FIG. 3 The effect of stopping iron fertilization after 50 years (dotted line) is depicted for the business-as-usual and constant-emission scenarios. The solid line is the unfertilized scenario, the dashed line is the scenario for continuous fertilization.

resulting from iron fertilization gives an equilibrium warming of 3.1 °C instead. On the other hand, the unfertilized constant-emission scenario, which reaches 505 p.p.m. in 2090, gives a significantly smaller equilibrium warming of 2.2 °C, which is reduced to 1.4 °C with the 90 p.p.m. additional oceanic uptake resulting from iron fertilization. These numbers can be compared with the 0.9 °C equilibrium warming that can be expected from the present atmospheric CO_2 content of 355 p.p.m. It should be kept in mind that the transient warming is smaller than, and not necessarily proportional to the equilibrium warming, due primarily to the uptake of heat by the ocean.

The most important conclusion we draw from our calculations is that, although the effect of iron fertilization is large enough to justify further study, the effect of a significant change in the emissions of CO_2 is even larger. We emphasize the preliminary nature of our calculations and the fact that all the assumptions we have made have been biased so as to yield an upper limit. ☐

1. Booth, W. Washington Post. A1 20 May (1990).
2. Baum, R. Chem. Engng News 68, 21–24 (1990).
3. Martin, J. H., Fitzwater, S. E. & Gordon, R. M. Global biogeochem. Cycles 4, 5–12 (1990).
4. Knox, F. & McElroy, M. B. J. geophys. Res. 84, 2503–2518 (1984).
5. Siegenthaler, U. & Wenk, T. Nature 308, 624–626 (1984).
6. Sarmiento, J. L. & Toggweiler, J. R. Nature 308, 621–624 (1984).
7. Sarmiento, J. L., Toggweiler, J. R. & Najjar, R. Phil. Trans. R. Soc. A325, 3–21 (1988).
8. Martin, J. H. & Fitzwater, S. E. Nature 331, 341–343 (1988).
9. Martin, J. H. & Gordon, R. M. Deep-Sea Res. 35, 177–196 (1988).
10. Martin, J. H., Gordon, R. M., Fitzwater, S. & Broenkow, W. W. Deep-Sea Res. 36, 649–680 (1989).
11. Martin, J. H. Paleoceanography 5, 1–13 (1990).
12. de Baar, H. J. W. et al. Mar. Ecol. Prog. Ser. 65, 105–122 (1990).
13. Banse, K. Limnol. Oceanogr. 35, 772–775 (1990).
14. Dugdale, R. C., & Wilkerson, F. P. Global biogeochem. Cycles 4, 13–20 (1990).
15. Anderson, G. C. & Morel, F. M. M. Limnol. Oceanogr. 27, 789–813 (1982).
16. Morel, F. M., & Hudson, R. J. in Chemical Processes in Lakes (ed. Stumm, W.) 251–270 (Wiley, New York, 1985).
17. Peng, T.-H. & Broecker, W. S. Nature 349, 227–229 (1991).
18. Toggweiler, J. R. & Sarmiento, J. L. in The Carbon Cycle and Atmospheric CO₂: Natural variations Archean to Present Vol. 32, Geophysical Monograph Series (eds. Sundquist, E. T. & Broecker, W. S.) 163–184 (American Geophysical Union, Washington, DC. 1985).
19. Broecker, W. S. Peng, T.-H., Östlund, G. & Stuiver, M. J. geophys Res. 90, 6953–6970 (1985).
20. Weiss, R. F., Bullister, J. L., Warner, M. J., Van Woy, F. A. & Salameh, P. K. Ajax Expedition Chlorofluorcarbon Measurements (Scripps Institution of Oceanography Reference 90-6, La Jolla, 1990)
21. Broecker, W. S. Global biogeochem. Cycles 4, 1–2 (1990).
22. Houghton, J. T., Jenkins, G. J. & Ephraums, J. J. (eds) Climate Change, The IPCC Scientific Assessment (Cambridg, University Press, 1990).
23. Siegenthaler, U. & Oeschger, H. Tellus 39B, 140–154 (1987).
24. Peng, T. H., Takashi T. & Broecker, W. S. Tellus 39B, 439–458 (1987).

Biases from natural sulphurization in palaeoenvironmental reconstruction based on hydrocarbon biomarker distributions

Math E. L. Kohnen, Jaap S. Sinninghe Damsté & Jan W. De Leeuw

Organic Geochemistry Unit, Faculty of Chemical Technology and Materials Science, Delft University of Technology, De Vries van Heystplantsoen 2, 2628 RZ Delft, The Netherlands

BIOMARKERS (chemical fossils) are sedimentary organic compounds whose basic skeletons suggest an unambiguous link with known contemporary natural products, and were synthesized by biota present at the time of the deposition of the sediment. These compounds are commonly used to assess palaeoenvironmental conditions of deposition of Recent and ancient sediments[1-3]. Saturated hydrocarbons are relatively easy to analyse and contain a lot of geochemical information, and are therefore the most widely used class of biomarkers in palaeoenvironmental reconstruction[2-5]. Hydrocarbon biomarkers are biosynthesized as such or are derived from functionalized biosynthetic lipids, such as alkenes, alcohols and acids, by diagenetically induced defunctionalization. Functionalized lipids may, however, also undergo an abiogenic reaction with hydrogen sulphide or polysulphides ('natural sulphurization') during the early stages of diagenesis, and this may lead to selective removal of specific hydrocarbon biomarker precursors. Here we investigate the influence of natural sulphurization on hydrocarbon biomarker signatures in immature sediments from Italy and off Peru. We show that, if not taken properly into account, this process may lead to a severe bias in the interpretation of the geological record.

Sedimentary functionalized lipids react with reduced sulphur species (H_2S and HS_x^-) to form organic sulphur compounds (OSCs) and sulphur-bound lipid moieties in macromolecules (see ref. 6 for a review). The onset of sulphurization of organic matter is controlled by the reactive iron (for example, ferrihydrite and haematite) content of the sediment, because organic matter reacts with reduced sulphur more slowly than do sedimented iron minerals and thus does so only after reactive iron oxides have first been converted to iron sulphides. In the region of upwelling in the Peru margin, sulphur incorporation into sedimentary organic matter starts in the top metre of the sediment column[7], indicating that this process occurs in the early stages of diagenesis. Moreover, the identification of OSCs in a Recent Black Sea sediment (age $3-6 \times 10^3$ yr) also points to an early diagenetic sulphurization of organic matter[8]. Ten Haven et al.[9] examined the extracts of almost 100 thermally immature deep-sea sediments and found that approximately 70% of the samples contain OSCs. The widespread occurrence of OSCs, and the fact that reduced inorganic sulphur species are present in any anoxic organic-matter-containing Recent marine sediment[10], suggest that natural sulphurization of specific functionalized lipids is a ubiquitous process. It seems inevitable that this selective removal of the precursors of hydrocarbon biomarkers will alter the hydrocarbon biomarker distribution in immature sediments, and thus the interpretation of the geological record as revealed by their apparent distribution. Hydrocarbon biomarkers are used in many (palaeo)environmental reconstruction studies of immature sediments[11-16] and of par-

ticulate organic matter in the water column recovered from sediment traps[17]. Although the major biota contributing to the sedimentary organic matter are deduced from the presence of specific biomarkers (such as hydrocarbons, alcohols and acids), the absence of specific biomarkers does not necessarily imply that the biosynthetic precursors and the corresponding biota were not present in the palaeoenvironment. Similarly, the absence of carbonate micro-fossils in sediments deposited below the carbonate compensation depth does not imply the absence of such species in the environment.

To investigate the bias introduced into hydrocarbon biomarker signatures in immature sediments by natural sulphurization, we have analysed immature sediment samples from the Messinian Vena del Gesso basin (Northern Apennines, Italy)
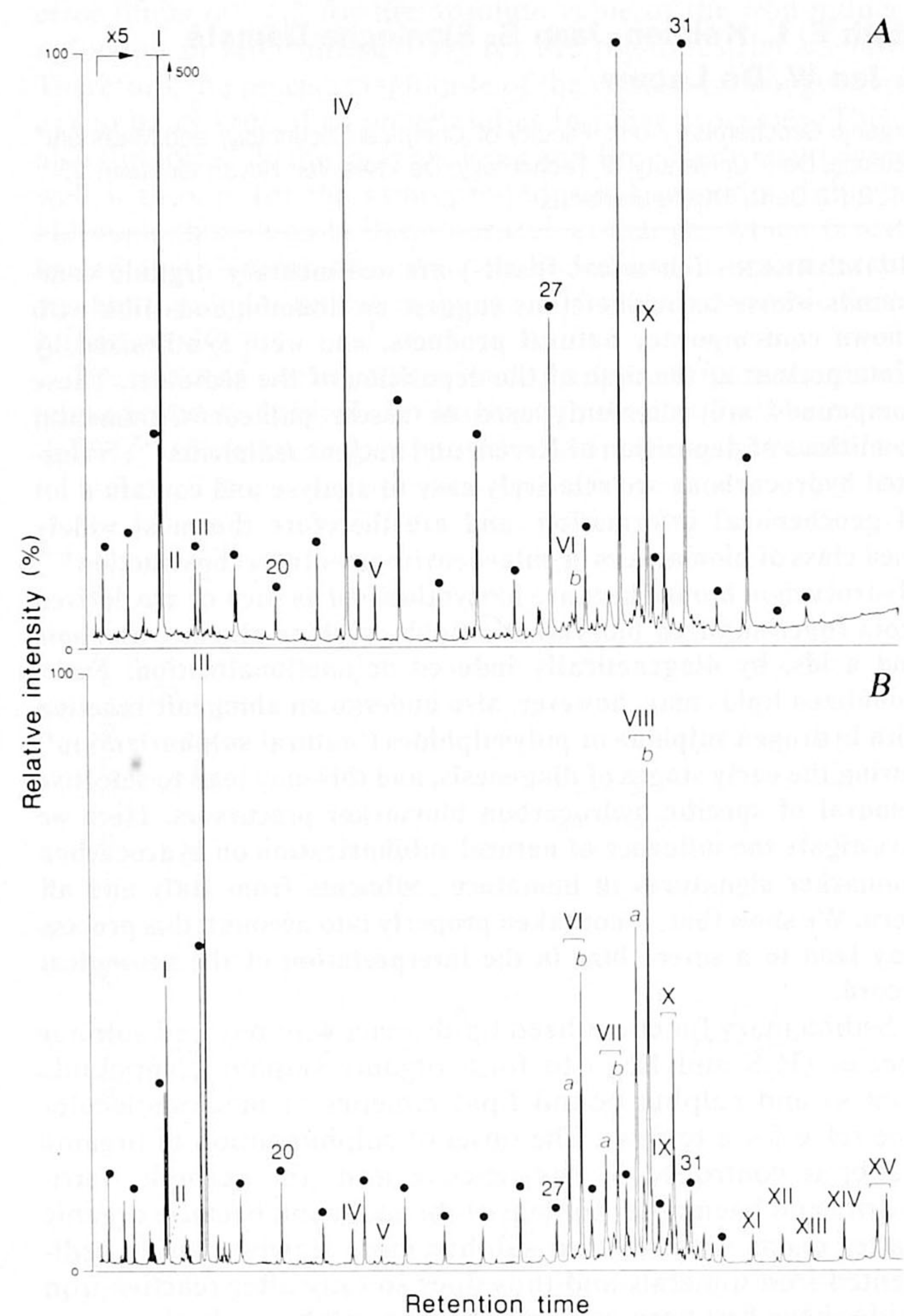

FIG. 1 Gas chromatograms (conditions: 25 m × 0.32 mm fused-silica capillary column coated with CP Sil-5 (0.12 μm); temperature program: 70–130 °C at 10 °C min^{-1}, 130–320 °C at 4 °C min^{-1}, held for 20 min, on column injection) of A, hydrogenated 'free' hydrocarbon biomarkers, and B, hydrogenated 'free + S-bound' hydrocarbon biomarkers isolated from the untreated and the desulphurized maltene fraction, respectively, of the extract from the Vena del Gesso sediment. The maltene fraction was separated from the extract (obtained by sonication using mixtures of CH_3OH and CH_2Cl_2) by precipitating the asphaltenes in n-heptane. Subsequently 6,6-d_2-3-methyleicosane (IV) was added as an internal standard. An aliquot of the maltene fraction was desulphurized using Raney nickel[19]. Both the reaction mixture obtained after desulphurization and an untreated aliquot of the maltene fraction were fractionated on a column into an apolar and a polar fraction as described previously[29]. A hydrocarbon fraction (R_f = 1.0–0.8) was isolated from the apolar fraction using thin-layer chromatography (SiO₂, 0.25 mm thickness) with n-hexane as developer. The hydrocarbon fractions were hydrogenated[8] and subsequently analysed with gas chromatography and GC-MS (GC-MS conditions were similar to those reported previously[32]). Key: a, 5β(H), 14α(H), 17α(H) steranes; b, 5α(H), 14α(H), 17α(H) steranes. Arabic numbers refer to number of carbon atoms of n-alkanes (indicated by black dots). Roman numbers refer to structures indicated in Fig. 2.

and the Peru upwelling area. The Vena del Gesso basin is an evaporitic basin filled with thick beds of gypsum associated with thinner carbonate and shaly intercalations[18]. The sample investigated (VDG-4A) is taken from a fresh outcrop of a non-evaporitic bituminous shale intercalation. The immature character of these consolidated sediments is reflected by the low vitrinite reflectance (~0.25%) of the trace indigenous vitrinite particles encountered. The Peru sediment is taken from ODP Leg 112, site 679 (11°03.81' S, 76°16.33' W), at a depth of ~1 m. Although both samples can be classified as thermally immature, the older and once more-deeply-buried Vena del Gesso sediment has a longer geological history and hence has undergone more diagenetic changes. Figure 1a shows the distribution of the hydrocarbon biomarkers of the Vena del Gesso sample. To release the naturally sulphurized hydrocarbon biomarkers, the maltene fractions (the fraction of sediment extract that is soluble in n-heptane) were desulphurized using Raney nickel, which cleaves C—S bonds selectively and quantitatively[19]. Both the 'free' and the 'free + S-bound' hydrocarbon biomarker fractions were hydrogenated before being compared. The distributions of the 'free' hydrocarbon biomarkers is significantly different to that of the 'free + S-bound' compounds (Fig. 1 and Table 1), clearly demonstrating the bias introduced by natural sulphurization, and the consequent possibility of incomplete or even erroneous reconstructions of depositional environments.

In the Vena del Gesso sediment, the distribution of the long-chain n-alkanes (C_{25}–C_{33}) is dramatically changed after desulphurization (Fig. 1). This is also expressed by the change in the 'carbon preference index' (the ratio of odd- to even-carbon-numbered n-alkanes[20]; Table 1), which is a frequently used measure of the contribution of terrigenous organic matter in sediments[18]. Based on the investigation of only the 'free' long-chain n-alkanes, one might come to the conclusion that the organic matter in this sediment contains an appreciable terrigenous contribution, whereas, after taking into account the naturally sulphurized long-chain n-alkanes, it can be concluded that there is only a small contribution of terrestrial organic matter. Pristane (II, see Fig. 2) and phytane (III) are acyclic isoprenoid biomarkers that are ubiquitous in sediments; the pristane/phytane ratio is thought to reflect the oxicity of the depositional environment[22], although more recently this ratio has also been interpreted in terms of palaeosalinity[23,24]. Although this parameter is not often applied to Recent sediments (such as the Peru sediment), it is frequently used in consolidated immature sediments (such as the Vena del Gesso sediment). In
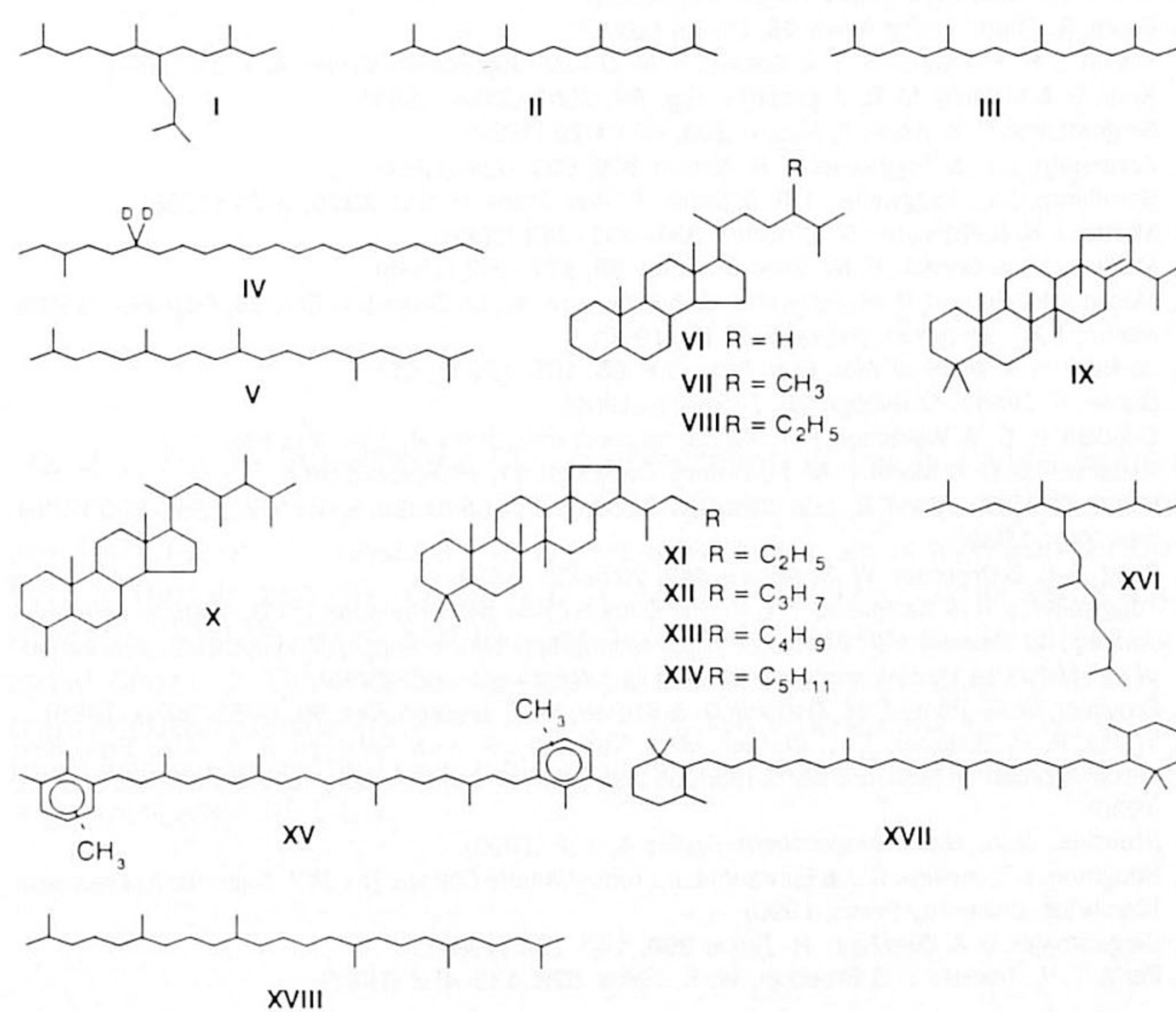

FIG. 2 Structures of compounds.

TABLE 1 Concentrations of selected biomarkers and biomarker ratios in the 'free' hydrocarbon and the 'free + S-bound' hydrocarbon fractions

	Vena del Gesso-4a			Peru upwelling area		
	'Free'	'Free + S-bound'	Naturally sulphurized fraction*	'Free'	'Free + S-bound'	Naturally sulphurized fraction*
Octadecane	9.0×10	5.5×10^3	98	2.0×10^3	2.0×10^3	0
Octacosane	1.7×10^2	1.7×10^3	90	2.0×10	3.2×10	38
Nonacosane	9.6×10^2	1.9×10^3	49	3.4×10	5.8×10	41
Pristane (II)	2.2×10^2	3.3×10^2	33	3.6×10	3.5×10	0
Phytane (III)	9.0×10	1.1×10^4	99	7.1×10	1.4×10^3	95
C_{20} HBI†(I)	4.0×10^3	4.6×10^3	13	<1	<1	n.a.
C_{25} HBI† (XVI)	<1	<1	n.a.	<1	1.2×10^2	100
PME‡ (V)	1.0×10^2	2.5×10^2	60	5.0×10	7.0×10	29
Squalane (XVIII)	<1	<1	n.a.	1.5×10^2	1.7×10^2	12
Cholestanes§ (VI)	1.6×10^2	1.2×10^4	99	3.0×10	2.0×10^2	85
Dinosterane (X)	<1	8.5×10^3	100	<1	<1	n.a.
Pentakishomo-Hopane‖ (XIV)	<1	1.1×10^3	100	<1	<1	n.a.
Diaromatic Carotenoid (XV)	<1	4.3×10^3	100	<1	<1	n.a.
β-Carotane (XVII)	<1	<1	n.a.	2.0×10	1.2×10^4	100
CPI#	8.0	1.1	n.a.	1.3	1.2	n.a.
Pristtane/phytane¶	2.5	2.9×10^{-2}	n.a.	5.5×10^{-1}	2.5×10^{-2}	n.a.

n.a. = not applicable. Concentrations of biomarkers (mg per kg extract) are obtained by integrating their peak areas and that of the internal standard (IV) in the FID trace.

* [('S-bound')/('free + S-bound')] × 100 (in %).

† HBI = highly branched isoprenoid.

‡ PME = 2,6,10,15,19-pentamethyleicosane.

§ $5\alpha(H), 14\alpha(H), 17\alpha(H)$-cholestane and $5\beta(H), 14\alpha(H), 17\alpha(H)$-cholestane.

‖ $17\beta(H), 21\beta(H)$, 22R-pentakishomohopane.

¶ Peak area of pristane is determined in an FID trace obtained using a DB17 column.

CPI = Carbon preference index (ref. 20) of the n-alkanes (C_{24}–C_{34}):

$$CPI = \frac{1}{2} \left[\frac{C_{25} + C_{27} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right].$$

both samples, the pristane/phytane ratio is changed drastically after desulphurization (Table 1), demonstrating that it may be heavily biased in immature sediments. This bias stems from the fact that the precursors of phytane react selectively with inorganic sulphur species during early diagenesis[24]. The contribution of marine organic matter is also underestimated when using the regular steranes (VI–VIII), which are those derived from sterenes after hydrogenation, as biomarkers for algal material, because these compounds are present only at very low levels in the 'free' hydrocarbon fraction whereas they are highly prevalent in the 'free + S-bound' hydrocarbon fraction (Fig. 1 and Table 1).

In both samples, several diagnostic biomarkers are virtually absent in the 'free' hydrocarbon biomarker fraction but are present in significant amounts after desulphurization (Fig. 1 and Table 1), demonstrating again that studies using solely the 'free' hydrocarbon biomarkers may miss valuable information about the depositional environment. Dinosterane (X), a biomarker for dinoflagellate algae[25], shows up only after desulphurization: its presence is in agreement with microscopic examinations, which reveal dinoflagellate cysts in the sediment. The presence of sulphur-linked diaromatic carotenoids (XV) attests to the activity of photosynthetic bacteria in the depositional environment of the Vena del Gesso sediment[26,27]. Another clue to bacterial activity is furnished by the appearance of pentakishomohopane (XIV) after desulphurization (Fig. 1). The presence of a C_{25} highly branched isoprenoid alkane (XVI) in the desulphurized sample of the Peru sediment (Table 1) is reminiscent of the presence of C_{25} highly branched isoprenoid alkenes in other samples[28], which have possibly been biosynthesized by diatoms in the palaeoenvironment. The most striking bias in the biomarker distribution is illustrated by the β-carotane carbon skeleton (XVII) in the Peru sediment: this compound is absent in the hydrocarbon fraction, but it is present as a major 'S-bound' moiety and thus dominates the 'free + S-bound' hydrocarbon biomarker distribution (Table 1).

On the other hand, the abundances of a number of biomarkers (for example, a C_{20} highly branched isoprenoid alkane (I), pristane (II), 2,6,10,15,19-pentamethyleicosane (V), squalane (XVIII)) in the naturally sulphurized fraction are relatively low (Table 1), indicating that 'free' hydrocarbon biomarkers in immature organic-sulphur-rich sediments are lipids that did not react with sulphur during early diagenesis, probably because they were biosynthesized without a reactive functionality.

It follows from these results that, in sediments with a high organic-sulphur content, the sulphur-bound biomarkers should be taken into account for a complete and thus more correct characterization of the (palaeo)environment. This can be achieved easily by simple desulphurization, which releases the naturally sulphurized biomarkers. Preliminary results[29] indicate that the same bias can be expected for the distributions of oxygenated biomarkers (such as alcohols, acids and ketones), compounds that are also used frequently to reconstruct palaeoenvironments from analysis of immature sediments[30,31]. □

1. Johns, R. B. (ed.) Biological Markers in the Sedimentary Record (Elsevier, Amsterdam, 1986).
2. Brassell, S. C. & Eglinton, G. in Organic Marine Geochemistry (ed. Sohn, M. L.) 10–32 (American Chemical Society, Washington, 1986).
3. Volkman, J. K. in Lacustrine Petroleum Source Rocks (eds Fleet, A. J., Kelts, K. & Talbot, M. R.) 103–122 (Blackwell, Oxford, 1988).
4. Mackenzie, A. S. in Advances in Petroleum Geochemistry Vol. 1 (eds Brooks, J. & Welte, D. H.) 115–214 (Academic, London, 1984).
5. Philip R. P. Fossil Fuel Biomarkers. Methods in Geochemistry and Geophysics Vol. 23 (Elsevier, Amsterdam, 1985).
6. Sinninghe Damsté, J. S. & de Leeuw, J. W. in Advances in Organic Geochemistry 1989 (eds. Durand, B. and F. Behar) 1077–1101 (1990).
7. Mossmann, J., Aplin, A. C., Curtis, C. D. & Coleman, M. L. in Proc. ODP Sci. Results 112 (eds Suess, E. et al.) 455–464 (Ocean Drilling Program, College Station, Texas, 1990).
8. Kohnen, M. E. L. et al. Geochim. cosmochim. Acta 54, 3053–3063 (1990).
9. Ten Haven, H. L., Rullkötter, J., Sinninghe Damsté, J. S. & de Leeuw, J. W. in Geochemistry of Sulfur in Fossil Fuels (eds Orr, W. L. & White, C. M.) 613–632 (American Chemical Society, Washington, DC, 1990).
10. Berner, B. A. Phil. Trans. R. Soc. Lond. 315, 25–38 (1985).

11. Simoneit, B. R. T. & Mazurek, M. A. *Init. Rep. DSDP* **63**, 837–853 (1982).
12. Rulkötter, J., von der Dick, H. & Welte, D. H. *Init. Rep. DSDP* **64**, 837–853 (1982).
13. Von der Dick, H., Rulkötter, J. & Welte, D. H. *Init. Rep. DSDP* **71**, 1015–1032 (1983).
14. Rulkötter, J., Mukhopadyay, P. K. & Welte, D. H. *Init. Rep. DSDP* **75**, 1069–1087 (1984).
15. Volkman, J. k., Allen, D. I., Stevenson, P. L. & Burton, H. R. in *Advances in Organic Geochemistry 1985* (eds Leythaeuser, D. & Rullkötter, J.) 671–681 (1986).
16. Grimalt, J. & Albaigés, J. *Geochim. cosmochim. Acta* **51**, 1379–1384 (1987).
17. Wakeham, S. G. *Geochim. cosmochim. Acta* **54**, 1325–1336 (1990).
18. Vai, G. B. & Ricci Lucci, F. R. *Sedimentology* **24**, 211–244 (1977).
19. Sinninghe Damsté, J. S., Rijpstra, W. I. C., de Leeuw, J. W. & Schenck, P. A. in *Advances in Organic Geochemistry 1987* (eds Novelli, L. & Matavelli, L.) 593–606 (1988).
20. Bray, E. E. & Evans, E. D. *Geochim. cosmochim. Acta* **22**, 2–15 (1961).
21. Eglinton, G. & Hamilton, R. J. in *Chemical Plant Taxonomy* (ed. Swain, T.) 187–217 (Academic, New York, 1963).
22. Didyk, B. M., Simoneit, B. R. T., Brassell, S. C. & Eglinton, G. *Nature* **272**, 216–222 (1978).
23. Ten Haven, H. L., de Leeuw, J. W., Rullkötter, J. & Sinninghe Damsté, J. S. *Nature* **330**, 641–643 (1987).
24. De Leeuw, J. W. & Sinninghe Damsté, J. S. in *Geochemistry of Sulfur in Fossil Fuels* (eds Orr, W. L. & White, C. M.) 417–443 (American Chemical Society, Washington, DC, 1990).
25. Summons, R. E., Volkman, J. K. & Boreham, C. J. *Geochim. cosmochim. Acta* **51**, 3075–3082 (1987).
26. Liaaen-Jensen S. in *Marine Natural Products* (eds Faulkner, D. J. & Fenical, W. H.) 1–73 (Academic New York, 1978).
27. Liaaen-Jensen S. in *Photosynthetic Bacteria* (eds Clayton, R. K. & Sistrom, W. R.) 233–248 (Plenum, New York, 1978).
28. Nichols P. D., Volkman, J. K., Palmisano, A. C., Smith, G. A. & White, D. C. *J. Phycol.* **24**, 90–96 (1988).
29. Meunier-Christmann, C. thesis, University of Strasbourg (1988).
30. Ten Haven, H. L., Baas, M., de Leeuw, J. W. & Schenck, P. A. *Mar. Geol.* **75**, 137–156 (1986).
31. Ten Haven, H. L., Rullkotter, J., Stein, R. & Welte, D. H. in *Proc. ODP Sci. Results* **112**, (eds Suess, E. *et al.*) 591–606 (Ocean Drilling Program, College Station, Texas, 1990).
32. Kohnen, M. E. L., Sinninghe Damsté, J. S., Rijpstra, W. I. C. & de Leeuw, J. W. in *Geochemistry of Sulfur in Fossil Fuels* (eds Orr, W. L. & White, C. M.) 444–485 (American Chemical Society, Washington, DC, 1990).

Hydrothermal activity and metallogenesis in the Lau back-arc basin

Y. Fouquet*, U. Von Stackelberg†, J. L. Charlou*, J. P. Donval*, J. Erzinger‡, J. P. Foucher*, P. Herzig§, R. Mühe‖, S. Soakai¶, M. Wiedicke§ & H. Whitechurch#

* IFREMER Centre de Brest, BP 70, 29280 Plouzane, France
† Bundesanstalt für Gewissenschaften und Rohstoffe (BGR), 3000 Hannover 51, Germany
‡ Institut für Geowissenschaften, Justus-Liebig-Universität, 6300 Giessen, Germany
§ Institut für Mineralogie und Lagerstättenlehre, RWTH Aachen, 5100 Aachen, Germany
‖ Geologisches Institut, Universität Kiel, 2300 Kiel 1, Germany
¶ Ministry of Lands Survey and Natural Resources, Nuku'alofa, Tonga
# Ecole et Observatoire de Physique du Globe de Strasbourg, 5 rue Descartes, 67084 Strasbourg Cedex, France

IN 1989, the submersible Nautile discovered one of the most active hydrothermal fields on the modern ocean floor, in the Lau back-arc basin (Fig. 1). The field contains high-temperature white and black smokers, and as we report here, its characteristics contrast strongly with those of the hydrothermal fields found at normal mid-ocean ridges. The main differences are the acidity (pH as low as 2), chemistry and temperature (up to 400 °C) of the hydrothermal fluids, the composition of the ore deposits, and the volcanic and tectonic environments. The fluids also have very high concentrations of trace metals, and primary gold is present in the accompanying mineral deposits. Our data show that these back-arc deposits in the Lau Basin are intermediate between typical mid-ocean-ridge mineralization and massive sulphide deposits of the Kuroko type.

The Lau Basin is a typical example of an active back-arc basin between a remnant (Lau ridge) and an active volcanic arc (Tofua volcanic arc) (Fig. 1a). The northern spreading axis at the centre of the basin consists of tholeiitic basalt. The southern segment, located 75 km closer to the Tofua volcanic arc, is made up of a differentiated series of Fe–Ti basalts, andesites, dacites and rhyolite[1-4]. This area shows a clear influence of the subducted slab on the composition of the lava[4,5].

Here we report observations from the Valu Fa ridge, the southernmost part of the southern segment between 21° and 23° S, only 40 km west of the Tofua volcanic arc[2,6-10] (fig. 1b). The water depth ranges from 1,700 to 2,000 m. The sulphide deposits are underlain by basaltic andesites and andesites at the Vai Lili field and by andesites and dacites at the Hine Hina field. The physical properties of the crust and construction processes are such that they do not produce the same fissures, faults and offsets that occur in typical mid-ocean ridge (MOR) systems. In particular, the high gas content of the magmas produces highly vesicular and brecciated lavas which facilitate extensive circulation of sea water and hydrothermal fluids in the crust and create pathways for ascending hydrothermal solutions[8,11,12]. These conditions provide an effective mechanism for abundant and widespread sea-floor and sub-surface mineralization.

Very-high-temperature black (320–400 °C) and white smokers (250–320 °C) were discovered at the central Valu Fa Ridge[6] (Fig. 1b, area 2). About 10 groups of smokers were observed in area 2. The active zone, not entirely mapped, is at least 400 m long and 100 m wide and controlled by a normal fault. In the Vai Lili area the hydrothermal plume rises up to 200 m (ref. 6) above the bottom. The temperature anomalies on the bottom are up to 30 °C a few metres from the vents, compared with only some tenths of degrees at hydrothermal sites in MOR systems. This is due to the importance of intense diffuse discharge from the side of the chimney and from the highly porous and brecciated andesite at the base. Away from the sulphidic chimneys there are important zones of widespread low-temperature discharge (100 × 100 m) where the ambient sea-

TABLE 1 Composition of Lau Basin, mid-ocean ridge and Kuroko sulphide deposits

	White Church (zone 3)	Vai Lili (zone 2)	Hine Hina (zone 1)	Mid-ocean ridge	Kuroko
N*	13	11	5	33	39
SiO_2(wt%)	25.12	10.48	1.76	5.15	
Al_2O_3 (wt%)	1.79	1.39	1.12	0.08	
S (wt%)	18.21	28.51	43.64	35.12	16.20
Ca (wt%)	0.14	1.48	0.07	4.49	
Fe (wt%)	7.17	10.46	34.57	25.96	13.72
Cu (wt%)	3.32	7.05	3.32	7.83	1.88
Zn (wt%)	11.17	26.27	10.87	8.17	6.25
Pb (wt%)	0.23	0.17	0.59	0.05	1.78
Ba (wt%)	20.84	11.76	2.09	0.08	
Mn (p.p.m.)	799	783	44	100	
Co ((p.p.m.)	2	2	5	960	
Ni (p.p.m.)	2	11	4		
As (p.p.m.)	473	1,581	4,586	154	
Se (p.p.m.)	2	0	22	163	
Sr (p.p.m.)	3,166	1,621	1,037	498	
Mo (p.p.m.)	46	30	20	50	
Ag (p.p.m.)	107	143	517	49	215
Cd (p.p.m.)	338	784	323	233	
In (p.p.m.)	<10	92	<10		
Sn (p.p.m.)	<10	5	2		
Sb (p.p.m.)	86	41	25		
Au (p.p.m.)	2	0.6	1.7	0.26	1.58

Calculated average of representative sulphide samples from the three main hydrothermal fields from the Valu Fa Ridge (zones 1, 2, 3). Metal content of dried substances were determined by X-ray fluorescence (P. Cambon and J. Etoubleau, IFREMER/Brest). Gold was analysed by neutron activation method. Values for mid-ocean ridge (East Pacific Rise, 13° N) are from ref. 26 and values for Kuroko from ref. 27.

* N, number of determinations.