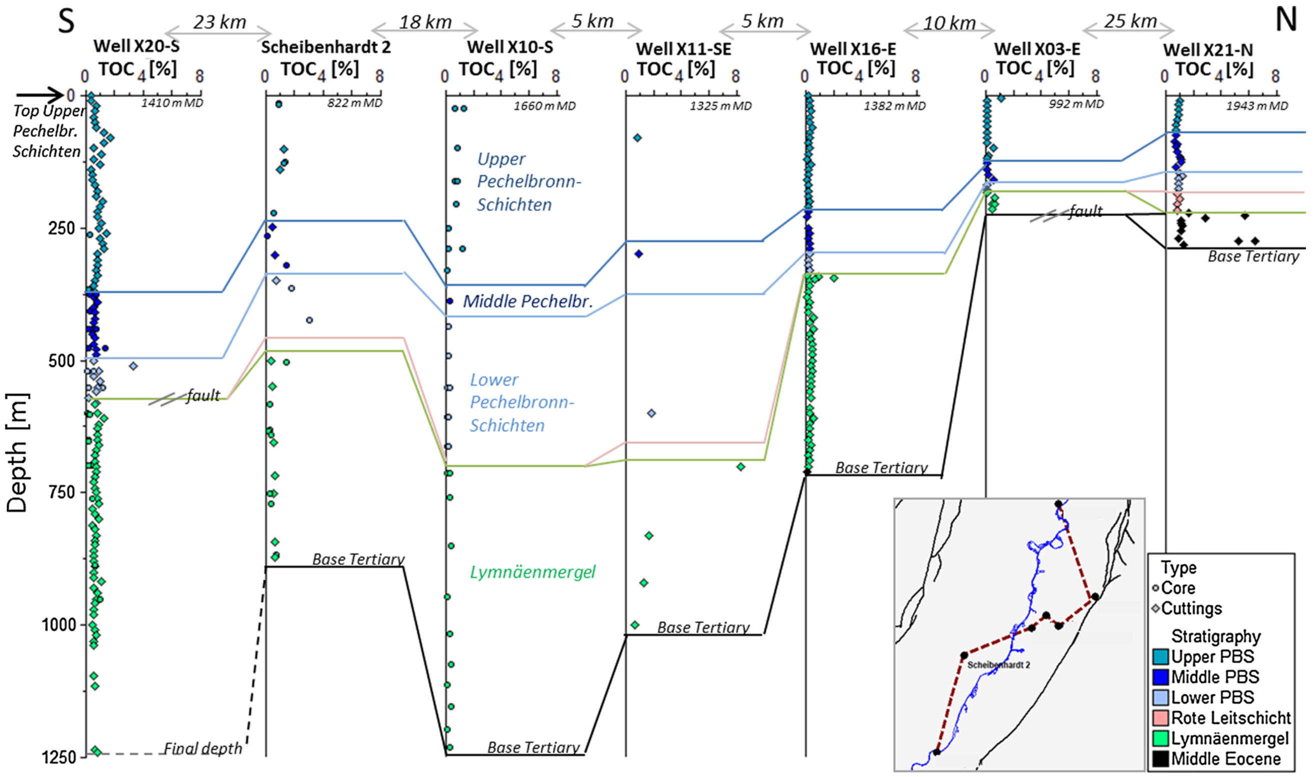

Fig. 6 TOC profiles for Pechelbronn-Schichten (PBS), 'Lymnäenmergel,' and Middle Eocene layers. Only single coaly layers in the Lymnäenmergel and Middle Eocene show source rock potential. *Remark* The marker unit 'Rote Leitschicht' is likely not always consistently identified in former well reports

wax oils' indicate terrestrial or deltaic to marginal marine depositional environments of the source rocks with high input of terrestrial land plants (Hunt 1996). For example, high wax oil from well 'Echo 6' in the northern URG was analyzed by Rückheim (1989) and he correlated it with a Lower PBS source rock. Furthermore, a significant contribution of high wax oils is known from the Hessbach and Winden oil fields as well as from the major Landau oil field (Fig. 1). The latter field is characterized by several reservoirs and mixed oils of oil family BC and BCD (Bruss 2000). Hence, oil reservoirs sourced by the oil family B source rocks exist preferentially in the western to middle part of the URG (Bruss 2000), but also in the northern URG. Bruss (2000) concluded an origin of these high wax oils in the Lower and Upper PBS, although high-quality source rock layers are not known in these units in the central URG (e.g., Welte 1979). Thus, the question where oils of family B are derived from still remains to be answered.

An overview profile of TOC records between the Eocene Basal Clay and the Rupelian clays from S to N is shown in Fig. 6. It suggests that major parts of the PBS and 'Lymnäenmergel' do not have any significant source rock potential due to low TOC values typically <1 %. As an exception, a minor coal layer situated near the top of the 'Lymnäenmergel' in well X11-SE shows a remarkable higher TOC content. However, this coaly layer does not show a uniform facies and lateral distribution. Furthermore, in well X21-N (in the vicinity of the city of Speyer) Middle Eocene (Middle Lutetian) layers occur with at least two coaly beds at the base and the top of this formation showing high TOC contents >5 % (5 m cuttings interval). In Fig. 6 also the progressive thinning of the early Tertiary sequence in northern direction is obvious.

Figure 7 shows TOC and Rock–Eval results of all early Tertiary samples (up to the Rupelian clays) in the central and northern URG. The Eocene Basal Clay, the 'Rote Leitschicht' ('red layers'), and the marine Middle PBS do not have any significant source rock potential or only very marginal potential (cf. Fig. 3). Highest source rock potential occurs in sapropelic coals of Middle Eocene Age (symbols shown with black filling, Fig. 6; equivalents to the Bouxwiller-Fm.). The coal layers correspond to basal Tertiary sediments that were deposited in terrestrial to limnic environments succeeding the 'Eocene Basal Clay.' Geochemical data characterizing the source rock potential of the Bouxwiller-Fm. is rare, although lignite seams and sapropelic coals are known from Lobsann (at Pechelbronn) or the reference outcrop at Bouxwiller for a long

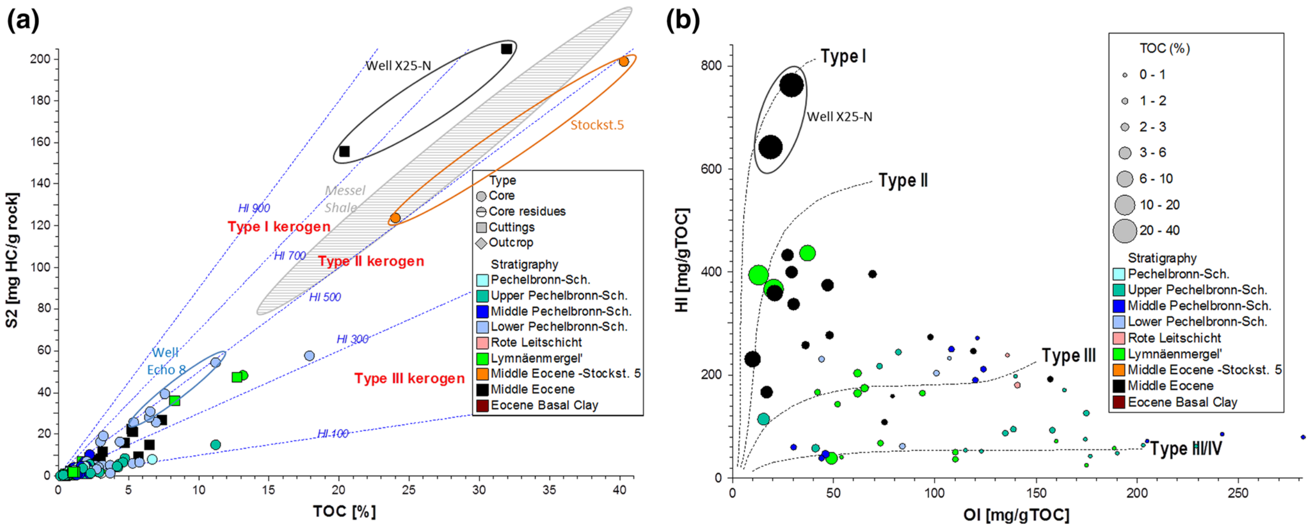

Fig. 7 **a** TOC versus S2 values of early Tertiary source rocks and **b** HI versus OI (Pseudo-van Krevelen) diagram. Own data (shown in Table 2) are compared to published data including data from Rückheim (1989), Radke et al. (1991) and internal reports; Messel shale data by Welte (1997; TOC 28.3 ± 6.1 %, HI 553 ± 43 mg HC/g TOC) and Bauersachs et al. (2014)

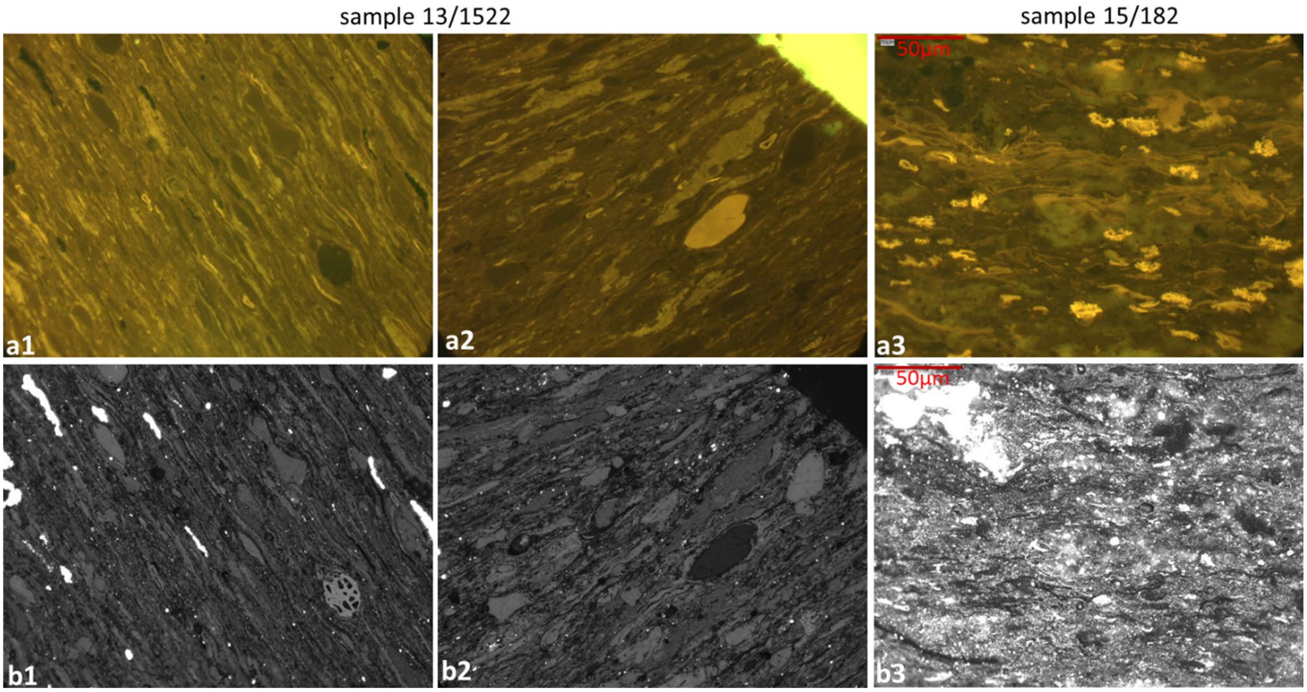

Fig. 8 Microscopic analyses of the OM in the Middle Eocene source rocks. **a** Incident light fluorescence mode; **b** reflected white light (each picture cut from 300 × 200 µm). **a1**, **a2**, **b1**, **b2**): small dark vitrinite in a liptinitic ground mass with sporinite. Most vitrinites are elongated and structureless with resinitic impregnation. **a3**, **b3** High quantities of sporinite in a liptinit groundmass with small structureless vitrinite

time (e.g., Sittler 1985). Here, hydrogen- and sulfur-rich lignites of about 2.2 m thickness occur with a TOC content of 44–50 % (Ménillet et al. 1979). Sediments of contemporaneous age show very heterogeneous source rock parameters and thicknesses. They do not occur in the entire graben, although Middle Eocene sediments are known even from the southwestern Mainz Basin in the North (Fig. 1; Schäfer 2012:21). Unfortunately, only cuttings of this unit are available. At well X25-N (close to Speyer) a 10-m interval (2 × 5 m cuttings) of these coaly layers shows extraordinary high hydrocarbon generation potential by TOC values of 20–32 %, and S2 values of 156–205 mg HC/g rock referring to HI values of 642–762 mg HC/g TOC (cf. Table 2; 13/1522–23). VR_r of 0.60 % and T_{max} values of 442–443 °C indicate an early oil window maturity for these sapropelic coals or coaly shales.

These sapropelic Middle Eocene coaly samples (e.g., 13/1522, Table 2) are characterized by abundant small, dark and structureless vitrinites (detrovitrinites), which show often a degraded appearance and a brownish fluorescence (Fig. 8). Large wood particles are missing, but elongated gelified vitrinites occur supporting the indication of putrefaction. Liptinite occurs in great quantity dominated by liptodetrinite, sporinite and waxy, structureless macerals. Distinct large telalginite is not present. Thus, the distinct lamination and dominance of dark detrovitrinites and detroliptinites indicates a suboxic to anaerobic paralic swamp environment. Other samples of this stratigraphic unit show an oxic depositional environment with type III kerogens and lower HI values (Fig. 7).

In parts, samples of these Middle Eocene coaly layers are highly enriched in sporinite. A sample from well X29-N showed conspicuous miospores (probably pollen) reaching lengths of 12–15 µm (Fig. 8a3, b3). The surface of the exine is densely covered by club-shaped elements (clavae), typically about 1.5 µm high and with a diameter of <1 µm at the apex. The pollen may be most probably assigned to the dispersed miospore genus *Ilexpollenites,* but other genera cannot be excluded as no palynological preparations were available of this sample.

Kinetic investigations of the sapropelic coals from well X25-N showed a narrow distribution of activation energies indicating homogenous oil-prone organic matter (Fig. 9a). A sapropelic coal sample from the top part of the 'Lymnäenmergel' (border to Lower PBS) from well X111 shows also a narrow distribution of activation energies which indicates similar oil-prone organic matter for these coaly beds. The relatively low activation energies indicate a significant oil generation at low maturity levels as compared to typical type II kerogens of the Posidonia Shale or Fish Shale (Fig. 9b). The sulfur content is moderate to high (1.6–1.7 %) in these Eocene samples as compared to other coals and may indicate an influence of marine ingressions in the swamp or marsh environments.

A lateral consistency of the investigated coaly layers is not given, however. At the uppermost part of the 'Lymnäenmergel' a coaly layer is also known from well X11-SE (Fig. 6) as well as from a prominent outcrop at Rot-Malsch (Fig. 1), where a very thin lignite seam marks the border between the 'Lynmäenmergel' to the Lower PBS (Barth 1970).

Rock–Eval data of the coaly shale from the 'Lymnäenmergel' indicate hydrogen-rich type III kerogen, whereas the sapropelic coals from well X25-N shows hydrogen-rich organic matter similar to waxes or type I kerogens (Fig. 7).

The high hydrocarbon generation potential of the sapropelic coal samples is obvious from Fig. 9c, which is even higher than that of the Posidonia Shale. However, for the Posidonia Shale higher S1 + S2 values than these published by Bruss (2000; 63 mg/g) are known, e.g., from the Swabian Alb (e.g., Frimmel 2003; Röhl and Schmid-Röhl 2005). But, the Eocene coals are of limited extent and thickness in contrast to the Posidonia Shale that extends over a large area as an excellent petroleum source rock of significant thickness (Song et al. 2015).

Nevertheless, the oldest Tertiary source rocks in the URG correspond to sapropelic coals and coaly shales of the early rift sediments from the Middle Eocene (Bouxwiller-Fm.), top part of the 'Lymnäenmergel' and Lower PBS. Geochemical data (e.g., Pr/Phy values, Table 3) indicate typical oil family B source rocks (high wax oils). These source rock layers correspond to relatively thin coaly shales (ca. 5–15 m) showing partly high TOC contents (>15 %) and high wax contents due to increased input of terrestrial land plants characterized by terrigenous type II–III kerogen and partly oil-prone sapropelic coals.

Oil shales from well Stockstadt 5

At well Stockstadt 5 in the northern URG (Fig. 1) a 64-m-thick Middle Eocene succession occurs representing the earliest Tertiary sediments with about 14-m-thick oil shales at the top (Straub 1955). These sediments are considered as local maar lake deposit and local Messel Shale equivalent (Straub 1955; Hillebrand and Leythaeuser 1992), but are of significantly younger Eocene (Late Middle to Upper Eocene) age than the famous lower Lutetian Messel Shale (ca. 47.8 Ma; Nix 2003—unpublished biostratigraphic investigations; Lutz et al. 2013). The Middle Lutetian Bouxwiller-Fm. is also younger than the Messel Shale and has thus roughly the same age as the oil shales from well Stockstadt 5. The origin of these sediments at Stockstadt 5 is still disputed (Grimm et al. 2011), but Lutz et al. (2013) suggest a maar-diatreme volcano and corresponding maar lake deposits. These Middle Eocene oil shales have been analyzed by Rückheim (1989) and Hillebrand and Leythaeuser (1992) who report TOC values of 12–40 % and HI values of 493–673 mg HC/g TOC (Fig. 7). These Eocene layers display excellent source rock properties, but are locally restricted.

Due to the suggested maar lake origin of the Stockstadt 5 oil shales the indicated type II kerogen from Fig. 7a cannot correspond to anoxic marine organic matter. Instead a mixture of type III and I kerogen is likely due to a lacustrine depositional setting surrounded by swamps and forests. A similar mixture is also known

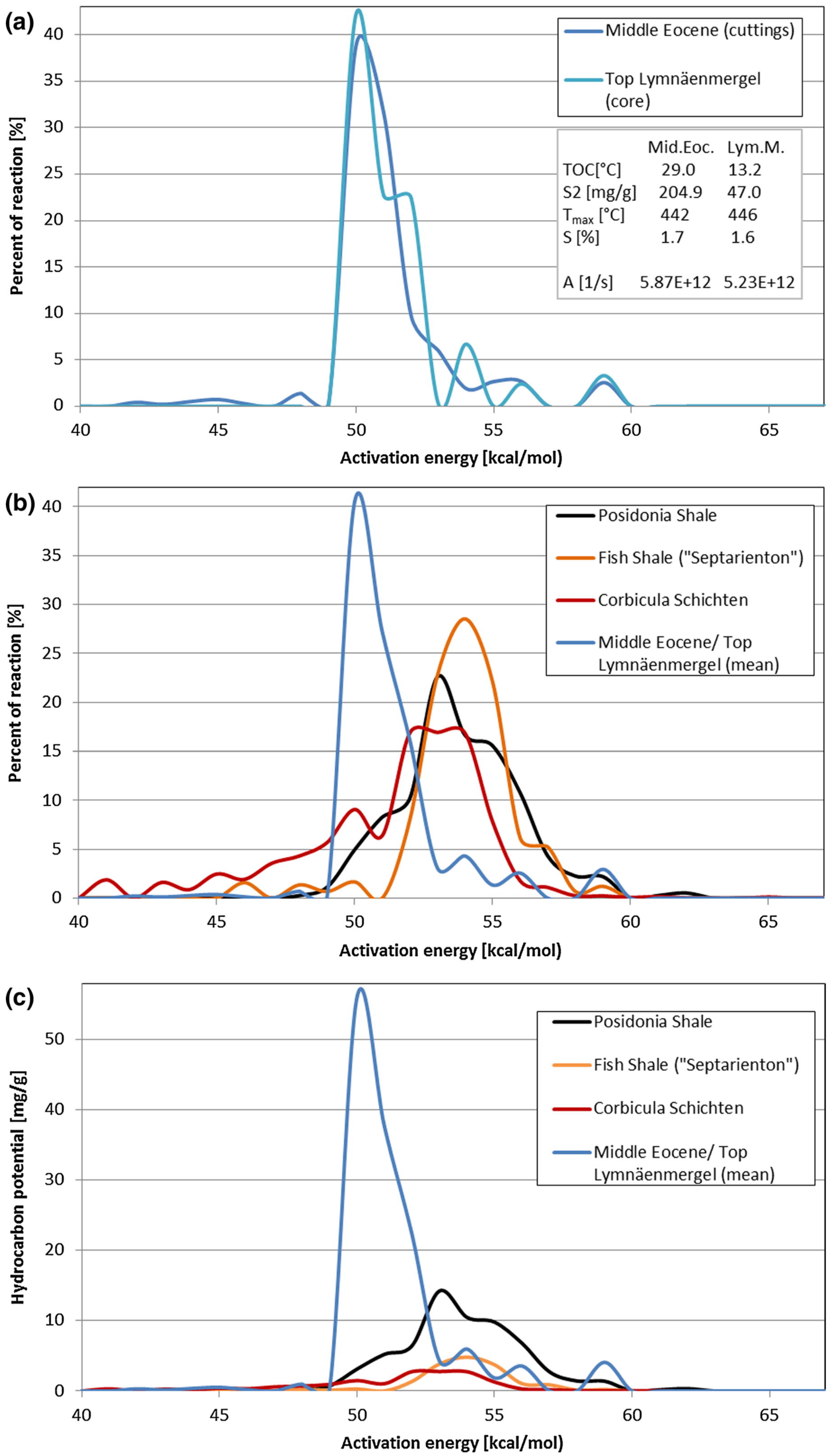

Fig. 9 **a** Bulk kinetics of Eocene samples (Middle Eocene equivalents to the Bouxwiller-Fm., 13/1522; Lymnäenmergel, 14/889); The frequency factor A, TOC content, S2 and T_{max} value, and the sulfur content are noted. **b** Comparison of bulk kinetics (%) and **c** comparison of the hydrocarbon potential versus activation energy of the Eocene samples, Posidonia Shale (Lias ε), Fish Shale (‘Septarienton’) and Corbicula-Sch. (modified after Bruss 2000); *Remark* for the hydrocarbon potential (S1 + S2) a mean value of the two Eocene sample was used ([223.6 mg/g + 52.9 mg/g]/2 = 138.3 mg HC/g rock); for the Posidonia Shale a value of 63 mg HC/g rock as published by Bruss (2000) was used. However, considerably higher values for this unit are known

for the Messel Shale showing typically about 80 % of type I kerogen and 20 % of type III kerogen (Littke et al. 1997). These lake deposits are not able to generate large amounts of oil due to their limited extent and low maturity (0.33–0.39 % VR$_r$, T_{max} 431–437 °C, 20S/(20S + 20R) steranes: 0.17; Rückheim 1989; Hillebrand

and Leythaeuser 1992 at 1715 m depth at well Stockstadt 5). Nevertheless, they can be considered as local variety of oil family B source rocks. The respective Middle Eocene bog, swamp and lake deposits were heterogeneously distributed and later discordantly covered by the first marine ingression from the southern URG.

Fish Shale

The Rupelian Fish Shale is characterized by TOC contents of typically 3–5 %, HI values of 400–550 mg HC/g TOC and type II kerogen (Böcker and Littke 2014). For the southern URG also TOC values up to 8 % and S2 values of 35 mg/g are reported (Langford and Blanc-Valleron 1990) indicating a good to excellent source rock potential. However, a low maturity and thickness of the Fish Shale (typically 10 m, maximal ca. 30 m) has to be considered. A detailed source rock characterization of the Fish Shale is given by Böcker and Littke (2014).

Oils generated by the ‘Rupelian Clays’ (oil family D), especially by the Fish Shale (Bodenheim Fm./Hochberg-Subfm.), show typical marine characteristics, but with an input of land plants (Bruss 2000; Böcker and Littke 2014). A marine-suboxic depositional environment characterizes these oils, which show much similarity to Liassic oil family C (Bruss 2000). Unique characteristic of these oils is the occurrence of the highly branched isoprenoid (HBI) C_{25} originating from diatoms (Böcker and Littke 2014).

Corbicula- and Lower Hydrobienschichten

The Corbicula- and Hydrobienschichten are assumed to have a moderate source rock potential due to TOC values of 0.6–5 % and varying HI values (100–585 mg HC/g TOC) indicating mixed kerogen types of primary type IIS and subordinate type III (Bruss 2000; Lampe and Schwark 2012). Maximum TOC content of the Corbicula- and Hydrobienschichten is in the order of 5–6 % (Welte 1979; Lampe and Schwark 2012). The thickness and facies of the source rocks layers within these beds is assumed to be quite heterogeneous due to a high segmentation of the basin during the deposition of these beds (cf. Bruss 2000).

Early mature, sulfur-rich oils of oil family A are assumed to be derived from the Corbicula- and Lower Hydrobienschichten representing an anoxic-evaporitic-salinar facies (Bruss 2000). These oils show also a minor influence of terrigenous organic matter (Bruss 2000). High sulfur contents (up to 2.9 %), low API gravities (18°API) as well as dominant even numbered n-alkanes and low pristane/phytane ratios (<0.4) are characteristic (Bruss 2000).

Results and discussion

Oil families in the URG

Oil–oil correlation by gas chromatographic parameters

Results of gas chromatographic analyses of the saturated hydrocarbon fraction are summarized in Table 3 providing important data regarding the origin of crude oils in the URG. Bruss (2000) differentiated four groups of crude oils with characteristic n-alkane distributions. Several additional oils analyzed here fit these groups and have been added to these four oil families (Fig. 10). In addition, a group of crude oils exists representing mixtures which do not fit to these oil families (not shown in Fig. 10).

Eye-catching is the unique n-alkane distribution of oil family B (high wax oils) revealing high proportions of high molecular weight n-alkanes (nC_{27}, nC_{29}, nC_{31}) that are typically originating from terrestrial higher-plant epicuticular waxes (Eglinton and Hamilton 1963, 1967; Hedberg 1968). Bruss (2000) determined also slightly dominant odd numbered long-chain n-alkanes (nC_{25} to nC_{35}). Oil from well Rülzheim 1 (Meletta-Schichten reservoir; Table 4) analyzed by Gamintchi (1979) clearly matches the oils from this family and was added to this group, e.g., Minfeld oil field, well Scheibenhardt 2, and Deidesheim.

The n-alkane distributions of oil family A show a pattern with an even–odd-predominance of n-alkanes and a slightly bimodal distribution with a maximum between nC_{22}–nC_{30}. This pattern characterizes early mature oils generated by carbonatic to evaporitic-salinar source rocks (Welte and Waples 1973; Hollerbach 1985; Bruss 2000). A residual oil sample from the Hydrobienschichten from well ‘Alpha 4’ (located close to the city of Worms; Fig. 1) analyzed by Rückheim (1989) shows clearly such a GC pattern of oil family A (Fig. 10) and should be attributed to the Corbicula- and Hydrobienschichten source rocks. An origin of the high-paraffinic oils of the oil fields Dudenhofen, Worms and Frankenthal (location see Fig. 1) from the Corbicula- and Hydrobienschichten was already suggested by Schad (1962a).

Oils of oil family C show a similar pattern compared to oil family D, but most oils of family C show slightly increased quantities of shorter n-alkanes and lower quantities of higher n-alkanes when compared to family D. Both oil families C and D are derived from marine algae and phytoplankton, i.e., from marine petroleum source rocks. Bruss (2000) assumed an origin of family D from the Rupelian Clays (Fish Shale) and of family C from the Liassic Posidonia Shale.

Pristane/Phytane (Pr/Phy) values separate marine-derived oils (oil families C and D), the high wax oils of

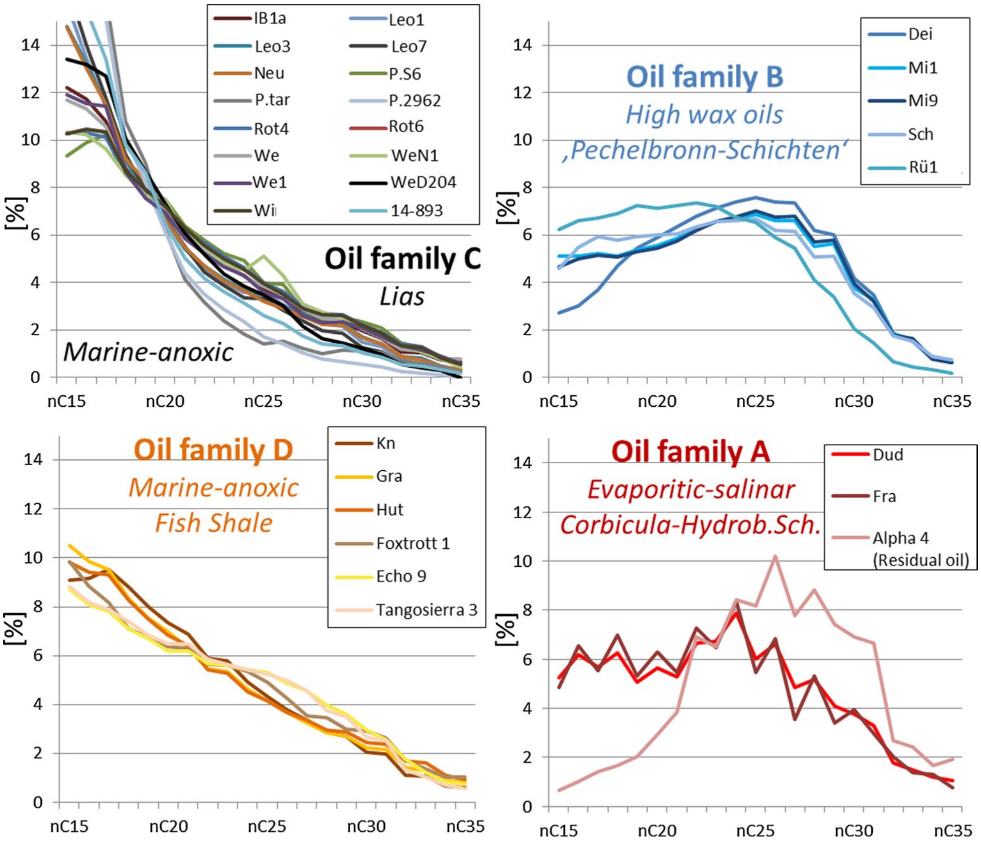

Fig. 10 Overview of normalized n-alkane distribution pattern (Sum nC_{15}–nC_{35} = 100 %) from gas chromatograms of reservoired oils in the URG. The oils are separated into the four oil families with their respective source rock: **a** Corbicula- and Hydrobienschichten; **b** Pechelbronn-Schichten-Early graben deposits; **c** Liassic black shales; **d** Fish Shale (Modified after Bruss 2000; 18 GC traces from Bruss 2000; 4 traces by Rückheim 1989; 1 trace by Gamintchi 1979; and 7 own samples). Mixed oils as for example Landau or Hessbach oils are not shown (Leopoldshafen oils are major Liassic oils with a very minor admixture of Fish Shale oil). Minor differences in *n*-alkane distribution might correspond to different GC equipment, heating rates, etc.

oil family B with increased terrestrial land plant input, and the evaporitic-salinar oils from oil family A. Oil family A oils show very low Pr/Phy values of 0.2–0.4, and the high wax oils very high Pr/Phy values of >3–3.5. In contrast, the marine Liassic oils show typically values of 1.4–1.8 (partly 2.2—Leopoldshafen 3) and the Fish Shale oils similar values of predominantly 1.5–1.7, but partly 2.4–2.5 (Offenbach 1 and Rülzheim 2 oils; cf. Bruss 2000; Rückheim 1989).

As a result, Pr/Phy values can give an indication about the oil family. For example, three oils from the Hydrobienschichten and Corbicula-Schichten analyzed by Hollerbach (1980b) with Pr/Phy values of 0.1–0.4 clearly correlate with oil family A. Other examples are oils published by Richard (1994) from oil field Scheibenhard showing a Pr/Phy value of 3.4 and the oil sample Maxm2 showing a Pr/Phy value of 3.0 which clearly correspond to oil family B.

These differences can also be seen in Pr/nC_{17} versus Phy/nC_{18} values (Fig. 11). A clear separation of oil family A and B is visible compared to marine-derived oils of oil family C and D is visible. Family D oils plot slightly above oil family C oils, which indicate an increased terrestrial input in the Fish Shale compared to the Liassic black shales. Moreover, two oils of oil family D (Offenbach 1, Rülzheim 2) do not fit the trend of Knielingen, Huttenheim, Graben and 'Echo-T.' oils (Fig. 11; Table 4). An increased terrestrial input for these two oils (Offenbach 1, Rülzheim 2) compared to the other Fish Shale oils is indicated. Moreover, these oils do not show the typical n-alkane distribution of oil family D and have been grouped to mixed oils with bimodal distributions. Bruss (2000) concluded an oil family D origin (Fish Shale) based on hopane and sterane investigations.

Furthermore, an increased level of maturity is indicated by rather low Pr/nC_{17} versus Phy/nC_{18} values for several Liassic oils compared to Fish Shale oils (e.g., IB1a, P.2962). However, Pr/nC_{17} versus Phy/nC_{18} values of the oils AB2 and IT1b, analyzed by Bruss (2000), indicate a lower maturity level of these Liassic oils located at the very eastern graben shoulder compared to other Liassic oils.

Oil–oil correlation by carbon-isotopic composition

One of the most useful parameters for oil–oil correlations in the URG is the stable carbon-isotopic composition of the saturated versus the aromatic hydrocarbon fraction (Fig. 12). Next to a source-related separation of crude oils into groups originating from terrigenous and marine sources (Sofer 1984), also age-related differences in the isotopic composition occur. A clear isotopic difference between Liassic-derived oils and Tertiary-derived oils is observed in crude oils from the URG (Bruss 2000). Purely

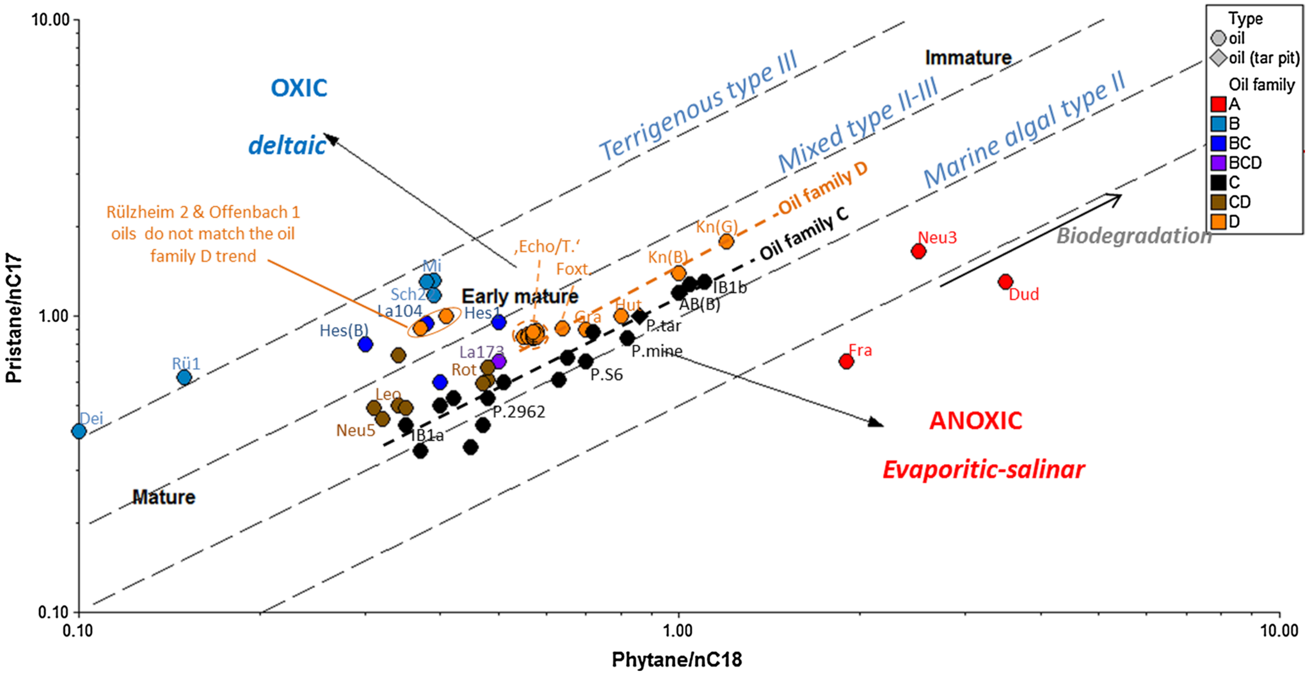

Fig. 11 Pristane/nC_{17} versus Phytane/nC_{18} diagram; arrows indicate the depositional environment, exposure to oxygen and direction of increasing biodegradation. For abbreviations see Table 3

Tertiary-derived oils are characterized by significantly heavier δ^{13}C-isotopic signatures as compared to Liassic-derived oils as well as mixed Liassic and Tertiary oils. This heavier isotopic composition reflects an increased quantity of terrestrial contributions in the oils as well as an increased diversity of land plants present during the Tertiary. The Tertiary oils show also an increased input of terrigenous organic matter. This is deduced from for the high wax content of oil family B, as well as high concentrations of the biomarker oleanane (indicative for angiosperms) in the oils generated by the Fish Shale (Böcker and Littke 2014). The Sofer (1984) reference lines for terrigenous and marine oils indicate an increased input of terrigenous organic matter, especially for the high wax oils of oil family B as well as mixed oils such as Hessbach and Winden. Liassic oils typically plot in the marine area, but other marine oils generated by the Fish Shale (Hut, Gra) do not plot in the typical area for marine oils suggested by Sofer (1984).

A further aspect that influences the carbon-isotopic composition is the provenance of organic matter (Peters et al. 2005a). Source rock alterations as well as thermal maturation effects and secondary processes (e.g., migration and biodegradation) can cause variations in the compound class distributions of related oils and thus in the carbon-isotopic composition by up to 2 ‰ (Sofer 1984; Peters et al. 2005a).

Four oils of oil family B (Minfeld 1, Minfeld 9, Scheibenhardt 2 and Rülzheim 1) which are regionally closely located (Fig. 1) show very similar values in their isotopic composition. Hence, a common kitchen area of these oils is suggested (Fig. 12). Based on its geochemical characteristics oil of the well Deidesheim 2 belongs also to oil family B and shows a similar maturity level (Bruss 2000); however, its isotopic composition strongly differs from the cluster of all the other family B oils shown in Fig. 12. This suggests that oil of well Deidesheim 2, which is located about 40 km to the north of the latter oils, has been generated in a different kitchen area as the other oil family B oils.

In analogy, the three samples of oil family A oils which show a similar character in their organic composition (e.g., n-alkane distributions) but their carbon-isotopic composition is considerably different (Fig. 12), indicating three different kitchen areas for these oils, which are separated about 40 km from each other.

Bulk geochemical parameters

Due to major exploration and production periods dating back to the 1930s and 1950–1960s the availability of oil samples of former URG oil fields for new geochemical investigations is rather limited nowadays. Hence, parameters of former analyses can be considered instead to achieve information about the potential source rocks of these abandoned oil fields.

Typical parameters that were routinely determined in the past include API gravity, sulfur and paraffin content, setting

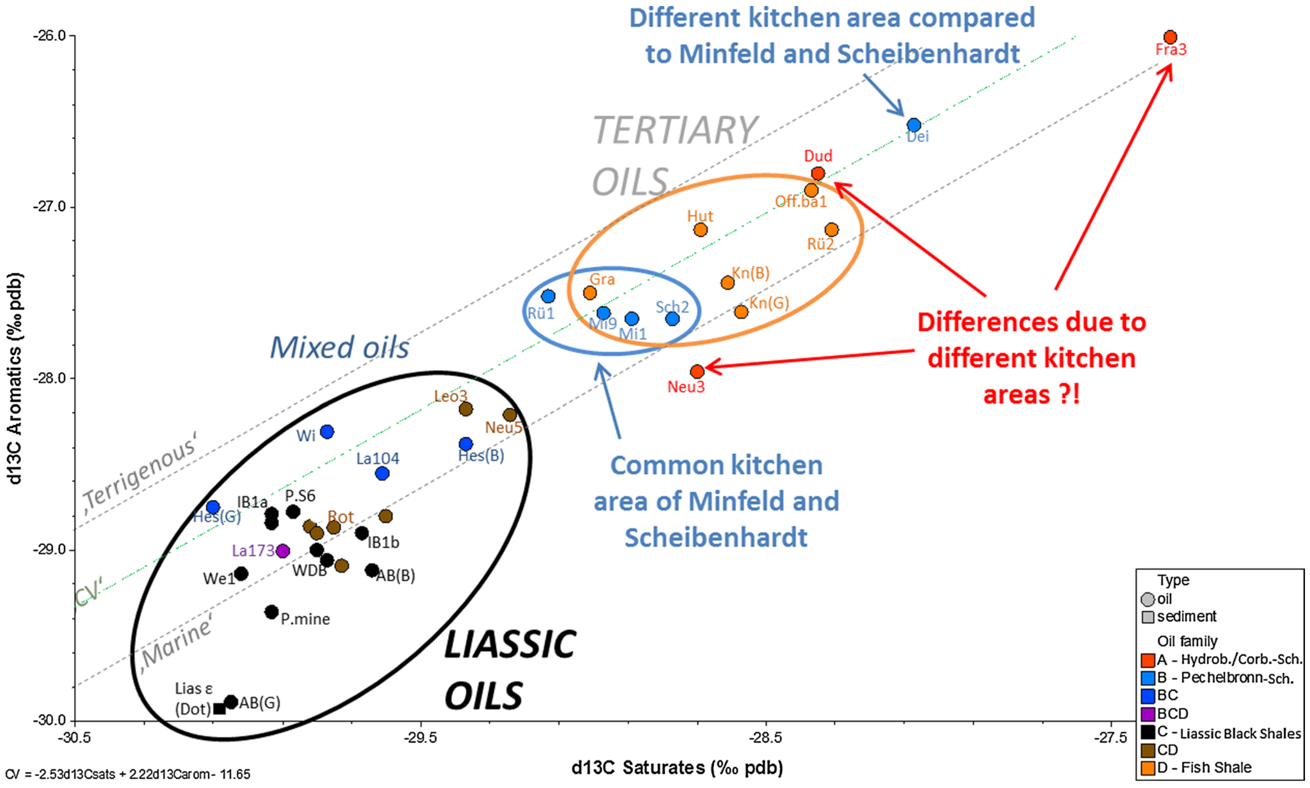

Fig. 12 Carbon-isotopic composition of saturated and aromatic hydrocarbon fractions of crude oils in the URG ('Sofer plot'). Summary of isotopic analyses by Gamintchi (1979), Bruss (2000) and internal studies. Sample Lias ε (Dot) is an extract from the Lias ε quarry at Dotternhausen analyzed by Gamintchi (1979). For abbreviations see Table 4. *Remark* The statistical Canonical Variable (CV) by Sofer (1984) was created for *n*-alkanes > $n\text{C}_{15}$ whereas Bruss (2000) and Gamintchi (1979) used the entire saturated fraction

point (pour point) and viscosity. These bulk parameters can still give valuable information about the type of crude oil as well as the oil family. For example, high wax oils (oil family B) contain a very high quantity of higher n-alkanes (paraffins), which originated from terrestrial land plants (Hedberg 1968). A high paraffin (higher n-alkanes) content results in highly viscous oil and a significantly higher setting point (nowadays the pour point is used—the pour point is roughly setting point + 3 °C; Feßmann and Orth 2002) when compared to typical high-quality marine oils (e.g., non-altered Posidonia Shale oils of oil family C). Typical examples are the high wax oil family B oils from Deidesheim and Minfeld, which show very high setting points of 37 °C and 28–33 °C (Veit 1962; Bruss 2000). Solidification below this temperature of the setting (or pour) point is usually attributed to precipitation of waxes from the parent oil (Peters et al. 2005a).

The setting point appears to be a very useful tool to differentiate oil families. Typically, non-biodegraded pure Liassic oils show very low setting points of <0 °C, whereas purely Tertiary oils of oil families A, B as well as D show higher values of >10 °C for (Fig. 13). However, this parameter has to be used with caution because secondary alteration of crude oils can cause significant changes in the setting point; e.g., Pechelbronn oils, which are affected by biodegradation, show a wide range in setting points. Another highly indicative parameter with respect to oil–source rock correlations is the sulfur content. Bruss (2000) showed that oil family A has by far the highest sulfur content of the four oil families in the URG.

In order to achieve new oil–source rock correlations, first all oils with known oil–source rock correlation were analyzed and subsequently oils without a known source rock were compared to the existing bulk geochemical parameters data set. As an example, in 1952 highly viscous heavy oil was 'produced' from well Wolfskehlen 4 (only 580 l plus 3600 l oil 'foam') from the Hydrobienschichten (sample Wol4 in Fig. 13; sulfur 10.3 %, API 9°, setting point 16 °C—LBEG 1952). Similar highly viscous heavy oil has been produced from the Hydrobienschichten reservoirs in the well Darmstadt 2a (API 11°, setting point +29 °C; 846–925 m depth; LBEG 1954) and from well Stockstadt 135 (API 14°; LBEG 1960), again in the Hydrobienschichten. These oils with the given low API gravities clearly show an oil family A character and would be very unusual for oil family B, C or D oils. Another heavy

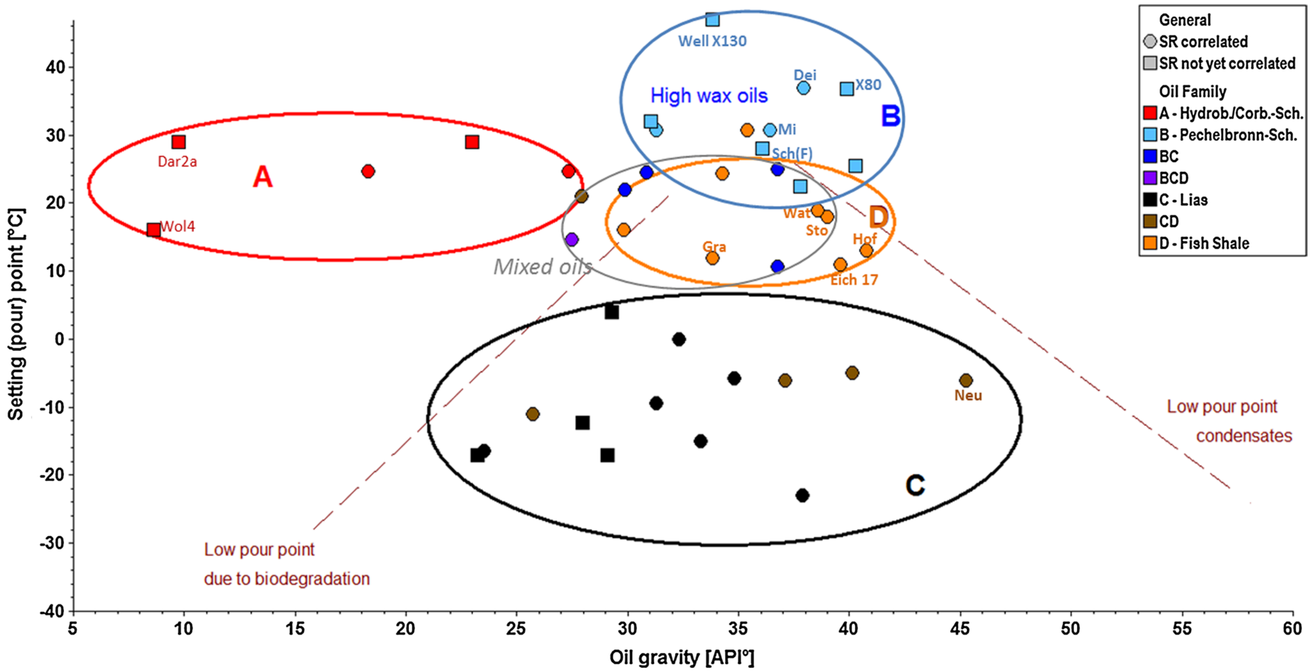

Fig. 13 API gravity versus setting/pour point for produced oils from the URG. Mean values for each oil field are displayed. *Round symbols* show oils where the source rock (SR) has already been identified by GC and GC–MS analyses. *Squared boxes* show oil samples where only former field data (bulk parameters) are available, and a source rock has not yet been correlated. Data partly from LBEG (Landesamt für Bergbau, Energie und Geologie, Hannover) yearly reports

oil sample of well X71 stems from the Corbicula-Schichten and shows an unusual high paraffin content of 33 % (Fig. 14), thus revealing a different character than other oil family A oils. However, the sulfur content and an API gravity of 23° of the X71 oil sample clearly correlate with oil family A.

Very viscous high wax oils show typically the highest setting points in the URG and have been produced in the central and northern URG; e.g., well Eich 17 produced oil with a setting point of 52 °C from basal Tertiary reservoirs (LBEG 1959). Several oil samples that were produced from the PBS in field X80 have a paraffin content of about 28–35 %, are low in sulfur and show a setting point of about 30–43 °C. They can clearly be correlated with the high wax oils of oil family B (Figs. 13, 14). The same can be assumed for oil with a setting point of 47 °C produced from base Tertiary/Top Rotliegend sandstones in well X130.

API gravity can also be used to achieve valid information about the oil family, but should be used in combination with other parameters because of maturity, migration, biodegradation and source-related dependencies (Peters et al. 2005a). The oil with the highest API gravity of about 45° was produced from oil field Neureut (LBEG 1959; Fig. 13). This light oil has a major Liassic origin but also Fish Shale admixtures (Bruss 2000) and probably indicates an increased maturity level in the area of Karlsruhe (so-called Rastatt Trough, Fig. 1). This is supported by low Pr/nC_{17} versus Phy/nC_{18} values indicating an increased maturity level (Fig. 11).

Exemplary oil–source rock correlations

Oil–source rock correlation can be performed in several ways. For example, GC–MS analyses obtain highly specific source and age-related biomarkers, which have been used intensively for oil–source rock correlations in the URG by Rückheim (1989), Hillebrand and Leythaeuser (1992) and Bruss (2000), who achieved major source rock correlations for numerous oils. A short synopsis of previous work supplemented by new data and information is given in the following.

- The Posidonia Shale (Lias ε) as excellent source rock has been considered as source rock of oil family C oils (Bruss 2000). This is obvious from distributions of steranes which show a nearly identical pattern, e.g., Weingarten oil and an extract of the Lias ε (Fig. 15a). Particularly, when comparing these sterane traces to extracts of Tertiary source rocks (e.g., Fish Shale, PBS—see Böcker and Littke 2014) the correlation is striking. However, further Liassic rocks have also a significant source rock potential, especially the Lias α (Fig. 3). Sterane distributions show a nearly identical pattern for

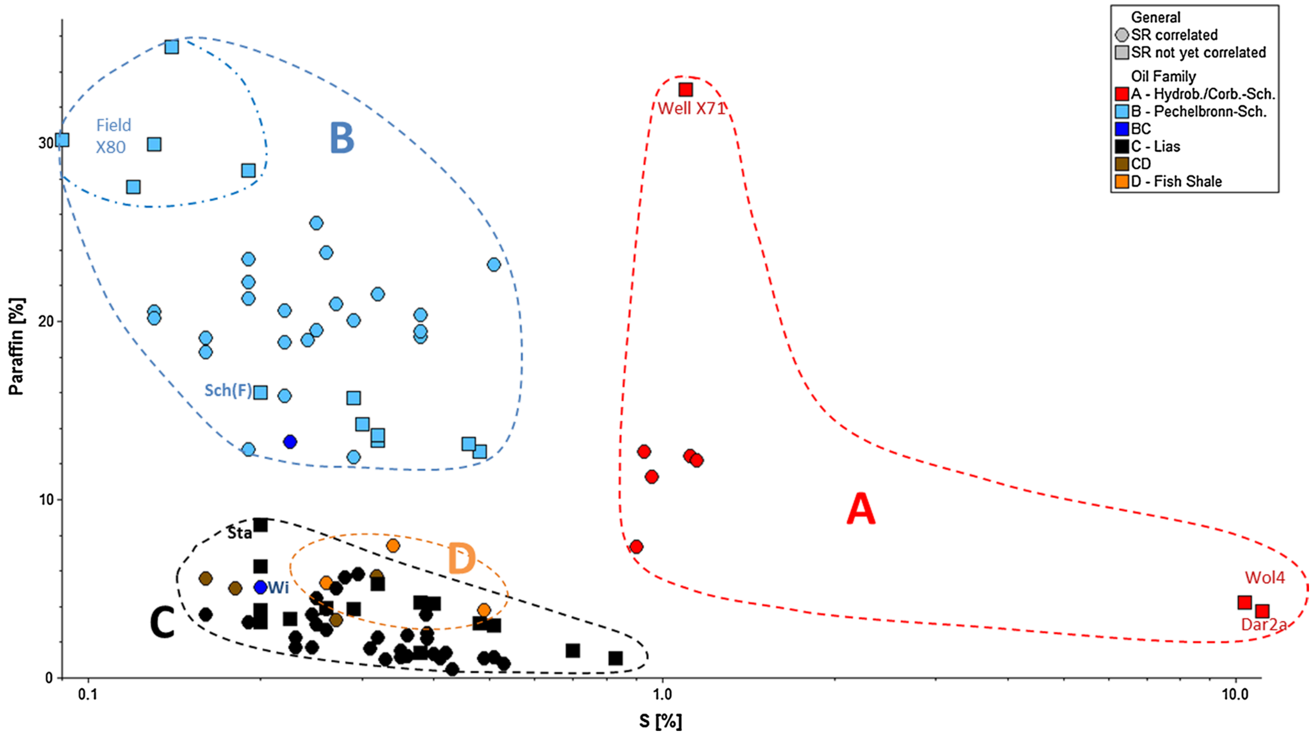

Fig. 14 Sulfur versus paraffin content of oil samples from the URG. Sulfur content on logarithmic scale, paraffin content on linear scale. *Round symbols* show oils where the source rock (SR) has already been identified by GC and GC–MS analyses. *Squared boxes* show oil samples where only former field data (bulk parameters) are available. Data partly from LBEG yearly reports

an oil of family C (Leopoldshafen oil—showing also very minor admixtures of ca. 5 % of Fish Shale oil, determined by, e.g., very little quantities of the HBI C_{25} (see below)) and a Lias α source rock extract (Fig. 15). From a geochemical point of view there is no major difference in the composition of steranes and hopanes (not shown) which would allow a further differentiation of Lias ε and Lias α oils. Hence, it is suggested that the Lias α is also co-generating oils of oil family C.

- Oleanane is a very useful age-related biomarker. Due to its origin from angiosperms (e.g., Peters et al. 2005b) it allows to differentiate between Liassic and Tertiary oils in the URG. Concentrations of oleanane testify undoubtedly a Tertiary origin of the oil or admixtures from Tertiary source rocks (Fig. 16a; cf. Bruss 2000).
- In some oils a highly branched isoprenoid (HBI) C_{25} (2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecan) is occurring which originates from diatoms (Bruss 2000; Summons et al. 1993). Major HBI C_{25} occurrences are known from the Fish Shale (Bruss 2000; Böcker and Littke 2014), but also the salinar Corbicula-Schichten show concentrations of this molecule (Waples et al. 1974). Bruss (2000) used the HBI C_{25} as diagnostic indicator for oil family D oil (Fish Shale). Oil family A oils (with origin in the Corbicula-Schichten and Hydrobienschichten) showed no HBI C_{25} occurrences, although this molecule has been detected in these source rocks (Bruss 2000). Therefore, the HBI C_{25} is used as unique marker for Fish Shale oil (or admixtures; Fig. 16b) but should be used in combination with other characterizing parameters, e.g., Pr/Phy or OEP values.

Overview and distribution of oil families

All in all, four distinct oil families can be differentiated and correlated with their source rocks (Table 1). An overview of the regional distribution of the oil families in the central and northern URG is given in Fig. 17 (the four oil families are marked by different colors; reservoirs with mixed oil families are shown with the subordinate oil family as colored cross). The map reveals lateral migration of oil stemming from the Liassic black shales (oil family C) toward the eastern (e.g., Weingarten oil field) and western margin (e.g., Pechelbronn). The reservoirs at Pechelbronn have been charged by Liassic source rocks, as shown in several studies (Gerling et al. 1988; Blümel et al. 1989; Richard 1994; Bruss 2000; this study). Furthermore, long-distance migration of Liassic oil occurs in the central segment of the URG in areas where the Liassic source rocks are already eroded (regions north of the doted in, e.g., Landau, Römerberg).

Nearly all reservoirs in the Alsace area are sourced by Liassic source rocks (cf. Richard 1994). There, only the

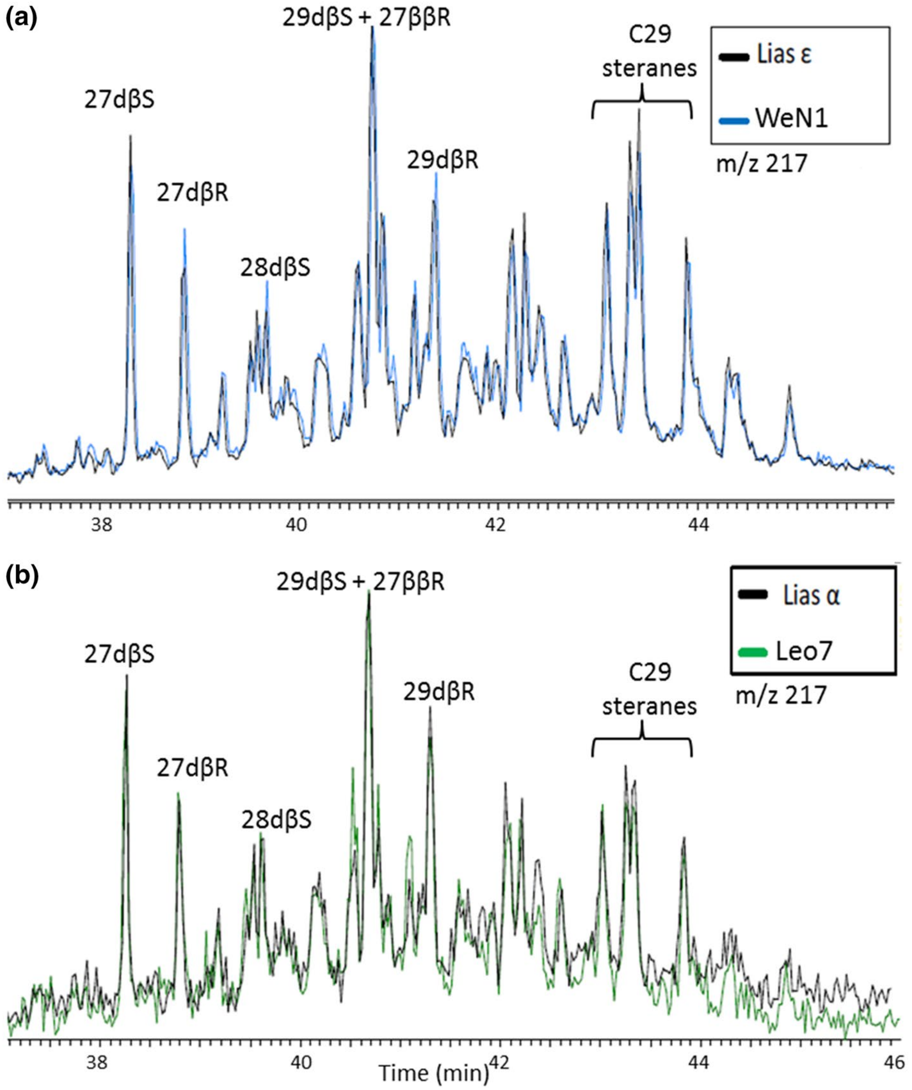

Fig. 15 **a** Lias ε (11/466; TOC 7. 4 %, HI 482 mg HC/g TOC, T_{max} 429 °C, VR_r 0.62 %) steranes compared to those of Weingarten oil and **b** Lias α (11/451: 8.9 % TOC, HI 115 mg HC/g rock, T_{max} 431 °C, VR_r 0.8 %) steranes compared to those of a Leopoldshafen oil. Generic peaks are identified for orientation

reservoirs Scheibenhard and Schelmenberg have a Tertiary (oil family B) origin. The lack of oils generated by oil family B source rocks at the eastern rim and in the southern URG indicates poor hydrocarbon generation potential of these source rocks in the eastern and southern part of the graben (cf. Fig. 11; TOC typically <1 %). Oils of family D as Huttenheim, Graben or Rot deduce an oil-mature Fish Shale source rock in this eastern area. Therefore, a poor quality of oil family B source rocks has to be considered as major reason for missing family B oils at the eastern rim.

Oils generated by the Rupelian Fish Shale (oil family D) occur especially in the central URG, but also in the northern URG. In the latter region, oil is predominantly produced from the PBS (especially Upper PBS) and mainly generated by the Rupelian Fish Shale (oil family D). Partly, high wax oils (family B) occur in the Lower PBS (e.g., oil 'Echo 6'; Rückheim 1989) and also in Rotliegend reservoirs. The oil fields Eich-Königsgarten, Stockstadt, Hofheim and Wattenheim were producing from the Upper PBS and are major oil family D oils. But, also subordinate quantities of oil family B are obvious from the fields Eich-Königsgarten and Stockstadt as high wax oils occur also in the Upper PBS reservoirs (Rückheim 1989; Hillebrand and Leythaeuser 1992). These minor admixtures of high wax oil (oil family B—typically occurring in the Lower PBS) to oil reservoirs in the Upper PBS (typically sourced by the Fish Shale—oil family D) are mostly reported in proximity of faults (Hillebrand and Leythaeuser 1992). Furthermore, oils of family D occur also in the Lower PBS reservoirs (Hillebrand and Leythaeuser 1992). Hence, faults might be suggested as important migration pathways or the Middle PBS may act not as perfect seal.

In any case, the reservoirs in the northern URG are predominantly sourced by the Fish Shale. This is obvious from GC traces showing typical n-alkanes distributions of

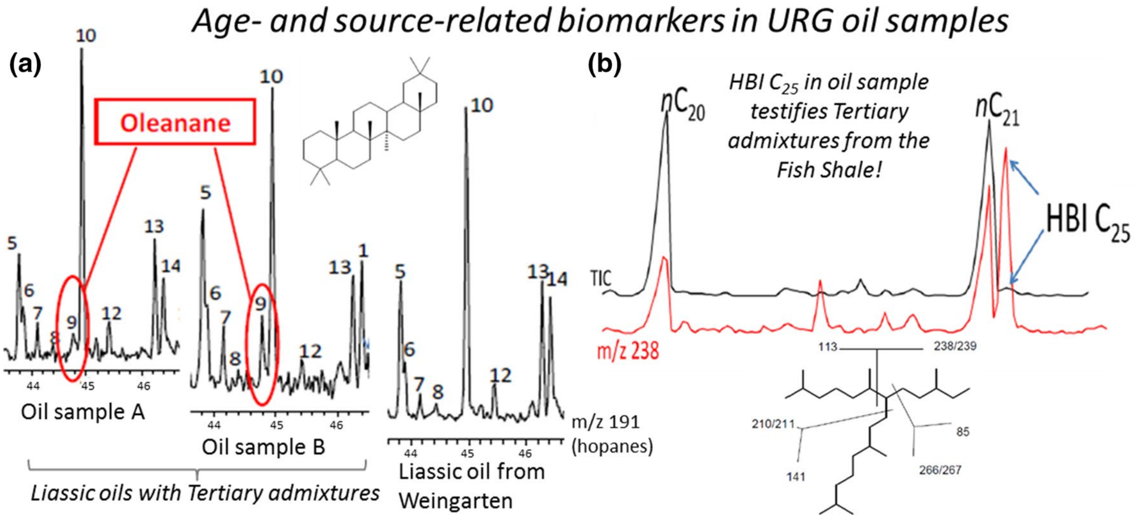

Fig. 16 **a** *m/z* 191 ion chromatograms of three oil samples identifying Oleanane (peak 9) occurrences in mainly Liassic-derived oils; **b** *m/z* 238 ion chromatogram and total ion current (TIC) showing a Fish Shale specific C_{25} highly branched isoprenoid (HBI) in a mainly Liassic-derived oil testifying admixtures of this source rock

marine-anoxic oils, which are very similar to those of pure Fish Shale oils such as Huttenheim, Graben and Knielingen (Fig. 3). Significant oleanane concentrations testify a Tertiary source rock of these oils (cf. Fig. 9 in Rückheim 1989).

In the southern part (south of Scheibenhard) oil family D reservoirs are missing due to an immature to early oil window mature Fish Shale source rock in this area as shown by Böcker and Littke (2014). The major quantity of oil family D oils is trapped in the underlying Upper PBS, e.g., oil field Eich-Königsgarten and Stockstadt. Several reservoirs in the overlying 'Gray Beds' and BNS occur especially in the central graben area, but are typically characterized by relatively thin and poorly connected sandstones suggesting rather short lateral and vertical migration distances.

Early mature oils of family A characterized by low API gravities and generated by the Corbicula- and Hydrobienschichten (e.g., Dudenhofen, Frankenthal and Worms) indicate a kitchen area of these source rocks in the Late Tertiary to Quaternary subsidence center, the Heidelberg-Mannheim-Graben (Figs. 1, 17). Additionally, oil from well Neureut 3 testifies that oil family A is not restricted to the northern URG and oil from this oil family can also occur in the area of Karlsruhe.

Gas families in the URG

In order to determine gas families and gas kitchen areas the composition of hydrocarbon gases (e.g., wetness ratios) and the gas/oil ratios (GORs) of existing oil reservoirs are of main interest. Figure 18 shows the distribution of gas/oil ratios of oil fields in the northern and central URG compared to thermogenic gas reservoirs and microbial gas reservoirs.

Thermogenic (wet) gas reservoirs occur only in the central URG, e.g., in Keuper sandstones at Spöck, and Oligocene sandstones at Hagenbach, Hayna and Rülzheim (at Hayna and Rülzheim also oil is produced—at Hayna a high-paraffin oil probable of oil family B; LBEG 1958, 1960). A kitchen area for thermogenic gas in the central graben area, the Rastatt Trough, is recognizable matching also the wet gas kitchen area of the Posidonia Shale (cf. VR_r map Lias ε in Böcker and Littke 2015). Another Liassic wet gas kitchen area might be present in the surrounding area of the Schaeffersheim (Alsace). Here, reservoirs in Middle Jurassic strata (Dogger) contain thermogenic gas (82 % C_1—Sittler 1985). Hence, a Liassic origin of the thermogenic wet gas is indicated. The Römerberg oil field shows a low GOR (mean ca. 7), indicating that the major Lias ε source rock did not reach the gas window in the kitchen area (Fig. 18), although a loss of gas during migration processes has to be considered.

In contrast, near surface gas reservoirs (400–1200 m) in the Ried group (also called 'Young Tertiary I and II'; cf. Fig. 2) and Hydrobienschichten contain typically very dry gas, e.g., reservoir Eich (Fig. 18; dryness 97 %; LBEG 1953), Pfungstadt and Frankenthal (dryness 100 %; LBEG 1956, 1958). These gases show generally a homogenous composition and occur especially in the 'Young Tertiary I' in the northern URG (Straub 1962). Plein (1993) and Mauthe et al. (1993) suggested a 'biogenic' origin of these gases from marls of the Hydrobienschichten, but without showing analytical data. A probably biogenic origin is also suggested by Dill et al. (2008). A microbial origin of

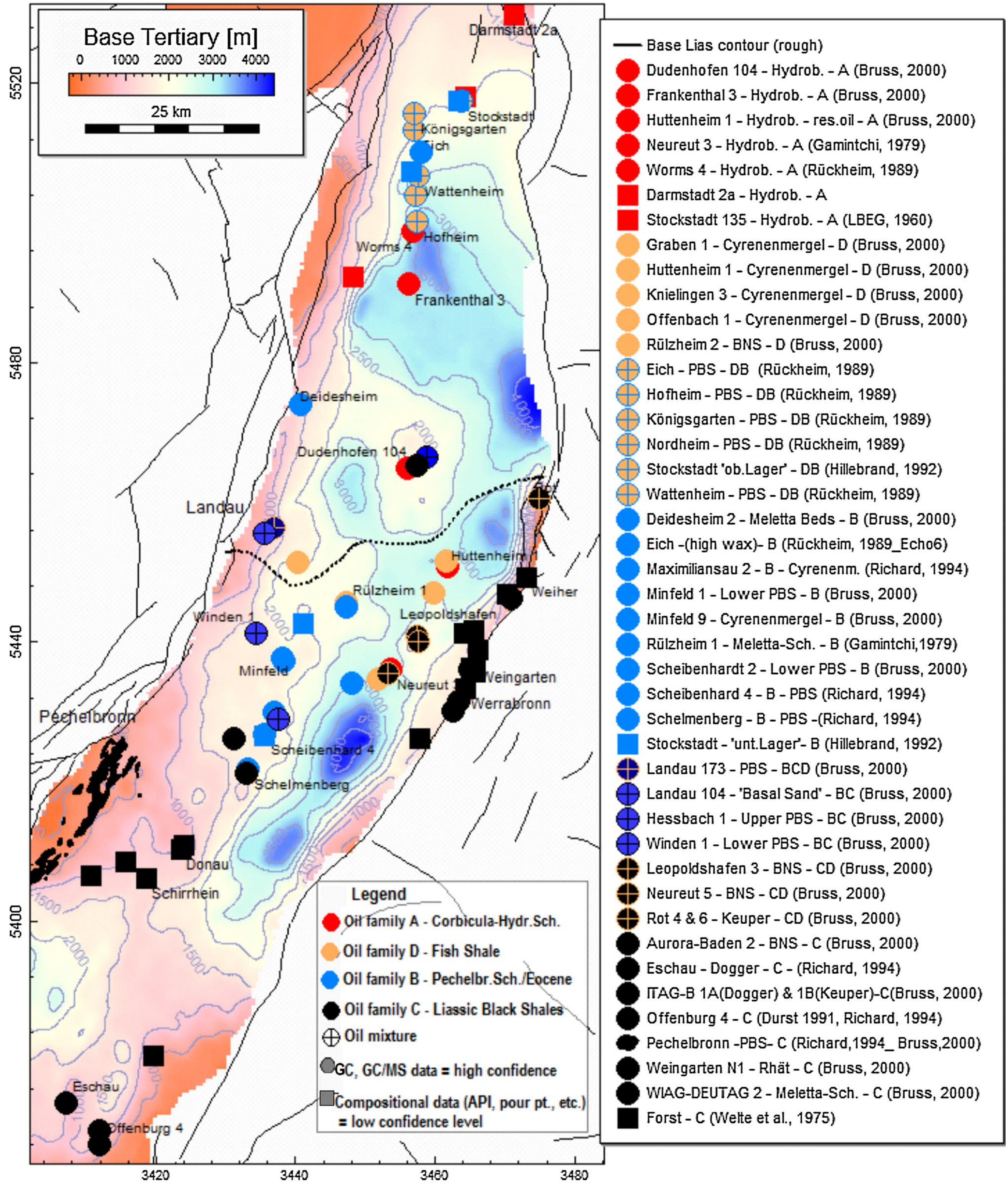

Fig. 17 Oil family map. A map of the base Tertiary is shown in the background and a rough outline of the base Lias is marked (*black line*). *Round symbols* indicate oil–source rock correlations with detailed geochemical data; *squared boxes* display correlations based on bulk geochemical parameters. The reservoir unit of each oil sample is given in the legend. Structural map taken from Sokol and Nitsch (2013). The area of the Pechelbronn oil field is taken from Sittler (1985)

these gases is confirmed by gas samples from the Hydrobienschichten (600 m depth) in the area of Speyer showing $\delta^{13}C$ (CH_4) values of ca. −60 ‰ V-PDB. Another example where a predominant microbial origin is inferred is the Schaffhouse gas field in the Alsace area with >98 % C_1 producing relatively close to surface from the 'Gray Beds' (Blumenroeder 1962; Fig. 18). In addition, for a gas blow out from Miocene strata at about 300 m depth at Bienwald in the year 1900 (Eisbacher and Fielitz 2010; Fig. 18) a microbial origin has to be considered.

Next to the microbial conversion of oil into gas, the source rocks for the existing microbial gas family are expected in younger Miocene depocenters.

Microbial gas typically occurs in sand-shale sequences containing continental type III kerogens where increased quantities of CO_2 are available, rather than in marine carbonatic-evaporitic sequences (Rice 1993; Hunt 1996). Hence, organic-rich marls in the Worms-Subgr. the 'Young Tertiary' sequence with several lignite layers interbedded (Grimm et al. 2011), and possibly also the BNS or Cyrenenmergel with known lignites, can be considered as potential source rock for microbial gas. Due to high sedimentation rates during Tertiary times several stratigraphic units and depocenters might have sourced microbial gas. However, due to a cluster of microbial gas in the area of the Heidelberg-Mannheim-Graben, the 'Young Tertiary' and Miocene sediments in this area are assumed as major source of the microbial gas.

Migration and migration pathways as related to the early graben formation

The distribution of oil families in the central and northern URG as shown in Fig. 17 is controlled by different migration pathways and sealing stratigraphic units. For example, the occurrence of several purely Tertiary-derived oils in the central URG suggests that expelled Liassic oil remained at deeper levels and did not reach the upper reservoirs. Within the Tertiary sequence above the Rupelian Clays migration likely took place in relatively thin, often discontinuous sands, which result in several small reservoirs containing oil family D and A oils.

In contrast, major oil reservoirs such as Landau and Römerberg occur in areas where the Liassic black shales are already eroded and testify lateral long-distance migration of Liassic oil in NW direction (Böcker et al. 2014). This transport is controlled to a major extent by the early graben formation. A central aspect to understand the migration mechanism is the structural configuration of the Mesozoic layers after the Late Cretaceous to Paleocene uplift and erosion event (cf. Böcker and Littke 2015).

Figure 19a displays the stratigraphic units that are present below the base Tertiary unconformity. Before the formation of the URG (ca. 75–50 Ma) an uplift center formed in the NW-NNW of the central URG area more or less orientated perpendicularly to the strike direction of the Liassic or Keuper outlines. These strike directions are also (roughly) consistent with the Alpine deformation front indicating a main stress field perpendicular to these directions. Hence, a major NNW-SSE-directed stress field existed during the early formation of the URG. Volcanic activities in the surrounding northern URG area during 76–48 Ma support these considerations (Fig. 19b). This first phase was followed by a significant volcanic phase from about 44–35 Ma in the Hocheifel (Horn et al. 1972; Grimm et al. 2011), suggesting a second uplift phase during the Middle Eocene. Volcanism in the Hocheifel with >400 volcanic eruption centers and an area of about 1000–1200 km^2 took place between about 44.3 (±0.4) and 35 Ma (Steingötter 2005; Grimm et al. 2011) and thus coincides with the age of the 'Lymnäenmergel.' Hence, also the Eifel volcanism in the Eocene has to be considered as important uplift center affecting the distribution of the incoming Eocene transgressions ('Lymnäenmergel,' Rote Leitschicht) from the southern URG. During this period, the 'Lymnäenmergel' were deposited in closed lagoon and transgressed over Dogger and Liassic sedimentary rocks in the south-southeastern parts of the central URG. Northwest of a line Landau-Speyer-Heidelberg these Upper Eocene marine ingressions of the 'Lymnäenmergel' are missing (Fig. 20; Doebl and Teichmüller 1979) or these formations occur in thin marginal facies in the northwestern part of the central URG (e.g., at Landau or Speyer; cf. Fig. 12). Eocene equivalents are also known from the southern Mainz Basins (Schäfer 2012). There competent Keuper sandstones and Muschelkalk limestones likely built a kind of barrier (comparable to the southwest German 'cuesta landscape,' 'Schichtstufenland') for the incoming southern ingressions.

In summary, the tectonic setting before the graben formation resulted in a major SSE-SE-directed dip—or tilt in direction to the Alps—of the Mesozoic strata, which was enhanced during the Eocene ingressions coming from the south and depocenters of the 'Lymnäenmergel' and 'Rote Leitschicht' in the southeastern central URG (Figs. 19, 20).

Considering expelled Liassic oil (main phases of oil expulsion in the Miocene), major sealing units as the Opalinuston-Fm. (Dogger α) above the Liassic source rocks in combination with more ductile basal Tertiary marls overlying a fractured Mesozoic subcrop result in a major topography-driven, NW-NNW-directed migration of Liassic oil within the Mesozoic succession (Fig. 20). Therefore, the Dogger α, a 80- to 150-m-thick claystone overlying the Liassic sequence (Geyer and Gwinner 2011), is a well known as pronounced seal and characterized by very low hydraulic conductivities typically in the order of 10^{-13} to 5×10^{-13} m/s (e.g., Heitzmann

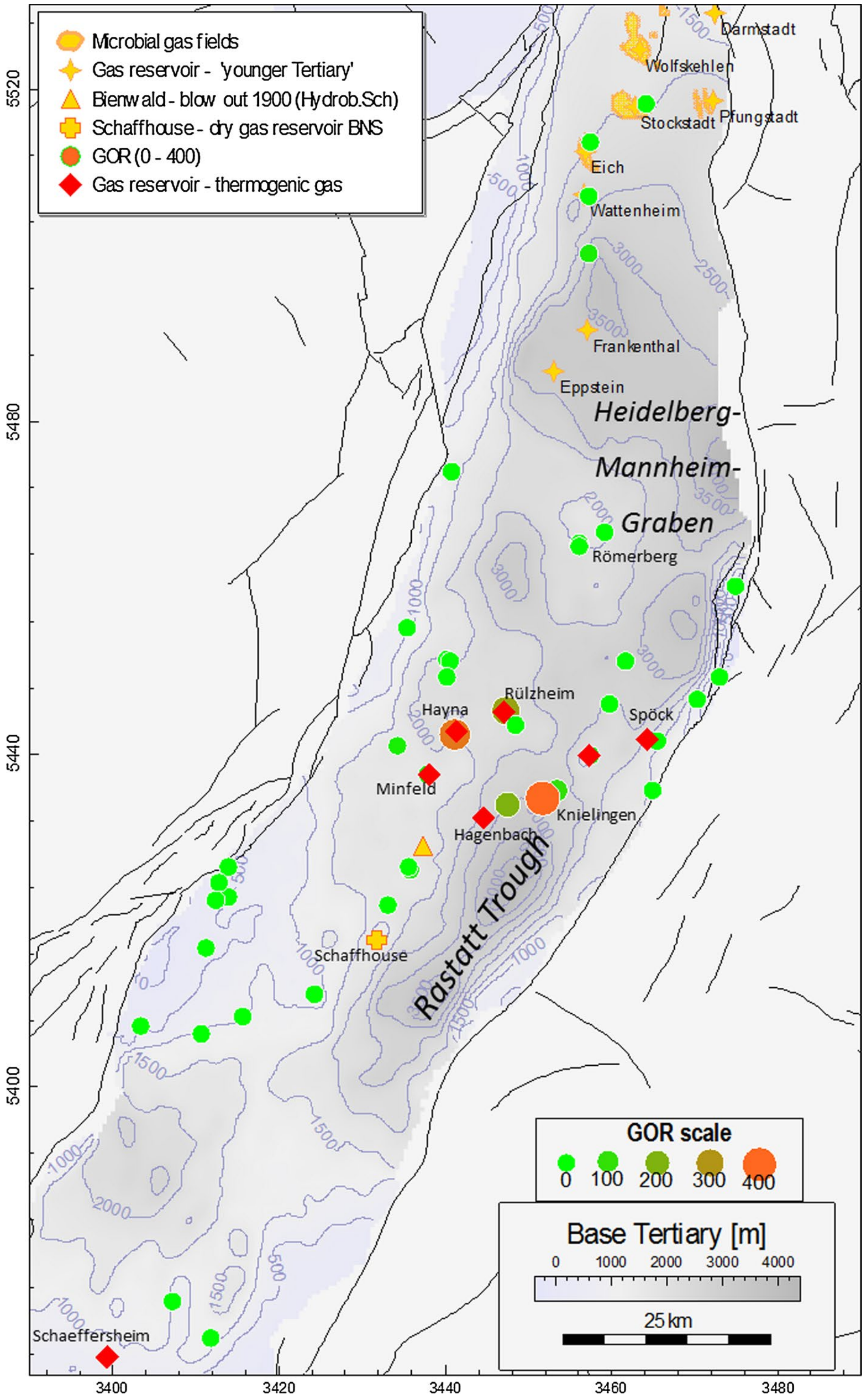

Fig. 18 Distribution of gas/oil ratios (GOR values; cf. Table 4) of existing oil reservoirs compared to thermogenic (associated) gas reservoirs and microbial gas reservoirs which occur mainly in the Hydrobienschichten and Young Tertiary (for oil reservoirs without significant quantities of gas, e.g., Pechelbronn, GOR < 5 was used). The location of microbial gas fields is according to Straub (1962), thermogenic gas reservoirs after Durst (1991)

and Bossart 2001). Furthermore, fault zones in the Opalinuston do not represent preferential flow-paths, which is attributed to an efficient self-sealing ability and results in (expected) long-term conductivities of 10^{-10} to 10^{-12} m/s (e.g., Meier et al. 2002; Blümling et al. 2007). Conclusively, the Opalinuston acts as vertical barrier (seal) for expelled oil of the Posidonia Shale. This is supported by minor test production of light oil directly from the Posidonia Shale, e.g., at Rüppur 1 (LBEG 1956), indicating also that oil remained to a specific quantity within the Posidonia Shale. The same mechanism can be assumed for expelled oil from the Lias α source rocks, which are overlain by the 30- to 65-m-thick clayey Obtususton-Fm. (Lias β claystones). As a result, predominately lateral

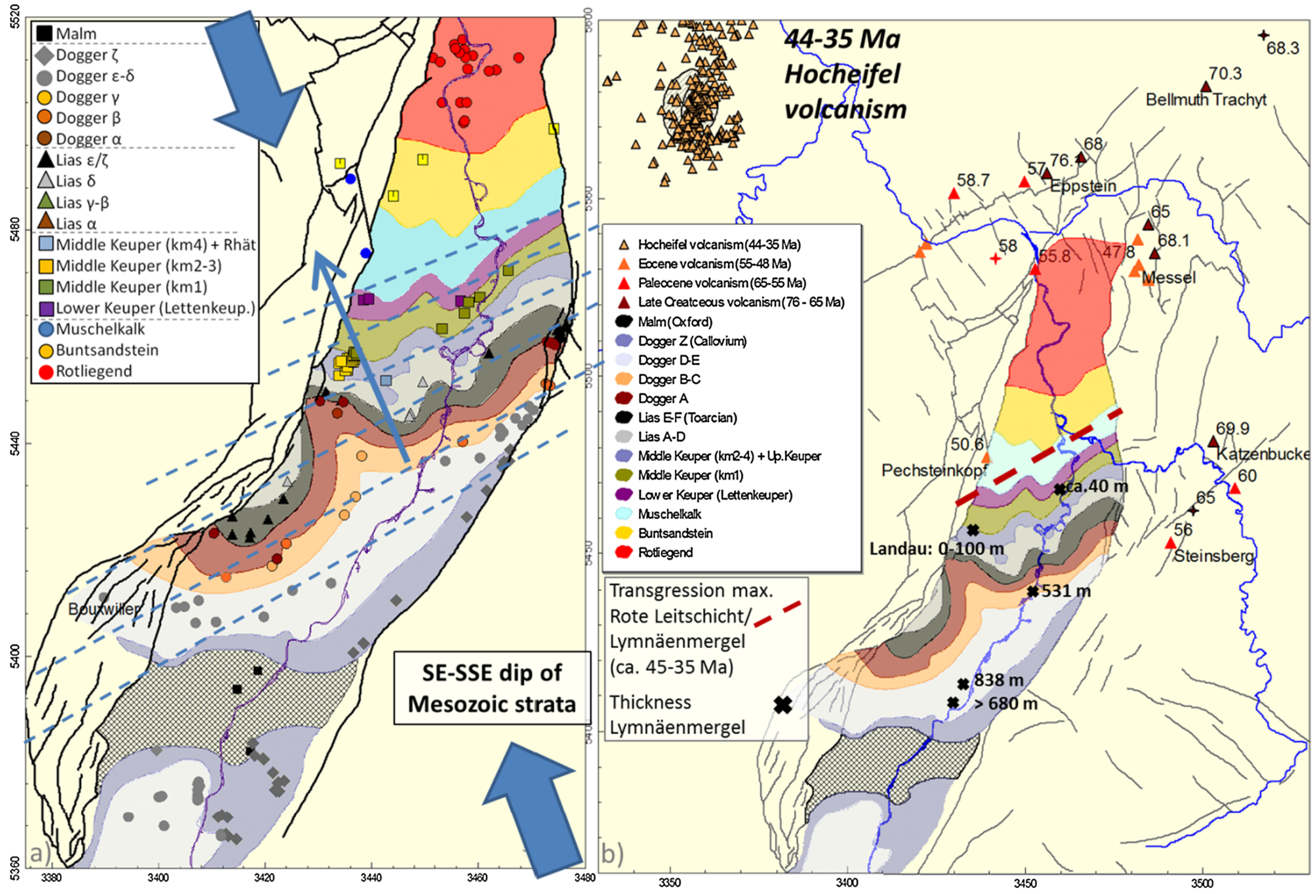

Fig. 19 **a** Preserved sedimentary rocks below the Base Tertiary unconformity. Trend lines of the eroded layers are more or less parallel to the Alpine deformation front and identify an uplift center in the NW of the URG area. A SSE-SE-directed dip of the Mesozoic subcrop is obvious. Due to the narrow shape of the northern URG subcrop lines of Keuper, Lias and Dogger sedimentary rocks should be considered to identify trend lines rather Rotliegend and Buntsandstein outlines. **b** Volcanic activity in the URG area during the early formation of the URG between 80 and 35 Ma. Two major volcanic periods occurred (ca. 76–48 Ma and the Hocheifel volcanism at ca. 44–35 Ma). Location and age of volcanic rocks after Lorenz and Lutz (2004) and Grimm et al. (2011)

migration pathways of expelled Liassic oil within fractured Liassic carbonates or in underlying Keuper sandstones (e.g., so-called Rhätsand, Stubensandsteine 1–4, Schilfsandstein, Lettenkeupersand; cf. Fig. 2) can be assumed. Particularly, the 'Stubensandsteine 1–4' are considered as (step by step) migration pathways in deeper Mesozoic levels due to discharge in northern to western directions (cf. Geyer and Gwinner 2011). Thus, the enhanced lateral migration of expelled Liassic oil (by Lias α and ε source rocks) in older stratigraphic units and NW directions, as detected in the major reservoirs Römerberg and Landau, is considered to take place within the Liassic sequence and Keuper sands and fractures. Expelled Lias α oil clearly migrates more easily in the underlying Keuper sandstones or fractured Keuper layers. Hence, faults are not a necessary condition for a migration of expelled Liassic oil into older stratigraphic layers.

The indication of sealing Liassic, Dogger α and Tertiary layers is supported by highly varying geothermal gradients at Soultz-sous-Forêts, Rittershofen or Landau geothermal wells. From Soultz-sous-Forêts hydrothermal convection cells are known to decrease significantly above the Buntsandstein-Muschelkalk successions, which implies a major sealing quality of the clayey Liassic Black Shales and overlying Tertiary marls (with significantly lower hydraulic conductivities) compared to the fractured Buntsandstein, Muschelkalk and Keuper sequence at Soultz-sous-Forêts (Pribnow and Schellschmidt 2000; Eisbacher and Fielitz 2010; Genter et al. 2010). Hence, the Base Tertiary unconformity, the base Lias and base Opalinuston-Fm. horizons are considered as important seals and fractured Mesozoic sediments below these seals are assumed as key migration pathways.

At Pechelbronn—with the Pechelbronn-Schichten as main reservoir—it is obvious that faults affect the

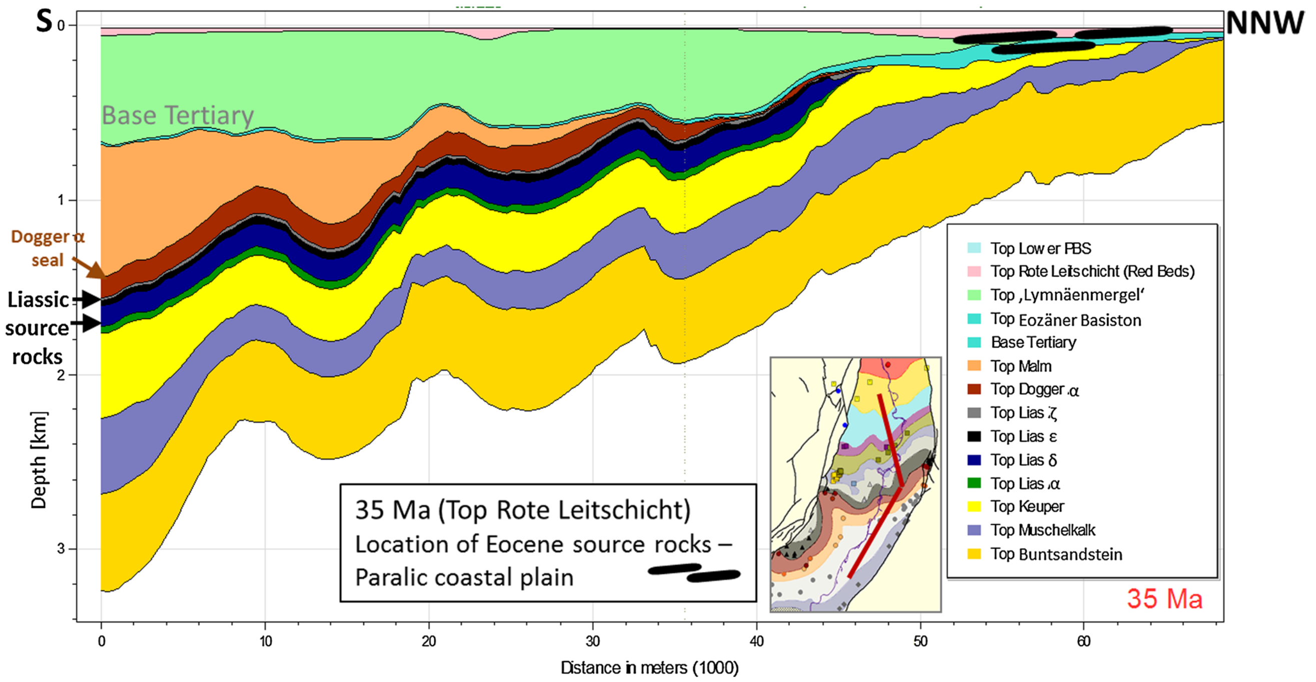

Fig. 20 Basin configuration at 35 Ma—Eocene paralic coastal plain source rocks occur in the marginal parts of the early basin. Major uplift phases in the N-NW URG area in the Late Cretaceous–Eocene result in predominately northwestern migration pathways of expelled Liassic oil during the main phase of oil migration (Oligocene–Miocene)

migration pathways significantly. The Liassic source rocks, which charged the Pechelbronn reservoirs, are only very early mature in the close vicinity (ca. 0.55 % VR_r—Blümel et al. 1989; 'immature'—Richard 1994). Therefore, a moderate-to-long-distance lateral migration is necessary to charge the structure (>15–20 km). In consequence, a major lateral migration of Liassic oil below the Dogger α clays has to be considered, favored by a dense fracturation with numerous synthetic faults displaying migration pathways and entry points into Oligocene layers and enabling migration in these levels above. Groundwater flow pattern supports the regional oil migration as stated by Blümel et al. (1989), who showed that the Pechelbronn area acts as focal groundwater discharge area for topography induced cross-formational flow dominating the regional groundwater regime. In this sense, the asymmetric graben geometry, characterized by a dominating master fault in the central and northern URG at the western rim, enhances the predominately northern to western migration pathways of expelled Liassic oil (Fig. 1).

Lateral and facial variations of source rocks in the URG

Principal source rocks in the URG are the Liassic Black Shales, coaly shales deposited in the early stages of the rift event (mostly Eocene), the marine Rupelian Fish Shale, and to a minor extend the evaporitic to salinar Corbicula- and Hydrobienschichten.

The marine-anoxic source rocks as Lias ε, Lias α and the Rupelian Fish Shale are considered as laterally very homogenous with regard to facies (in terms of petroleum generation potential) in the central URG area (e.g., Böcker and Littke 2014, 2015). The transgression of the Rupelian Fish Shale flooded the entire URG and the bituminous Lias ε and α shales are even more widely distributed. The main element of uncertainty is not whether these layers occur in oil shale facies, but the thickness and maturity of these source rocks are crucial points controlling the quantity as well as composition of generated hydrocarbons.

For early Tertiary source rocks of oil family B (bituminous coals, and coaly shales and marls of the Bouxwiller-Fm., 'Lymnäenmergel,' Lower PBS) the distribution and occurrence of potential source rocks is controlled by other factors. Depocenters during the brackish ingressions of the 'Lymnäenmergel' as indicated in Fig. 6 show nearly no significant source rock potential. Instead, the main source rock layers are relatively thin coals and coaly shales, which were deposited in local depressions with mires and bog-like environments during the early rift stages typically close to the base Tertiary unconformity. Hence, the distribution of these source rocks seems to be restricted to bogs before the Eocene transgressions or to depressions in the hinterland of marking topographic swells, which were not or nearly not transgressed during the Eocene (as indicated in Fig. 20). Further source rock layers occur in local sub-basins likely affected by processes of alluviation; for example, in some wells coaly shales occur at the top of the 'Lymnäenmergel' (cf. Fig. 12 and sample 14/889). Consequently, a heterogeneous distribution of high wax family B oils occurs with reservoirs in the Mesozoic subcrop to sandy basal Tertiary sequence (e.g., Landau—reservoirs below basal Tertiary marine ingressions) and reservoirs in the Lower PBS (e.g., Minfeld, Scheibenhardt 2, northern URG). Partly, oils of family B occur also above the seals of the Middle PBS and Rupelian clays indicating migration pathways via faults (e.g., at Stockstadt or at Deidesheim (oil from the Meletta-Schichten)).

In the northern URG the PBS are usually the oldest Tertiary deposits (Grimm et al. 2011). The thickness of the PBS decreases toward the North to values in order of only 60–70 m (e.g., oil field Eich, 45 km north of Speyer). Here, the source rocks for the high wax oils occur again close to the Base Tertiary within the Lower PBS (Rückheim 1989). The lowermost section of the Lower PBS (ca. 10 m above the Base Tertiary) typically shows the best source rock characteristics (e.g., Fig. 13 well 'Echo 8,' Rückheim 1989). Hence, particularly the very early rift layers show good source rock properties and seem to be the major source for the high wax oils with an increased input of terrestrial organic matter.

Conclusions

The petroleum system of the URG comprises multiple reservoir rocks and four major oil families represented by four distinct source rock intervals, i.e., the Liassic black shales (oil family C), basal Tertiary coals and coaly shales (B), the Rupelian Fish Shale (D), and the Corbicula- and Hydrobienschichten (A). Transgressive units such as the Base Tertiary ('Lymnäenmergel'), the Middle Pechelbronn-Schichten (PBS), the Rupelian Clays and the Cerithienschichten are acting as major seals for expelled oil and subdivide the petroleum system.

- Oldest oils originated from the Liassic black shales (oil family C) with the Posidonia Shale as main source rock and the Arietenkalk-Fm. (Lias α) as second source rock interval. The Posidonia Shale can be characterized as excellent source rock and main source rock of the major oil fields Pechelbronn, Landau and Römerberg. Expelled Liassic oil migrated mainly laterally within the fractured Mesozoic subcrop. The structural configuration of the Mesozoic layers favored migration of expelled Liassic oil in NW directions due to an uplift center of the Late Cretaceous-Paleocene erosion event in the N-NW of the northern URG and Eocene depocenters in the SE area of the central URG. Therefore, upward migration was hindered by Dogger α claystones and subsequently by more ductile basal Tertiary marls and clays enabling lateral topography-driven migration in NW directions. Locally, this migration mechanism was interrupted by faults, which act as entry points into stratigraphically younger and older units.
- Major source rocks of the high wax oil family B are coaly basal Tertiary source rocks showing partly high source rock potential. In the northern URG these source rocks occur especially in the Upper Eocene Lower PBS, whereas in the central URG Middle Eocene layers (equivalents of the Bouxwiller-Fm.) and partly the uppermost part of the 'Lymnäenmergel' show excellent source rock potential. For these oil family B source rocks several different kitchen areas are suggested with migration pathways of expelled oil reaching sands in the overlying PBS and 'Gray Beds' and also the underlying fractured Mesozoic subcrop.
- The Rupelian Fish Shale acts as important source rock and is the main source rock in the northern URG (oil family D). Expelled oil from the Fish Shale migrated into the underlying Upper PBS and the overlying 'Gray Beds.' In the Upper PBS longer-distance lateral migration was possible, whereas the relatively thin, poorly connected sands in the 'Gray Beds' did not allow for such long-distance migration.
- At several locations very viscous, sulfur-rich oils occur (oil family A), mainly in Corbicula- and Hydrobienschichten reservoirs. These oils originated from early mature evaporitic-salinar source rocks within the Corbicula- and Hydrobienschichten and occur especially in the area of the Heidelberg-Mannheim-Graben.

In addition to oil fields several thermogenic gas fields can be correlated with Liassic wet gas kitchen areas. Furthermore, several gas fields close to surface contain microbial gas and occur mainly in Miocene subsidence centers. The major part of the hydrocarbons was derived from the Liassic black shales with the Posidonia Shale as most important source rock in the URG.

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