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Origin of Nama Basin bitumen seeps: Petroleum derived from a Permian lacustrine source rock traversing southwestern Gondwana

Roger E. Summons [a,*], Janet M. Hope [b], Roger Swart [c], Malcolm R. Walter [d]

[a] *Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA 02139, USA*
[b] *Research School of Earth Sciences, Australian National University, Canberra 0200, Australia*
[c] *P.O. Box 24287, Windhoek, Namibia*
[d] *Australian Centre for Astrobiology, Macquarie University Biotechnology Research Institute, Sydney, NSW 2109, Australia*

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Abstract

Biodegraded bitumens associated with quartz and calcite veins in the Cambrian Fish River Subgroup sediments of the Nama Group of southern Namibia have a geochemical signature diagnostic for organic matter that was deposited in a saline lacustrine palaeoenvironment. In particular, they contain abundant gammacerane, β-carotane and 3β-methylhopanes while 24-isopropyl cholestanes and dinosteroids are not detectable. Sealed tube hydrous pyrolysis of asphaltene and polar fractions yielded saturated hydrocarbons amenable to C isotopic analysis, and these analyses show unusually low δ^{13}C values. These combined characteristics are also present in immature bitumens from the Permian Irati Formation of Brazil and a saline lacustrine facies of the Whitehill Formation in the Karoo Basin, South Africa. We conclude that the bitumens originated from Whitehill equivalent strata of the Kalahari Basin deposited in what was an extensive saline lacustrine basin in southwestern Gondwana during the Early Permian. In southern Africa, source rocks of the Whitehill Formation are generally immature for petroleum generation and it is therefore likely that the Nama bitumens were expelled by contact metamorphism during emplacement of Karoo dolerite sills and dykes in the Jurassic.

1. Introduction

Vein bitumens and hydrocarbon rich fluid inclusions have been reported from several localities in the Neoproterozoic–Cambrian Nama Group of the Nama Basin, Namibia (Kvenvolden and Roedder, 1971; Walter et al., 1996). If these bitumens were of Nama age their biomarker and isotopic compositions may be informative about events during the Neoproterozoic–Cambrian transition. Irrespective of their age, they could also provide useful information on the depositional setting/environment of prospective source rocks and potential petroleum resources. Accordingly, we undertook a geochemical study to determine their possible origins.

The Nama Basin extends for over 350,000 km^2 across southern Namibia, western Botswana and the northwestern tip and southwestern margins of South Africa, with extensive outcrops only in

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[*] Corresponding author.
E-mail address: rsummons@mit.edu (R.E. Summons).

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Namibia. The Nama Sequence developed as a foreland basin in response to the developing Damara and Gariep orogens to the north and west respectively (Gresse and Germs, 1993; Germs, 1995). The Nama sequence was deposited approximately 600–530 Ma, thus spanning the Precambrian–Cambrian boundary (Germs, 1995; Grotzinger et al., 1995). The Nama is largely undeformed, being folded only at its edges. Temperatures appear to have reached at least 200 °C in the undeformed portions, determined from illite crystallinity data (Meert et al., 1997). A major unconformity separates the Nama Group sediments from the overlying Carboniferous–Permian sequence, which form the basal section of the Karoo Group. In southern Namibia the Karoo age sequence is thought to have been separated from the main Karoo Basin by a highland (Visser, 1987) and is known as the Kalahari Basin. No Triassic section is found in the Kalahari Basin and the youngest Karoo rocks are intrusive and extrusive igneous rocks of the Jurassic Stormberg Group. These outcrop extensively over southern Namibia. The final phase of basin formation was the development of the Cenozoic Kalahari Basin (Haddon and McCarthy, 2005). This developed as a successor basin to the Karoo Basin but, although aerially extensive, it is not of any significant thickness in southern Namibia.

Hydrocarbon occurrences have been reported from several localities in southern Namibia. Occurrences of bitumen veins occur in the youngest unit of the Nama, the Cambrian Fish River Sub-Group (Altebäumer and Altebäumer, 1990). The best outcrops are in the Fish River itself near Berseba (see Fig. 1 for locality). These veins strike approximately east–west and are commonly associated with calcite. Maximum vein thickness is 5 cm. The bitumen is brittle, vitreous and has a conchoidal fracture. It was previously assumed that the bitumen was derived from the Nama sequence.

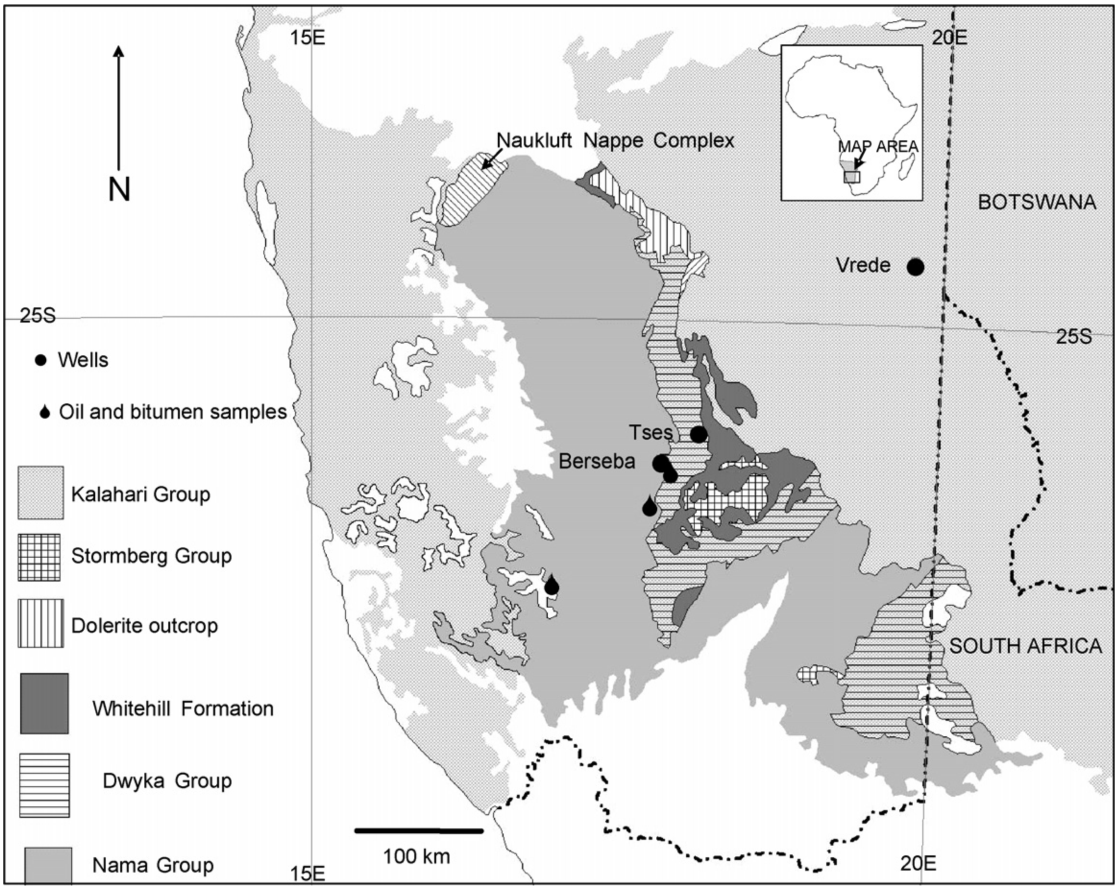

Fig. 1. Map showing the locations of Nama Basin (Namibia) bitumen samples relative to outcrops of Neoproterozoic–Cambrian Nama Group and major units of the Phanerozoic cover.

A second type of occurrence is on the farm Heigums 205 where a quartz fault breccia contains light hydrocarbons which ooze out of fissures, particularly when the rock is hammered. A third type of occurrence is found on Geiaus 6 where quartz crystals contain inclusions of water and oil. The quartz crystals are contained in calcite filled veins in a dyke of probable Gannakouriep age (715 Ma). Fresh samples of these were not collected in the study but samples were obtained from collectors. The ensuing data, however, proved not to be useful since they contained insufficient hydrocarbon for rigorous characterisation.

Unambiguous determination of the origins of hydrocarbon in bitumens, seeps and fluid inclusions requires direct access to, and comparison with, representative source rock samples. However, aspects of the palaeoenvironment and geological age of petroleum source rocks can be evaluated using biomarker patterns and isotopic data (Seifert and Moldowan, 1981; McKirdy et al., 1994; Murray et al., 1994; Dowling et al., 1995; George et al., 1998; Peters et al., 2004). Molecular proxies for vascular plants and algal plankton that radiated in the Mesozoic and Cenozoic have been particularly useful for placing age constraints on seeps and petroleum accumulations of unknown affinity (Summons et al., 1992; Thomas et al., 1993; Moldowan et al., 1994; Holba et al., 1998; Sinninghe Damsté et al., 2004). Bacterial and archaeal biomarkers, as well as some particular steroids, are useful for constraining the palaeoenvironmental setting of petroleum source rocks (Moldowan, 1984; Summons and Powell, 1987; Sinninghe Damsté et al., 1995; Farrimond et al., 2000; Peters et al., 2004). C isotopic trends in petroleum *n*-alkanes can also provide invaluable insights into source and maturity in support of data on the distributions of biomarker hydrocarbons (Murray et al., 1994; Edwards et al., 2004).

In this paper we report the geochemical characteristics of some biodegraded bitumens found in veins within Nama Group sediments with inferences leading to identification of the probable source in the Permian Whitehill Formation of the Karoo Supergroup.

2. Materials and methods

2.1. Sample descriptions and bulk data

Bulk geochemical data for bitumens from the Nama Basin studied here are provided in Table 1. Pedigrees for the samples are as follows:

#8633 (MRW Field code 950915.4) is from a massive vein bitumen within a silty sandstone. Collection coordinates: 26° 05.905′S; 17° 50.623′E.

#8634 (MRW Field Code 950915.5) is from a fractured sandstone with small bitumen masses collected from Gevaams Farm Westside of Fish River Valley. Coordinates: 26° 21.840′S, 17° 42.736′E.

#8638 (MRW Field Code 950916.1c) was collected from Heigums 105 Farm. It was a brecciated quartzite in fault zone, and the rocks gave a strong diesel smell when hammered. An oil film spreads for a few millimeters on broken surfaces. Coordinates: 26° 54′00″S; 16° 57′40″E.

Sediment samples from the Nama Group were screened by Rock–Eval pyrolysis, and results are summarised in Table 2. Rock–Eval parameters for samples from Permian Paraná and Karoo basins selected for comparison with Nama bitumens are shown in Table 3.

2.2. Analytical protocols

Rock–Eval and TOC analyses were conducted at Geoscience Australia using established protocols.

The samples were subjected to Soxhlet extraction in dichloromethane:methanol 3:1. Gas chromatographic analyses of the intact ‘whole’ extract (EOM) were conducted on small aliquots of all samples according to the following method. Samples of

Table 1
Description, extract yields and carbon isotopic compositions data for three Nama Basin, Namibia, sediments containing vein bitumen

GA sample #	Information	EOM %	Asph % EOM	Sats % EOM	Aroms % EOM	Pols % EOM	δ^{13}C Sats ‰	δ^{13}C Aroms ‰
8633	Massive vein bitumen	3.7	15.2	21.0	32.6	42.4	−21.6	−22.3
8634	Sandstone with bitumen masses	0.1	6.4	22.5	37.3	42.4	−23.8	−23.4
8638	Brecciated quartzite with oil in fractures	0.2	0.4	73.0	10.7	9.0	−21.7	−20.8

Table 2
Summary of Nama Basin, Namibia, sediment samples screened by Rock–Eval & TOC

# Samples	Well	Depth m	TMAX* (°C)	S 1 (mg/g)	S 2 (mg/g)	S 3 (mg/g)	P I	S2/ S3	P C	TOC (wt%)	H I	O I
3	Berseba-1	N/A	440 ± 30	0.0	0.0	0.1	0.0	0.9	0.0	0.1	18	48
5	Tses-1	1526–1551	480 ± 30	0.0	0.0	0.1	0.0	0.2	1.0	0.01	0	25
5	Weshof-1	51–98	450 ± 20	0.0	0.0	0.0	0.0	0.0	0.0	0.1	9	9
12	Tahiti 1	34.5–49.1	445 ± 20	0.0	0.0	0.3	0.2	0.2	0.0	0.4	5	122
52	ND-2	48.5–516.5	445 ± 20	0.0	0.0	0.0	0.0	0.0	0.0	0.3	4	8
1	Aranos Basin AGIP 9	221.9	439	0.2	5.9	0.0	0.0	0.0	0.5	8.1	73	0
1	AGIP 10	257.6	431	0.0	1.1	0.1	0.0	7.8	0.1	3.9	28	4
1	AGIP 11	227.5	378	0.0	0.0	0.0	0.0	0.0	0.0	0.2	6	0
1	AGIP 11	286.1	249	0.1	0.0	0.0	0.8	0.0	0.0	3.3	1	0
1	ACP 4	246.4	364	0.0	0.1	0.7	0.2	0.2	0.0	5.6	2	13
1	ACP 4	296.7	462	0.0	1.5	0.0	0.0	0.0	0.1	5.0	30	0
1	ACP 4	312.6	445	0.3	6.8	0.0	0.0	0.0	0.6	7.9	86	0
1	Karoo Fm. "pseudocoal"	n/a	472	2.2	43.8	17.2	0.0	2.5	3.8	90.0	49	19

Averaged data are given for those wells showing multiple samples.

Table 3
Rock–Eval parameters of four potential source rock analogues from the Irati Fm. (Paraná Basin, Brazil) and the Whitehill Fm. (Karoo Basin, South Africa)

GA Sample #	Information	TMAX (°C)	S 1 (mg/g)	S 2 (mg/g)	S 3 (mg/g)	P I	S2/S3	P C	TOC (wt%)	H I (mgHC/g TOC)	O I (mgCO$_2$/g TOC)
1999001	Irati Fm., o/crop, thin laminated shale	426	7.05	46.80	1.45	0.13	32.28	4.47	8.32	563	17
1999002	Irati Fm., o/crop, black shale and dull bitumen vein	431	8.50	79.45	1.65	0.10	48.15	7.30	10.55	753	16
1999003	Irati Fm., o/crop, bright bitumen mosaic in weathered grey shale	430	7.68	83.22	1.59	0.08	52.34	7.54	11.08	751	14
1999004	Whitehill Fm., black laminated shale	431	1.25	2.75	1.55	0.31	1.77	0.33	2.97	93	52

the EOM, containing an internal standard ($ai\mathrm{C}_{22;}$ 3-methylheneicosane, 99+% purity, ULTRA Scientific added at 10 μg/mg EOM), were injected onto the vaporising injector, operated at 300 °C in the split mode, of a Varian 3400 instrument. The GC was fitted with an HP Ultra-1 capillary column (50 m × 0.22 mm ID × 0.5 μm film). The carrier gas was hydrogen and the oven was held at 30 °C for 20 min prior to being programmed to 310 °C at 8 °C/min.

After gentle removal of the extraction solvent, the extracts were weighed and separated into asphaltene, saturated hydrocarbon, aromatic hydrocarbon and polar fractions. The saturated hydrocarbon fractions were further separated into *n*-alkanes (silicalite adduct = SA) and branched/cyclic hydrocarbons (silicalite non-adduct = SNA) by passing a pentane solution through silicalite molecular sieve (West et al., 1990). The non-adduct (SNA) was used for GC–MS analysis and CSIA of the isoprenoids. The *n*-alkanes were obtained from the SA fraction by destruction of the sieve with hydrofluoric acid and analysed for the carbon isotopic compositions of individual compounds.

GC–MS of saturated hydrocarbon fractions was conducted on aliquots containing internal standards ($ai\mathrm{C}_{22;}$ 10 μg/mg and D_4-ααα-ethylcholestane, Chiron, 100 ng/mg) in full scan and selected ion recording (SIM) modes on an HP 5973 instrument and using a 50 m × 0.2 mm (ID) × 0.11 μm film

HP-5 capillary column, with helium as carrier gas. The GC oven was programmed from 60 to 310 °C at 4 °C/min. Injection was in split mode (100:1).

GC–MS was also conducted on the SNA fraction containing a deuterated internal standard (D_4-ααα-ethylcholestane, 100 ng/mg) using an Autospec Q instrument, in multiple reaction monitoring (MRM) mode, using a common series of transitions to detect C_{19}–C_{26} cheilanthanes ($M^+ \rightarrow 191$), C_{26}–C_{30} steranes ($M^+ \rightarrow 217$), C_{30} methylsteranes ($414 \rightarrow 231$), C_{27}–C_{35} triterpanes ($M^+ \rightarrow 191$), C_{31}–C_{36} methylhopanes ($M^+ \rightarrow 205$) and the deuterated stigmastane internal marker for quantitation and retention time standard ($404 \rightarrow 221$). The GC was equipped with a 60 m × 0.25 mm (ID) × 0.25 μm film DB-1 capillary column, used hydrogen as carrier gas and the GC oven was programmed from 60 to 310 °C at 4 °C/min. Injection was in the splitless mode.

Bulk carbon isotopic measurements were made by combustion of the sample (ca. 1–2 mg @ 850 °C 12 h) in evacuated sealed vycor tubes using cupric oxide as an oxygen source. After isolation and drying of the product CO_2 on a vacuum line, the $\delta^{13}C$ values were measured using the sample manifold and dual inlet system of a Finnigan MAT 252 isotope ratio mass spectrometer. Values are reported in ‰ relative to Vienna Peedee Belemnite (VPDB). Compound specific isotopic analyses (CSIA) were conducted on individual *n*-alkanes and, where possible, pristane and phytane according to methods previously reported (Murray et al., 1994; Dowling et al., 1995). Typical reproducibility for this analysis was ±0.4‰ for *n*-alkanes and ±0.8‰ for acyclic isoprenoids (which are often accompanied by co-eluting branched or cyclic alkanes).

Compound identifications were made by comparisons of mass spectra and retention times of reference standards or known compounds in reference bitumens and oils.

2.3. Source rock screening analysis

To survey potential Neoproterozoic–Cambrian sediments, approximately one hundred samples from Nama Basin and nearby boreholes Berseba-1, Tses-1, Weshof-1, Tahiti-1 and ND-1, Agip-9 to -11, ACP-4 and numerous water wells on local farms were analysed by Rock–Eval and TOC (data not shown for individual samples). All were interpreted as having insignificant potential for petroleum generation and unlikely to yield useful amounts of extractable hydrocarbons for biomarker analysis. The highest carbon content was for a sample of bright graphitic material (also known as pseudocoal), with no hydrocarbon potential, encountered in the Permian Karoo Fm. Otherwise the Neoproterozoic–Cambrian samples had TOC <0.6% and, without exception, the S2 values were below those considered indicative of petroleum potential. Averaged data for Rock–Eval and TOC for these samples are given in Table 2 and suggest the samples were over mature.

Additional outcrop samples from the Permian Karoo Basin, the Paraná Basin of Brazil and time equivalents from the Falkland Islands were also screened. However, the majority of these samples were weathered and the Rock–Eval analysis data showed $S2 < 0.5$ mg/g and $HI < 50$ mg/g despite there being significant organic carbon present in some. It was clear from these data that a large majority of Permian samples had coaly, Type III organic matter (OM) with little petroleum generation potential and were unlikely candidates for the source rock of the Nama bitumens. In contrast, the three fresh samples of Irati outcrop from a Petrobras Quarry and one sample of core from a lacustrine facies of the Whitehill Fm. of South Africa had the dark appearance of organic rich shale and this was confirmed by Rock–Eval/TOC analysis (Table 3). The average HI and TOC of Irati samples were 689 and 10, respectively, indicating significant petroleum source potential. All samples are immature, with $T_{\max}$ in the range 426–431 °C. $T_{\max}$ for #19990004 may be suppressed somewhat due to the high PI value although biomarker data indicate that the maturity is still low. Although this particular Whitehill Fm. sample had lower TOC, S2 and HI values than the Irati outcrops, extract data suggested that the entrained organic matter had very similar geochemical qualities.

2.4. Asphaltene pyrolysis

Aliquots of ~50 mg of the asphaltene fractions from bitumens #8633, #8634 and #8638 were heated, together with 10 mg H_2O in sealed, evacuated pyrex tubes for 72 h at 350 °C. The resultant product yields and compositions are shown in Table 5. The saturated hydrocarbon fractions from the pyrolysates were analysed by GC

Table 4
Extractable bitumen compositions of four potential source rock analogues from the Irati Fm. (Paraná Basin, Brazil) and the Whitehill Fm. (Karoo Basin, South Africa)

GA sample no.	Rock g	EOM (ppm)	% Asph	% Sats	% Arom	% Pols	B/C % Sats
19990001	8.5	19432.6	10.9	22.2	33.2	Lost	92.0
19990002	18.7	22737.5	6.1	22.0	34.8	37.1	81.0
19990003	30.2	19361.1	7.0	25.0	40.3	27.7	69.0
19990004	16.9	9056.9	13.7	23.5	25.0	37.7	55.0

Table 5
Summary of yields from sealed-tube pyrolysis for Nama Basin bitumen asphaltene and polar fractions

GA sample #	Fraction pyrolysed	Amt (mg)	Sats (mg)	Arom (mg)	Pols (mg)
8633	Asph	40.5	0.6	5.5	1.7
8633	Pols	41.3	4.2	10.7	5.5
8634	Asph + pols	24.9	1.8	6.7	7.4
8638	Asph + pols	8	1	1.3	2.1

(Fig. 2), MRM GC–MS (e.g. Fig. 3) and SIM GC–MS (Table 6).

3. Results and discussion

3.1. Fluid inclusion hydrocarbons

In an initial survey, a number of large quartz and calcite samples were examined for hydrocarbon bearing fluid inclusions because these have been reported by previous workers (Kvenvolden and Roedder, 1971). Although no inclusions were positively identified microscopically in our work, we did identify numerous samples with black bituminous deposits along crystal boundaries. Their compositions were studied by progressively heating the crushed mineral and examining the products of each stage studied by GC–MS (Hoffmann et al., 1988). Hydrocarbons released at 100–300 °C had a very similar pattern to hydrocarbons in the massive vein bitumens (discussed below) in that there was low Pr/Ph, abundant acyclic isoprenoids and even carbon preference. Hydrocarbons released at 300–550 °C contained alkene–alkane pairs and probably result from thermal cracking of a residue of macromolecular OM. We also examined the same samples by crushing under solvent and GC analysis of the extract. These also showed patterns that appeared to be altered petroleum hydrocarbons but were probably contaminated with biogenic hydrocarbons derived from more recent organic matter. Because of their low abundance, the uncertain history of the samples and the likelihood of ambiguous results, we did not proceed with any further work on these ‘fluid inclusion’ samples.

3.2. Massive vein bitumens

Massive vein bitumens occur at several points along the Fish River outcrops of the Fish River Subgroup sediments at localities shown in Fig. 1. Numerous samples were collected and bulk geochemical parameters of the three that were studied in detail are given in Table 1. These comprised two typical vein bitumens (#8633 and #8634) and one sample (#8638) that contained lighter hydrocarbons that were released by hammering or crushing.

Fractionation of the massive vein bitumen samples by column chromatography yielded saturated hydrocarbon fractions that, from their bulk compositions and inspection of GC-FID traces, were biodegraded to various degrees. The most obvious sign of biodegradation is the loss of most *n*-alkanes and acyclic isoprenoids and the presence of a large unresolved complex multiplet in two of the samples. Two examples are shown in Fig. 2a and b. Although samples #8638 (Fig. 2a) and #8634 (Fig. 2b) had overtly different chromatograms, it is evident from the compositional data that the former is a much better preserved bitumen retaining a higher proportion of saturated hydrocarbons. The bulk isotopic data for saturated and aromatic hydrocarbon fractions were very similar to those reported by Kvenvolden and Roedder (1971). The hypothesis that the oils were genetically related was further supported by GC analyses showing low Pr/Ph ratio and the presence of abundant acyclic isoprenoids $<C_{20}$.

GC–MS analyses in scan, SIM and MRM modes (data not shown) gave a consistent geochemical picture for all massive and vein bitumen samples which was manifested as a very distinctive pattern

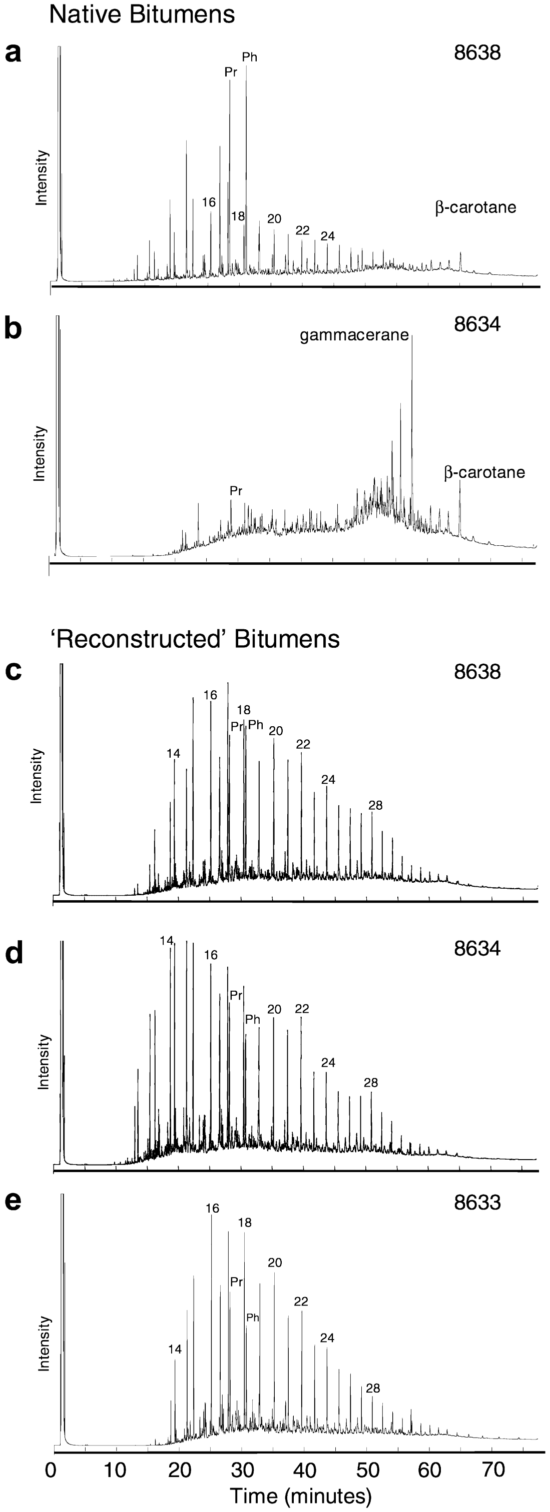

Fig. 2. GC-FID chromatograms for two massive vein bitumen samples showing different degrees of biodegradation (a and b) and three samples (c–e) reconstructed by sealed-tube pyrolysis of asphaltene or polar fractions.

of sterane and triterpane isomers. The bitumens appeared to be biodegraded products of low to moderate maturity oils that featured a low abundance of rearranged steranes and hopanes and C_{29} $\alpha\beta$-hopane dominant over its C_{30} counterpart which, together, suggest a source rock with low clay content such as a carbonate or marl (Peters et al., 2004). C_{30} desmethyl steranes were not detectable and, together with the high abundances of regular steranes, gammacerane, β-carotane and 3β-methylhopanes, the biomarker assemblage indicates that the precursor oils originated from rocks deposited in a saline lacustrine palaeoenvironment (Moldowan, 1984; Peters et al., 2004). For example, the characteristics of the Nama bitumens were reminiscent of samples from the Green River Formation of western USA (Collister et al., 1992), the Beatrice oil from the North Sea (Peters et al., 1989; Duncan and Buxton, 1995) and of saline lacustrine oils of the Atlantic Margin basins (Mello and Maxwell, 1990). One key age diagnostic feature of the samples was the virtual absence of 4-methylsteranes and triaromatic dinosteroids in the Nama bitumens and a sign that the hydrocarbons are Palaeozoic in age, or possibly older (Moldowan and Talyzina, 1998; Summons et al., 1987, 1992) [although it is known that dinosteranes do occasionally occur in low abundance in older samples (Summons and Walter, 1990; Moldowan and Talyzina, 1998)]. The paucity of dinoflagellate biomarkers clearly distinguishes the Nama bitumens from Mesozoic saline lacustrine oils of the Atlantic margins which have dinosteroids in abundance (Mello and Maxwell, 1990; Mello et al., 1993; Schiefelbein et al., 1999).

In seeking to match the biomarker pattern more closely to known hydrocarbon accumulations, and because moderate to severe biodegradation skews diagnostic biomarker ratios (Seifert and Moldowan, 1979; Volkman et al., 1983; Peters et al., 2004), we conducted sealed tube hydrous pyrolysis experiments on polar and asphaltene fractions in an effort to generate hydrocarbons closer to the original patterns that would have prevailed in the precursor, non-biodegraded oils (Jones et al., 1988; Sofer, 1988). The yields and bulk composition of these pyrolysates is reported in Table 5. GC-FID traces for three representative samples are shown in Fig. 2c–e. These display a common suite of characteristics that includes an envelope of *n*-alkanes just beyond C_{38} with a slight odd over even carbon predominance below C_{18} and an overt even over odd predominance for C_{20}–C_{28}. Acyclic isoprenoids up to

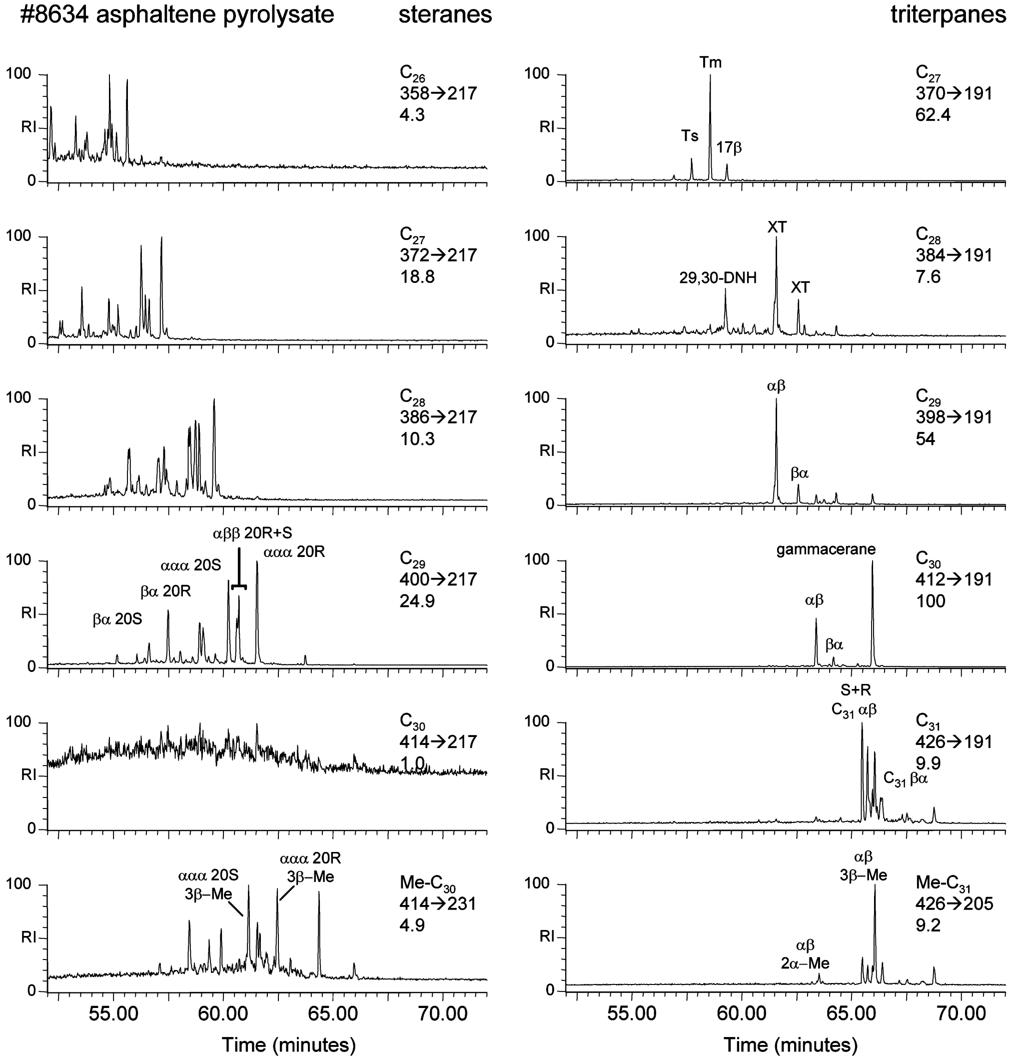

Fig. 3. Biomarker patterns obtained by MRM GC–MS analysis of saturated hydrocarbons formed during sealed-tube pyrolysis of the asphaltene fraction of Nama Basin bitumen sample #8634. Key compounds are identified by name and stereochemistry. Each chromatogram is identified by the mass transition and its intensity shown normalized relative to the most intense response, in this case, gammacerane present in the *m*/*z* 412 → 191 transition. The peak identified as 3β-methylhopane in the *m*/*z* 426 → 205 transition, which partially co-elutes with gammacerane, may comprise additional components. XT denotes interference peaks arising from related compounds and is due to an artifact of the MRM technique.

squalane are evident but dominated by $<C_{20}$ members with Pr/Ph ratio ∼1. Sterane and triterpane ratios are also similar to each other and significantly different to the saturated hydrocarbons of the native bitumens with reduced relative abundances of C_{29} αβ-hopane and gammacerane, confirming that the elevated profiles in those samples was the result of the relative resistance of these compounds to biodegradation.

MRM GC–MS analysis of these ‘reconstructed’ oils confirmed that the bitumen samples have a common genetic origin and a geochemical character typical of samples from saline lacustrine environments. The patterns of steranes and triterpanes are quite similar for all the samples and are illustrated for one of them (#8634) in Fig. 3. C_{29} steranes are dominant followed by C_{27} with C_{28} subordinate. C_{30} desmethyl steranes are barely evident in the 414→217 reaction chromatogram and, of the C_{30} methyl steranes, the 3βmethyl-ααα 20S and 20R isomers were the most intense peaks in the 414→231 reaction trace. 4α-Methyl steranes were present although they were at trace levels. The sterane isomers showed regular ααα dominant over αββ and

Table 6
Sterane, triterpane and cheilanthane source and maturity parameters derived from GC–MS analysis in SIM mode for samples of the Irati and Whitehill formations compared to a representative sample of hydrocarbons from the asphaltene pyrolysate from a Nama Basin bitumen

OilMod Ratios	19990001 SNA Irati shale	19990002 SNA Irati shale	19990004 SNA Whitehill Fm	8638K Sats Nama Asph Pyr
C19/C23	0.17	0.20	0.20	0.80
C22/C21	0.21	0.24	0.16	0.12
C24/C23	0.65	0.77	0.69	0.76
C26/C25	3.80	3.66	4.96	1.96
Tet/C23	1.77	2.32	2.51	0.58
C27T/Ts + Tm	0.02	0.02	0.01	0.01
C28/C30H	0.00	0.00	0.01	0.01
C29/C30H	0.41	0.50	0.52	0.93
C30X/C30H	0.01	0.02	0.02	0.03
OL/C30H	0.01	0.01	0.01	0.03
C31R/C30H	0.16	0.16	0.14	0.14
GA/C31 R	1.69	2.17	4.95	18.45
C35S/C34S	0.97	0.78	0.97	0.61
Ster/Terp	0.45	0.23	0.37	0.63
Rearr/Reg	0.10	0.05	0.02	0.15
%C27	41.30	41.10	45.80	31.80
%C28	10.80	15.60	18.80	18.38
%C29	47.70	43.10	35.40	49.82
C29 20S/R	0.16	0.21	0.19	0.67
Ts/Tm	0.24	0.22	0.30	0.17
C29Ts/C29H	0.14	0.09	0.11	0.07
29DM/C30H	0.01	0.01	0.01	0.07

The selected parameters were based on OilMod ratios developed by GeoMark Research for oil-source correlation studies (Zumberge, 1987; Peters et al., 2004; Zumberge et al., 2005). There is a significant degree of variability between the source rocks attributable to heterogeneity within these immature samples.

both dominant over diasteranes. The ratio $20S/(20S + 20R) \sim 0.4$ for this sample places its maturity level in the early oil window. However, there was some variability in the maturity parameters within the 'reconstructed' saturate fractions.

Oleanane was not detected and the most abundant triterpane was gammacerane, consistent with the hydrocarbons originating from a saline palaeoenvironment. C_{30} and C_{29} $\alpha\beta$ hopanes were equally abundant and the relative abundances of $\beta\alpha$-hopanes, Ts/Tm and 17β-trisnorhopane, like the steranes, is consistent with a maturity level at the very early stages of oil generation. Overall, the patterns were for oils sourced from rocks deposited in a Palaeozoic or older saline lake.

3.3. Potential source rocks

Rock–Eval screening of over 100 Neoproterozoic–Cambrian drill core and water well cuttings samples from the Nama and Aranos basins and Damar Orogen revealed no potential petroleum source rocks local to the massive and vein bitumens. Four samples comprising three outcrop sediments from the Petrobras-6 oil shale quarry in the Paraná Basin of Brazil and one piece of core from the Whitehill Fm. of South Africa were analysed by Rock–Eval and TOC and found to be excellent petroleum source rocks, although they were immature with respect to oil generation (Table 3). Four additional samples obtained from the Neoproterozoic Nama group, with low TOC and S2 contents, were also extracted for biomarkers. The compositions of these extracts were markedly different from the vein bitumens and are not discussed further because of likely contamination issues.

3.4. Results of extraction

Putative Early Permian source rock samples were further investigated by extraction and biomarker analysis as summarised in Table 4. The data confirm the hydrocarbon source potential of the Irati and Whitehill samples. Extract compositions are shown in Table 4 while source and maturity parameters derived from SIM GC–MS of their saturated hydrocarbon fractions are given in Table 6. All samples that yielded significant amounts of bitumen (five of eight samples extracted) proved, after silica gel chromatography, to yield a predominant polar and asphaltene component that reflects an originally low degree of thermal maturity.

3.5. Results of gas chromatographic analysis

Gas chromatograms of total extract (EOM), saturated hydrocarbons that were purified from the EOM and the branched and cyclic hydrocarbon fraction (B/C) are compared in Figs. 4 and 5. The samples are interesting in that they show a very low ratio of *n*-alkanes to branched and cyclic components and the diagnostic biomarkers β-carotane and gammacerane are prominent even in the crude total extract (EOM). A low relative abundance of *n*-alkanes is probably a manifestation of the low maturity of the samples but after adduction onto silicalite these proved to be sufficiently abundant for CSIA analysis along with the isoprenoid hydrocarbons present in the non-adduct fraction (SNA) Fig. 6.

3.6. Biomarker analysis from gas chromatographic–mass spectrometric analysis

Two types of biomarker analysis were undertaken on the putative source rock samples under

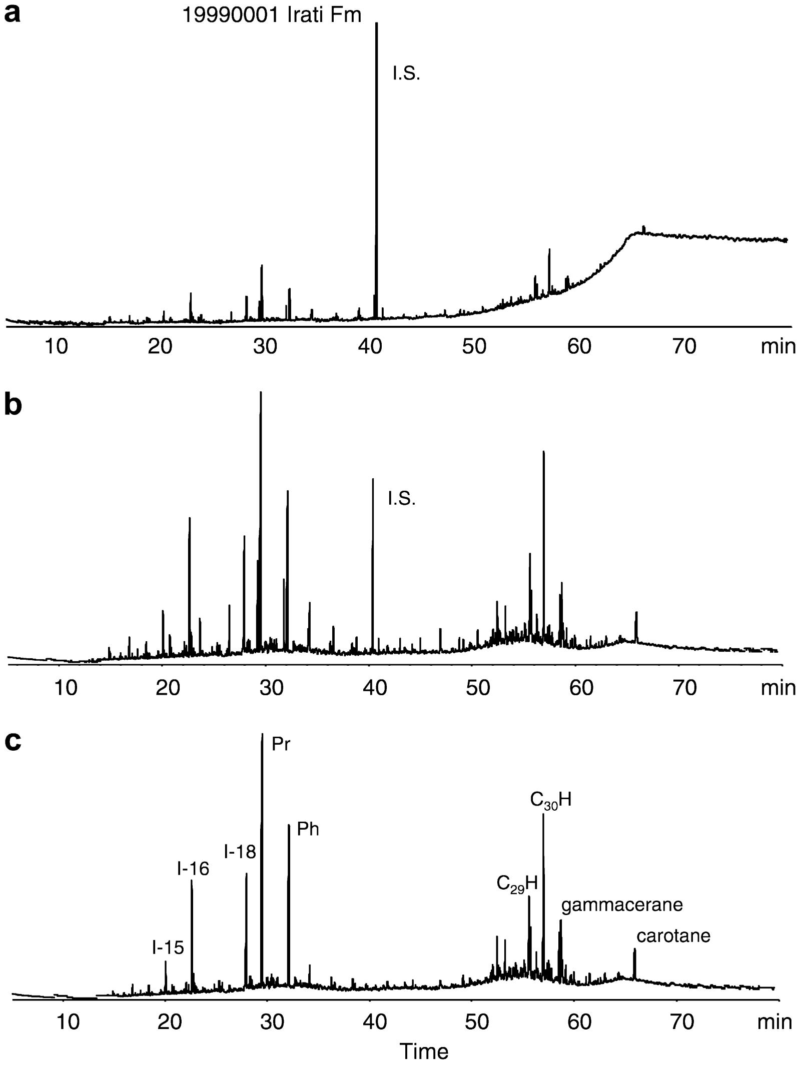

Fig. 4. GC-FID chromatograms for the total extractable hydrocarbons (a), saturated hydrocarbons (b) and silicalite non-adduct of the latter (c) obtained from a sample of Irati Fm. (GA# 19990001) and showing an enrichment of biomarkers that was typical of the three sediments from this formation.

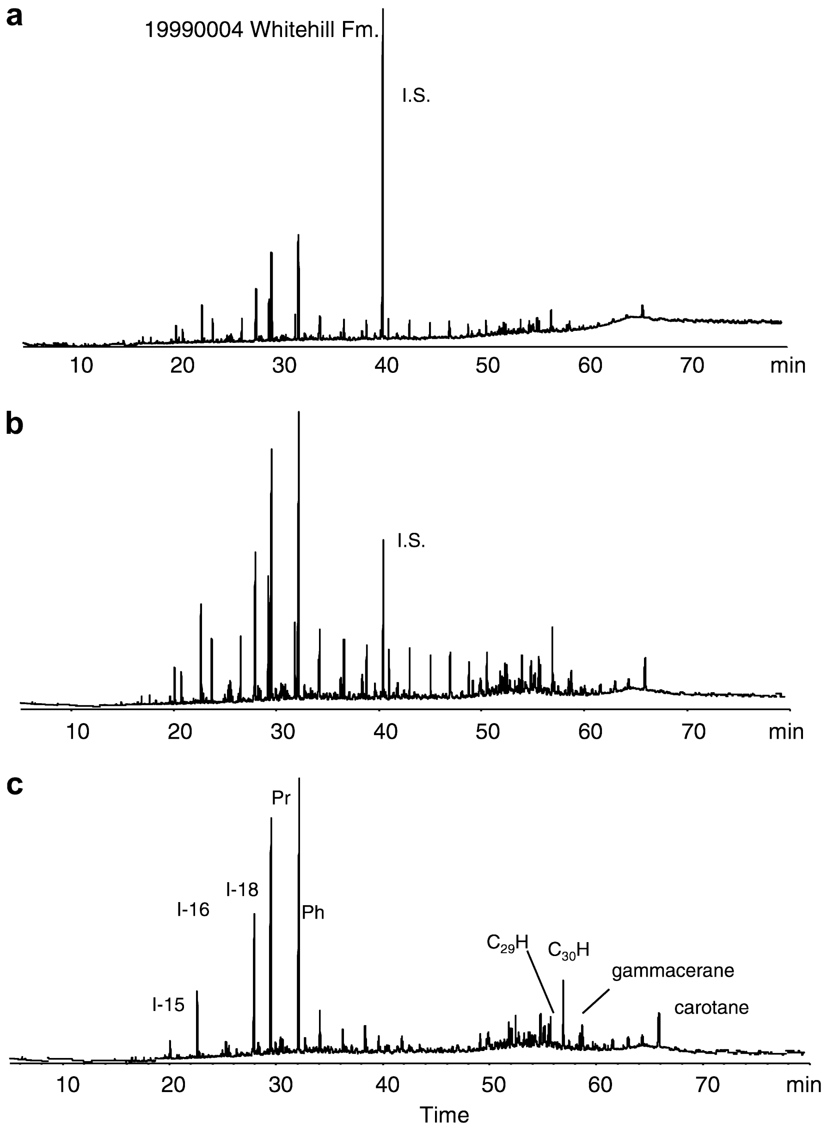

Fig. 5. GC-FID chromatograms for the total extractable hydrocarbons (a), saturated hydrocarbons (b) and silicalite non-adduct of the latter (c) obtained from a sample of Whitehill Fm. (GA# 19990004). Note the considerable variation in relative abundances of key compounds such as Pr/Ph ratio.

exactly the same protocols as used for the reconstructed Namibia bitumens. GC–MS in the full scan mode enabled confirmation of the identity of the isoprenoids, carotane and gammacerane in all the samples. GC–MS in the SIM mode yielded *m*/*z* 177, 191 and 217 ion chromatograms that are used to derive GeoMark's OilMod™ parameters (Zumberge et al., 2005). These are shown in Table 6 and provide a comprehensive source and characterisation of the Nama bitumens, together with the Irati and Whitehill samples, that is analogous to data in GeoMark's 'OILS' database and which can be used to classify and compare samples with a globally representative set of petroleum data (Peters et al., 2004). The geochemical signature of the Irati Shale samples is similar, as far as comparisons can be made, with data recorded earlier for this unit (Da Silva and Cornford, 1985). There is a reasonable correspondence between the data for the Irati and Whitehill samples, bearing in mind that the samples are relatively immature and one expects more variability in ratios corresponding to the natural variability of source rock facies as compared to the equivalent data from oils. All

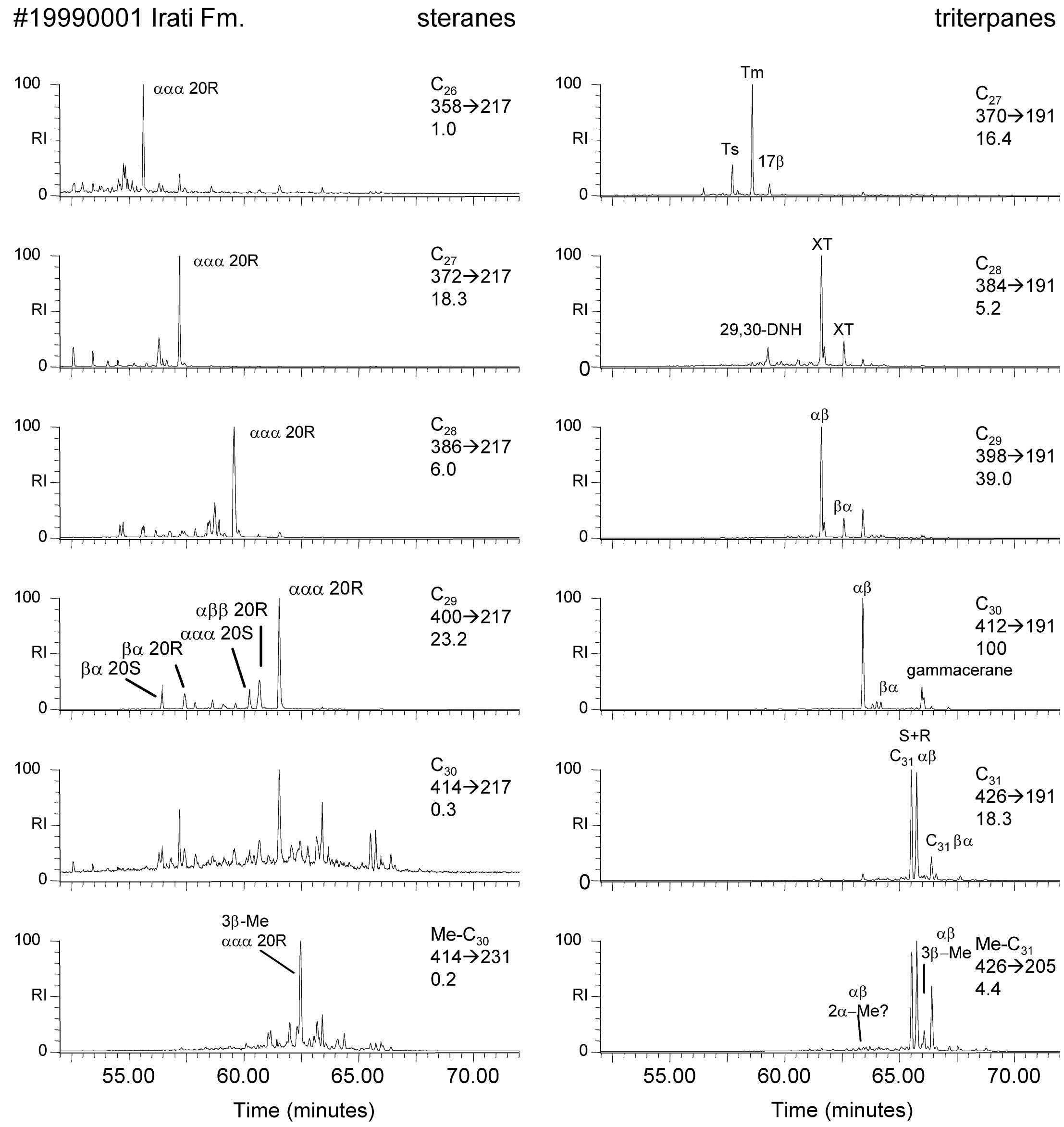

Fig. 6. GC–MS (MRM) data showing sterane and triterpane biomarkers in the branched and cyclic fraction of a sample from the Irati Fm. (GA #19990001) corresponding to the GC-FID trace shown in Fig. 4c.

signatures are consistent with a saline lacustrine source facies (Shi et al., 1982; Fu et al., 1989; Peters et al., 1989; Carroll et al., 1992; Collister et al., 1992; Duncan and Buxton, 1995; Carroll and Bohacs, 2001; Chen and Summons, 2001). There is also a good correspondence between patterns of the Irati (Fig. 6) and Whitehill (Fig. 7) shale samples and the reconstructed Namibia bitumens as exemplified in sample #8638K, again bearing in mind the maturity differences and previous biodegradation of the latter sample.

GC–MS analysis was also undertaken in MRM mode to obtain details of the trace level biomarkers such as C_{30} desmethyl steranes, dinosteroids and methylhopanes that cannot be readily detected or accurately quantified in the GC–MS scan or SIM data. MRM data confirmed the saline lacustrine source facies for Namibia bitumens and their close correspondence to the Irati and Whitehill sediments as indicated by absence of marine signatures such as C_{30} desmethyl steranes, dinosteroids and 28,30-dinorhopane, and presence of indicators of an active

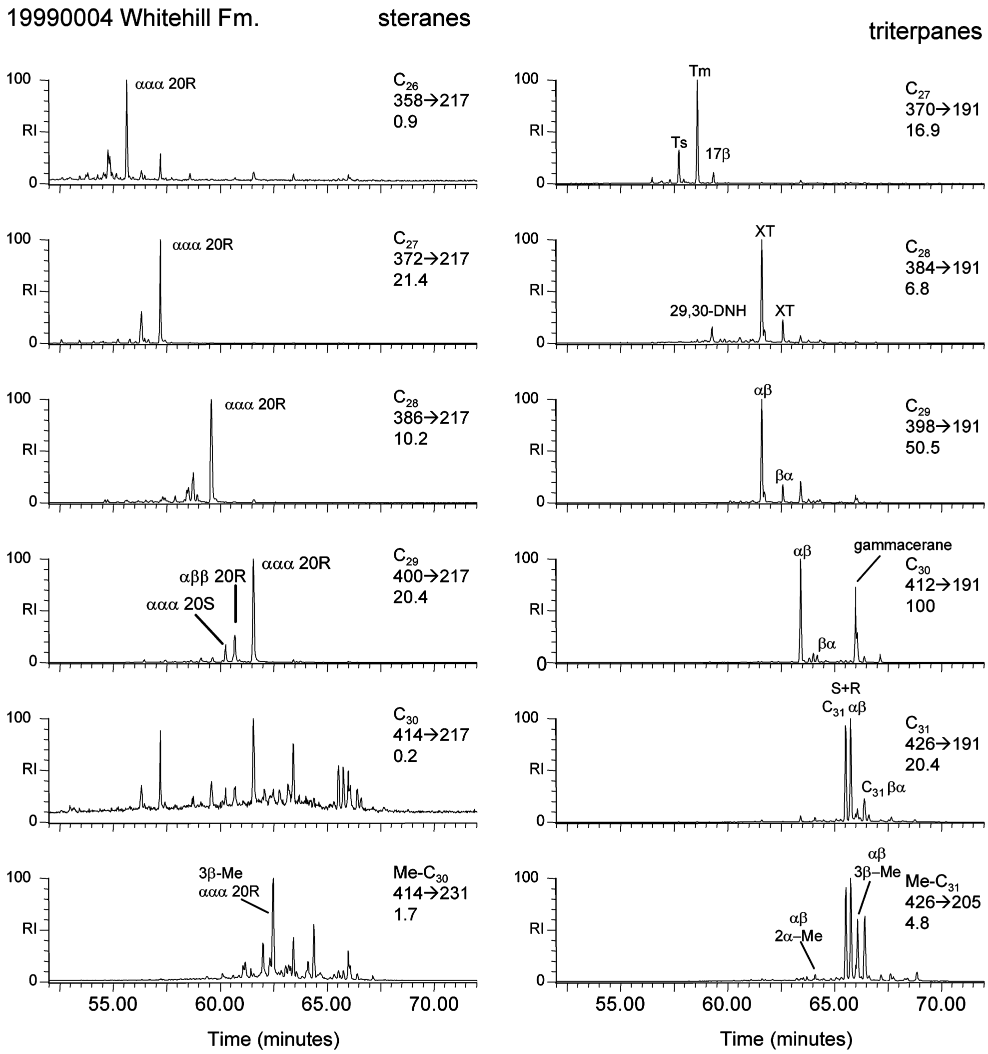

Fig. 7. Sterane and triterpane biomarkers detected by GC–MS (MRM) analysis of the branched and cyclic hydrocarbons from the sample of Whitehill Fm. (GA #19990004) corresponding to the GC-FID shown in Fig. 5c.

methane cycle through 3β-methylhopanes which is indicative of aerobic methanotrophy (Collister et al., 1992). The virtual absence of dinosteroids and 4-methylstigmastanes allows these Permian samples to be distinguished from the Pre-salt Cretaceous saline lacustrine oils of the Atlantic Margin (Mello et al., 1988,1993; Burwood et al., 1992; Schiefelbein et al., 1999). The palaeoenvironmental inferences that can be drawn from the biomarker data are summarised in Table 7.

3.7. Results of CSIA analysis

Compound specific carbon isotopic data for *n*-alkanes are shown in Fig. 8. In the top panel we show data for the Namibia bitumens that were obtained though adduction of *n*-alkanes formed by pyrolysis of asphaltene and polar fractions. Low MW (C_{12}–C_{20}) alkanes are relatively enriched in ^{13}C, have δ^{13}C values that are comparable to the bulk isotopic data given in Table 1 and are consistent with their origin from algal and bacterial sources. In three of the samples, *n*-alkanes >C_{20} tended to more depleted values, declining to values between −29‰ and −31‰ indicating a different origin and likely contribution from the lipids of vascular plants. The asphaltene pyrolysate of sample #8633 showed a somewhat different profile to that of the pyrolysates of polar fraction with a relatively ‘flat’ profile oscillating near −22‰. This sample is a very close match to the Irati and Whitehill shale samples (Fig. 8, lower). The variability evident in

Table 7
A summary of source and lithology dependent biomarker attributes for Irati and Whitehill formation samples compared to those of the Nama Basin bitumens and their palaeoenvironmental significance

Geochemical attribute	Interpretation	Nama Bitumens	Whitehill Bitumen	Irati Bitumens
Abundant gammacerane	High salinity waters	Yes	Yes	Yes
Abundant β-carotane	Saline lacustrine environment	Yes	Yes	Yes
Absence of C_{30} steranes	Non-marine environment	Yes	Yes	Yes
C_{29} sterane predominance	Green algae; probable non-marine source	Yes	No c27 > c29	Yes
Low Pr/Ph and other acyclic isoprenoids abundant	Anoxic bottom waters; possible signal from halophiles and/or methanogens	Yes	Yes	Yes
Low rearranged steranes and hopanes	Clay starved sediment or indicative of immature samples	Yes immature	Yes low maturity	Yes low maturity
C_{29}/C_{30} hopane ratio <1	Generally observed in clastic (or low carbonate) source rocks	Yes	Yes	~1
Low 2α-methylhopane abundance	High 2α-MeH indicative of input of OM from cyanobacteria	Yes	Yes	Yes
High 3β-methylhopane abundance	Strong methane cycle indicates low sulfate water body	Yes	Yes	Yes
Abundant 28,30-DNH	Euxinic marine environment	No	No	No
Abundant dinosteroids	Pre-Triassic petroleum; Dinosteroids rare in Proterozoic to Early Paleozoic samples	No	No	No
Heavy carbon isotope signature (−22‰ to −24‰)	Lacustrine and/or hypersaline environment. Heavy values also consistent with Permian oils from all sources	Yes	Yes	Yes

the Nama samples is almost certainly reflecting heterogeneity in source facies, maturity and alteration (biodegradation) histories.

The Irati and Whitehill formation samples showed a range of patterns typical of lacustrine systems where the *n*-alkanes showed a 'flat' profile for $>C_{20}$ and no evidence for ^{13}C depleted waxy hydrocarbons from plants. The lower MW hydrocarbons showed evidence for a variable input from a ^{13}C depleted source. Isotopically, the lightest *n*-alkanes in all the shale samples are C_{17} and C_{18} which are the carbon numbers typical of lipids from bacteria, including cyanobacteria. The *n*-alkane isotope profile for the Whitehill sample #19990004 is identical to the Irati sample #19990002 within the experimental error of 0.4‰. The Irati sample #19990001 has the most ^{13}C depleted C_{13}–C_{20} *n*-alkanes suggesting it has higher contributions from bacterial and/or cyanobacterial sources in this particular sample. While this isotopic evidence for an enhanced cyanobacterial contribution is at odds with only finding traces of 2-methylhopanes in this sample, we also note that the production of 2β-methylbacteriohopane polyols occurs selectively within the cyanobacteria and is found in roughly 35% of the cultured species studied to date (Talbot et al., 2008). Overall, the Irati, Whitehill and Nama bitumen samples show similar bulk and compound specific isotopic data typical of OM that has formed in an environment characterised by low DIC availability. This was earlier rationalised as being due to microbial blooms (Faure and Cole, 1999).

The two data sets (alkanes from biodegraded samples obtained by pyrolysis versus those present in fresh, immature bitumen) need to be viewed in the context of relative maturity of the samples and also their degree of alteration. For example, the shale extracts are low maturity bitumens isolated from rocks where the bulk of the kerogen will not have generated hydrocarbons. Consequently the immature samples with relatively low amounts of *n*-alkanes might not have isotopic compositions representative of all the organic matter in the sample. In other words, the *n*-alkane versus $\delta^{13}C$ profiles of immature or marginally mature bitumens might differ somewhat from those for oils formed at peak generation. For example, Collister et al. (1992) found significant differences in *n*-alkanes extractable from a Green River sample compared to those released from kerogen by pyrolysis at 280 or 350 °C.

Fig. 9 compares the averaged $\delta^{13}C$ values for the acyclic isoprenoids Pr and Ph compared to the averaged values of adjacent n-C_{17} and n-C_{18} alkanes. Pristane and phytane had very similar

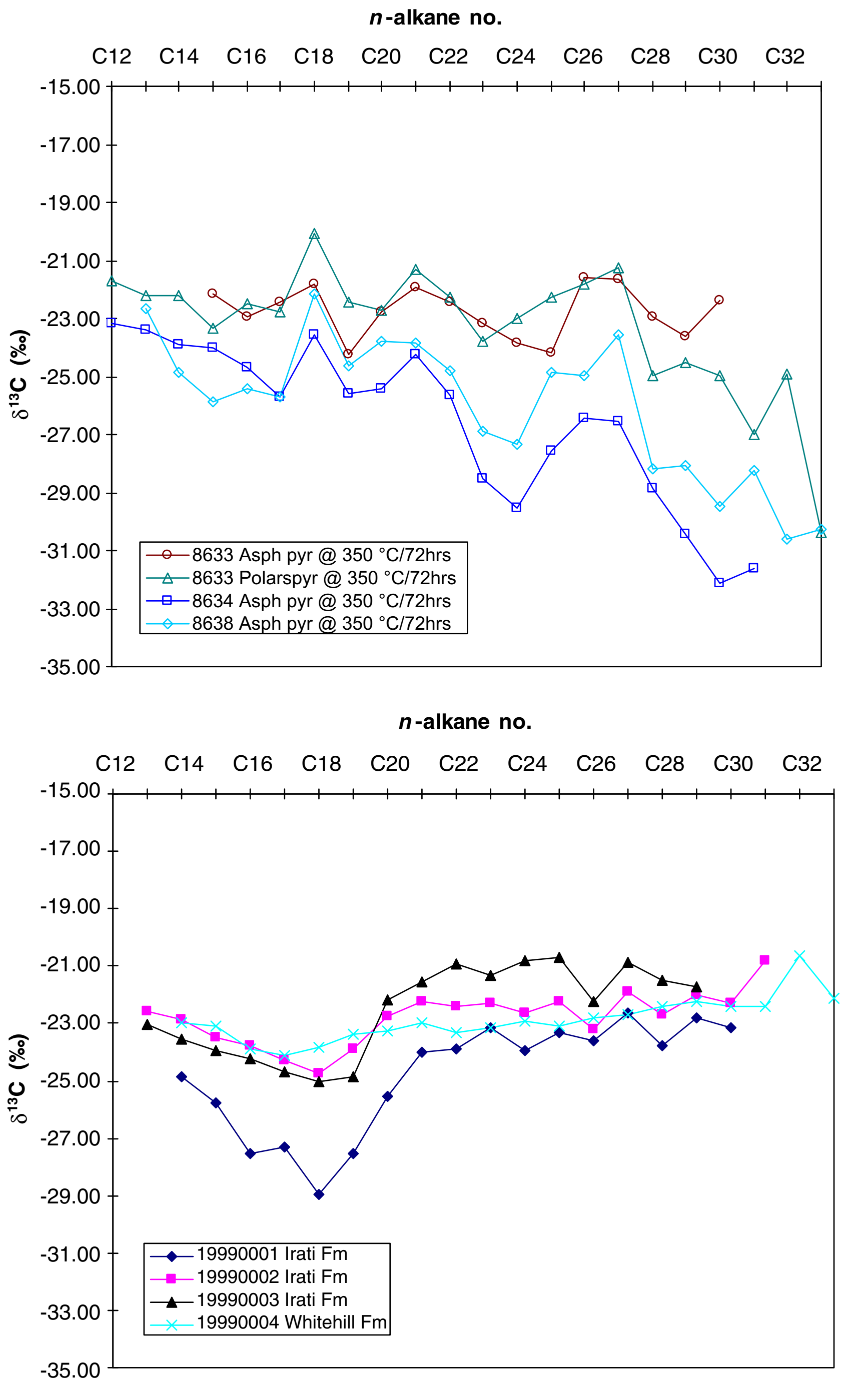

Fig. 8. Top panel shows the isotopic compositions of hydrocarbons produced by hydrous pyrolysis of the asphaltene/polar fractions of three Nama Basin bitumen samples. The lower panel shows equivalent data for hydrocarbons in three samples of Irati Fm. and the Whitehill Fm. sample.

isotopic compositions (within 0.4‰) for all the shale samples and were very slightly ^{13}C enriched compared to the adjacent C_{17} and C_{18} *n*-alkanes. The δ^{13}C data for pristane and phytane, as expected, were more variable for the reconstructed bitumens. The cross plot of Fig. 9 illustrates how isoprenoids in the ‘reconstructed’ Nama samples are ‘correctly’ ordered, that is, more enriched in ^{13}C with respect

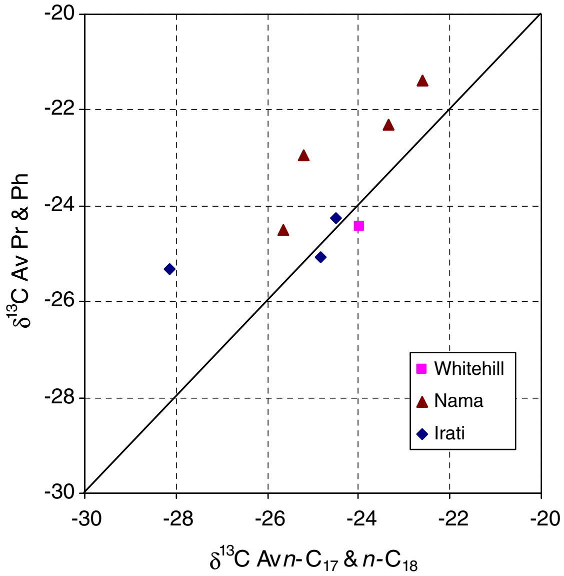

Fig. 9. Cross plots of carbon isotopic compositions of *n*-alkane versus acyclic isoprenoids in the suite of hydrocarbons in the Irati Fm. (diamonds), Whitehill Fm. (square) and Nama Basin reconstructed oils (triangles).

to co-occurring acetogenic lipids (Hayes, 2001). This is a key result because it supports the use of this kind of sealed tube pyrolysis for geochemical correlation efforts. One sample from the Irati Formation falls on a trend with the Nama samples while others from the Irati and Whitehill fm. fall close to the 1:1 line. None of the samples show ‘abnormal’ ordering as is common in Neoproterozoic sediments (Logan et al., 1997).

3.8. Palaeogeographic reconstructions and likely origin of the Nama bitumens

The consolidation of the southern continental landmasses after about 600 Ma resulted in the Gondwana Supercontinent. The Paraná Basin of Brazil, the Falkland Islands, the Kalahari Basin in southern Namibia and the Karoo Basin of South Africa probably formed an intracratonic basin in the centre of this landmass and was apparently isolated from the world oceans. Isolation of this vast inland sea is indicated by the endemic fauna of the Whitehill and Irati shales (Oelofsen, 1987). The Kalahari Basin appears not to have been directly contiguous with the main Karoo Basin to the south but was separated by a highland (Visser, 1995; Faure and Cole, 1999). However connection of both the Kalahari and Karoo Basins to the west into the Paraná Basin is clear from the occurrence of the endemic Mesosaurid swimming reptiles in all the basins (Oelofsen, 1987; Werner et al., 2002; Werner and Stollhofen, 2000). Additionally, the Black Rock Member of the Port Sussex Formation, Falkland Islands, has been lithostratigraphically correlated with the Whitehill of southern Africa (Trewin et al., 2002).

The ^{13}C enrichment and similarity of organic matter from other southwestern Gondwana basins has been noted previously (Faure and Cole, 1999) where it was attributed to drawdown of DIC by algal blooms. This may well be the case but, in any event, the close correlation of organic geochemical parameters reflecting both algal and bacterial inputs, together with evidence for elevated salinity in roughly coeval Early Permian samples from the Paraná, Kalahari and Karoo Basins signifies a close correspondence in palaeoclimate and depositional environments (Table 7).

Maturation studies on the Whitehill Formation in the Kalahari Basin are hampered by the widespread occurrence of Jurassic dolerite sills and dykes which locally influence the maturity of the shales. Weathering also severely affects the pyritic, organic shales which have TOCs in Namibia of up to 10%. Hence, little unaltered outcrop is found. The Irati Shale of the Paraná Basin is a thin but exceedingly organic rich rock where a maximum TOC of 24% has been recorded with values oscillating between 8% and 13% TOC (Milani and Zalán, 1999). However the maximum burial of the equivalent unit in the Kalahari Basin appears to have been in the order of only 1–1.5 km. Therefore, petroleum generation by burial maturation would be unlikely. This is supported by work on the thermal maturity of outcrop shales which indicates that the Whitehill is immature at all locations unaffected by dolerite magmatism.

Atypical petroleum has been described from the Irati Fm. in Brazil (Araujo et al., 2000; De Araujo et al., 2005). In this petroleum system the Irati shale has been intruded by numerous sills and dykes of Cretaceous age (138–127 Ma) related to the breakup of southwestern Gondwana. The thermal effect of the intrusive bodies extends above and below the bodies to a distance equivalent to the thickness of the body. Multiple intrusions have resulted in multiple, small hydrocarbon generation episodes. These would have been too small to fill giant reservoirs. Lateral migration would also have been limited. A similar hydrocarbon generation mechanism is invoked for the occurrence of the seeps and bitumens in southern Namibia where extensive intrusion by dolerite sheets and dykes occurred in the Jurassic (178 Ma) (Anderson and McLachlan, 1979). Similarly large reservoirs would not be filled. Tectonic movement of southern Namibia since this time, in particular during separation of South America and Africa and uplift near the end Tertiary, could have caused breaching of any possible accumulations. Based upon this reasoning, the potential for finding large hydrocarbon accumulations is limited.

4. Conclusions

Palaeogeographic and palaeoenvironmental reconstructions from previous studies, in combination with the organic geochemistry data presented here, suggest very similar paleoenvironmental settings for the Karoo, Kalahari and Paraná Basins during the Early Permian. A range of source specific biomarkers that were measured by GC, GC–MS and GC–MS–MS show that organic rich sediments in these basins bear a geochemical signature diagnostic for organic matter that was deposited in a saline lacustrine palaeoenvironment. They contain abundant gammacerane, β-carotane and 3β-methylhopanes while 24-isopropyl cholestanes and dinosteroids are not detectable. Moreover, the rocks appear to have high potential for petroleum generation. However, where encountered so far, their local burial histories appear to have been insufficient to generate significant petroleum deposits. Some oil that has been generated from these rocks occurs as biodegraded vein bitumens found within the Fish River sub-group of the Nama Basin of Namibia. These likely have a similar origin to oil bearing fluid inclusions found in quartz crystals from surrounding localities. It's probable that these Nama Basin hydrocarbons were generated by contact metamorphism during emplacement of dolerite sills and dykes during the Jurassic.

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