Pristane/phytane ratio as environmental indicator

SIR—The discussion by ten Haven et al.[1] concerning the use of pristane (Pr) to phytane (Ph) ratio as an environmental indicator has missed the point of much of the early literature, and misconstrues the significance of some recent data. The problem of error in the measurement of Pr concentrations caused by coelution of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane must be kept in perspective. The compound is poorly resolved from Pr on most good-quality capillary columns and has been identified in only one very unusual and geologically young crude oil and in few recent sediments[2]. There is not sufficient evidence that it is present in sufficient concentration to influence significantly the measurement of Pr concentrations in most ancient sediments and oils.

Bituminous coals and oils originating from higher plants are known[3,4] to have high Pr/Ph ratios (5–10) in comparison with marine oils and sediments (<1–3). Further, Pr/Ph ratios increase from 1–2 in brown coals to a maximum of 4–10 in bituminous coals, and significant Pr generation occurs at the threshold of oil generation. These observations were rationalized in terms of the preferential formation of phytanic acid by oxidation of phytol, followed by the conversion of phytanic acid to Pr during catagenesis[3,4], and have been completely ignored by ten Haven et al.[1]. Clearly, high Pr/Ph ratios (≥3) are indicative of an input from terrestrial organic matter that has a high probability of being exposed to oxidation before or during deposition. But as the depositional conditions and source inputs control the distribution of Pr and Ph precursors, it is inappropriate for Pr/Ph ratios to be used as a redox indicator in low-maturity samples without consideration of the precursors and the maturity level.

Most marine, organic-rich sediments and oils have a narrow range of Pr/Ph ratios (0.8–2.5)[5], and with increasing maturity there can be a gradual increase in Pr/Ph ratio within this range. This has been associated in one case[6] with other evidence of oxidation of organic matter during deposition. The proposal that Pr/Ph ratios cannot reflect the redox conditions of the final resting place of organic matter[1] is a question of semantics because all sediments ultimately become reducing during burial; it is the depositional history that is the critical factor in determining the extent of oxidation of organic matter, not the final resting place.

Pr/Ph ratio cannot be used as a palaeoenvironmental indicator at low maturity level[2] and this is implicit in the early literature[3,4]. At higher maturation levels, high Pr/Ph ratios (> 3.0) are reliable indicators of input of terrestrial organic matter[4] and very low values are characteristic of anoxic, and often hypersaline, environments[1,2]. The significance of values between 0.8 and 2.5 in mature normal marine sediments and oils is more difficult to assess. Whether the origin of pristane is ultimately phytol or tocopherols[7] may be irrelevant to the application of the Pr/Ph ratio as a redox indicator. Tocopherols are claimed to have greater preservation potential than phytol and its derivatives[7]. The effect of some oxidative degradation of organic matter during deposition would be selectively to preserve tocopherols, giving rise to higher Pr/Ph ratios during subsequent maturation. The use of Pr/Ph ratios as a correlative tool was originally based on many empirical observations which have now expanded greatly and are still valid. Any qualification to the explanations for the origins of Pr and Ph do not invalidate the fundamental observations.

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TEN HAVEN ET AL. REPLY — We agree with Powell that pristane (Pr) to phytane (Ph) ratios close to unity should be interpreted with great caution and that fewer difficulties arise with extremely high (as in coals) or extremely low (as in sediment from hypersaline environments) Pr/Ph ratios. In these latter cases, the Pr/Ph ratios are probably influenced by specific sources of the organic matter and specific depositional environments, where the redox condition is only one of the factors.

The main point of our paper[1] concerns the generalizations and oversimplifications implied in the use of the Pr/Ph ratio as an indicator of the level of oxygen at the site of organic matter deposition into sediments. In much recent work (mainly that dealing with sediments containing immature organic matter), a Pr/Ph ratio of unity has become a kind of magic number to differentiate between palaeo-oxygen levels, commonly with reference to Didyk et al.[8]. We made several new arguments[1] based on novel geochemical findings to emphasize the restricted use of the Pr/Ph ratio as a palaeoenvironmental indicator. Note that the intermediates in the diagenetic scheme of Didyk et al.[8], who studies the conversion of phytol in a few recent sediments, have not been verified in many cases. Moreover, it is becoming obvious that many precursors of both pristane and phytane have to be taken into account[2,7]. The selective preservation of these precursors will be different in different sedimentary environments. In other words, the ultimate Pr/Ph ratio is determined by a large variety of known and unknown precursors, their selective preservation and their pathways of diagenesis.

The coelution of pristane with 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane on apolar stationary phase is a new result. Sediments containing mature organic matter and a few crude oils have been checked for the presence of this compound. In addition to other examples[2,9] sapropels from an open marine environment in the Mediterranean (typical potential oil-source rocks) are known to contain this new compound in concentration three times as high as pristane[10].

Of course, we do not object to using the Pr/Ph ratio as a correlative tool when samples of the same origin and maturation level are compared with one another (as in oil/source-rock correlation).

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Radiocarbon dating

SIR—Radtke proposes electron-spin-resonance analysis as a means of identifying shell and coral samples that are unsuitable for radiocarbon dating[1]. An alternative is to date samples by 'first-order assay'[1], which provides reliable ages for material less than 10,000 years old and, in so doing, distinguishes between Holocene and earlier samples. Each analysis (excluding labour) costs about £0.50; the requisite liquid scintillation counters are commoner than electron-spin-resonance spectrometers in universities and, of course, radiocarbon laboratories.

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