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# Oil-source rock correlation of the Lower Palaeozoic petroleum system in the Baltic Basin (northern Europe)

Shengyu Yang[1], Hans-Martin Schulz[2], Niels Hemmingsen Schovsbo[3], Jørgen A. Bojesen-Koefoed[4]

1. Helmholtz Centre Potsdam–GFZ German Research Centre for Geosciences, Sec. 3.2, Organic Geochemistry, D-14473 Potsdam, Germany; henryyang@gfz-potsdam.de
2. Helmholtz Centre Potsdam–GFZ German Research Centre for Geosciences, Sec. 3.2, Organic Geochemistry, D-14473 Potsdam, Germany; schulzhm@gfz-potsdam.de
3. Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark; nsc@geus.dk
4. Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark; jbk@geus.dk

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**Abstract**

The correlation of lower Palaeozoic marine source rocks with reservoired oils by biomarkers is complex due to the uniform early Phanerozoic biomass (bacteria and algae) and the lack of land plant and animal input. Accordingly, the main source rocks for the most prolific oil province in the Baltic Basin are still a matter of debate.

Ten source rocks and 15 oil samples from five north European countries bordering the Baltic Sea Basin were analysed by gas chromatography (GC) with flame ionization detector, GC-MS (mass spectrometry), and GC-MS/MS to detect acyclic isoprenoids, and aliphatic, aromatic, and NSO (nitrogen, sulphur and oxygen) biomarkers. Chemometric tools were applied to screen for meaningful source- and age-related biomarkers and to highlight genetics. Extended tricyclic terpane ratios, $C_{24}$ tetracyclic terpane/$C_{26}$ tricyclic terpane ratios, and relative $C_{29}$ sterane concentrations are considered the most promising biomarkers in differentiating Llandovery shales from Cambrian to Ordovician Alum Shale and for correlation with its expelled oil. The uranium irradiation related $C_{26}$-$C_{28}$ triaromatic steroid concentrations provides possible distinguishing criteria for the source potential of the different Alum Shale units. Enhanced oil maturation by volcanic intrusion is highlighted by sterane biomarkers and polycyclic aromatic hydrocarbons.

The Alum Shale is here considered the main source rock for oil accumulations in lower Palaeozoic reservoirs of the Baltic basin. Oil seepage occurring in Ordovician limestone was mainly generated by the Middle Cambrian Alum Shale, and Middle Cambrian sandstone reservoirs were mainly sourced by Upper Cambrian and Lower Ordovician Alum Shale with

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higher maturity. Considerations about the assessment of migration distance are based on carbazole concentrations and $C_{29}$ sterane isomerization.

Advanced studies to unravel detailed lower Palaeozoic oil-source rock correlations are based on meaningful biomarkers; offer approaches to significantly reduce the exploration risk in this area, and could be applied to similar early Palaeozoic petroleum systems in other basins.

## 1. Introduction

Lower Palaeozoic successions in the Baltic Basin (northern Europe) host both conventional oil and gas accumulations, and unconventional hydrocarbons in the source rocks itself. Petroleum accumulations occur in Middle Cambrian sandstones onshore and offshore Poland (Karnkowski et al., 2010; Więcław et al., 2010b), in the Kaliningrad Oblast (Brangulis et al., 1993), and in Lithuania (Zdanavičiūtė, 2012). Scattered Upper Ordovician limestone oil reservoirs were also discovered in Latvia (Kanev et al., 1994) and around the Swedish Gotland island (Sivhed, 2004). The two most important lower Paleozoic source rocks in the Baltic Basin and surrounding areas are the Alum Shale (Middle Cambrian to Lower Ordovician) and the Llandovery (Lower Silurian) black shale which are both promising targets for shale gas exploration (Zdanavičiūtė and Lazauskienė, 2009; Schulz et al., 2010; Schovsbo et al., 2011).

Although oil has been produced from Middle Cambrian sandstone and Upper Ordovician limestone in the Baltoscandian countries for decades, there is a lack of convincing evidence about the main source rock(s) since these are very alike with respect to most conventional geochemical and organic petrographic tools. All potential source rocks are marine shales containing type II kerogen (algal and bacterial origin) (Kanev et al., 1994; Nielsen and Schovsbo,

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2006; Więcław et al., 2010a) and the analyses of established proxies like the pristane/phytane (Pr/Ph) ratio or routine biomarkers delivered insufficient evidence in clearly unravelling the differences between the different marine shaly source rocks. The main complicating issue is the uniformity of shale due to the lack of higher terrigenous land plant input during the early Palaeozoic and a relatively monotonous depositional environment. Although using data about light hydrocarbon distributions, selected biomarkers, and carbon isotope data, Kanev et al. (1994) and Więcław et al. (2010b) were unable to separate the shales and concluded that all shales of Middle Cambrian to Lower Silurian age are potential source rock candidates for lower Palaeozoic petroleums reservoired in the Baltica basin. In contrast, Zdanavikiute and Bojesen-Koefoed (1997) and Pedersen et al. (2007) suggested that Llandovery shales are the main contributors for oil in Middle Cambrian sandstones according to Pr/Ph ratios and sterane data, while Schleicher et al. (1998) and Kotarba and Lewan (2013) argued that the petroleum was mainly generated by the Alum Shale based on biomarker and carbon isotope data. Dahl et al. (1989) assumed that the oil in limestone reservoirs on Gotland was sourced from the Alum Shale which presumably was heated locally by volcanic activity, and referred to characteristic sterane, tricyclic terpane and homohopane distributions. However, the lack of Alum Shale occurrence in the near subsurface is a reasonable counterargument (Sivhed, 2004). In summary, great uncertainties exist despite previous investigations.

In this contribution we present analytical data of samples taken on a broader regional scale than previous studies in the Baltic Basin. The samples are from five Baltoscandian countries and comprise Cambrian to Silurian source rocks and oils from Middle Cambrian and Ordovician reservoirs. Conceptually, we correlated results about maturity, source, and age-specific information. Chemometric tools were applied to classify the oil samples into clusters. Specific

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biomarker combinations considered effective in differentiating source rock extracts and oils from different ages in this area were introduced first. In addition, oils matured by regional deep burial versus locally from volcanic heating are differentiated. This contribution offers a practical solution for further exploration activities in the Baltic Basin by providing the best tools to differentiate lower Paleozoic source rocks and oils in general that are applicable not only in Baltic Basin but also elsewhere.

## 2. Regional Petroleum Geology

### 2.1 Regional Geodynamics and Basin Evolution

The Baltic Basin covers part of the Baltic Sea, Kaliningrad Oblast, Northern Poland and the western parts of the Baltic States (Figure. 1). It overlies the western margin of the East European craton with its Precambrian crystalline basement and comprises of sediments deposited from the Early Cambrian to present day. The basin fill is thin in the north-eastern part (less than 100 m [300 ft] thickness in Estonia) and increasingly thickens south-westward towards the Teisseyre-Tornquist Zone (over 4000 m [13000 ft] thickness in northern Poland) which forms the southern boundary of the basin (Ulmishek, 1990).

Since its formation, the Baltic Basin underwent four main geodynamic evolution stages each with different burial dynamics until the late Palaeozoic. These different episodes were the main controlling factors for the tectonic and sedimentary features of the basin (Šliaupa and Hoth, 2011).

(1) During the passive continental margin stage (Vendian–Late Ordovician) the basin started to develop as a passive margin basin from latest Vendian to Early Cambrian times in response to

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the break-up of the Rodinia supercontinent (Poprawa et al., 1999; Kosakowski et al., 2010). This initial basin stage gave rise to coarse-grained siliciclastics of Ediacaran age. With progressing continental separation, marine transgressions flooded the basin, and marine shale, sandstone and carbonate sedimentation occurred from the Cambrian to Ordovician Periods (Nielsen and Schovsbo, 2006).

(2) The foreland basin stage (Late Ordovician–Early Devonian) developed due to the docking of the Avalonian plate to the western margin of the Baltica plate, mainly during the Late Ordovician–Silurian times (Vejbæk et al., 1994; Poprawa et al., 1999). The subsidence increased during the Silurian when up to 4500 m [14700 ft] of siliciclastic and calcareous sediments were deposited.

(3) A more continuous but slower subsidence took place during the Devonian and characterises the intra-craton basin stage (Šliaupa and Hoth, 2011). Lagoonal and deltaic deposits covered the area during that time (Ūsaityt, 2000).

(4) A thermal doming and sag basin stage developed during the Carboniferous–Permian transition. The basin subsidence ceased in the Mississippian time, thereafter, significant uplift and erosion affected the margin of the basin (Sopher et al., 2016). In response to the thinning of the lithosphere, diabase sills and dykes intruded into the Baltic Basin (Motuza et al., 1994) and Scandia (Priem et al., 1968; Obst, 2000).

## 2.2 Source Rocks

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Several marine shales with a considerable petroleum generation potential are of early Palaeozoic age (Figure 2), while carbonate deposits contain total organic carbon (TOC) contents less than 0.2 wt.% which denote them as non-source rocks (Šliaupa and Hoth, 2011). The Middle Cambrian–Lower Ordovician Alum Shale and the Llandovery shale are considered as the two most important and potential source rocks because of their wide occurrence, considerable thicknesses and high TOC contents (Kanev et al., 1994).

Named after the hydrated potassium and aluminium-bearing sulphate [$KAl(SO_4)_2 \cdot 12H_2O$], the Alum Shale consists of fine-grained, blackish mudstone and shale of Middle Cambrian, Late Cambrian (Furongian) and Early Ordovician (Tremadocian) age (Nielsen and Schovsbo, 2006) (Figure. 2). The thickness of the Alum Shale is regionally variable. To the west of the Baltic Basin, an approx. 180 m (590 ft) thick Alum Shale was found in the Danish offshore (Nielsen and Schovsbo, 2006). Within the basin, the Alum Shale reaches its maximum thickness of ca. 100 m [300 ft] in the Teisseyre-Tornquist Zone, and wedges out eastward and northward due to erosion (Buchardt et al., 1997). The Alum Shale is not present to the east and north of Kaliningrad-South Gotland line (Figure 1) except for a maximum seven meter (23 ft) thick Tremadocian Alum Shale in northern Estonia (Loog et al., 2001). Covering a time span of 23 million years (500-477 Ma), the three Alum Shale subseries (Middle Cambrian, Upper Cambrian and Lower Ordovician) differ in their organic and inorganic geochemical composition (Thickpenny, 1984). High TOC contents, typically up to 10 wt.% and high sulphur contents dominate in the Lower Ordovician and Middle Cambrian Alum Shale whereas the Upper Cambrian Alum Shale is featured by TOC contents of up to 22 wt.% and high silica contents (Schovsbo et al., 2015; Kosakowski et al., 2016).

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Formed in a deep water environment, the Llandovery shale is a dark grey to black shale or marlstone. This shale is rich in TOC (up to 16 %wt.) and its hydrocarbon generation potential is known in the southern and eastern part of the basin (Zdanavikiute and Bojesen-Koefoed, 1997). A typical thickness of the layer in the eastern part of the basin is 5-25 m (16-82 ft) (Kanev et al., 1994), but increases to 100 m (300 ft) in offshore Poland (Modliński and Podhalańska, 2010).

Besides these two layers, the locally distributed Caradoc Upper Ordovician shales can also be considered as possible source rocks (Kanev et al., 1994). In Sweden and Lithuania, the Upper Ordovcian shales are named as Fjäcka Shale and the Mossen Shale with TOC contents of up to 6 wt.%. However, these two shales have maximum thickness of 10 m (32 ft) (Högström and Ebbestad, 2004; Zdanavičiūtė and Lazauskienė, 2004), typically less than five m (16 ft) thick (Šliaupa and Hoth, 2011), and occur very locally. The equivalent shale in Poland is called Sasino Shale (Stouge and Nielsen, 2003; Modliński and Szymański, 2013). It has typical TOC between 1-2.5% with variable hydrogen index values, ranging from 11 to 359 mg hydrocarbon/gTOC, and is considered to be deposited in a sub-oxic environment (Więcław et al., 2010a). The limited distribution and hydrocarbon generation ability of the Upper Ordovician shales make them possibly regional source rocks rather than main contributors of the oil accumulations found all around the basin.

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### 2.3 Reservoirs

The Middle Cambrian sandstones and the Upper Ordovician limestone reefs are the reservoir rocks for most of the petroleums found in the lower Palaeozoic strata in the Baltic Basin (Figure 2). Petroleums trapped in sandstone occur in Poland, Russia (Kaliningrad) and Lithuania while

oil reservoired in limestone reefs occur on the Swedish island of Gotland and in Latvia (offshore and onshore) (Figure 1).

The trap style in the sandstone reservoirs are mosly asymmetric brachy-anticlinal domes as a result of the Caledonian orogeny. The effective porosity and permeability in the southwestern part of the Baltic Basin are generally low with values around 5-14% and 5-24 mD caused by intensive quartz cementation (Schleicher et al., 1998; Semyrka et al., 2010), whereas higher porosities characterise the eastern basin part. For instance, reservoir porosity can be as high as 20% in western Lithuania and 34% in Kaliningrad (Zdanavičiūtė, 2012).

In the northern part of the Baltic Basin, oil is produced from about 100 limestone reef structures in the Ordovician limestone sequence (Sivhed, 2004). In general, the reefs are located at shallow depth of only a few hundreds of metres (feet). The onshore reefs are generally rather small with a maximum diameter of 800 meters (2600 ft) and an height of up to 50 meters (160 ft), but can be up to two km (6560 ft) in diameter offshore (Tuuling and Flodén, 2009). The oil is produced from fractures, cavities, and vuggy porosity of the limestone (Chatzis, 2014).

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### 2.4 Maturation and Accumulation

Subsidence during the Caledonian orogeny is the main maturation control, especially in the southwestern part of the Baltic basin. Volcanic intrusions during Permo-Caboniferous times led to a localized high maturation of the Palaeozoic shales offshore Kaliningrad (Motuza et al., 1994; Motuzaa et al., 2015), island Bornholm in the Baltic Basin (Obst, 2000), and in central Sweden (Dahl et al., 1989), but only slightly contributed to the overall thermal maturation (Karnkowski et al., 2010). The 1-D burial reconstruction carried out by Kosakowski et al. (2010) and the 2-D

basin modelling by Wróbel and Kosakowski (2010) indicate that the onset of petroleum generation from the lower Palaeozoic source rocks occurred from the Early Devonian through the Mississippian period. The peak of hydrocarbon generation took place from the Late Devonian to the Mississippian time and main expulsion almost concurrently happened. During Permian and Mesozoic times tectonic activities led to remobilization with following adjustment of accumulations.

During the passive continental margin stage, normal fractures were widely developed in the basin and served as petroleum migration paths. For example, oil produced in the southwestern Baltic basin migrated eastward and northward up to shallower Ordovician limestone reservoirs through fractures, sandstones, and unconformity connections. Migration from younger source rock to older reservoirs in the Baltic Basin and into surrounding areas can also be observed. Examples are pyrobitumens found in Lower Cambrian sandstones on Bornholm island (Denmark) (Møller and Friis, 1999) as well as asphaltite in central Swedish bedrock fractures (Sandström et al., 2006) where there is no effective source rock beneath. This is either caused by downward migration due to the overpressure and abundance of fractures, or more likely due to the upward charging from younger source rocks into the tectonically uplifted older strata as suggested by Wróbel and Kosakowski (2010).

## 3. Samples and Methods

### 3.1 Samples

15 Llandovery shales and Alum Shale samples were investigated in the frame of this study (Table 1). Of these five Upper Cambrian Alum Shale samples from Sweden were also available,

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but did not deliver sufficient extraction amounts for geochemical investigations and were excluded.

15 oil samples from five countries have been analysed (Table 1). Two oil samples from the Brattefors quarry were taken directly from a fresh oil seepage after the mining company had cut a Middle Ordovician limestone which are similar to Figure 20b as described by Buchardt et al. (1997). The other samples are from boreholes in the basin area.

The oil samples cover most of the oil producing areas in the Baltic Basin (Figure 1). Previous geochemical results of analysed oil samples from the Baltic States were reported by Bojesen-Koefoed et al. (2001). This basic data set provides a meaningful geographic and stratigraphic distribution, and is used in this study to build on with further conceptual approaches and techniques to unravel the oil-source correlation of the early Palaeozoic petroleum system in the Baltic Basin.

### 3.2 Methods

Soxhlet extraction was carried out on powdered shale and solid bitumen samples for 24 hrs at 50 °C. A dichloromethane and methanol mixture (99:1) was used as solvent. In a next step, asphaltenes were precipitated from the extracted bitumen as well as from the crude oil samples before medium pressure liquid chromatography (MPLC) fractionation. Aliphatic and aromatic hydrocarbons, and NSO (nitrogen, sulphur and oxygen) compounds were separated from the maltene fraction after MPLC as described by Radke et al. (1980).

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Gas chromatography with flame ionization detector (GC-FID) was carried out on the aliphatic hydrocarbon fractions of all samples. The instrument was equipped with a HP Ultra 1 capillary column. The oven temperature was programmed from 40 °C to 300 °C with a 5 °C/min heating rate.

Biomarkers from aliphatic, aromatic, and NSO compounds were detected by gas chromatography-mass spectrometry (GC-MS). Gas chromatography-mass spectrometry-mass spectrometry (GC-MS/MS) was applied to detect aliphatic biomarkers for better peak separation. GC-MS test runs were based on a Trace GC Ultra system coupled to a DSQ mass spectrometer. The GC was equipped with a PTV injection system and a fused silica capillary column, and was heated from 50 °C to 310 °C at a rate of 3 °C/min. GC-MS/MS measurements were performed on a Finnigan MAT 95XL mass spectrometer coupled to a HP 6890A gas chromatograph with a PTV injection system and a SGE BPX5 fused silica capillary column. The GC oven temperature was programmed from 50 °C to 310 °C with a heating rate of 3 °C/min, followed by an isothermal phase of 30 min.

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## 4. Results

### 4.1 GC-FID

All samples show very high signal/noise ratios for normal alkanes and acyclic isoprenoids, and pristane/$nC_{17}$ and phytane/$nC_{18}$ ratios are generally low (Table 1 and Figure 3). The biodegradation scale of Peters and Moldowan (1991) suggests that all samples are non- to slightly biodegraded (Table 1). Thus, a very weak impact from biodegradation on the following oil-source correlation is expected.

No significant odd or even carbon number predominance of *n*-alkanes pattern was observed in the samples. Most of the samples have Pr/Ph ratios between 1.0-3.0, except the three Llandovery shale extracts from the B3 well with Pr/Ph ratios higher than 3.0 (Table 1).

### 4.2 Aliphatic Biomarkers

Based on the m/z 191 and m/z 217 traces of aliphatic biomarkers, at least two endmember types can be identified. For example, the Llandovery shale extracts are characterized by higher concentrations of $C_{24}$ tetracyclic terpane and $C_{28}$-$C_{29}$ tricyclic terpane peaks are significantly smaller than $T_s$ and $T_m$ (Figure 4A). The sterane and diasterane biomarkers of the Llandovery shale samples are dominated by $C_{27}$ and $C_{29}$ homologues (Figure 4B). In contrast, the $C_{24}$ tetracyclic terpane contents in the Alum Shale extracts and reservoir oil are very low, and $T_s$ and $T_m$ peaks are less predominant (Figure 4A). Furthermore, these samples show obviously higher $C_{28}/C_{29}$ steranes ratio in comparison with the Llandovery shale extracts (Figure 4B).

All samples have low concentrations in gammacerane and $C_{35}$ homohopane. Accordingly, confident interpretations of these biomarkers can only be achieved in a few samples (Table 1). Other redox-, precursor-, and age-related biomarkers, like 28,30-Bisnorhopane, dinosteranes, and 24-norcholestanes were not identified applying through GC-MS/MS analysis from any of the samples. 24-*iso*-/*n*-propylcholestanes were only recognized in sample Deb.

### 4.3 Aromatic and NSO Biomarkers

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Naphthalenes, phenanthrenes, and dibenzothiophenes can be clearly identified in all samples, while the aromatic steroid concentrations differ significantly (Figure 5). The Lower Ordovician and Upper Cambrian Alum Shale samples show no or very little $C_{26}$-$C_{28}$ triaromatic steroid distribution patterns and all oils from Middle Cambrian reservoirs are also depleted in these compounds (Table 1 and Figure 5). When comparing the polycyclic aromatic hydrocarbons (PAHs), most samples are marked by very low pyrene/phenanthrene ratios, only oil samples from the Brattefors quarry are characterized by pyrene concentrations higher than phenanthrene.

In the investigated NSO fractions, the carbazole concentrations vary among the samples. In general, shale extracts are always rich whereas only four oil samples from Middle Cambrian sandstone and oil seepage in the Brattefors quarry show identifiable carbazoles signals (Table 1).

### 4.4 Oil Family Assignments

Chemometric tools which use multivariate statistics to remove noise and to show affinities among samples are very helpful in oil-source correlations (Peters et al., 2013; Peters et al., 2016). Source-related and age-related biomarkers were chosen to as meaningful input parameters for principal component analysis (PCA) and hierarchical cluster analysis (HCA), instead maturity dependent parameters were not integrated (Table 1).

The PCA results point to differences between Llandovery shale extracts and the rest of the samples. The key signals for correlation are extended tricyclic terpane ratios (ETR), $C_{24}$TeT/$C_{26}$TT, and $C_{29}$ sterane distributions, whereas other ratios are relatively less significant (Figure 6A). Two main clusters can be grouped by HCA data (Figure 6B), and the Llandovery shale extracts are clearly separated from the Alum Shale extracts and the oils. However,

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additional sub-clusters can be identified within cluster I: the Alum Shale extracts and two oil samples from the Brattefors quarry are closely related, and the oil sample Gec appears to be a mixture of the two end members (Figure 6).

It has to be pointed out that almost none of the source-related and age-related biomarkers used here are totally maturity independent and vertical and horizontal heterogeneities of the source rock can also significantly influence the result of the oil-source correlation. Thus, detailed discussions on the results are necessary.

## 5. Discussion

### 5.1 Maturity

The maturity assessment is not only important in evaluating the influence of local hydrothermal overprints, but also helpful in unravelling the impact of maturity on oil-source correlations. A good correlation can be found between the maturity biomarker ratios diasterane/sterane and Ts/Tm (Figure 7A). It has to be pointed out that both of these two maturity parameters can be influenced by mineralogy (Rubinstein et al., 1975; McKirdy et al., 1981), for example, carbonate-rich source rocks are characterized by small values of these ratios. However, the mineralogical impact on the maturity seems unlikely, since all samples are marine siliciclastic sediments. The $C_{29}$ sterane epimer ratios are also considered as important maturity parameters and most of the samples show maturities within their thermodynamic equilibrium thresholds (Figure 7B).

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In general, the four maturity parameters show that two Llandovery shale samples (Gen and Ruk) and one Alum Shale (B7) sample are in the oil window whereas all other shale samples are immature or in the early stage of oil generation (Figure 7).

The maturity parameters show that the oils in the Ordovician reefs were mainly charged from source rocks during the early oil window except for the two samples from Brattefors. Oils in Middle Cambrian reservoirs are generally more mature. Of these the C9 and Gec oils are suggested to represent in peak oil window (Figure 7B).

### 5.2 Volcanic Intrusion Induced Maturation

The Bra/a and Bra/b oil samples taken from Middle Ordovician limestones in the Brattefors quarry present 20S/(20S+20R) sterane ratios which are significantly higher than the thermodynamic equilibrium threshold (Figure 7B). This implies that these samples are likely to have experienced abnormally fast heating during maturation (Strachan et al., 1989). Furthermore, only these two samples have high pyrene/phenanthrene ratios. The pyrene/phenanthrene ratio in petroleum is generally low, and elevated values for this ratio are suggested to be caused by pyrolytic maturation (Budzinski et al., 1997). Because rapid heating and high temperatures can cause the breaking of bonds in organic matter leading to small molecular fragments, mostly free radicals recombine to form PAHs by pyrosynthesis as the temperature drops (Huang et al., 2015b). For instance, PAHs are enriched in artificial pyrolysates (Brocks et al., 2003), hydrothermally generated oil (Simoneit and Lonsdale, 1982), sediments influenced by forest fires (Venkatesan and Dahl, 1989), or oils generated by nearby volcanic intrusions (Huang et al., 2015b).

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The regional maturity pattern reveals that potential source rocks are immature in south central Sweden (Figure 1), and that there is a lack of pathways for the oil to migrate from the basin centre. Due to the widespread occurrence of Permo-Carboniferous diabases in this area, oil samples from the Middle Ordovician Brattefors limestone are genetically related to this volcanic intrusion period (Dahl et al., 1989). Similar sterane maturity and PAHs characteristics as for the Brattefors oil is missing in the other investigated samples, so that oil formation in the Baltic State area is the result of geological burial.

## 5.3 Correlation

### 5.3.1 Acyclic Isoprenoids

Traditionally Pr/Ph was often applied to differ oxic from anoxic depositional environments (Didyk, 1978). However, palaeosalinity (ten Haven et al., 1987), maturity (Dzou et al., 1995), and organic matter type input (Goossens et al., 1984) were also considered as influencing factors. Thus, Pr/Ph values between 0.8-3.0 offer a broad interpretation window, and are not exclusively indicative for a depositional environment assignment (Peters et al., 2005).

In our sample set, three Llandovery shale samples from well B3 have Pr/Ph ratios higher than 3.0 (Table 1 and Figure 3), and, despite other considerations, could reflect terrestrial organic matter input under oxic conditions (Peters et al., 2005). However, an advanced terrestrial plant community is widely believed not to have flourished before the Devonian (Kenrick and Crane, 1997), but recent studies reveal the occurrence of first eutracheophytes in the Late Ordovician (Gerrienne et al., 2016), and that sediments across the Upper Ordovician Lower Silurian boundary in Sweden host spores (Badawy et al., 2014). Accordingly, some terrestrial organic

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matter can have been admixed into marine depositional environments during the foreland basin stage. In summary, the high Pr/Ph ratios in some Llandovery shale samples are reasonable indications that the depositional environment during the Early Silurian was more strongly oxidized than during deposition of the Alum Shale.

5.3.2 Terpanes

The routine BNH/H ratio, Gammacerane index and C35 homohopane index are not indicative in differentiating the Lower Palaeozoic samples in this study, because most of these biomarkers were not detected by GC-MS and GC-MS/MS analyses. As suggested by PCA, extended tricyclic terpane ratio (ETR) and the $C_{24}$ tetracyclic/$C_{26}$ tricyclic terpane ($C_{24}$TeT/$C_{26}$TT) ratio were compared and a nice correlation can be found (Figure 8). The Llandovery shale extracts show very low ETR values and enrichments in $C_{24}$ tetracyclic terpanes, whereas the Alum Shale extracts and oil samples from Upper Ordovician limestone reservoirs plot in the lower right part of the template (Figure 8).

ETR (ETR=[$C_{28}$+ $C_{29}$]/ [$C_{28}$+ $C_{29}$+Ts]) was taken as an age-related biomarker ratio in differentiating Jurassic reservoired oil from Triassic (Holba et al., 2001; Hanson et al., 2007) and is relatively resistant to thermal maturation and biodegradation (Holba et al., 2002). The ETR values correlate well with the gammacerane index and Pr/Ph ratio (De Grande et al., 1993; Hao et al., 2011), and are thus considered indicators for salinity and alkalinity.

The $C_{24}$ tetracyclic terpane is considered as a biomarker in evaluating depositional environments (Volk et al., 2005; Tao et al., 2015) and can be enriched in carbonate rocks (Palacas et al., 1984), evaporites (Clark and Philp, 1989), or rocks with terrestrial organic matter input (Philp and

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Gilbert, 1986). Furthermore, the tetracyclic terpanes are regarded to be more resistant against biodegradation than tricyclic terpanes due to the more stable stereoisomerism (Aquino Neto et al., 1981; Williams et al., 1986). Thus, the $C_{24}TeT/C_{26}TT$ ratio would increase with intensified biodegradation level. However, the application of the PM scale (Peters and Moldowan, 1991) shows that the bitumen in the Llandovery shale has undergone very slight biodegradation (Table 1), i.e. only a few *n*-alkanes have been depleted (see GC-FID traces in Figure 3). The more biodegraded oil samples, e.g. Adz and Ber exhibit only very low $C_{24}TeT/C_{26}TT$ ratios (Table 1 and Figure 8). In summary, the biodegradation of these samples is not as pronounced as to control the tetracyclic/tricyclic terpane distribution.

The scattered distribution of oil samples and the Alum Shale extracts in Figure 8 can be explained by the combination of facies variations and maturity changes. Deposited in a vast area the Alum Shale is characterized by vertical and horizontal variations during deposition across the area. For instance, the lithostratigraphic unit of the Alum Shale in south central Sweden differs from those within basinal areas (Nielsen and Schovsbo, 2006).With increasing maturity, the ETR is anticipated to be decreased, because of the relative Ts enrichment in the denominator of the ratio. Also, Farrimond et al. (1999) and Huang et al. (2015a) pointed out that the $C_{24}TeT/C_{26}TT$ ratio would slightly increase especially after peak oil generation although this is not the case in our sample set. These maturation controls can partly explain why the more mature oil samples in the Middle Cambrian sandstone reservoir have lower ETR and higher $C_{24}TeT/C_{26}TT$ ratios than the oil from the Upper Ordovician limestone. Summarising the above and independent on secondary processes, the oil samples can be regarded as genetically closer to the Alum Shale than to the Llandovery shale.

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Although both were deposited below wave base under dysoxic to anoxic conditions, the Alum Shale and Llandovery shales differ in depositional features. The Alum Shale was deposited in a large and shallow epicontinental sea (Thickpenny, 1984; Schovsbo, 2002), while the Llandovery shale was formed in a foreland basin with open circulation to the ocean. The salinity differences indicated from biomarkers might reflect differences in water column stratification between the two settings, and the Alum Shale was deposited in a water column with stratification. In general, organic lean shale, sandstone and carbonate intercalations can be found more frequently in Lower Silurian shales than in the Alum Shale (Lazauskiene et al., 2003; Modliński and Podhalańska, 2010) which implies a less stratified, more unstable, and shallower-water environment during deposition.

### 5.3.3 Steranes

The ternary diagram about the $C_{27}$, $C_{28}$, and $C_{29}$ distribution is meant to enable the distinction of source rocks or oils from different ecosystems or depositional settings (Huang and Meinschein, 1979).

The Llandovery shale samples can be clearly separated from the rest of the samples due to their elevated $C_{29}$ proportions. The Alum Shale extracts and the oil samples overlap (Figure 9) and thus confirm marine depositional conditions (Moldowan et al., 1985). The oil sample Gec could be partly co-sourced by the Llandovery shale which is indicated by very similar sterane distributions (Figure 9). With an elevated $C_{29}$ concentration, the C9 oil could also be influenced by Llandovery shale (Figure 9). Samples with $C_{29}$ sterane concentrations larger than 60% are typically associated with an organic material dominated by terrestrial precursors (Huang and

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Meinschein, 1979), and may be related to the early advanced plant development in this area. Alternatively, the $C_{29}$ steranes can also be retraced to green algae, e.g. Chlorophyceae (Grantham and Wakefield, 1988; Kelly et al., 2011; Katz and Everett, 2016). Consequently, the precursor of the organic matter in the Llandovery shale can be clearly differentiated from those organisms which delivered the organic matter preserved in the Alum Shale and most of the oil samples.

The Deb oil is the only sample with identifiable 24-*iso*-/*n*-propylcholestanes. This $C_{30}$ sterane is interpreted as an indicator of marine algae (Moldowan et al., 1990) or demosponges (Love et al., 2009). $C_{30}$ steranes were not found in the Alum Shale and in oils in Cambrian reservoirs (Moldowan et al., 1990). These data are based on the analyses of a limited sample set and lead to the conclusion that the precursor sterols for the formation of $C_{30}$ steranes appeared between the Early Ordovician and the Devonian. However, the detection of $C_{30}$ steranes is dependent on instrument sensitivity and is often due to contamination from lubricating oil during drilling (Antcliffe and Stouge, 2013). Since the $C_{30}$ sterane signals in the Deb oil sample are generally weak, it is hard to explicit the geological meaning of these compounds in this sample so far.

To briefly summarize the above findings, the lower Palaeozoic oil found in the Baltic Basin is primarily generated from the Alum Shale. The Llandovery shale could add only a subordinate contribution to these oils in the area.

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### 5.4 Heterogeneity within Alum Shale

The Alum Shale is vertically and horizontally highly heterogenous in terms of lithology (Thickpenny, 1984), depositional environment (Schovsbo, 2001), rock types (Schovsbo et al., 2015), mineralogy (Snäll, 1988), artificial pyrolysates (Horsfield et al., 1992; Bharati et al.,

1995), and uranium concentrations (Schovsbo, 2002; Kosakowski et al., 2016). For example, the Upper Cambrian and Lower Ordovician Alum Shale in the northern part of the basin are rich in uranium (> 100ppm) (Schovsbo, 2002) which was either produced by hydrothermal activity (Mossman et al., 1993; Oliver et al., 1999) or controlled by the depositional environments (Schovsbo, 2002), while the Middle Cambrian Alum Shale is generally poor in uranium. However, only minor variations in source-related and age-related aliphatic biomarker compositions can be found among the three units. Nevertheless, triaromatic steroids distribution could be helpful in differentiating them.

Two Alum Shale extracts lack in or have very low $C_{26}$-$C_{28}$ triaromatic steroid concentrations although $C_{20}$-$C_{21}$ triaromatic steroids can be identified in all samples (Table 1 and Figure 5) and the strong resistance of triaromatic steroids against biodegradation (Peters and Moldowan, 1991; Larter et al., 2012) argues against a removal by biodegradation. In general, triaromatic steroids are considered as aromatization products from monoaromatic steroids. During thermal maturation the $C_{26}$-$C_{28}$ / $C_{20}$-$C_{21}$ triaromatic steroid concentrations will decrease due to the preferential degradation of the long-chain triaromatic steroids (Mackenzie et al., 1981; Beach et al., 1989). The $C_{26}$-$C_{28}$ triaromatic steroids are expected to be entirely cracked to shorter chained compounds during condensate or wet gas generation stages (Peters et al., 2005). The Baltic samples without $C_{26}$-$C_{28}$ triaromatic steroids are either immature or in the peak oil generation stage which implies that those compounds were not thermally cracked. Dahl et al. (1988) and Lewan and Buchardt (1989) found that the $C_{26}$-$C_{28}$ triaromatic steroid concentrations in the Alum Shale are inversely proportional to its uranium content and concluded that the uranium irradiation initiates the cleavage of the aliphatic side chains of high molecular weight steroids to form lower molecular weight steroids. This theory fits the results of our work as the two Alum

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Shale extracts without $C_{26}$-$C_{28}$ triaromatic steroids are from the uranium-rich Upper Cambrian and Lower Ordovician Alum Shale (Table 1), and as the Middle Cambrian Alum Shale samples with significantly higher $C_{26}$-$C_{28}$ triaromatic steroid responses are generally lean in uranium concentrations (Schovsbo, 2002). Importantly, the oil sample from the Middle Cambrian sandstone reservoirs contains no $C_{26}$-$C_{28}$ triaromatic steroids and is probably sourced from the uranium-rich Alum Shale interval. In contrast, the oil samples in the Upper Ordovician reef reservoirs all have high triaromatic steroid compounds and thus can be genetically linked with the Middle Cambrian Alum Shale. However, further geological or geochemical evidence is required to support this hypothesis. The weak response of $C_{26}$-$C_{28}$ triaromatic steroids in the Brattefors oil samples is either an original one or caused by the high temperature influence during volcanic intrusions.

The horizontal heterogeneity within the three stages of Alum Shale needs to be taken into account due to depositional variability. For example, the uranium concentration of the Upper Cambrian and Lower Ordovician Alum Shale changes significantly in different areas (Schovsbo, 2002; Kosakowski et al., 2016) and source-related and age-related aliphatic biomarkers also show certain quantitative variability in a lateral sense (Figure 8 and 9). However, the limited access to Alum Shale samples with oil window maturity prevents a comprehensive reconstruction about the horizontal heterogeneities.

### 5.5 Migration and Mixing

The distribution of pyrrolic nitrogen compounds is considered to reflect migration distances, the abundance of carbazoles and the benzo[a]carbazole/benzo[c]carbazole isomer ratio both decrease with increasing migration distance (Li et al., 1995; Larter et al., 1996). However, Horsfield et al.

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(1998) and Bakr and Wilkes (2002) have pointed out that the benzocarbazole isomer ratio is also influenced by maturity and depositional environment. Nevertheless, the carbazole concentration seems to reflect the migration distance because the NSO compounds undergo retention due to geochromatographic effects and their lesser affinity to hydrocarbons (van Duin and Larter, 1998; Silliman et al., 2002). All oil samples from Upper Ordovician limestone reservoirs are depleted in carbazole compounds (Table 1). Only four oil samples from Middle Cambrian reservoirs (C9, B8, Deb, and Gec) have clear carbazole signal responses (Table 1), and indicate relatively short migration distances from the source rock. This conclusion is supported by the biomarker migration index theory suggested by Seifert and Moldowan (1981) and Carlson and Chamberlain (1986) as these four oil samples plot along the source sample maturity trend line in the $C_{29}$ sterane isomer maturity diagram (Fig. 7B). This feature corresponds to the first order kinetic conversion lines and oil samples Sak and Gus are shifted to the right of the trend line due to strong fractionation during migration (Figure 7B). In other words, the source rock for the oil in the reservoirs is "close by" and this phenomenon fits the regional maturity trend (Figure 1). Although the Alum Shale is regarded to be the main source rock for the lower Palaeozoic petroleum, contributions from the Llandovery shales to some reservoirs is possible. For example, the Gec oil sample is generally grouped between the Alum Shale and the Llandovery shale in the chemometric analysis (Figure 6), and is characterized by a similar terpane distribution as the Alum Shale (Figure 8) while the $C_{29}$ sterane ratio resembles the Llandovery shale (Figure 9). The maturity of the Deb oil sample is among the least mature ones considering Ts/Tm and Diasterane/sterane ratios (Figure 7A), but $C_{29}$ sterane isomers indicate a higher maturity than most of the oil in Upper Ordovician reef reservoirs. This inconsistency in maturity could also be caused by multi-charging processes from the same source through time, since carbonate-rich

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source rocks are not involved here. Most likely the oil in the Middle Cambrian sandstone reservoirs is exclusively sourced by the uranium-rich Alum Shale, because $C_{26}$-$C_{28}$ triaromatic steroids would occur in this oil if other source rock were involved.

## 6. Conclusions

1. Chemometric tools are efficient in screening decisive oil-source rock correlation biomarkers and showing genetic affinity relationship of samples.
2. Oil samples from Brattefors quarry in south central Sweden were heated by volcanic intrusions with high pyrene/phenanthrene ratios and have $C_{29}$ S/R sterane ratios significantly beyond the normal thermodynamic threshold. Oil reservoired in basinal areas is generated by normal geological burial processes.
3. ETR, $C_{24}$ tetracyclic terpane/$C_{26}$ tricyclic terpane, and relative $C_{29}$ sterane concentrations are the most useful biomarkers in differentiating Llandovery shale from Alum Shale. The uranium irradiation induced decrease of $C_{26}$-$C_{28}$ triaromatic steroids in Alum Shale can be a practical key signal to link oil to the specific sub-stages of the Alum Shale.
4. Alum Shale is the main source rock for the oil in the lower Palaeozoic sandstone and reef reservoirs in the Baltic Basin. A contribution from the Middle Cambrian Alum Shale to the oil in Upper Ordovician limestone reservoirs is noticeable. In contrast, oil in Middle Cambrian siliciclastic reservoirs was mainly sourced from more mature Upper Cambrian and Lower Ordovician Alum Shale.
5. The evaluation of migration distances can help in understanding the accumulation processes. Possible oil mixing occurs in some Lithuanian wells where the Llandovery shale occurs with good source rock properties.

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## Authors

Shengyu Yang is a Ph.D. candidate at the Helmholtz Centre Potsdam–GFZ German Research Centre for Geosciences under the auspices of the Technical University of Berlin. He received bachelor and master degrees, both in petroleum geology, from China University of Petroleum and China University of Geosciences, respectively. His current major scientific interests include biomarker, compositional petroleum generation kinetic and basin modelling.

Hans-Martin Schulz is a senior research scientist at the Helmholtz Centre Potsdam–GFZ German Research Centre for Geosciences. He holds a diploma in geology and a Ph.D., both from the RWTH Aachen University, Germany, and is lecturer for petroleum geology at the Clausthal University of Technology, Germany. His research interests include organic–inorganic interactions in conventional and unconventional oil and gas systems, and nanogeomaterials.

Niels Schovsbo is a senior research scientist at the Geological Survey of Denmark and Greenland. He received his Ph.D. in geochemistry from the University of Copenhagen in 2001. His research focus is on stable isotope geochemistry, major and trace element chemostratigraphy, and reservoir properties of low permeable chalk and shales.

Jørgen A. Bojesen-Koefoed is a senior research scientist with the Geological Survey of Denmark and Greenland. He holds a M.Sc. from the University of Copenhagen and a Ph.D. from the Technical University of Denmark. He works primarily with applied petroleum geochemistry and petrology, with main focus on Greenland and the Arctic in general.

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## FIGURE CAPTIONS

**Figure 1.** Simplified map of the Baltic Basin and its possible oil kitchen. The thermal maturity of the Alum Shale measured on vitrinite-like macerals (Buchardt et al., 1997). Symbols indicate the source rock and oil samples locations.

**Figure 2.** Simplified stratigraphy of the lower Palaeozoic petroleum system in the Polish part of the Baltic Basin.

**Figure 3.** Diagram of pristane/*n*-$C_{17}$ vs.phytane/*n*-$C_{18}$ with two representative GC-FID traces. Depositional environment and biodegradation can be evaluated accordingly (Peters et al., 1999).

**Figure 4.** Comparison of terpane and sterane traces of three representative samples. Traces shown here were provided by GC-MS for direct visual comparison purpose. Ts/Tm ratios and sterane biomarkers presented in table 1 and figures were interpreted from GC-MS/MS to ensure better data quality.

**Figure. 5.** The distributions of triaromatic steroids (m/z=231) in three Alum Shale extracts and two typical oil samples. $C_{20}$-$C_{21}$ triaromatic steroids can be detected from all samples, but some samples show no or very low $C_{26}$-$C_{28}$ responses.

**Figure 6.** (A) Principal component analysis on oil samples based on representative biomarkers and (B) hierarchical cluster result in grouping the oils into two groups.

**Figure 7.** Cross plots of terpane and sterane biomarkers show the maturities of source rock and oil samples. Yellow stripes in panel B manifest the thermodynamic equilibrium intervals of the sterane isomer. Diasterane/sterane radio is calculated from [total $C_{27}$ to $C_{29}$ β, α 20S+20R diasterane]/ [total $C_{27}$ to $C_{29}$ α,1β,1β and α,α,α 20S+20R] steranes (Peters et al., 1990). Ts/Tm is the ratio of $C_{27}$-trisnorneohopane over $C_{27}$-trisnorhopane (Seifert and Moldowan, 1978). Sterane maturity biomarkers are calculated from $C_{29}$ sterane epimer ratios as described by Mackenzie et al. (1980).

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**Figure 8.** The terpane biomarker cross-plot can efficiently separate Llandovery source rocks from the rest. $C_{24}$ TeT and $C_{26}$ TT are abbreviations for $C_{24}$ tetracyclic terpane and $C_{26}$ tricyclic terpane respectively. The extended tricyclic terpane ratio (ETR) (Holba et al., 2001) is calculated from $(C_{28}+C_{29})/(C_{28}+C_{29}+Ts)$ in m/z191. The size of the dot demonstrates the maturity of each sample to evaluate the maturity dependency of the biomarkers.

**Figure. 9.** Ternary diagram showing the relative distribution of $C_{27}$, $C_{28}$ and $C_{29}$ iso-steranes [5α,14β,17β(H) 20S+20R]. The Llandovery shale extracts and oil sample Gec are featured by high concentrations in $C_{29}$ iso-sterane.

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## TABLE CAPTION

**Table 1.** Stratigraphic and geochemical information of shale extracts and oils samples. PM Rank is an evaluation on bidegradation level after (Peters and Moldowan 1991).Parameters with superscripted "C" were used in Chemometric analysis. TT, TeT, H, St, and TAS are abbreviations for tricyclic terpane, tetracyclic terpane, hopane, sterane, and triaromatic steroids, respectively. GI is short for 10*gammacerane/(hopane+gammacerane). Biomarker signal qualities of $C_{26}$-$C_{28}$ triaromatic steroids and carbazoles are presented. "++" describes those according compounds can be clearly identified. "+" demonstrates biomarkers can be interpreted from weak signals. "-" represents those no corresponding biomarkers can be identified.

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| | Name | Well/place | Age | PM Rank | Pr/Ph$^{C}$ | Pr/nC$_{17}$ | Ph/nC$_{18}$ | C$_{22}$/C$_{21}$TT$^{C}$ | C$_{24}$/C$_{23}$TT$^{C}$ | ETR$^{C}$ | C$_{24}$TeT/C$_{26}$TT$^{C}$ | C$_{23}$TT/H | GI | H C$_{35}$S/C$_{34}$S | St$_{27}$ISO$^{C}$ | St$_{28}$ISO$^{C}$ | St$_{29}$ISO$^{C}$ | DiaSt/St | St$_{29}$ S/(S+R) | St$_{29}$ ββ/(ββ+αα) | Ts/Tm | C$_{26}$-C$_{28}$ TAS | Carbazoles |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Source rock | Gen | Geniai-1 | Llandovery | 1 | 2.16 | 0.73 | 0.40 | 0.24 | 0.40 | 0.53 | 0.56 | 0.88 | - | 0.35 | 0.25 | 0.12 | 0.63 | 1.40 | 0.47 | 0.42 | 0.60 | ++ | ++ |
| | Ruk | Rukai-2 | Llandovery | 1 | 1.95 | 0.46 | 0.26 | 0.30 | 0.42 | 0.55 | 0.62 | 0.84 | - | - | 0.25 | 0.16 | 0.59 | 1.42 | 0.49 | 0.54 | 0.70 | ++ | ++ |
| | B3/a | B-3 | Llandovery | 2 | 4.49 | 1.52 | 0.34 | 0.32 | 0.45 | 0.45 | 0.67 | 0.72 | - | - | 0.21 | 0.17 | 0.62 | 1.04 | 0.35 | 0.32 | 0.42 | ++ | ++ |
| | B3/b | B-3 | Llandovery | 1 | 3.17 | 1.18 | 0.44 | 0.27 | 0.38 | 0.28 | 0.61 | 0.25 | - | - | 0.20 | 0.11 | 0.69 | 1.16 | 0.41 | 0.35 | 0.61 | ++ | ++ |
| | B3/c | B-3 | Llandovery | 1 | 3.35 | 1.00 | 0.37 | 0.24 | 0.39 | 0.35 | 0.51 | 0.32 | - | - | 0.21 | 0.15 | 0.64 | 1.09 | 0.42 | 0.34 | 0.47 | ++ | ++ |
| | Ott | Ottenby | L.Ordovician | 1 | 1.38 | 0.46 | 0.35 | 0.22 | 0.60 | 0.68 | 0.29 | 1.06 | - | - | 0.28 | 0.21 | 0.51 | 0.73 | 0.41 | 0.45 | 0.47 | - | ++ |
| | Kak/a | Kakeled | U. Cambrian | 1 | 1.71 | 0.37 | 0.28 | 0.21 | 0.61 | 0.86 | 0.20 | 0.86 | - | - | 0.28 | 0.25 | 0.47 | 1.08 | 0.38 | 0.36 | 0.41 | - | ++ |
| | Dju | Djupvik | M.Cambrian | 2 | 1.64 | 1.76 | 1.04 | 0.20 | 0.57 | 0.77 | 0.20 | 1.07 | 0.73 | 0.40 | 0.25 | 0.20 | 0.55 | 0.77 | 0.32 | 0.31 | 0.34 | ++ | ++ |
| | Kak/b | Kakeled | M.Cambrian | 1 | 1.55 | 0.68 | 0.53 | 0.21 | 0.47 | 0.82 | 0.18 | 0.85 | - | - | 0.31 | 0.23 | 0.46 | 0.86 | 0.40 | 0.38 | 0.38 | ++ | ++ |
| | B7 | B-7 | M.Cambrian | 1 | 1.61 | 0.27 | 0.20 | 0.24 | 0.54 | 0.74 | 0.31 | 0.62 | - | - | 0.30 | 0.23 | 0.47 | 1.35 | 0.48 | 0.48 | 0.70 | ++ | ++ |
| Reservoir oil | Bra/a | Brattefors | M.Ordovician | 2 | 1.53 | 1.10 | 0.78 | 0.23 | 0.64 | 0.85 | 0.20 | 2.36 | 0.82 | 0.38 | 0.35 | 0.15 | 0.50 | 2.41 | 0.57 | 0.58 | 0.76 | + | ++ |
| | Bra/b | Brattefors | M.Ordovician | 2 | 1.32 | 2.02 | 1.65 | 0.24 | 0.61 | 0.84 | 0.18 | 2.42 | 0.80 | - | 0.34 | 0.17 | 0.49 | 1.99 | 0.58 | 0.62 | 0.74 | + | ++ |
| | BÅ/a | BÅ-6 | U.Ordovician | 2 | 1.03 | 1.10 | 0.68 | 0.21 | 0.80 | 0.83 | 0.22 | 0.91 | - | 0.41 | 0.29 | 0.19 | 0.52 | 1.38 | 0.42 | 0.51 | 0.56 | ++ | - |
| | BÅ/b | BÅ-6 | U.Ordovician | 1 | 1.06 | 0.97 | 0.67 | 0.22 | 0.79 | 0.84 | 0.21 | 1.08 | - | - | 0.28 | 0.18 | 0.54 | 1.46 | 0.43 | 0.52 | 0.60 | ++ | - |
| | Gus | Guseuskaya -4 | U.Ordovician | 1 | 2.15 | 0.90 | 0.46 | 0.23 | 0.72 | 0.82 | 0.20 | 0.75 | - | 0.38 | 0.27 | 0.21 | 0.52 | 1.24 | 0.38 | 0.56 | 0.55 | ++ | - |
| | Rut | Rute-1 | U.Ordovician | 1 | 1.98 | 0.52 | 0.31 | 0.23 | 0.81 | 0.83 | 0.22 | 1.04 | - | - | 0.27 | 0.26 | 0.47 | 1.30 | 0.45 | 0.57 | 0.63 | ++ | - |
| | Adz | Adze-6 | U.Ordovician | 2 | 2.06 | 1.39 | 0.75 | 0.23 | 0.71 | 0.86 | 0.17 | 0.81 | - | - | 0.25 | 0.22 | 0.53 | 1.55 | 0.41 | 0.54 | 0.48 | ++ | - |
| | Ber | Bernatai | U.Ordovician | 2 | 1.95 | 3.42 | 2.16 | 0.19 | 0.77 | 0.86 | 0.18 | 0.68 | 0.78 | 0.42 | 0.27 | 0.20 | 0.53 | 1.42 | 0.44 | 0.54 | 0.49 | ++ | - |
| | E6 | E-6 | U.Ordovician | 1 | 2.13 | 0.99 | 0.54 | 0.23 | 0.76 | 0.84 | 0.16 | 0.82 | - | 0.37 | 0.26 | 0.24 | 0.50 | 1.45 | 0.43 | 0.49 | 0.52 | ++ | - |
| | Sak | Sakuciai-1 | M.Cambrian | 1 | 2.58 | 0.60 | 0.26 | 0.20 | 0.79 | 0.63 | 0.29 | 0.89 | - | - | 0.24 | 0.25 | 0.51 | 2.04 | 0.40 | 0.60 | 0.72 | - | - |
| | C9 | C9-1 | M.Cambrian | 0 | 2.11 | 0.38 | 0.21 | 0.23 | 0.81 | 0.73 | 0.17 | 0.98 | - | - | 0.29 | 0.15 | 0.56 | 2.15 | 0.51 | 0.60 | 0.79 | - | + |
| | B8 | B-8 | M.Cambrian | 0 | 2.01 | 0.43 | 0.24 | 0.20 | 0.82 | 0.75 | 0.22 | 1.20 | - | - | 0.26 | 0.23 | 0.51 | 1.71 | 0.46 | 0.54 | 0.68 | - | + |
| | Deb | Debki-8 | M.Cambrian | 0 | 1.78 | 0.35 | 0.22 | 0.21 | 0.81 | 0.67 | 0.43 | 1.07 | - | 0.39 | 0.27 | 0.22 | 0.51 | 0.90 | 0.46 | 0.57 | 0.57 | - | ++ |
| | Gec | Genciai-3 | M.Cambrian | 1 | 2.69 | 0.74 | 0.31 | 0.22 | 0.75 | 0.67 | 0.31 | 1.32 | - | - | 0.19 | 0.18 | 0.63 | 2.47 | 0.52 | 0.66 | 0.74 | + | + |
| | D5 | D5-1 | M.Cambrian | 1 | 2.05 | 0.57 | 0.24 | 0.21 | 0.78 | 0.71 | 0.26 | 1.21 | - | - | 0.26 | 0.21 | 0.53 | 1.45 | 0.43 | 0.58 | 0.56 | - | - |

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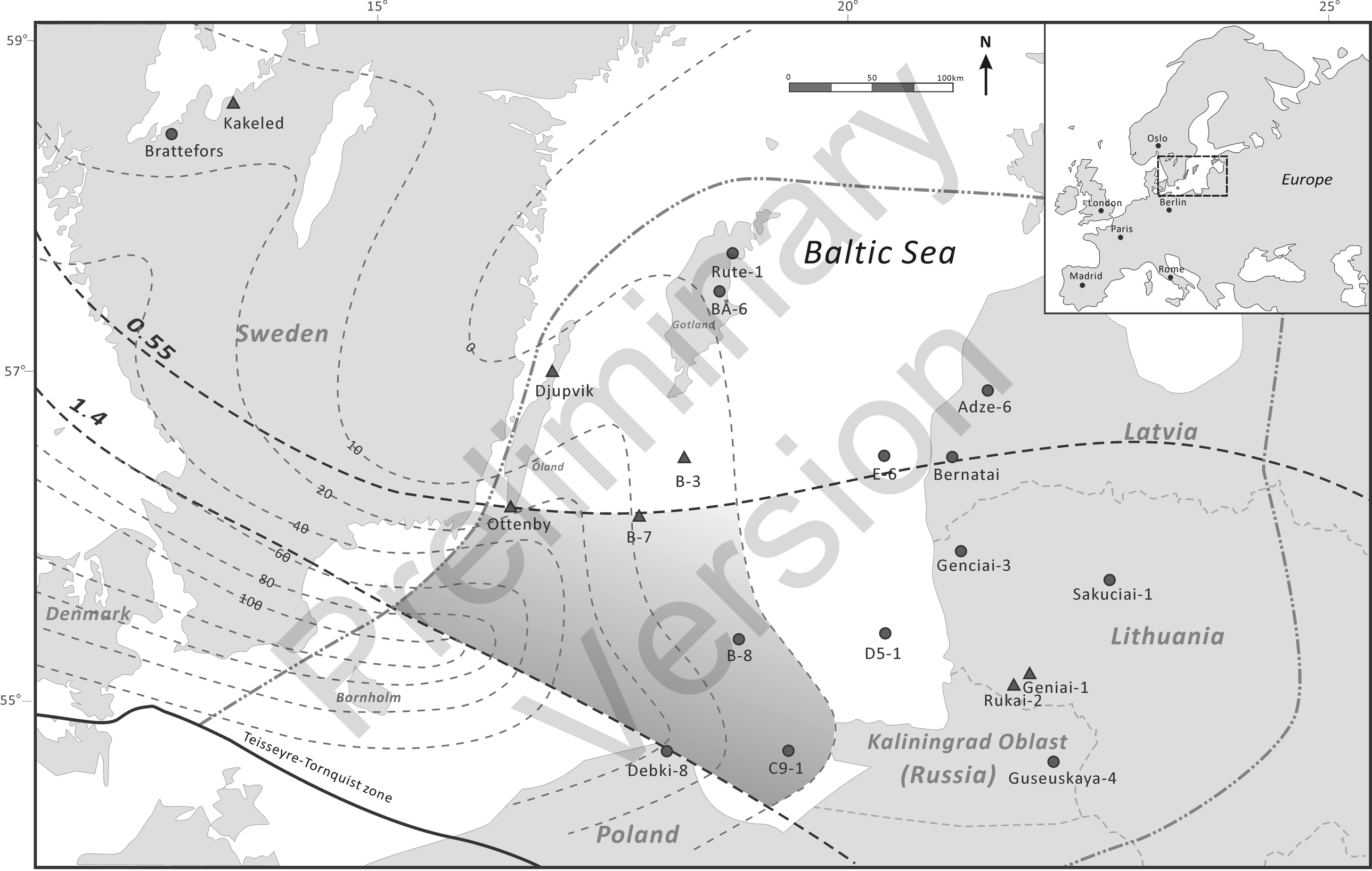

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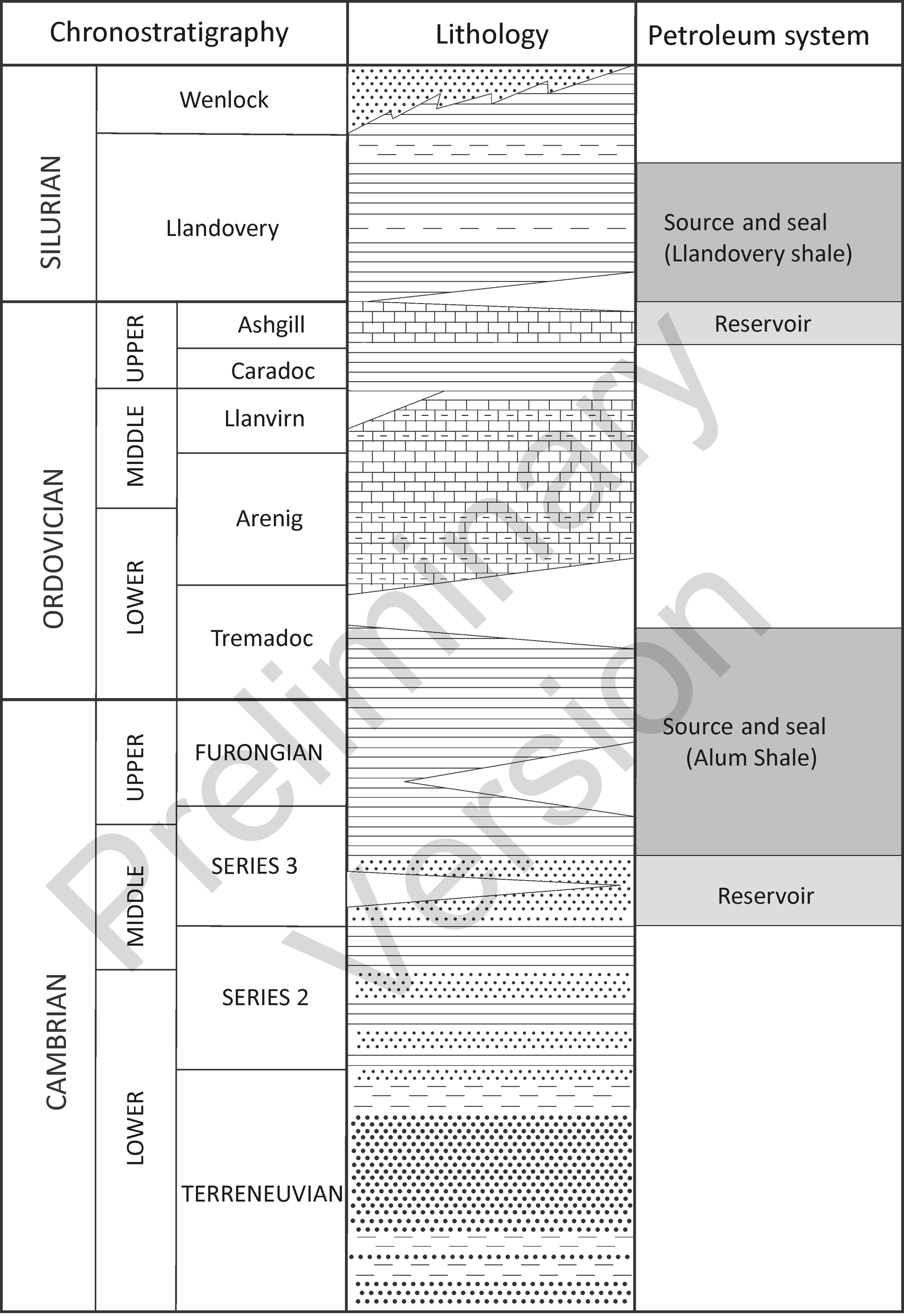

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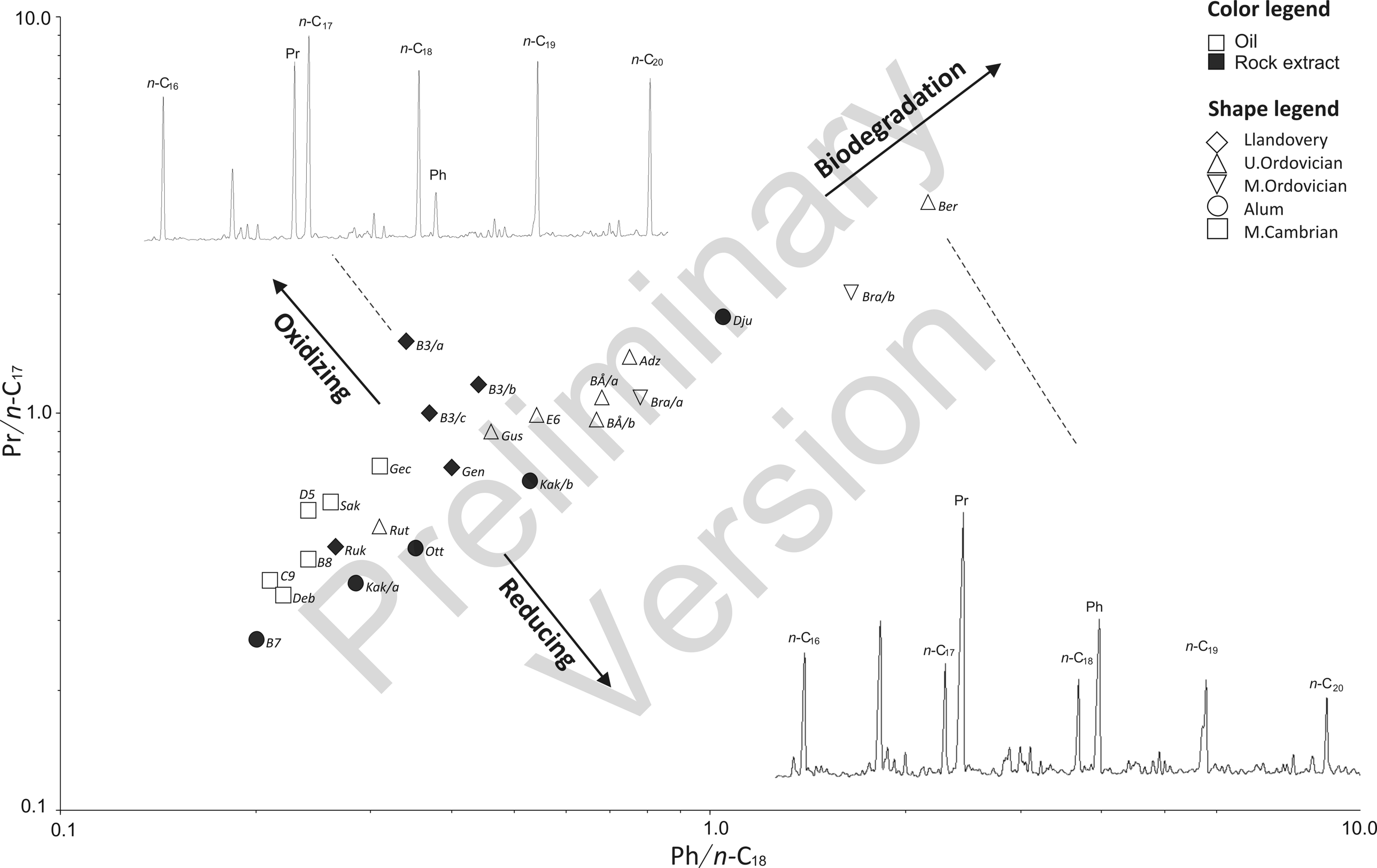


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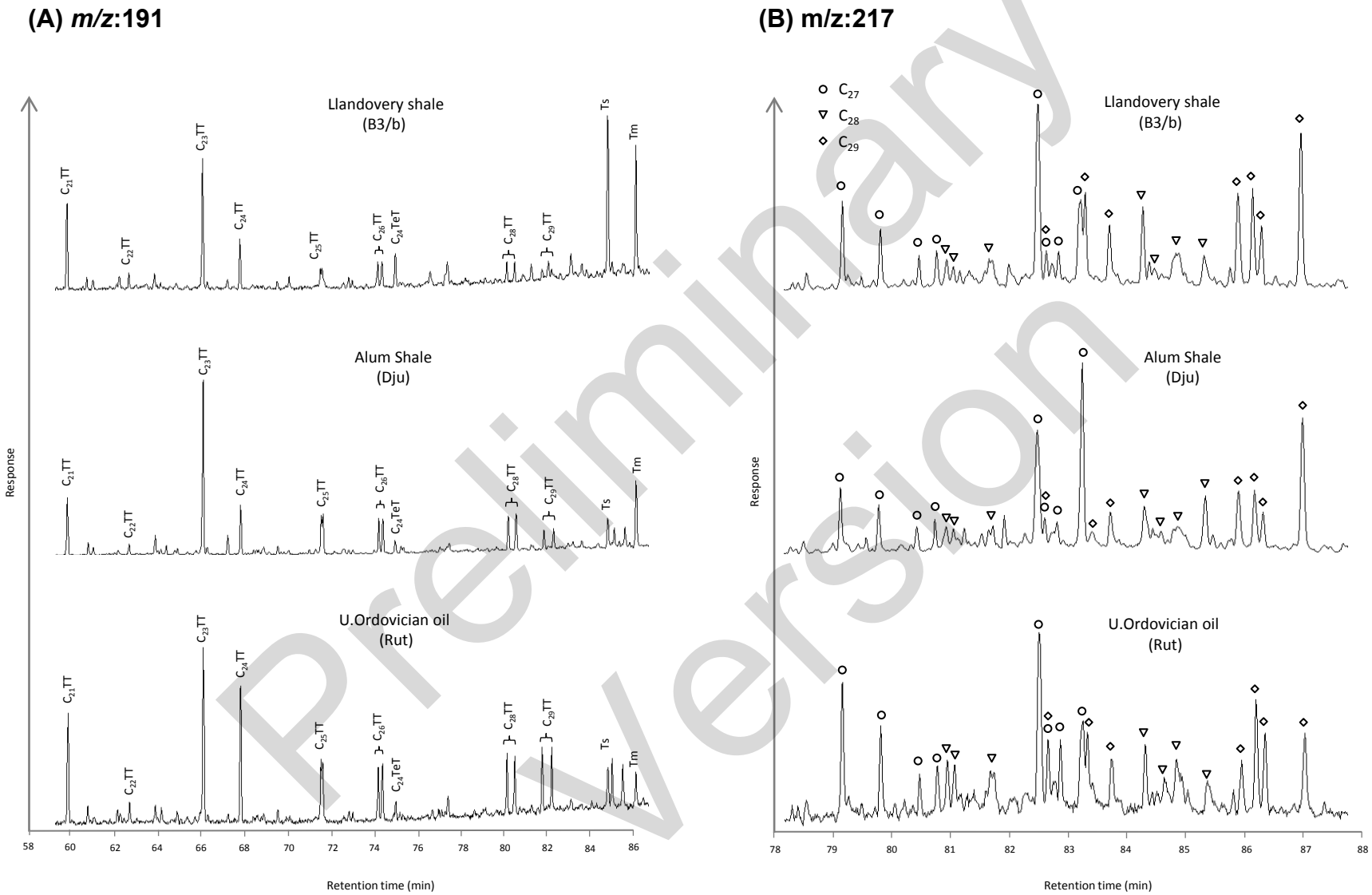


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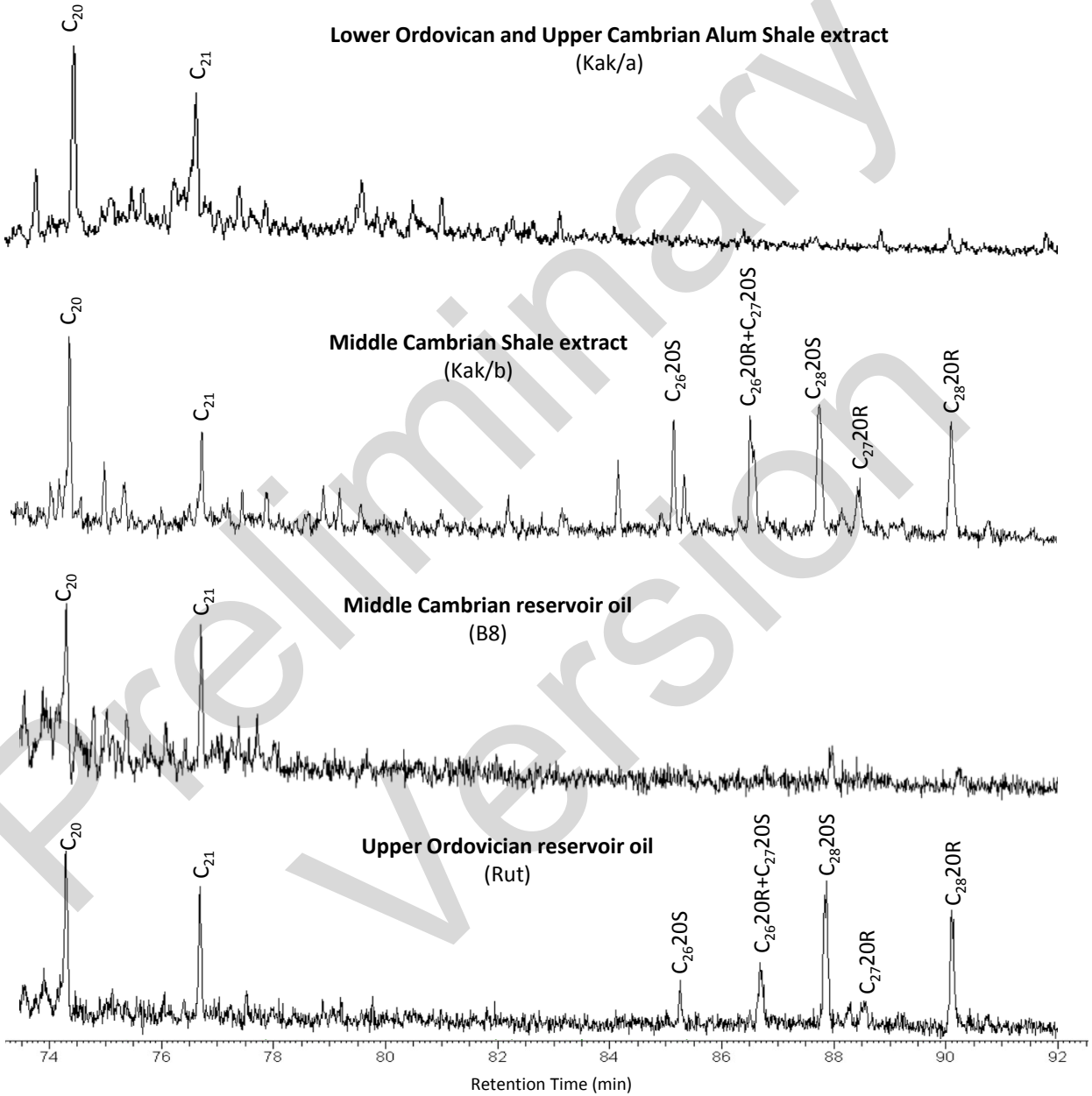


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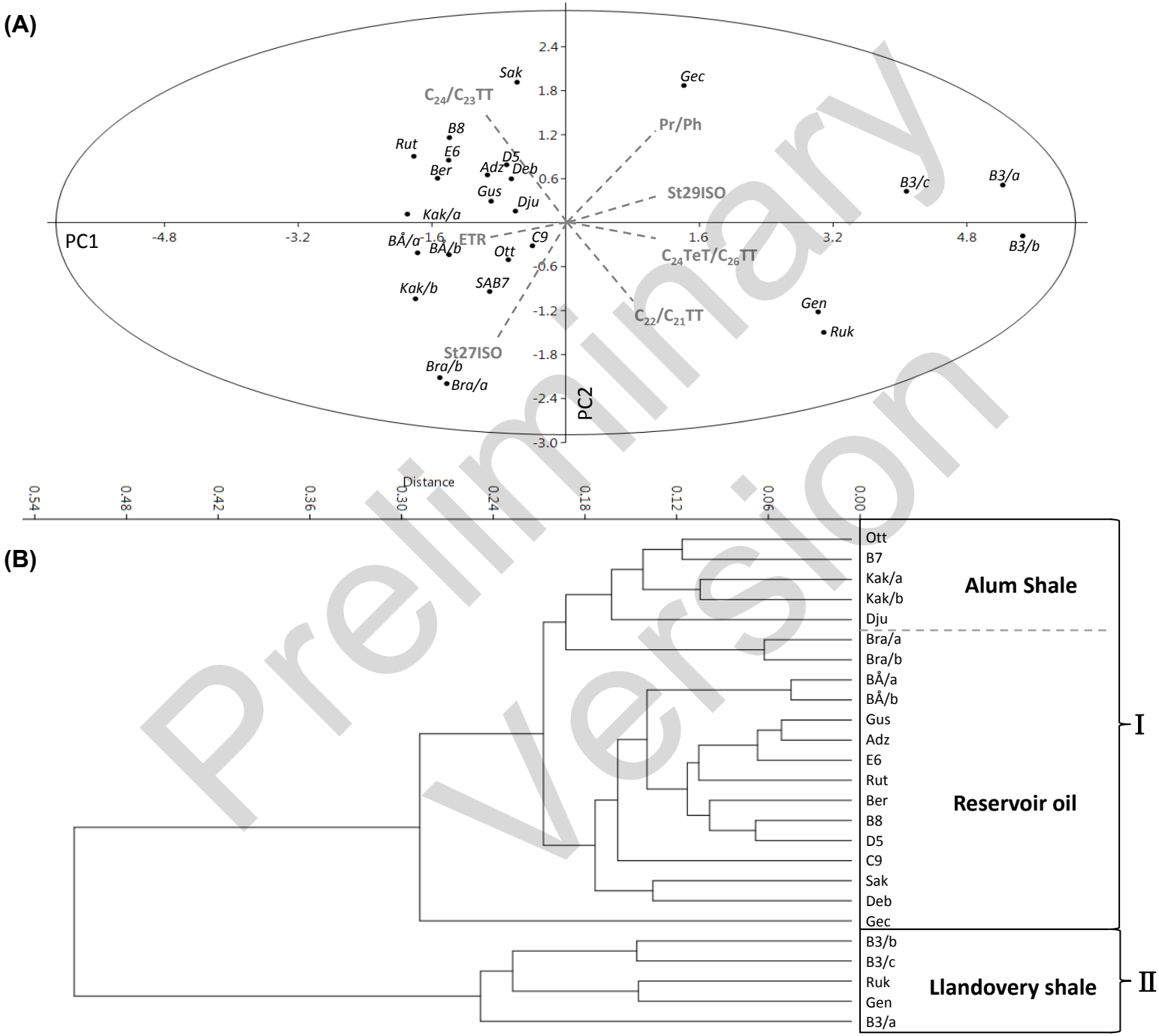


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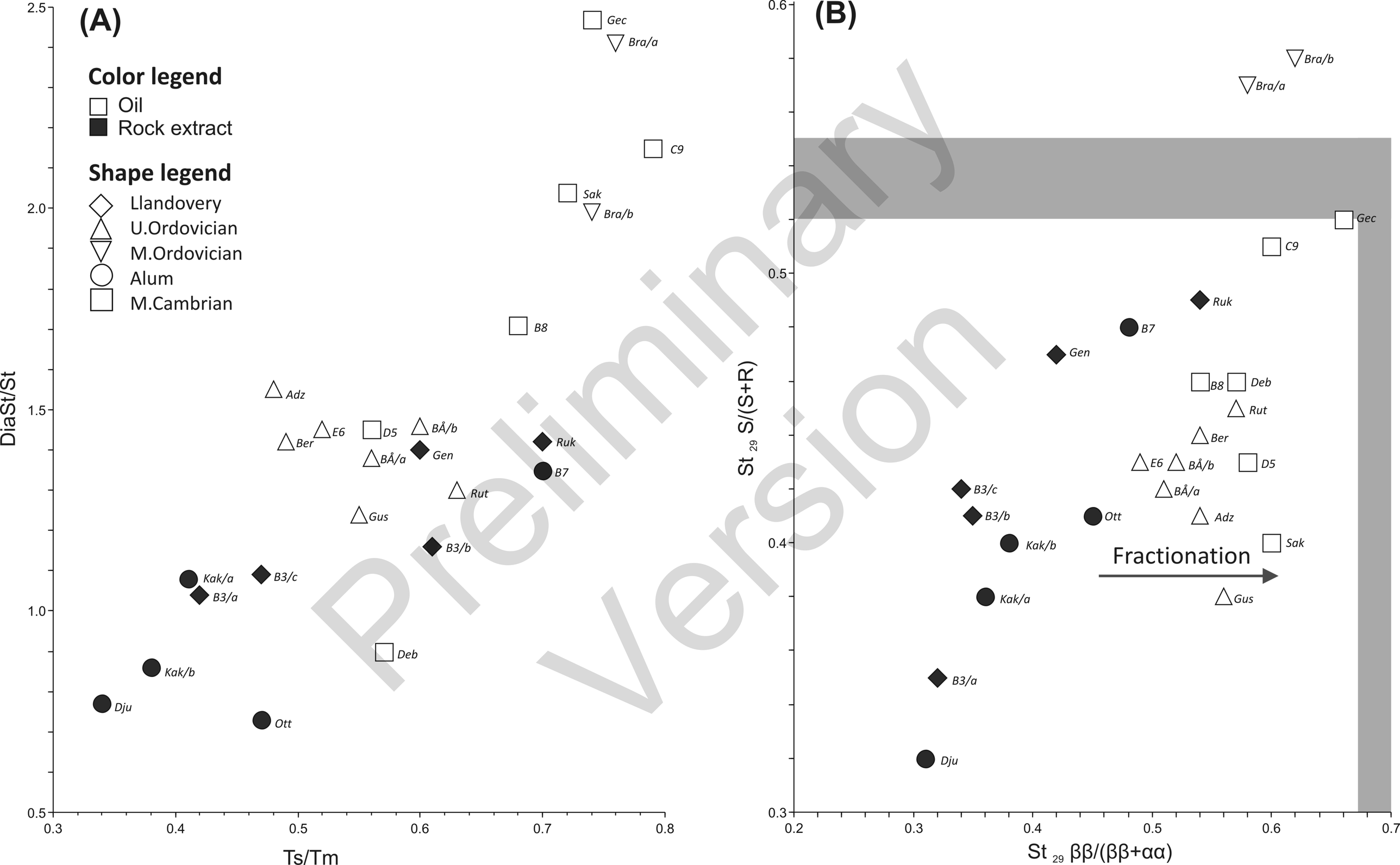
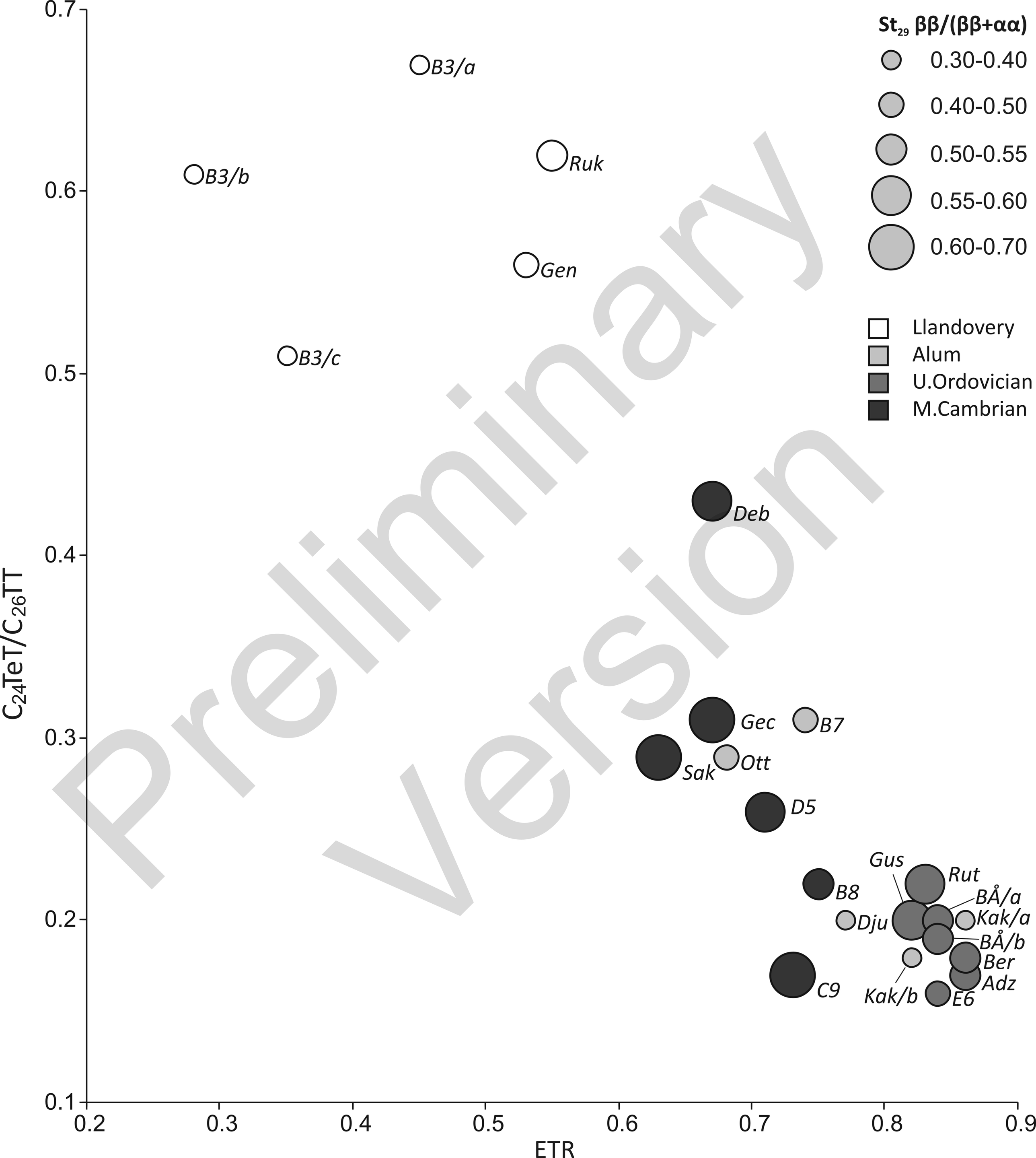
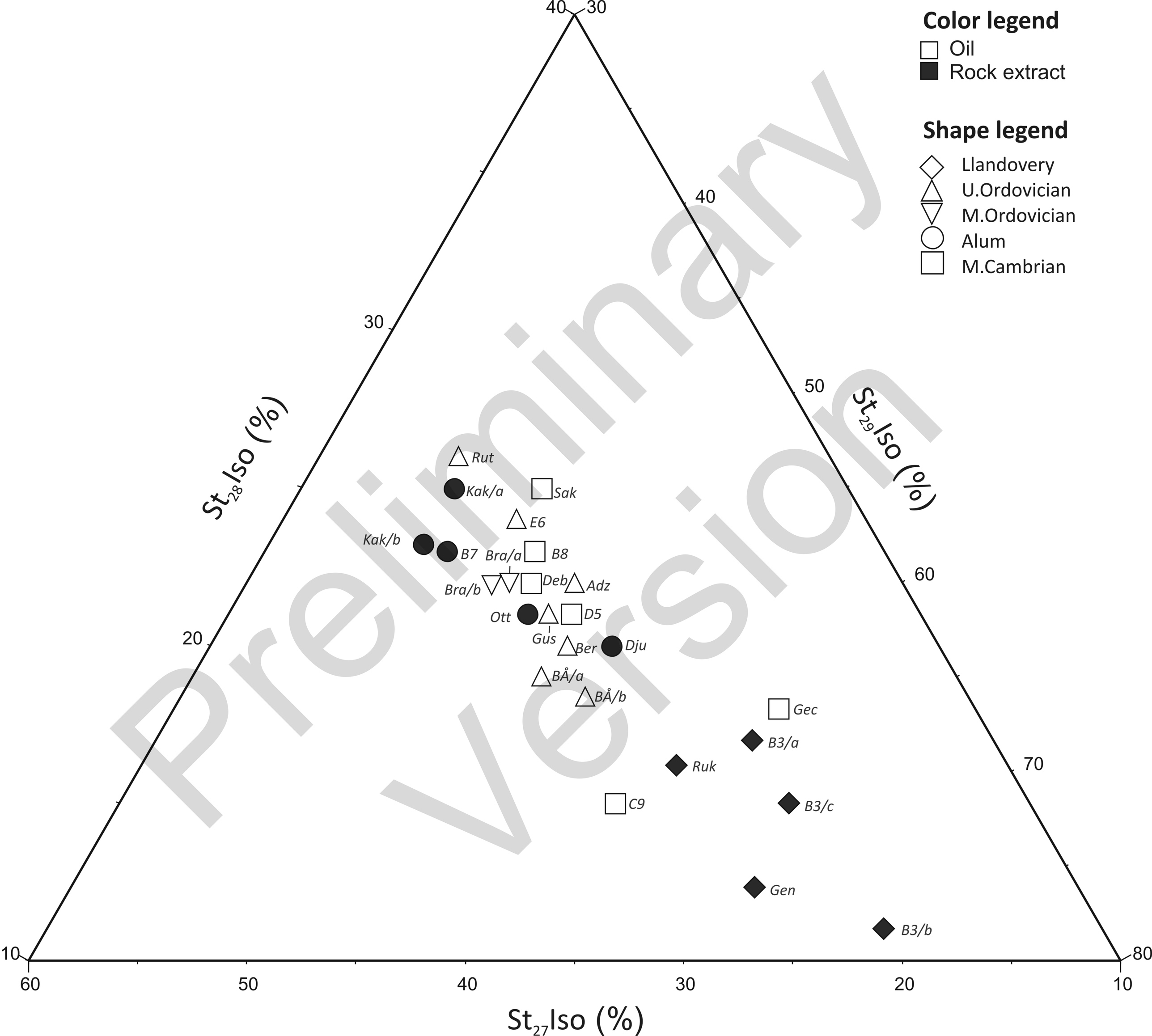
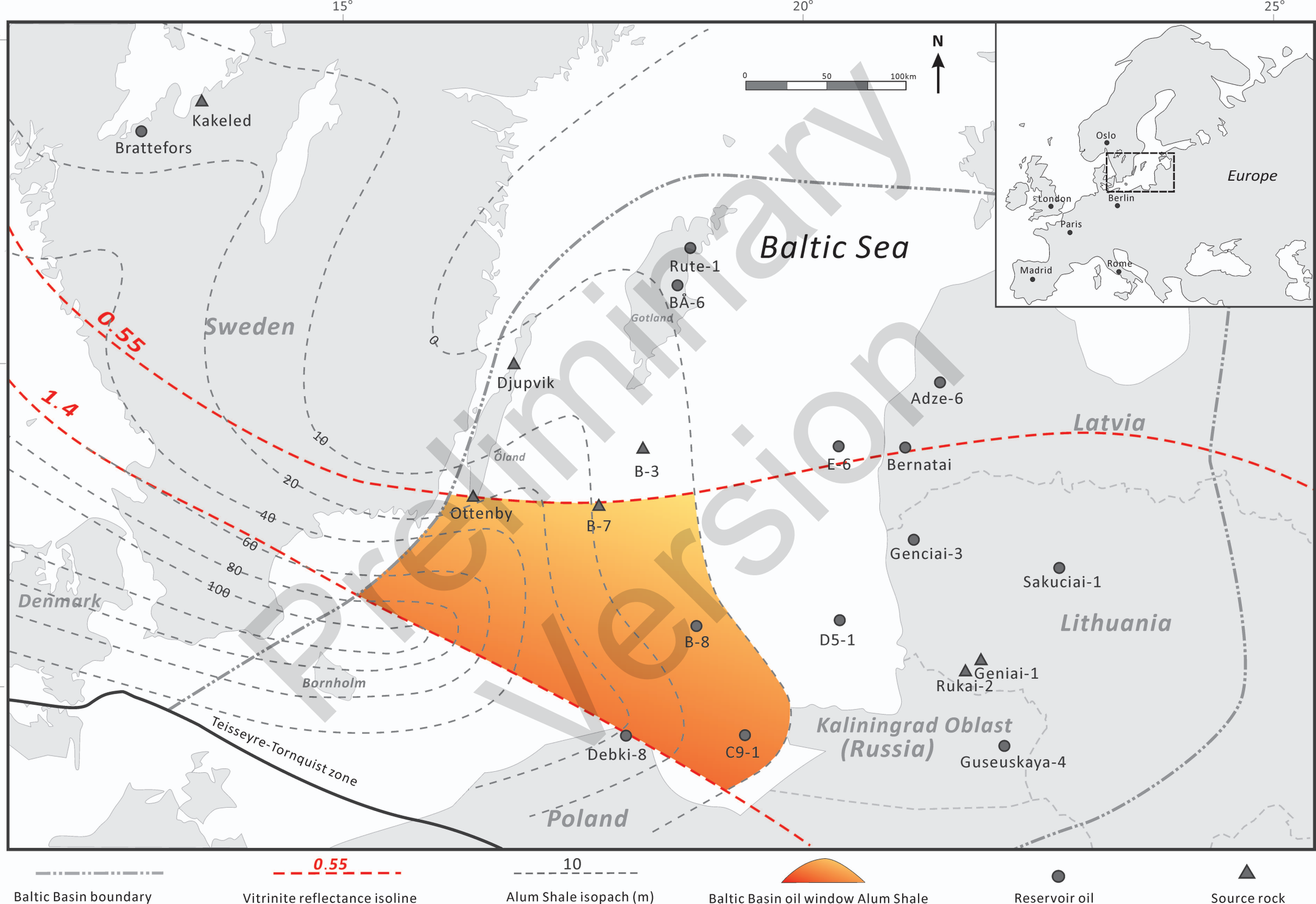
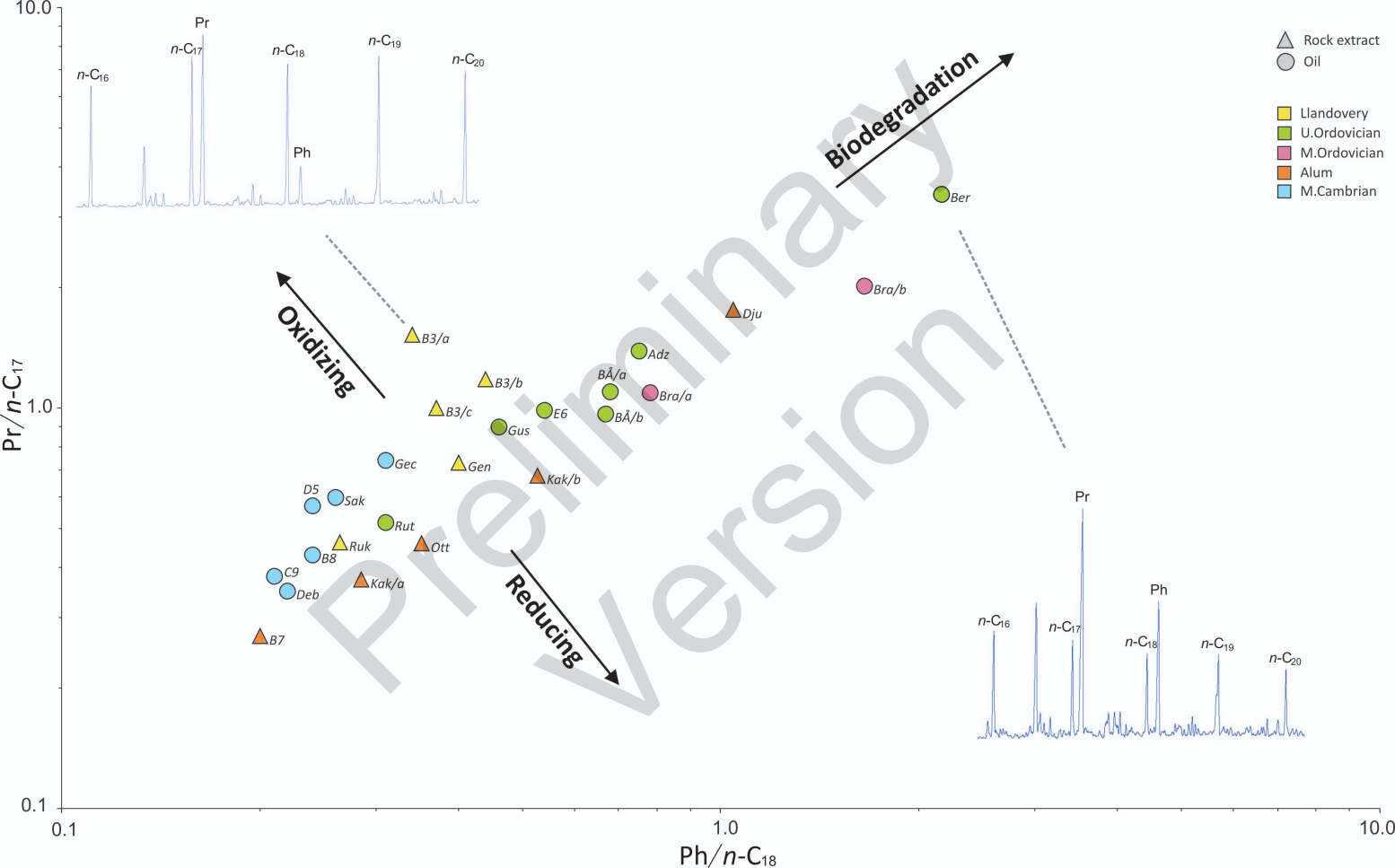

(A)
Color legend
Oil
Rock extract
Shape legend
Llandovery
U.Ordovician
M.Ordovician
Alum
M.Cambrian
DiaSt/St
Ts/Tm
Gec
Bra/a
C9
Sak
Bra/b
B8
Adz
E6
D5
BÅ/b
Ber
BÅ/a
Gen
Ruk
B7
Rut
Gus
B3/b
Kak/a
B3/c
B3/a
Deb
Kak/b
Dju
Ott
(B)
St 29 S/(S+R)
St 29 ββ/(ββ+αα)
Fractionation
Preliminary Version

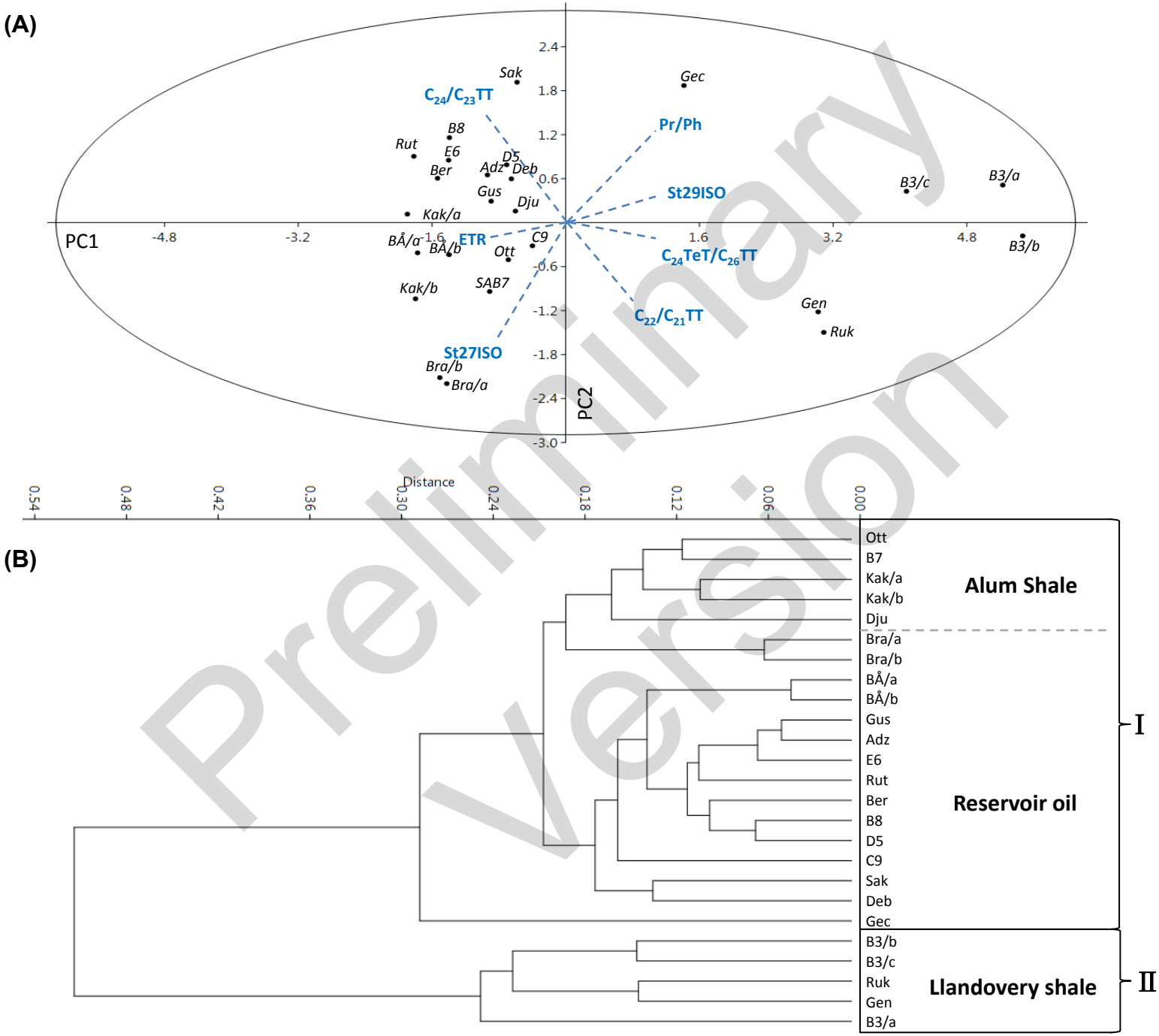


Preliminary version

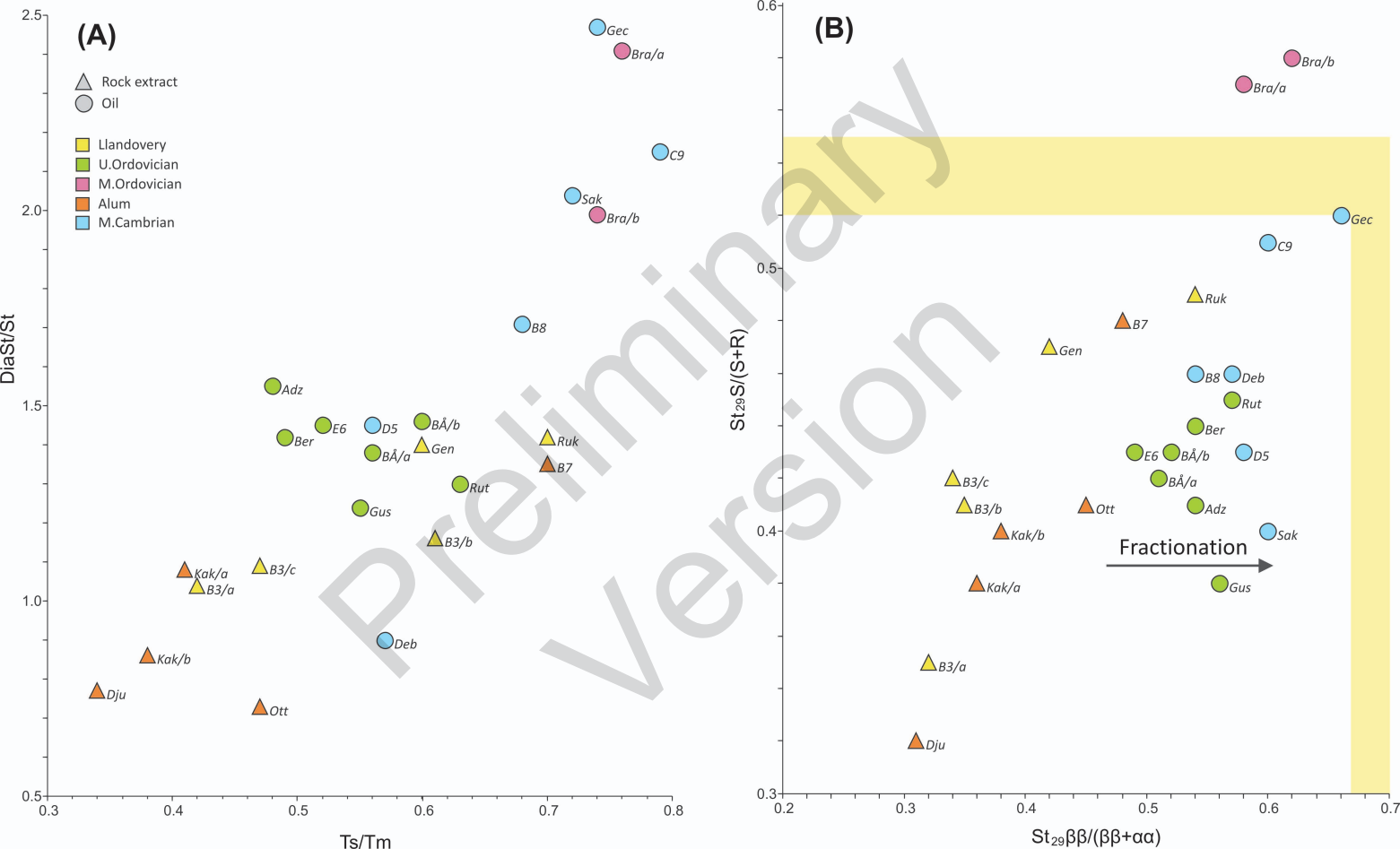

Color legend
Oil
Rock extract
Shape legend
Llandovery
U.Ordovician
M.Ordovician
Alum
M.Cambrian
St28Iso (%)
St29Iso (%)
St27Iso (%)
Rut
Kak/a
Sak
E6
Kak/b
B7
Bra/a
B8
Bra/b
Deb
Adz
Ott
D5
Gus
Ber
Dju
BÅ/a
BÅ/b
Gec
B3/a
Ruk
C9
B3/c
Gen
B3/b
Preliminary version

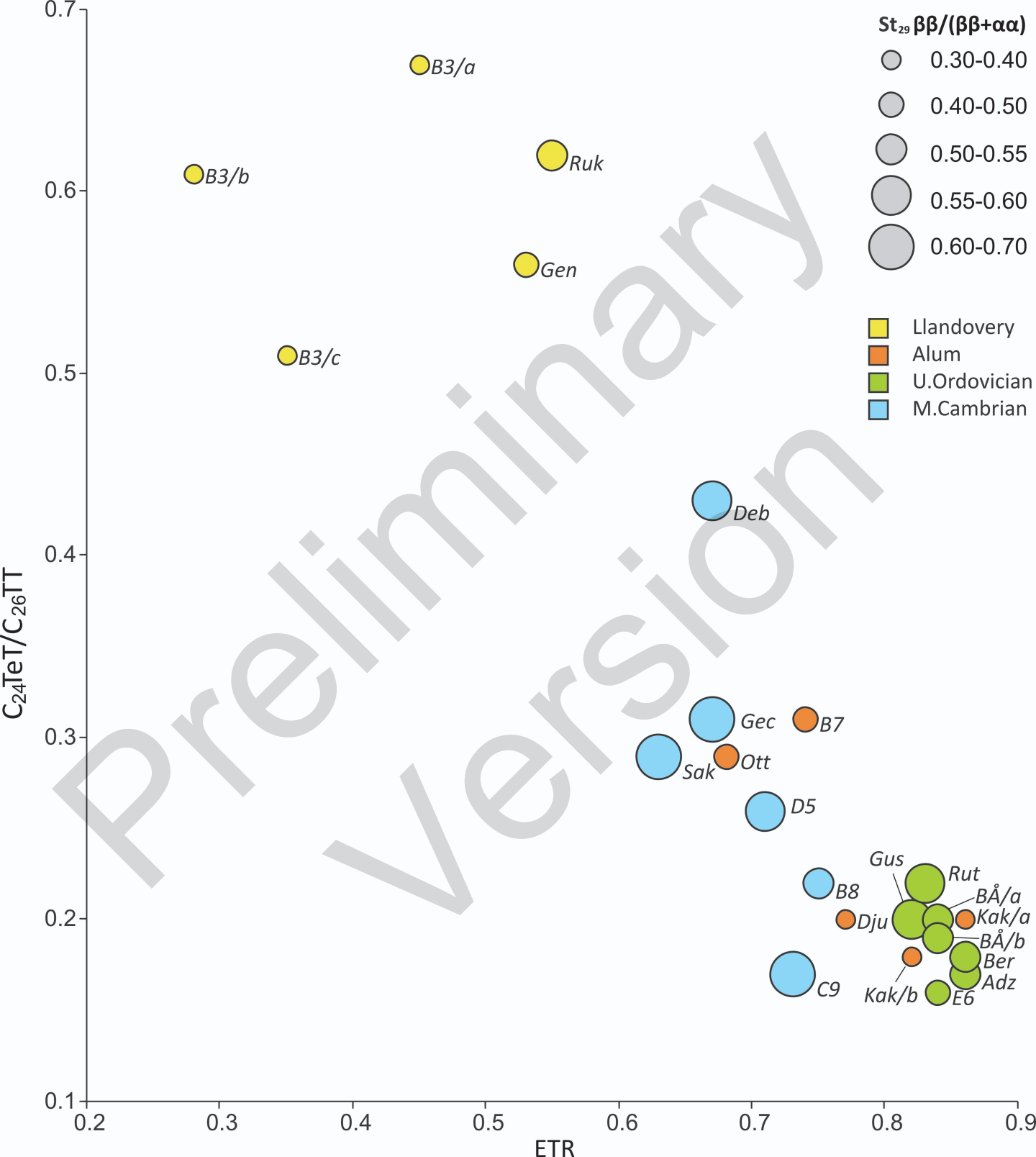

15°
20°
25°
59°
57°
55°
N
0
50
100km
Kakeled
Brattefors
Baltic Sea
Rute-1
BÅ-6
Gotland
Sweden
0.55
1.4
Djupvik
Adze-6
Latvia
Öland
B-3
E-6
Bernatai
10
20
40
60
80
100
Ottenby
B-7
Genciai-3
Sakuciai-1
Denmark
Lithuania
B-8
D5-1
Geniai-1
Rukai-2
Bornholm
Kaliningrad Oblast
(Russia)
Teisseyre-Tornquist zone
Debki-8
C9-1
Guseuskaya-4
Poland
Oslo
Europe
London
Berlin
Paris
Madrid
Rome
Preliminary version
Baltic Basin boundary
0.55
Vitrinite reflectance isoline
10
Alum Shale isopach (m)
Baltic Basin oil window Alum Shale
Reservoir oil
Source rock

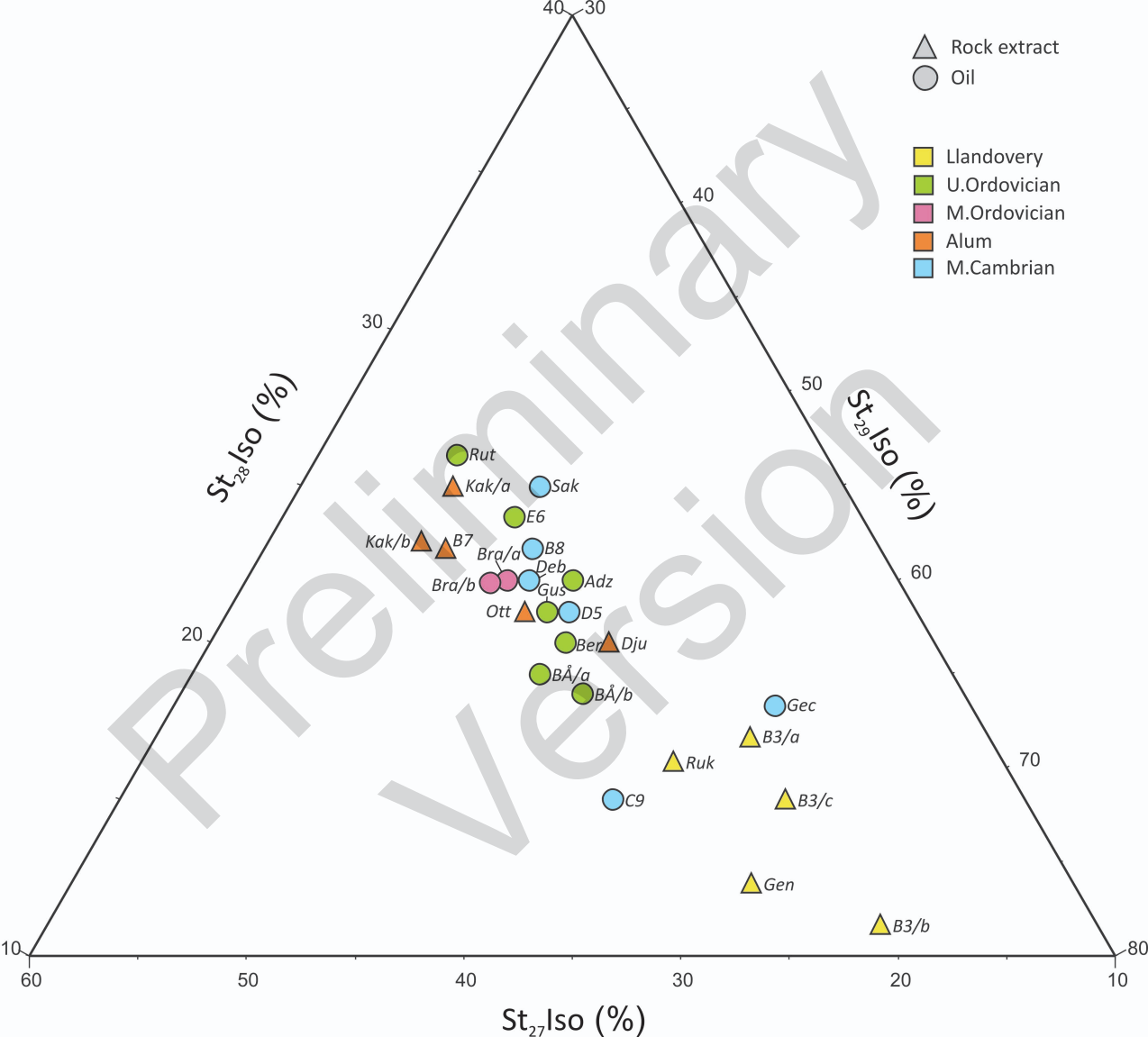

Rock extract
Oil
Llandovery
U.Ordovician
M.Ordovician
Alum
M.Cambrian
Biodegradation
Oxidizing
Reducing
Preliminary Version
n-C16
Pr
n-C17
n-C18
Ph
n-C19
n-C20
Ber
Bra/b
Dju
B3/a
Adz
B3/b
BÅ/a
Bra/a
B3/c
E6
BÅ/b
Gus
Gec
Gen
Kak/b
D5
Sak
Rut
Ruk
Ott
B8
C9
Kak/a
Deb
B7
10.0
1.0
0.1
Pr/n-C17
Ph/n-C18




Preliminary Version


(A)
Rock extract
Oil
Llandovery
U.Ordovician
M.Ordovician
Alum
M.Cambrian
DiaSt/St
Ts/Tm
Gec
Bra/a
C9
Sak
Bra/b
B8
Adz
E6
D5
BÅ/b
Ber
BÅ/a
Gen
Ruk
B7
Rut
Gus
B3/b
Kak/a
B3/c
B3/a
Deb
Kak/b
Dju
Ott
(B)
St29S/(S+R)
St29ββ/(ββ+αα)
Fractionation
Preliminary Version


St29 ββ/(ββ+αα)
0.30-0.40
0.40-0.50
0.50-0.55
0.55-0.60
0.60-0.70
Llandovery
Alum
U.Ordovician
M.Cambrian
B3/a
B3/b
Ruk
Gen
B3/c
Deb
Gec
B7
Sak
Ott
D5
Gus
Rut
B8
BÅ/a
Dju
Kak/a
BÅ/b
Ber
Adz
C9
Kak/b
E6
C24TeT/C26TT
ETR
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Preliminary Version


Rock extract
Oil
Llandovery
U.Ordovician
M.Ordovician
Alum
M.Cambrian
St28Iso (%)
St29Iso (%)
St27Iso (%)
Rut
Kak/a
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E6
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Bra/b
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Adz
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D5
Ben
Dju
BÅ/a
BÅ/b
Gec
B3/a
Ruk
C9
B3/c
Gen
B3/b
Preliminary Version