



Review

Organic geochemistry and mineralogy. I. Characterisation of organic matter associated with metal deposits

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ABSTRACT

As geochemical appraisals of mineral regions of commercial prospectivity evolve, the organic matter associated with metal rich ores has attracted greater attention. Petroleum basin and modern seafloor hydrothermal vent studies have suggested that organic matter can have a significant influence on the behaviour of mineralising fluids. There have been many isolated reports of certain organic compositional or morphological (e.g. pyrobitumen) features showing an apparent relationships with hydrothermal fluids or minerals, raising expectations that organic based parameters might be useful to mineral exploration. However, the understanding of organic–inorganic relationships in Earth systems is far from complete. For example, the detailed mechanics of the interaction of organics with hydrothermal fluids over geological time remain largely undefined. Organic geochemistry studies have traditionally involved the measurement and interpretation of the hydrocarbon composition of sedimentary rocks. Here we review the types of aliphatic hydrocarbons, aromatic hydrocarbons and metalloporphyrins often detected from organic geochemical investigations in mineral-rich regions. Such molecular data can be particularly diagnostic of biochemical sources and the palaeo-environments at the time mineral associated organic matter was deposited. Sub-surface trends of hydrocarbon alteration may also reflect major biogeochemical processes such as thermal maturity and biodegradation. Organic geochemistry data can also occasionally provide information about the nature (e.g., origin, composition, temperatures) and migration pathways of hydrothermal fluids and can make a contribution to holistic ore genesis models. The well preserved organic matter associated with the economic “Here’s Your Chance” Pb–Zn–Ag Mine (Paleoproterozoic Barney Creek Formation, McArthur Basin, Australia) and the transition metal-rich Early Permian Kupferschiefer Formation (Germany–Poland) have attracted significant attention. A more detailed summary of the organic character of these deposits is provided to highlight the contribution organic geochemistry can make to understanding mineralisation processes. Most organic geochemical studies of highly mineralised regions, however, have not adequately addressed the significance of organic matter to mineralisation. A slightly different analytical focus than traditionally used for exploration appraisal of petroleum hydrocarbons may be required to properly evaluate the significance of organic species to the mobilisation, transport and deposition of ore metals. The characterisation and subsequent thermodynamic modeling of organic substances and complexes within metalliferous hydrothermal systems will contribute to a better understanding of the nature and role of organic–inorganic fluids or other affiliated organics in ore systems.

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1. Introduction

The ubiquity of organic matter (OM) in sedimentary rocks and the high organic load of several significant mineral deposits – e.g. Pb, Zn and Ag deposits of Australia's McArthur Basin (Logan et al., 2001; Summons et al., 1988), Cu and Fe deposits of Europe's Kupferschiefer formation (Püttmann et al., 1989) and Cu deposits of the Nonesuch formation (N. Michigan, USA; Ho et al., 1990; Ho and Mauk, 1996) – have supported a general view that OM plays a role in some forms of mineralisation. Questions that are often raised with respect to the role of OM in mineralisation include: Where does the OM come from? Is it syngenetic with ore formation or transported from an exogenous source prior, during or after ore formation? What diagenetic processes and temperatures from burial or through interaction with hydrothermal fluids has it been exposed to? What are the actual roles of OM in the formation, mobilisation or accumulation of metal ores? There has been insufficient scientific study of organic–mineral interactions to confidently answer these questions. Organic compounds can react with metal and sulfur species through a variety of redox and other processes, and may influence physico-chemical properties important to mineralisation (e.g., pH; mineral solubilities, precipitation temperatures, rock porosity and permeability). Migrating oil and metal bearing brines may passively co-inhabit the same hydrothermal fluids or accumulate in the same highly porous reservoir rocks (Montacer et al., 1988). Acids and other organic compounds may promote rock porosity to help create favorable reservoir structures (Knauss et al., 1997). It has also been suggested that high mineral concentrations may catalyse the abiotic production of organic compounds such as by Fischer–Tropsch reactions of such basic gases as H₂, CO₂ and H₂O (Gize, 1999b).

Several books and special journal issues have been dedicated to the research of organic–inorganic interactions in Earth systems. These include *Bitumens in Ore Deposits* (Parnell et al., 1993), Springer Verlag, Berlin (1993); *Organic Matter and Mineralisation: Thermal Alteration, Hydrocarbon Generation and Role in Metallogenesis* (eds. M. Glikson and M. Mastalerz) Kluwer Academic Publishers,

Dordrecht (2000); a special 1996 issue of *Ore Geology Reviews* *Organics and Ore Deposits*; a 1999 issue of *Economic Geology* dedicated to *Organic Matter and Ore Deposits: Interactions, Applications and Case Studies* and a 2000 edition of *Reviews in Economic Geology on Ore Genesis and Exploration: The roles of organic matter* (eds. T.H. Giordano, et al., E.g., see Introduction Leventhal and Giordano, 2000). Many of these review articles and a good number of other studies have focused on mineral locations where organic concentrations are notably high. In addition to the aforementioned metal-rich McArthur Basin, Kupferschiefer and Nonesuch deposits there have been many isolated accounts of organics associated with large deposits of Mississippi Valley Type (MVT) Pb–Zn deposits (e.g., Disnar and Sureau, 1990; Gatellier and Disnar, 1989) and other metals including U (e.g., Gize, 2000; Kribek et al., 1999; Landais, 1993, 1996; Leventhal et al., 1987; Nakashima et al., 1999); Au (Fairmaid et al., 2011; Gize, 1999b, 2000; Hulen and Collister, 1999; Large et al., 2011; Thomas et al., 2011; Yang and Lentz, 2010), Hg (Gize, 1999b, 2000), Ni (Lott et al., 1999), Mb (Lott et al., 1999) and V (Lewis et al., 2010).

The previous attention highlights the suspected importance of OM to the occurrence of mineral deposits, and the potential benefit of organic parameters to exploration for valuable metals. However, Gize (1999a), in his introductory editorial to the special organic edition of *Economic Geology*, lamented that despite intensive organic research of some of the world's major metal deposits the role and sources of OM in ore genesis remained unknown or contentious. Over a decade later, few would confidently claim to understand the relevance of organics to mineralisation processes.

Several studies in which advanced organic geochemistry has been applied to mineral deposits have identified hydrocarbon biomarkers of major organic precursors and molecular alterations indicative of important Earth processes such as thermal maturity and biodegradation (e.g., Logan et al., 2001; Rieger et al., 2008). Apparent trends between biomarker parameters or other hydrocarbon ratios with metal rich ores have also on occasion been recognised (e.g., Hulen and Collister, 1999; Spangenberg and Macko, 1998).

The purpose of this present review is to describe ways that OM associated with mineral systems have been typically analysed and the type of information about metal deposits this can provide. It is not intended to be an exhaustive account of all previous literature relating to *Organic–Mineral* associations, but rather the aim is to outline the insightful outcomes from a number of reliable organic geochemical studies which serve as exemplifiers for the benefits of the applied organic geochemistry of mineralogical systems. The value of organic geochemistry in understanding mineralisation processes is perhaps best demonstrated by insightful outcomes from the particularly well studied organic matter associated with the economic “Here’s Your Chance” Pb–Zn–Ag Mine (Paleoproterozoic Barney Creek Formation, McArthur Basin, Australia) and the transition metal-rich Early Permian Kupferschiefer Formation (Germany–Poland). Organic geochemical studies adjacent to these two metal deposits and the contribution of this research to ore genesis models are separately described. We also aim to highlight the limitations of traditional organic geochemistry approaches for studying the mechanics of organic–mineral interactions. We exclude detailed discussion of ore deposit studies reporting biomarker distributions which appear inconsistent with the thermal history or age of the host rocks and where extract yields fall into a range where trace-level contamination becomes a concern.

In order to facilitate a comprehensive and easy to follow presentation of organic compounds associated with minerals and analytical techniques employed in their characterisation, we provide an [Appendix A](#), depicting all structural types of molecules discussed complemented by a glossary that lists all abbreviations (used for brevity) and brief descriptions of organisms, compounds or processes.

1.1. Guilt by association

The importance of organic–inorganic interactions to the formation of metal sulfides and other mineral deposits has often been inferred from a general correlation of high subsurface concentrations of both organics (e.g. 1–15 wt.%) and minerals containing valuable metals (e.g., [Large et al., 2011](#); [Thomas et al., 2011](#)). Analytical methods such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and X-ray fluorescence (XRF) can measure trace metal concentrations with high sensitivity, including detection of non visible, but potentially economic levels (e.g., Au at >250 ppm; [Large et al., 2011](#)). The total organic carbon (TOC) contents of OM can be analysed by a number of analytical methods. [Simoneit and Giže \(2000\)](#) provide an informative introduction into analytical techniques commonly used to characterize the organic matter in ore deposits, including sample preparations, bulk methods (e.g., R-E pyrolysis; [Crick, 1992](#); [Crick et al., 1988](#)) for measuring composition of main elements (C, H, O, N) and also useful for establishing the OM quality or type ([Tissot and Welte, 1978, 1984](#)) and spectroscopic methods probing molecular composition.

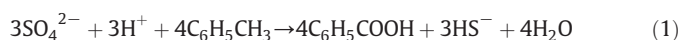
1.2. Organic mineral relationships

High organic concentrations and related morphological features (e.g., pyrobitumen, a hydrocarbon mineraloid formed by thermal solidification of petroleum) have occasionally proved useful for mineral exploration. For instance, the association of OM and sulfide mineralisation has been used to help explore for Zn–Pb minerals from Triassic–Cretaceous formations in northern Tunisia ([Montacer et al., 1988](#)). Residual petroleum (i.e., pyrobitumen) from Late Cretaceous sources was also correlated with Cu–(Ag) mineral deposits in northern Chile ([Cisternas and Hermosilla, 2006](#)). Still relatively little is known about the mechanistic role that organics play in the genesis of the ore associated with these and most deposits, although such information could add considerable value to exploration endeavors. Progression beyond a superficial correlation of the concentrations of organic and inorganic species to a more detailed investigation of the sub-surface interactions of organic substances

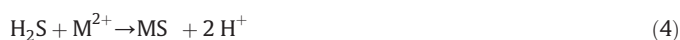
and metal-rich ores will help clarify the frequency and extent to which organics contribute to the formation of different mineral deposits.

Several previous studies provided evidence of a deeper connection between co-occurring minerals and OM. Losses of OM with mineralisation, such as evident in the Nonesuch Formation ([Ho et al., 1990](#)) and Barney Creek Sediments of the Here’s Your Chance (HYC) deposit ([Chen et al., 2003](#); [Logan et al., 2001](#)), have been attributed to the oxidation of the OM or excessive thermal maturation on exposure to hydrothermal fluids. OM can also facilitate the biogenic (e.g. sulfate reducing bacteria; SRB) or abiogenic (e.g. thermochemical sulfate reduction; TSR) reduction of sulfates, and the subsequent precipitation of metal sulfides ([Connan and Orgeval, 1973](#); [Disnar et al., 1986](#); [Germanov, 1965](#); [Montacer et al., 1988](#); [Nooner et al., 1973](#); [Pering, 1973](#); [Powell and MacQueen, 1984](#)). Ore precipitation – as well as OM maturation – associated with hydrothermal fluid would also account for TSR and pyrobitumen formation ([Spangenberg and Macko, 1998](#)). Hydrothermal fluids may also introduce exogenous OM (e.g., HYC – [Williford et al., 2011](#)).

[Rieger et al., 2008](#) proposed the following reaction scheme to represent the oxidation of bitumen or OM to produce sulfides which could subsequently react with mineralised salts. The organic reactant is represented by toluene (C₆H₅–CH₃; structure *I* of [Appendix A](#)) and the oxidation product by benzoic acid (C₆H₅–COOH).



[Chen et al. \(2003\)](#) proposed a similar model for TSR of OM in the HYC deposit of the McArthur Basin, also suggesting that bacterial sulfate reduction (BSR) could occur in cooler zones.



Others have proposed similar processes, with different organic reactants such as high-molecular weight (MW) normal (*n*-) alkanes (*III*, [Appendix A](#)) to produce *n*-carboxylic acids ([Machel et al., 1995](#)). However, the actual reactants and products in natural systems remain largely unknown. The oxidation of metal sulfides by oxygen-charged brines can result in high abundances of elemental sulfur (S⁰), which can then initiate the dehydrogenation and aromatisation of saturated hydrocarbons ([Giže, 1999b](#)). This process can also include incorporation of S⁰ to form aromatic sulfur containing compounds.

Where sulfur is deficient some transition metal species may react with biological porphyrins to yield organic-metal complexes ([Giže, 1999b](#)). Several studies of Kupferschiefer deposits have reported high abundances of both organic sulfur compounds (OSCs, e.g., *IV–VIII*) and Fe(III), Ni, VO²⁺ based metallo-porphyrins (e.g., *IX, X*; [Czechowski, 2000](#); [Eckardt et al., 1989](#); [Grice et al., 1996a, 1996b, 1997](#); [Kucha, 1983](#); [Kucha and Przybyłowicz, 1999](#); [Pancost et al., 2002](#); [Schwark and Püttmann, 1990](#); [Wolf et al., 1989](#)), and evidence for basin-wide syngenetic origin of Ni- and VO-porphyrins (and some Fe-porphyrins) in non-mineralised sediments and loss of Ni-porphyrins in heavily mineralised areas.

1.3. Microbially mediated ore precipitation

Research on biologically induced mineral precipitation is progressing rapidly and bacterially associated examples below are a small selection. Detailed discussions on this topic were tackled by [Ehrlich \(1999\)](#), [Bazylinski and Frankel \(2003\)](#) [Haferburg and Kothe \(2007\)](#) and [Reith et al. \(2007\)](#). Biologically induced mineralisation results when metabolic activities of microorganisms yield by-products that are reactive to metals

and can initiate nucleation and growth of minerals (Bazylnski and Frankel, 2003). Mineralisation occurs actively when minerals form in synergy with chemical reactions in the cell, such as when iron and manganese oxides precipitate around the cyanobacterial cell with the increase in oxygen concentration and pH during photosynthesis (Fortin and Beveridge, 2000). Other examples of enzymatically-driven intracellular deposition are magnetite (Fe_3O_4) (Frankel et al., 1979), greigite (Fe_3S_4) and pyrite (FeS_2) in a magnetotactic bacteria (Frankel et al., 1979; Mann et al., 1990); uraninite (UO_2) and technetium(VII) oxide in Fe(III)-reducing bacteria (Lloyd et al., 2002); and octahedral Au colloids in a soil bacteria (Southam and Beveridge, 1994). Interestingly, spherical nanoparticles precipitated from abiotic experiments are distinct from octahedral, framboid like and foils of Au precipitated from Au(I)-thiosulfate complex in cells of a microbial consortia consisting mainly of sulfate-reducing bacteria that was isolated from a Au mine in Witwatersrand Basin (Lengke and Southam, 2007).

Moreover, mineral precipitation on the cell surface and in the bulk phase is a continuum between active and passive involvement of the organism. Commonly, bacterial cell surfaces have an overall negative charge mostly from carboxyl, phosphate and nitrogenous groups that become active sites for metallic cations to adsorb (Beveridge, 1988; Fortin et al., 1997; Tsezos and Volesky, 1981). Anions such as carbonate, phosphate and sulfate can react with the adsorbed metal ions and form precipitates that act as nucleation sites. An example is the uranyl phosphate salt $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ found on cell surfaces of *Citrobacter* (Macaskie et al., 1992). Ferrous iron adsorbed to the cell surface of sulfate-reducing bacteria (SRB) may react with biogenic H_2S to produce greigite, pyrrhotite (Fe_{1-x}S , $x = 0$ to 0.2) (Fortin et al., 1994), mackinawite (tetragonal FeS), marcasite (orthorhombic FeS_2) and pyrite (Freke and Tate, 1961; Rickard, 1969). Moreover, sulfides of Fe, Cu, Zn and Pb may precipitate in the vicinity of SRB cells (Ehrlich, 1999; Miller, 1950; Temple and Le Roux, 1964). In addition, some dissimilatory metal reducing bacteria can take advantage of the electrochemical potential of mineral surfaces to extract energy and reduce and precipitate metals as a consequence (Nealson et al., 2002).

The precipitation of mineralised skeletons and shells is biologically controlled (Bazylnski and Frankel, 2003; Lowenstam, 1981) and commonly involves an organic framework that constrains size, crystallinity, chemical composition, nucleation and growth of specific minerals (Lowenstam and Weiner, 1989). Chitons for example, have a complex array of enzymes and biochemical processes to reinforce their teeth with magnetite providing them with structural and mechanical strength to scrape algae from rock surfaces (Lowenstam, 1962).

Biologically mediated mineral formation is more efficient than abiotic precipitation (e.g., in vivo transformation of FeS to FeS_2 ; Donald and Southam, 1999). The kinetic advantage of biogenic mineral formation, however, is naturally limited to environments where organisms can thrive and is constrained by their ability to cope with conditions that accompany mineralisation such as radioactivity, metal toxicity and elevated temperatures. However, under favourable conditions, microorganisms can become extremely abundant, rapidly promoting micron and nano-scale processes that immobilize metals and influence mineral precipitation in and outside of the cell. As the cells die, the active sites on the cell surface and in the bulk phase can be enhanced or diminished with diagenesis. The evolution and transformation of these organic residues, which continue to influence the solubility, transport and precipitation of metals, will see them have a prolonged effect on ore formation. Perhaps present-day observations of microbial consortia can be correlated with molecular fossils in ore deposits to help establish a link to the active or passive roles of certain micro-organisms to mineral formation. This is an analytical template that has been established from petroleum exploration and paleoenvironmental reconstruction using organic geochemical and isotopic analyses.

In some cases, it is difficult to distinguish biogenic from abiotic minerals. However, fossilised microorganisms can give hints

of biogenicity (Rasmussen, 2000), although their syngeneity, genuine biological origin and role in mineralisation are often controversial. The most valuable, but by no means unambiguous indicator of microbial mineral precipitation in the rock record is the sulfur isotopic composition of sulfides (see Section 3.3 Sulfur Isotope Analysis; and 4.1 HYC deposit).

1.4. Traditional organic geochemistry

Decades of organic geochemical research on the hydrocarbon composition and properties of coal, oil and gases has resulted in a sophisticated understanding of the nature and history of sedimentary organics. Detailed analyses of OM composition can often provide information about biochemical precursors, depositional environment or alteration typical of different geological phenomena (e.g. Peters et al., 2005; Tissot and Welte, 1978, 1984).

The study of organic matter in sediments typically involves spectroscopic analysis of whole samples, or fractions resolved on the basis of physico-chemical properties. Even the tiny organic records occasionally present in fluid inclusions can be accessed with specialised analytical procedures (George et al., 2007; Stasiuk and Snowdon, 1997; see Section 5). Complimentary information can be provided by separate analysis of solvent extractable (i.e., bitumen) and non-extractable (i.e., kerogen) fractions. Demineralisation of geochemical samples with hydrofluoric acid, a technique used to isolate kerogen (Marshall et al., 2007; Saxby, 1976), can also yield hydrocarbons occluded in the kerogen-mineral matrix. Bitumens obtained by this technique have been referred to as “Bitumen II”, whereas the first extract obtained by organic solvent extraction is known as “Bitumen I”. Bitumen II is considered to be associated with the kerogen-mineral matrix (Sherman et al., 2007). Nabbefeld et al. (2010) compared both aliphatic and aromatic thermal maturity parameters (especially those related to the methyl phenanthrenes, e.g., *Xla*, and methyl naphthalenes, e.g., *Ila*, $\text{R} = \text{CH}_3$) in Bitumen I and Bitumen II for a variety of marine sediments spanning the Permian/Triassic boundary. It was found that the aromatic thermal maturity parameters are generally lower in Bitumen II than Bitumen I, and that the magnitude of this difference is greater with an increasing proportion of clay relative to organic carbon.

Kerogen is a poorly-understood macromolecular network of organic debris that is resistant to dissolution in organic solvents. However, analytical pyrolysis of kerogen, i.e. its thermal degradation, often yields hydrocarbon distributions that are similar to bitumen. These pyrolysates may also include organic compounds sequestered within metal sulfides or other minerals (Price, 1993; Spangenberg and Macko, 1998). Analytical pyrolysis has also been used to simulate the thermal maturation of organics in kinetic studies (e.g., Lewan et al., 2008) and represents a higher level of analytical sophistication than Rock Eval pyrolysis which is widely applied to establish the type of OM or its thermal maturity.

Biomarkers are the molecular fossils of biological compounds such as membrane lipids and pigments. After deposition of OM and with increasing accumulation of overlying sediments, lipids and other compounds undergo diagenesis losing chemical functional groups such as acid moieties and double bonds and eventually turning into mere hydrocarbon skeletons. However, these hydrocarbons often still structurally resemble their biogenic precursors, yielding taxonomic and environmental information. Encased in sedimentary rocks, hydrocarbon biomarkers may remain stable for hundreds of millions of years and, thus, are useful to reconstruct ancient microbial ecosystems. Certain biomarker features can also be indicative of specific depositional environments and geological processes, including microbial activity in the subsurface and thermal degradation induced by deep burial or hydrothermal activity (Peters et al., 2005). This type of information has made biomarkers prime targets of petroleum exploration studies (Peters et al., 2005), but their detection and interpretation in OM associated with ores remains an under-explored

area of research. The OM associated with ore deposits may contain hydrocarbons that are quite similar to conventional oils and bitumens (Spangenberg and Macko, 1998), although the high temperatures at which most metal ores form will lead to increasing proportions of polycyclic aromatic hydrocarbons (PAHs; e.g., Chen et al., 2003; Simoneit, 1994; Simoneit et al., 1992) and eventually complete destruction of all molecules.

The lipids of cell membranes are the major biochemical precursor of sedimentary biomarkers. These compounds span a vast range of structures reflecting subtleties in their biological or physico-chemical function. Membrane constituents are amphipathic, operating as a delicate temperature sensitive fluid phase, and primarily control the passage of water and solutes/nutrients between cells. Bacterial and eukaryotic membranes are predominantly composed of phospholipids including two aliphatic chain carboxylic acids which usually function optimally at temperatures of ~70 °C. Some membranes function at higher temperatures and at depth in petroleum reservoirs (Hallmann et al., 2008). These are typically composed of cyclic aliphatics to provide greater rigidity, with the number of rings increasing with operating temperature. The polycyclic sterols and hopanoids, the structural precursor of the important sterane (XII) and hopane (XIII) petroleum biomarkers ubiquitous in the geosphere, are important constituents of the lipid membranes of many eukaryotes and bacteria, respectively (Brocks and Grice, 2011; Peters et al., 2005). The structures of a number of biomarkers and other hydrocarbons common to sedimentary OM are given in the Appendix A.

The interpretation of hydrocarbon composition can also be complemented by stable isotopic analysis (Grice and Brocks, 2011). The information provided by bulk isotopic analysis of whole samples or their fractions is greatly extended by the capacity to measure the stable isotopic values (e.g., $\delta^{13}\text{C}$, δD , $\delta^{34}\text{S}$) of individual organic compounds (e.g. Amrani et al., 2009; Dawson et al., 2005; Freeman et al., 1990; Logan et al., 1995; Sessions et al., 1999). The application of stable isotopic methodologies to ore systems is reviewed in detail below (see 3.0).

2. Organic geochemistry of mineral deposits

The economic focus of the organic and inorganic geochemistry disciplines have been on commercially attractive fossil fuels and metal exploration targets, respectively. Consequently, hydrocarbons in mineral systems have attracted far less research than hydrocarbon fuels. Whilst petroliferous and metalliferous sediments occasionally coincide, occurrence of petroleum in mineral deposits is not common, probably partly because the elevated temperatures favouring the formation of many ore types already lead to thermal decomposition of liquid petroleum (Brocks and Summons, 2004). Nevertheless, a number of studies investigating the composition and properties of mineral associated organics of relatively low thermal maturity – or at least not exposed to metamorphic temperatures – have provided useful geochemical information relevant to ore formation.

Whilst interpretations of hydrocarbon compositional data are typically based on trends established from studying fossil hydrocarbons, the validity of applying traditional organic geochemical rules and interpretations to the organics in mineral systems may need to be re-established (Gize, 1999b). The geological alteration of OM may not always adhere to fossil fuel conventions, since the metal or sulfur species which are typically present in relatively high concentrations may significantly influence the fate of most organics (Gize, 1999b). In Fe-rich deposits, mineral oxidation such as of pyrite to haematite is most likely accompanied by the oxidation of the organic matter, for example alkanes to aromatics (Gize, 1999b). Therefore, the high concentrations of certain hydrocarbons in pyrite-rich ore deposits (e.g. Pb–Zn, Hg, Au) may be simply correlated with the high concentrations of pyrite rather than reflect an especially productive source rock. Nevertheless, recognition of trends relating to metal or sulfur

influences on organic alteration should also be useful for identifying ore genesis processes (Gize, 1999b).

Several previous studies of the OM in mineral systems have shown that the occurrence, concentration or stable isotopic values of some of the biomarkers associated with metal-rich ores can help identify the sources of organic matter and alteration relationships with mineralisation (e.g., Ho et al., 1990; Palinkas et al., 2009; Rieger et al., 2008; Spangenberg and Macko, 1998). Sophisticated information from source diagnostic biomarkers and the distinctive profiles or isotopic values of other hydrocarbon compounds indicative of geological processes can illuminate complex sub-surface redox chemistries and may greatly aid the search for large deposits of commercially valuable minerals. Table 1 lists several hydrocarbon biomarkers that have been reported from regions of high metal deposition and the types of source and process information they provide. A detailed account of the information provided by major hydrocarbon biomarker classes is also given below.

2.1. Analysis of hydrocarbon composition

The bitumen and kerogen fractions of sedimentary OM typically contain a large range of aliphatic and aromatic products that require powerful analytical capacity to resolve. Gas chromatography (GC) can provide very effective separation of many non-polar hydrocarbons, and when used in combination with mass spectrometry (MS) can unravel the complexities of hydrocarbon mixtures (see Fig. 3). GC–MS can be applied to the saturate and aromatic hydrocarbons of bitumen or kerogen pyrolysates, but the GC resolution of more polar organic compounds and products of large size (i.e., MW > 700) can be more challenging. These factors limit the GC–MS analysis of metal–organic complexes although advances in related analytical technologies such as Liquid Chromatography MS look promising for direct detection of high MW and polar organic compounds (Hughey et al., 2004).

2.1.1. Acyclic aliphatic hydrocarbon signatures

The aliphatic hydrocarbons detected in OM derive largely from alkanic acids, alcohols, alkanes and other straight chain biological lipids, and their distribution or relative abundances can be indicative of particular biogenic sources. For instance, a broad unimodal distribution of *n*-alkanes (III) peaking at *n*-C₁₇ in the Les Malines MVT ore deposit was described as a typical marine signature (Disnar, 1996). More specifically, the relatively high abundances of *n*-C₁₅ and *n*-C₁₇ detected in OM of the San Vicente Zn–Pb deposit (E. Pucará Basin, Peru; Spangenberg and Macko, 1998) was attributed to algal/cyanobacterial sources (Gelpi et al., 1970). In contrast, the high MW (>C₂₀) *n*-alkanes detected in the Vieille Mine ore deposit showed a relatively high abundance of odd-over-even carbon numbers (Disnar, 1996) which is quite diagnostic of terrestrial higher plants (Peters et al., 2005). Similarly, *n*-alkanes extending to C₄₀ were detected in the bitumen associated with CuS deposits of the Pabellón Formation near Copiapó, northern Chile (Rieger et al., 2008), and these very high MW waxy *n*-alkanes can be indicative of terrestrial or lacustrine input (Hunt, 1996; Tissot and Welte, 1978). In a further example, Logan et al. (2001) detected a rare predominance of even-numbered *n*-alkanes and odd-C branched monomethyl -alkanes (e.g., XVI) with an even predominance from C₁₆ to C₃₀ in 1.64 Ga old sedimentary rocks of the HYC deposit. According to Logan et al. (2001), these compounds may have formed by the decarboxylation or dehydration of long-chain aliphatic components from sulfide-oxidising bacteria (SOB). *n*-Alkane and monomethyl -alkane series showing a similar even carbon number predominance had been observed in living SOB mats (Logan et al., 1999) and modern hydrothermally generated petroleum (Simoneit, 1994).

The presence or relative abundances of isoprenoids (e.g., XIV, XV) and other branched alkanes may serve as indicators of certain

Table 1
Examples of the source and diagenetic/geological (i.e., alteration events) information provided by common hydrocarbon (HC) compounds detected in metal-rich deposits. The distribution/feature of aliphatic or aromatic products can often be interpreted as deriving from one of a range of source possibilities.

HC class	HC feature	Source/depositional information	Alteration events
<i>n</i> -Alkanes (III–appendix)	Unimodal, C ₁₇ peak (MVT) Short-chain homologues maximizing at <i>n</i> -C ₁₅ to <i>n</i> -C ₁₇ (MVT; Kupferschiefer [Kupf.]) Long-chain homologues (> <i>n</i> -C ₂₅) with a pronounced odd/even predominance (Kupf. – Grice et al., 1997; MVT – Disnar, 1996; Pabellón – Rieger et al., 2008)	Marine input (Disnar, 1996) Algal (Spangenberg and Macko, 1998) and cyanophyte sources (Schwark and Püttmann, 1990; Grice et al., 1997). - Terrestrial higher plants - Sulfide oxidising bacteria (Logan et al., 2001)	Vulnerable to biodegradation – susceptibility decreasing with increasing MW. Fractionation – high abundances of light <i>n</i> -alkanes attributed to fractionation during oil migration (Spangenberg and Macko, 1998) Effect of oxidising fluids – increasing abundances of short chain <i>n</i> -alkanes (< <i>n</i> -C ₁₇) relative to mid- and long chain homologues (Püttmann et al., 1989; Bechtel et al., 2000; Kotarba et al., 2005)
Isoprenoids (eg., XIV, XV)	C ₂₅ regular and C ₃₀ irregular isoprenoids (HYC) Increasing Pr/Ph values (Kupf./MVT) Dominant C ₁₅ , C ₁₉ and C ₂₀ isoprenoids (Cf. neighbouring <i>n</i> -alkanes) (Kupf.)	Archaeal source (Summons et al., 1988, Logan et al., 2001) Reducing or hypersaline environments (Schwark and Püttmann, 1990; Large and Gize, 1996; Spangenberg and Macko, 1998) High proportion of chlorophyll and bacteriochlorophyll (Schwark and Püttmann, 1990; Grice et al., 1996a, 1996b)	Vulnerable to thermal maturity Low Pr/ <i>n</i> -C ₁₇ and Ph/ <i>n</i> -C ₁₈ associated with mineralisation (e.g., Nonesuch Cu formation, Ho and Mauk, 1996) High Pr/ <i>n</i> -C ₁₇ and Ph/ <i>n</i> -C ₁₈ due to preferential oxidation of the <i>n</i> -alkanes (Bechtel et al., 2000). The ratios of <i>n</i> -alkanes vs. isoprenoids declines and the Pr/Ph ratio increases with mineralisation (e.g., Püttmann et al., 1989, 1990; Large and Gize, 1996, Bechtel et al., 2000, Kotarba et al., 2006)
Monomethyl-alkanes (eg., XVI, XVII)	High concentrations of isoprenoids and other branched alkanes (HYC) C ₁₆ to C ₃₀ monomethyl β-alkanes with odd-C branching and an even C nos predominance (HYC)	Prokaryotic input (Summons et al., 1988) Sulfide oxidising bacteria (Logan et al., 2001)	
Hopanes (XIII)	E.g., Kupf. – e.g., Grice et al., 1997; MVT – Slovenia Spangenberg and Hecler (2006) C ₃₅ homohopanes (Bahloul – Montacer et al., 1988)	Biomarkers for prokaryotic input Sulfate reducing bacteria	Hopane compounds variously susceptible to biodegradation and fractionation during transport Moretanes more decreased than other hopanes with MVT (Zn–Pb) mineralisation (Disnar, 1996)
Steranes (XII)	E.g., Kupf. – e.g., Grice et al., 1997; MVT – Slovenia Spangenberg and Hecler (2006) High C ₃₀ sterane concentrations; trace C ₂₆ steranes; diasterane ~ sterane distributions; 24- <i>n</i> -propylcholestane (HYC – Logan et al., 2001)	Biomarkers for eukaryotic input Marine deposition (e.g., Volkman, 1986)	Sterane compounds variously susceptible to biodegradation and fractionation during transport
Parent and alkylated aromatics (eg., XI, XIV–XVI, XXX–XXXIV, XXXVII)	Monoaromatic C ₂₄ fern/arborane (Kupf. – Schwark and Püttmann, 1990) Isorenieratane and trimethylsubstituted aryl isoprenoids (C ₁₁ – C ₂₁) (Kupf.)	Terrestrial microbial source (Hauke et al., 1992, 1995). Green sulfur bacteria (<i>Chlorobiaceae</i>) and sulfidic conditions in the photic zone (Summons and Powell, 1987; Grice et al., 1996a, 1996b, 1997)	Relative proportions of parent aromatics increase with thermal maturity Mineral zones dominated by parent aromatics include HYC (Chen et al., 2003); Kupferschiefer (Bechtel et al., 2000); and low temperature Cu–Fe–S deposits (Gize, 1999) Brocks et al., 2003 proposed Phen/MPhen as thermal maturity indicator.
S-aromatics (eg., IV–VIII)	High concentrations E.g., Kupf. – Püttmann et al., 1988a, 1988b, 1990, 1991; HYC – Chen et al., 2003; Pabellón – Rieger et al., 2008. Thioaromatics of naphthobenzo-, dinaphthobenzo- and phenanthrobenzothiophene. Pabellón – Rieger et al., 2008)	- High concentrations of reduced S from BSR or TSR - Not common fossil fuel hydrocarbons. - Product of reduced S reactant during Metallogenesis Naphthobenzo- and thiophene indicates mildly oxidizing conditions and at temperatures of about 300 °C (Rospondek et al., 2007)	Concentrations of S-aromatics increase with thermal maturity. Thioaromatic compounds and other heteroaromatics are more susceptible to epigenetic oxidation than normal aromatics (eg. Bechtel et al., 2000).
Porphyrins and degradation products (eg., IX–X)	Porphyrins, isorenieratane and maleimides. (Kupf. – Schwark and Püttmann, 1990)	chlorophyll and bacteriochlorophyll (Grice et al., 1996b, 1997)	

biological precursors. For instance, C₂₅ regular and C₃₀ irregular isoprenoids detected in McArthur River deposits were attributed to an archaeal source (Logan et al., 2001; Summons et al., 1988). Less is known about the biological provenance of pseudo homologous series of 5-methylalkanes with even C-numbers and 3-methylalkanes (XVI), and traces of 2-methylalkanes (XVII) that have been extracted from McArthur Basin sulfides (Logan et al., 2001; Mycke et al., 1988). Other C₁₈ to C₂₆ monomethyl alkanes, with methyl positions of 7-, 9-, and 11-, were also detected in these sediments. Although little is known about the biological sources of these methylalkanes, waxy bacterial lipids with similar methyl branching have been reported from a thermophilic bacterium (Pond et al., 1986). However, it is also quite possible that these molecules are anthropogenic artefacts because a third major series of branched alkanes, later identified as 5,5-diethylalkanes (Kenig et al., 2002, 2005), also detected in the McArthur Basin samples (Logan et al., 2001; Mycke et al., 1987),

were recently shown to be derived from polyethylene plastics that are often used as sample bags (Brocks et al., 2008).

Parameters or product ratios determined from *n*-alkane and isoprenoid abundances can also be used to collect information about the palaeo-environment at the time of organic matter deposition. Isoprenoids derived from the phytyl-side chain of e.g. chlorophyll can reflect the redox state of environments. Because pristane is the product of a decarboxylation process in aerobic environments, the pristane (XIV) to phytane (XV) ratio (Pr/Ph ratio) in oxidising environments is generally > 1, and in reducing environments < 1 (Didyk et al., 1978; Powell and McKirdy, 1973). Very low Pr/Ph ratios measured in Cu–Pb Mineralised zones of the Kupferschiefer (Fore-Sudetic Monocline, SW Poland) were correlated with lithofacies deposited in a reducing and hypersaline paleoenvironment (Large and Gize, 1996). Similar trends in Pr/Ph-ratios have been reported for the non-mineralised marginal Kupferschiefer of the Lower Rhine Embayment (Schwark and

Püttmann, 1990) and attributed to reducing conditions paralleled by enhanced salinity of bottom waters, as evidenced by specific methylchromane profiles. Increases in the Pr/Ph ratio evident at the base of the Kupferschiefer and at the transition from clay-rich to carbonate-rich zones, corresponding with the Cu to Pb zone transition, are likely due to increasing oxidation of OM during deposition and diagenesis. Similarly, consistently low Pr/Ph values detected in the San Vicente Zn–Pb deposit (Spangenberg and Macko, 1998) are consistent with a reducing depositional environment (Didyk et al., 1978).

2.1.2. Sterane and hopane biomarkers

The detection of hopanes (XIII), a class of bacterial pentacyclic terpenoids, and steranes (XII), the fossil hydrocarbon products of eukaryotic sterols, can provide especially diagnostic information about biological precursors and the biochemical and physico-chemical character of depositional environments. Several hopane and sterane biomarkers detected in Proterozoic deposits have helped resolve the evolutionary timeframe of several bacterial and eukaryotic groups.

Despite the geological persistence of these polycyclic hydrocarbons, their sedimentary concentrations are typically low because their lipid precursors are generally not abundant in the source organisms. Nevertheless, given the important biomarker value of hopane and sterane products they are frequently targeted by highly selective GC–MS analysis and have been used in several studies to characterise OM related to hydrothermal fluid dynamics and ore deposition. However, as sterane and hopane concentrations are commonly very low, particularly in the Precambrian and in sediments that have seen substantial thermal alteration, many accounts of these molecules in ore deposits may be influenced by biomarkers introduced through anthropogenic petroleum products such as drilling fluids and diesel exhausts (Brocks, 2011; Brocks et al., 2008).

Moreover, biological knowledge of hopanes and steranes has substantially improved in the last decade so that interpretations in older papers are sometimes inaccurate. For instance, some early studies considered high relative abundances of hopanes as evidence for significant microbial activity (e.g., Les Malines deposit; Disnar, 1996). However, it is now well established that taphonomic processes can very strongly influence the abundance of different biomarker classes so that an interpretation of strong or weak activity of particular organisms is difficult. An absence of hopanes has been similarly used to support the occurrence of abiotic processes such as TSR and sulfide formation (Spangenberg and Macko, 1998). One must also be careful with this converse argument, however, as the majority of bacteria, and almost all obligate anaerobic bacteria, do not produce hopanoids at all. Moreover, hopanes and steranes are also subject to various alteration phenomena, most notably thermal cracking and biodegradation (see 2.1.4), but also by fractionation during their transport by hydrothermal solutions (Disnar, 1996). Thus, absence of specific biomarkers in moderately mature bitumens is difficult to interpret, and absence of polycyclic structures from overmature OM should not be interpreted at all.

SRB may play an important role in the formation of low-temperature sulfide ore deposits. C₃₅ homohopanes (XIIIa), detected in the Pb–Zn rich Bahloul Formation in the Bou grine area of the Tunisian Atlas allegedly derive from such SRB (Montacer et al., 1988). However, there are currently no known hopanes, nor any other hydrocarbon class, that are diagnostic of sulfate reducers, so it remains unclear which group of organisms contributed these molecules. Studies of the Bahloul Formation also showed a correlation between Zn and Pb content and hopane/sterane ratio (Disnar and Sureau, 1990; Montacer, 1989), further suggestive of an intimate organic–Pb/Zn relationship.

In ancient sediments, steranes are predominantly derived from eukaryotic sources such as higher plants and microalgae. In post-Silurian sediments, high relative concentrations of the C₂₉ sterane stigmastane (XIIb) are often an indication of the significant contribution of organic debris from terrestrial plants (Huang and Meinschein, 1979; Volkman,

1986). Yet, high relative abundances of C₂₉ steranes detected in 1.5–1.6 Ga Mt Isa sulfides were originally attributed to cyanobacteria or prymnesiophycaen algae (Mycke et al., 1988). This interpretation is considered to be incorrect as cyanobacteria have been since shown not to produce steroids (Summons et al., 2006) and prymnesiophytes radiated much later in Earth history (De Vargas et al., 2007). As the Mt Isa deposit also suffered metamorphic temperatures and the same samples also contained plastic contaminants, the hydrocarbons probably derived from much younger allochthonous sources. One of the most valuable environmentally diagnostic biomarkers is 24-n-propylcholestane (XIIc), a steroid with a carbon skeleton exclusively found in chrysophyte algae and thus an indicator for marine depositional conditions (Volkman, 1986). The presence of this sterane in the Palaeoproterozoic Barney Creek Formation, the host of the HYC deposit, was accordingly interpreted as evidence for a marine depositional environment (Logan et al., 2001). However, newer investigations now suggest that the steranes in this formation are anthropogenic contaminants, removing one of the prime arguments that these deposits are of marine origin (Brocks et al., 2008).

In summary, the interpretation of steranes and hopanes extracted from rock in ore deposits is often plagued by secondary contamination and outdated biological interpretations. Thus, the full potential of these otherwise valuable and diagnostic indicators for ore exploration still needs to be realised.

2.1.3. Biological and geological alterations of aliphatic hydrocarbon signatures

Aliphatic hydrocarbons are susceptible to biological and geological processes that can alter biomarker signatures. Processes such as thermal maturation, biodegradation, water partitioning and mineral absorption of hydrocarbons have been robustly investigated in petroleum systems, leading to an exhaustive list of biomarker parameters that can yield information about these phenomena (Peters et al., 2005). However, it is currently unclear to what extent this information can be translated to organic matter in ore deposits.

A large range of biomarker parameters has been proposed to reflect thermal maturity (Peters et al., 2005) which increases with burial temperatures or pulses of geothermal heat from hydrothermal fluids (Simoneit, 1993a, 1993b; Simoneit et al., 1992) or igneous intrusions (e.g., George, 1992). Several early studies of organic–mineral systems attempted to use the Pr/Ph ratio as an indication of thermal maturity. Large and Gize (1996) did show Pr/Ph values mirrored Cu and Pb abundances in the Permian Kupferschiefer, implying a relationship with the increased thermal maturity driven by hydrothermal fluids. The Pr/Ph values of Les Malines MVT sediments were said to be consistent with a low maturity (Spangenberg and Macko, 1998) also reflected by mineral composition and other maturity indicators including the analytical T_{max} values measured by R–E pyrolysis (Spangenberg and Macko, 1998).

However, thermal maturity is usually more accurately reflected by the relative abundance of these isoprenoids relative to their neighbouring and thermally more stable *n*-alkanes (i.e. Pr/*n*-C₁₇ and Ph/*n*-C₁₈) – although even these ratios are vulnerable to other factors including migration, expulsion efficiency, water solubility and biodegradation. Pr/*n*-C₁₇ and Ph/*n*-C₁₈ values in OM of the Nonesuch Formation were shown to be lower in mineralised than unmineralised samples (Ho and Mauk, 1996). Intriguingly, increased abundance of isoprenoids relative to *n*-alkanes and a reduction in abundance of higher MW *n*-alkanes were also correlated with increased mineralisation at the San Vicente Zn–Pb deposit (Spangenberg and Macko, 1998). These authors suggested, incorrectly, that the apparent bias towards isoprenoids evident in the extractable hydrocarbons may be due to the increasing thermal maturities associated with mineralisation. Quite some scatter was noted in Pr/*n*-C₁₇ and Ph/*n*-C₁₈ values (Spangenberg and Macko, 1998), and other influences such as variations in depositional environment,

migration effects or biodegradation are likely to have had a bigger influence on these aliphatic hydrocarbons than thermal maturity.

Different hopane (*XIII*) and sterane (*XII*) isomers also show a range of degradation sensitivities to increased thermal maturation (from burial or exposure to hydrothermal fluids). For example, moretanes are more sensitive to thermal maturity than other hopanes, and their low values in the mineralised zones of the Les Malines deposit (Disnar, 1996) is consistent with a high thermal maturity, also reflected by higher values of other hopane based thermal maturity parameters.

Biodegradation is a sequential process, and the general consistency of hydrocarbon biodegradation trends led to the development of several biodegradation scales based on sequentially more susceptible structures (Peters et al., 2005; Volkman et al., 1984). *n*-Alkanes (*III*) are typically amongst the first hydrocarbons to be removed, with lighter homologues (C_6 – C_{12}) being most susceptible. This is followed by the quasi-step wise removal of other hydrocarbon classes depending on the capabilities of the microorganisms, but the general order is methyl alkanes, cycloalkanes, 1–3 ring aromatics, polyaromatics, asphaltenes, resins, diamandoids and porphyrins. Significant biodegradation has been observed in the bitumen of several MVT deposits (Connan and Orgeval, 1973; Gize and Barnes, 1987; Macqueen and Powell, 1983; Pering, 1973). Biodegradation of OM by microbial oxidation can be significant when Fe is low and sulfate abundant. When Fe(II) is present, however, it competes very successfully for sulfate which it reduces to pyrite. Under extreme conditions (e.g., near hydrothermal vents) the organics in Ferric oxide-rich ocean sediments can be effectively oxidised (Simoneit, 1993a). In petroleum reservoirs it has become accepted that biodegradation is preferentially an anaerobic process occurring at extreme depths (Hallmann et al., 2008; Jones et al., 2008).

Hydrocarbon composition can also be altered by preferential adsorptions during migration. The complex hydrocarbon compositions detected from Triassic rocks of the Vieille Mine (MVT deposit) included one sample which showed a range of organic features (e.g., high TOC, high carbon preference index [CPI], high concentrations of mid-MW range hydrocarbons such as *n*- C_{17} , *n*- C_{18} , pristane and phytane, and high sterane and hopane concentrations) distinct from all other samples from the mine (Disnar, 1996). These unusual characteristics were attributed to the molecular geochromatographic fractionation of migrating oil (Disnar, 1996; Zhao-An and Philp, 1987; Zhusheng et al., 1988).

Molecular fractionation during oil migration was similarly proposed to account for the relatively high abundances of light *n*-alkanes and high Pr/Ph ratios measured from the soluble fraction of pyrobitumens in the Upper Triassic–Lower Jurassic San Vicente Zn–Pb deposit (Spangenberg and Macko, 1998). It was further suggested that an increasing variation between Pr/*n*- C_{17} and Ph/*n*- C_{18} observed throughout the deposit may be due to differences in thermal maturity, depositional environment or migration effects of the mineralising fluid (e.g., Leythaeuser and Schaefer, 1984; McKirdy et al., 1984). OM in this deposit generally showed low Pr/Ph values thought to reflect a reducing and hydrogenating environment (Didyk et al., 1978; Spangenberg and Macko, 1998), but some samples had high Pr/Ph values probably reflecting more oxidising depositional conditions. It is unlikely that fractionation would significantly discriminate between Pr and Ph.

The Earth system is a complex biogeochemical environment and in many instances not all of the geochemical information provided by organic analysis is consistent with a singular source, depositional environment or geological processes. The Pr/Ph ratio, *n*-alkane maxima and other hydrocarbon features of extracts from Lower Cretaceous lavas of the Copiapó Cu–S deposits (N. Chile) showed a wide range of values (Rieger et al., 2008). These variations were interpreted to reflect the mixing of two or three different petroleum sources in the lava flows of the deposit. Inferences from molecular composition need to be interpreted with caution and in consideration with all available geochemical data and other related information.

2.1.4. Parent and alkylated aromatics

The aromatic hydrocarbon composition of sedimentary OM can provide additional information about depositional origins, biogeochemical processes and conditions supporting metal ore genesis. Aromatic hydrocarbons are particularly valuable for assessing levels of thermal stress and alteration. Whilst aromatic compounds can be geologically produced by oxidation of aliphatic reactants or by thermally mediated dehydrogenation processes – both schemes catalytically assisted by certain minerals – a number of aromatic biomarkers have been directly linked to many different biological sources. For example, the Permian Kupferschiefer deposits (Lower Rhine Basin, NW Germany) were reported to contain a range of parent and alkylated PAHs indicative of several different inputs (Schwark and Püttmann, 1990). These included i) a monoaromatic C_{24} fern/arboratriene (*XVIII*), presumably derived from ring-A-degradation of pentacyclic triterpenes (*XIII*), which is indicative of a terrestrial microbial source (Hauke et al., 1992, 1995); ii) isorenieratane (*XIX*) and sometimes (C_{11} – C_{21}) 2,3,6 trimethylsubstituted aryl isoprenoids (*XXa*) and methyl isobutyl maleimides (*XXI*) which are indicative of green sulfur bacteria (Chlorobiaceae) and sulfidic conditions in the photic zone of the water column (Grice et al., 1996a, 1996b, 1997; Summons and Powell, 1987); and iii) a dominant C_{29} -chroman (*XXII*) of unknown biological origin, although tentatively assigned to phytoplankton. There is some evidence that chroman ratios may be sensitive to fluctuations in marine salinity levels (Schwark et al., 1998; Sinningh-Damsté et al., 1987).

Aromatic hydrocarbons are also subject to the same sub-surface alterations as the aliphatic hydrocarbons. The effects of thermal maturation, biodegradation, water washing, and other alteration effects on the aromatic hydrocarbons of fossil organics have been extensively researched (e.g., Peters et al., 2005). The few studies to report on aromatic hydrocarbons in mineral-rich environments have shown them to reflect largely similar behaviour to the aromatics of fossil fuels. Thermal maturation has a particularly strong influence on aromatic composition, with the proportions of parent (i.e. unalkylated PAHs) and sulfur aromatics relative to alkyl-aromatics increasing with thermal exposures (Chen et al., 2003; Gize, 1999b). Accordingly, mineral zones are typically dominated by parent aromatics (e.g., HYC – Chen et al., 2003; low temperature Cu–Fe–S deposits – Gize, 1999b). Several hydrocarbon ratios reflecting the degree of aromatic methylation have been proposed as thermal maturity indicators (e.g., Phenanthrene (*XI*)/Methyl-Phenanthrene (*XIa*); Brocks et al., 2003a, 2003c). Metamorphic or very high thermal maturities will eventually destroy most aromatic hydrocarbon structures, which eventually break down to methane and graphite-like residues.

Broad distributions of alkyl aromatics have been detected in relatively low thermal maturity OM. Low concentrations of alkylated naphthalenes (*Ila*) and traces of alkylated biphenyls (*XXIII*) accompany more concentrated 3- to 5-ring PAHs (i.e., phenanthrene, *XI*; chrysene, *XXIV*; and perylene, *XXV*) in OM of the Cu–S rich Pabellón Formation (Copiapó, north Chile; Rieger et al., 2008) of early oil window maturity (based on benzothiophene, *V*, ratios and only trace presence of combustion sourced PAHs). Interestingly, the Pabellón OM showed a very unusual distribution of methylphenanthrenes (MP, e.g., *XIa*) isomers. Thermodynamically less stable 9- and 1-methylphenanthrene isomers (9-MP and 1-MP) were far more abundant than thermally favored 3-MP and 2-MP. In this hydrothermal system the MP distribution pattern must be influenced by an isomerisation mechanism other than thermal maturity (Radke et al., 1982). Alexander et al. (1995) did show that at low temperatures phenanthrene (*XI*) can kinetically react with methyl donors to yield predominantly 9-MP. Alternatively, these aromatics may simply occur in very immature OM.

Fluid type can also influence the extent of aromatisation (Gize, 1999b), with CO_2 fluid (particularly in absence of H donor) promoting high aromatic concentrations, including relatively high proportions of O-aromatics (i.e., high O/C ratio). Aromatics also have relatively

higher solubility in CO₂, whilst H₂O-rich fluids may promote abiotic hydrocarbon production, for example via the possible Fischer–Tropsch reactions of H₂O with other simple gases (Gize, 1999b).

PAHs can also be generated during the interaction of hydrothermal fluids with sedimentary organic matter, and the interaction of the hot flowing fluids with the produced hydrocarbons may lead to distinct molecular distributions along thermal gradients. For example, in the Guaymas spreading centre, hydrothermal fluids with temperatures of 60 °C to >400 °C rise through hundreds of meters of sediments deposited in a rift basin (Simoneit, 1993b). The hot fluids come into contact with sedimentary organic matter and generate hydrothermal petroleum in a rapid, pyrolytic reaction (Simoneit, 1985). The hottest fluids generate high relative abundances of parent (i.e. unsubstituted) PAH and dibenzothiophene (VI) while the saturated hydrocarbons resemble a gas condensate (Gieskes et al., 1988). As the generated hydrocarbons have relatively high solubilities in the near-critical to supercritical fluids, the products are transported along the path of fluid flow. While the fluids cool, different organic constituents start to condense according to ambient temperature and pressure conditions. PAH and elemental sulfur start to precipitate in the hottest areas, higher saturated hydrocarbons in intermediate temperature regions of ~20 to 80 °C and volatile compounds concentrate in cool horizons (Simoneit, 1985). In extreme cases, hydrothermal fractionation of organics may even lead to the precipitation of PAH minerals such as pendletonite which is nearly pure coronene (XXVI; Blumer, 1975). As a consequence of this redistribution by hot fluids, hydrothermal systems will likely show complex spatial heterogeneity of extractable organics. However, a detailed study of the hydrocarbon distribution in hydrothermal ore deposits may yield information about direction and temperature of fluid flow. Two examples are given in Section 4.1 ('HYC') and 4.2 (Kupferschiefer).

2.1.5. Sulfur hetero-aromatics

High concentrations of sulfur containing aromatics typically implies high concentrations of reduced sulfur such as from the oxidation of metal sulfides and BSR or TSR, although sulfur might also be acquired and transported by the migration of fluids through evaporates (Rieger et al., 2008). The reaction of reduced sulfur with unsaturated hydrocarbons can result in a range of aromatic organic sulfur compounds (OSCs) such as alkyl-thiophenes (IV), benzothiophenes (V) and dibenzothiophenes (VI; Rieger et al., 2008; Sinninghe-Damsté et al., 1989). Relatively high concentrations of dibenzothiophene, as well as parent PAHs, occur in black shales within the massive iron ore deposits of the Hamersley Basin in Western Australia, and at 2.5 billion years, these are also the oldest known clearly indigenous bitumens (Brocks et al., 2003b, 2003c).

High concentrations of S-heterocyclic aromatics, formed at the expense of aliphatic hydrocarbons (Püttmann, 1988), also occur in the Fe–Pb–S rich Kupferschiefer formation (Püttmann et al., 1988, 1990, 1991; Rospondek et al., 1994; Sun and Püttmann, 1996). The Kupferschiefer represents a classical example of where the oxidation of OM contributes to the precipitation of minerals from hydrothermal fluids, with the elevated temperatures and high pHs also favouring the production of OSCs (Gize, 1999b). High concentrations of OSCs have been similarly reported in the Pb–Zn–Ag rich HYC deposit in the McArthur Basin (Chen et al., 2003) and in Cu-sulfides of Chile's Lower Cretaceous Pabellón Formation (Rieger et al., 2008). The concentrations of OSCs in the McArthur Basin were also shown to correlate with the presumed temperature gradient across the deposit (Chen et al., 2003). The production of S-aromatics is less favored by some minerals such as pyrite poor MVT deposits (Gize, 1999b).

Rieger et al. (2008) contended that the high concentrations of highly condensed thioaromatics of naphthobenzothiophene (VI), dinaphthobenzothiophene (VII) and phenanthrobenzothiophene type must derive from the reactions of reduced sulfur produced from sulfur-bearing brines during metallogenesis, since these are not common fossil hydrocarbon

products (Rieger et al., 2008; Rospondek et al., 2007). Furthermore, benzonaphthothiophenes are only produced under mildly oxidising conditions and at temperatures of about 300 °C, as found in the hydrothermal petroleum occurrences of the Guaymas Basin (Rospondek et al., 2007). A lack of simple alkyl-thiophenes (IV) and benzothiophenes (V) excludes an early diagenetic origin (Sinninghe-Damsté et al., 1989).

3. Stable isotope analysis

Stable isotopic measurements can complement molecular distributions and provide additional information about organic sources and geological processes. It can be used to resolve sources, recognise source mixing and illuminate the timing and pathways of hydrocarbon migration (Grice and Brocks, 2011) and has been used to practically assist the exploration of sediment-hosted mineral deposits by helping trace the ore-fluid path and mineralisation process (Spangenberg and Macko, 1998). Stable isotopes, as opposed to radiogenic (unstable) isotopes, do not decompose therefore their natural abundances remain moderately constant, even over geological time. However, deviations in stable isotopic composition, or 'isotopic fractionation', occur in nature due to a combination of chemical and physical processes. Both equilibrium and kinetic processes can lead to 'isotopic fractionation'. Equilibrium effects occur as a consequence of temperature-dependent equilibrium isotope-exchange reactions leading to a change of the isotope distribution between different chemical materials, phases or molecules (Hoefs, 1987).

The range in stable carbon isotope ($\delta^{13}\text{C}$) values for major organic pools is shown in Fig. 1. The primary source of carbon is CO₂ and hydrogen is H₂O. At the base of the food chain aerobic photosynthesis is the main step that incorporates CO₂ and often with H₂O as an electron donor in the presence of sunlight. Chlorophyll *a* is the main pigment used by many algal and land plant communities. Some organisms, however, such as Chlorobiaceae (strict anaerobes) are primary producers and fix CO₂ utilising H₂S as an electron donor using longer wavelengths of light, hence their need to biosynthesise specific pigments e.g. bacteriochlorophylls (Grice et al., 1996b). Methanotrophic prokaryotes or methane oxidisers use methane as their carbon source which is generally provided by cohabiting methane producers (methanogenic Archaea). Methanogenic Archaea utilise hydrogen to reduce CO₂ to methane, or decarboxylate acetate to methane and CO₂. Other Archaea oxidise methane with sulfate (without oxygen). Heterotrophs feed on processed OM (e.g. herbivores and carnivores). Stable carbon and hydrogen isotopes of OM is determined by source of carbon and hydrogen and stable isotopic fractionations associated with biosynthesis (e.g., Hayes, 1983, 1993, 2001; Matthews and Hayes, 1978; Schouten et al., 1998; Summons et al., 2008; Zhou et al., 2010).

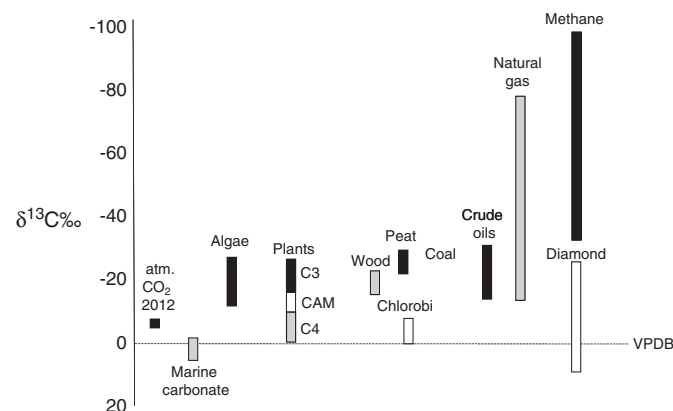


Fig. 1. Stable carbon isotopic ($\delta^{13}\text{C}$) values typical of different carbon sources.

3.1. Bulk (C, N, H) stable isotope analyses

Bulk isotope measurements are conducted by elemental analysis-isotope ratio mass spectrometry (EA-irMS). The elements hydrogen, carbon and nitrogen are the main constituents of OM and play critical roles in various biochemical, ecological, environmental, hydrologic and atmospheric processes. Thus stable isotopic compositions preserved in OM can provide powerful insights into such processes.

The $\delta^{13}\text{C}$ value of OM is initially determined by its genetic origin. The $\delta^{13}\text{C}$ of OM from Peru's San Vicente Zn–Pb deposit (E. Pucará Basin; Spangenberg and Macko, 1998) was interpreted to reflect the mixing of two or more organic sources. The $\delta^{13}\text{C}$ values of the saturate and aromatic fractions of San Vicente sediments were indicative of predominantly algal and bacterial lipid sources (Spangenberg et al., 1999). However, some samples showed $\delta^{13}\text{C}$ values more typical of a terrigenous source, attributed to retention and oxidation of migrating *n*-alkanes (III; Spangenberg et al., 1999). Carbon linked to the pyrobitumen of the El Soldado Cu deposit showed $\delta^{13}\text{C}$ values typical of petroleum (Rieger et al., 2008), suggesting that petroleum hydrocarbons may have actively participated in the formation of the Cu ore as proposed for other Cu deposits (Zentilli et al., 1997).

Thermal conditions have little effect on $\delta^{13}\text{C}$ values (Ho et al., 1990; Peters et al., 2005; Spangenberg and Macko, 1998 and references therein), although there may be preferential loss of isotopically light methane at extreme thermal conditions such as the onset of metamorphism or generation of anthracite coals (Des Marais, 1997; Spangenberg and Macko, 1998). OM in mineralised (Ho et al., 1990) and non-mineralised (Imbus et al., 1988) zones of the Nonesuch Formation showed similar $\delta^{13}\text{C}$ values (-31 to -34%), indicating negligible fractionation from the mineralisation process and associated oxidation of organic carbon. However, mineralised samples can become enriched in ^{15}N (Spangenberg and Macko, 1998), possibly due to preferential release of isotopically lighter, thermally less-stable aromatic compounds (Bakel and Philp, 1990) or the introduction of isotopically heavier nitrogen compounds by the ore fluid which may condense on the 'indigenous' kerogens (Williams et al., 1995).

3.2. Compound specific (C, H) isotopic analysis

The stable isotopic values of carbon, hydrogen, nitrogen and more recently sulfur of individual molecules can be measured by the combination of gas chromatography with isotopic ratio mass spectrometry (GC-irMS; e.g. Hayes et al., 1990; Grice and Brocks, 2011) or GC-ICP-MS in the case of compounds specific $\delta^{34}\text{S}$ analysis (Amrani et al., 2009). Hayes et al. (1990) were the first to develop the technique of CSIA in the field of organic geochemistry. Some of the first $\delta^{13}\text{C}$ measurements of individual biomarkers of Chlorobiaceae were performed by Summons and Powell (1986). In the fields of organic geochemistry and biogeochemistry, these measurements are used to elucidate aspects of biogeochemical cycling within a broad range of microbially-mediated processes (Freeman et al., 1990; Schouten et al., 1998; Summons et al., 1994, 1996; Zhou et al., 2010).

Lipids produced by different biosynthetic pathways can differ in $\delta^{13}\text{C}$ by as much as 20‰ within one organism (e.g. Schouten et al., 1998; Summons et al., 1994), although processes leading to these isotopic differences are still not fully understood (Hayes, 2001). Factors that can lead to carbon isotopic variation in an organism include the partial pressure of CO_2 ($p\text{CO}_2$), cell size and geometry (Goerick et al., 1994; Popp et al., 1998), growth rates (e.g., of phytoplankton; Laws et al., 1995) and plant water-use efficiency such as observed in C3, C4 and CAM plants (Ehleringer et al., 1993).

When reconstructing paleoenvironments of deposition (e.g. the Permian Kupferschiefer) based on CSIA it is critical to establish an 'isotopic reference' point against which values for various components can be compared. The C_{27} sterane cholestane (XIIa) and the C_{20} regular isoprenoid phytane (XV) are often reported in lacustrine and marine

environments and mainly derive from C_{27} sterols and chlorophyll *a*, respectively. Thus, $\delta^{13}\text{C}$ of steranes and phytane are a reference point for lipid components biosynthesised by algae. In the Kupferschiefer, the $\delta^{13}\text{C}$ of phytane was found to be similar to co-occurring algal-derived cholestane, consistent with a common algal origin (Grice et al., 1996b). This sediment also contains the biomarker methylethylmaleimide (XXVII), a degradation product predominantly derived from the macrocycle of chlorophyll *a* (Grice et al., 1996b, 1997). The maleimide was 3.5 to 4.5‰ more enriched in ^{13}C than phytane, if derived from the phytol side chain of the same chlorophyll (Grice et al., 1996b, 1997). When using CSIA $\delta^{13}\text{C}$ of biomarkers in sedimentary OM to reconstruct paleoenvironments, it is understood that stable carbon isotopic fractionation effects associated with biosynthesis are averaged out for sediments spanning hundreds to millions of years. Schouten et al. (1998) also suggests that cholestane is one of the most suitable 'isotopic reference' points of the photosynthetic organisms living in the euphotic zone.

In terms of stable hydrogen isotopes it is now well established that diagenetic and catagenetic processes over geological time (millions of years) can promote significant hydrogen exchange between biomarkers in the surrounding environment containing formation waters (e.g. Alexander et al., 1984; Dawson et al., 2005, 2007; Radke et al., 2005; Rigby et al., 1981; Sachse et al., 2004; Schimmelmann et al., 1999; Sessions et al., 2004).

δD of biomarkers can also be greatly influenced by thermal maturity reflecting a strong relationship with the alteration of indigenous δD signatures. Dawson et al. (2005) demonstrated the application of δD ratios of hydrocarbons (*n*-alkanes, III; pristane, XIV; and phytane, XV) to assess the maturity of petroleum source-rocks and crude oils from the Perth Basin (WA). Pristane and phytane were found to be significantly lighter compared to *n*-alkanes in the same sample, although this difference decreased with rising thermal maturity due to isotopic exchange. The *n*-alkane-isoprenoid δD signature of crude oils of different source facies, was consistent with values associated with mature-late mature sediments i.e., within the peak oil-generative window. The δD ratios for Pr and Ph correlate with % equivalent vitrinite reflectance (R_0), which further supports a relationship between maturation and isotopic enrichment in isoprenoids. The work by Dawson et al. (2005, 2007), Radke et al. (2005), and Pedentchouk et al. (2006) indicates that the δD measurement of hydrocarbons represents a useful maturity parameter which also accounts for different source-effects. Several researchers have shown that OM on interaction with hydrothermal fluids can exchange hydrogen with D-enriched fluid. Fig. 2 shows the δD of *n*-alkanes associated with several mineral deposits including HYC and Kupferschiefer to increase with the thermally sensitive methylphenanthrene (e.g., XIa) index (MPI-1; Dawson et al., 2007; Radke et al., 2005; Williford et al., 2011).

3.3. Sulfur isotope analysis

Organic sulfur is the second major pool of reduced S in sediments (after pyrite) and may be particularly enriched in metal rich regions, so has significant influence on the biogeochemical cycles of C, S and O including carbon burial and hydrocarbon formation (Werne et al., 2004). $\delta^{34}\text{S}$ of OSCs can help unravel the complexity of sedimentary S cycling and the extremely reactive nature of many intermediate inorganic S species that play a role in OM sulfuration.

Sulfides often form as the result of sulfate reduction and concomitant OM oxidation. Sulfur isotopes (i.e., $\delta^{34}\text{S}$) are useful to distinguish between OM that was microbially or thermally oxidised. Sulfide-rich fluids may form at temperatures $<100^\circ\text{C}$ through BSR and the oxidation of OM. Conversely, TSR and associated OM destruction occurs at temperatures usually above 130°C . These two major modes of sulfate reduction can be distinguished on the basis of the $\delta^{34}\text{S}$ value of the sulfides produced. TSR shows little or no net ^{34}S fractionation, e.g. as seen in Peruvian MVT deposits (Spangenberg and Macko, 1998), whereas BSR can lead to sulfides depleted in ^{34}S relative to sulfate by up to 65‰ (Canfield and Thamdrup, 1994). Strong isotopic depletion of

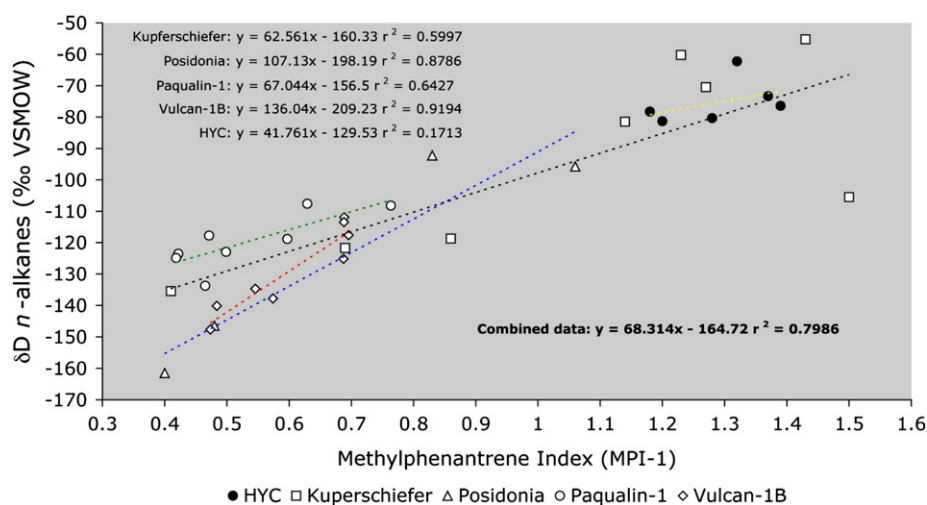


Fig. 2. δD of n -alkanes versus methylphenanthrene thermal maturity index (MPI-1) of the OM associated with several mineral deposits (HYC – Williford et al., 2011; Kupferschiefer and the Posidonia Shale – Radke et al., 2005; Vulcan, Paqualin – Dawson et al., 2007).

sulfides associated with BSR occurs, for example, in the massive HYCPb, Zn, Ag deposit – further discussed in Section 4.1.

However, isotopically heavy or depleted sulfides are not exclusively due to TSR or BSR, respectively. For example, in Archean sediments and other depositional settings with low aqueous sulfate concentrations, BSR may deplete the entire pore water sulfate reservoir (e.g. Shen et al., 2001), leading to minimal or no isotopic fractionation that may be mistaken as an indicator for TSR. Conversely, isotopically depleted sulfides may derive from mantle sources. $\delta^{34}S$ values measured for Fe (0.6‰) and Cu (−28‰) sulfides from Copiapó Cu deposits (Chile) were attributed to different sulfur sources rather than different modes of sulfate reduction (Cisternas and Hermosilla, 2006). The more depleted nature of the Cu sulfide was not attributed to BSR, since the > 150 °C temperatures of the hydrothermal fluid associated with Cu–S deposition are inconsistent with biological processes. Other data from this deposit indicated two separate hydrothermal fluids, an earlier one related to Fe sulfide formation and a later one for Cu-sulfide precipitation – probably involving isotopically light sulfur of probable magmatic origin. $\delta^{34}S$ differences of up to 12‰ between some minerals (e.g., sphalerite, galena and pyrite) and the major metal sulfides of the San Vicente MVT deposit were similarly attributed to different sources (Spangenberg et al., 1999).

The very recent development of compound specific $\delta^{34}S$ analysis (Amrani et al., 2009) has now made it possible to measure the $\delta^{34}S$ of organic sulfur compounds (OSCs). Given the tremendous diversity of organosulfur species, and their potential to record the isotopic compositions of sulfide in mineralising fluids through time, this new analytical capability offers considerable potential to study the role of OSCs in ore formation processes. Some organic molecules will tend to preserve isotopic records of biological sources and diagenesis. Significantly, the OM preserved by sulfuration often includes functionalised organic compounds (i.e., biomarkers), which retain a structural link to their biological source (Sinninghe-Damsté and de Leeuw, 1990). Whereas biomolecules with abundant functional groups are highly labile and subject to rapid microbial mineralisation, their reaction with reduced S species during diagenesis leads to cross-linking of molecules and a highly polymerised, stable molecular structure that is more resistant to low-temperature degradation (Adam et al., 1993; Kohnen et al., 1991).

4. Organic geochemical contributions to ore genesis models

4.1. HYC deposit

4.1.1. Barney Creek/McArthur basin (unmineralised OM)

The HYC ore body is hosted in the 1640 ± 3 Ma (Page and Sweet, 1998) Barney Creek Formation (BCF) of the McArthur Group. The BCF

was deposited in the north–south-trending Batten Trough, an intracratonic rift basin west of the present Gulf of Carpentaria. The basin extends over a known area of 25,000 km², but deposition probably continued to the north and east (Bull, 1998). The variable depositional thickness of the BCF, from a few tens of meters to local maxima of 1000 m, suggests a complex bathymetry with variable water depths across the basin. However, the formation shallows out towards the western and southern margins and is bounded to the north by an earlier Paleoproterozoic anticline. Although previously described as a shallow lacustrine or sabkha depositional setting (Jackson et al., 1988), the BCF is now commonly interpreted as a marine succession that accumulated in a quiet, sub-wave base environment (Bull, 1998; Jackson et al., 2000; Shen et al., 2002). The basin was probably connected to the ocean to the north-east or east, but the syndepositionally active Emu fault on the eastern perimeter may have formed a sill restricting exchange of basin waters with the ocean.

If syndepositional mechanisms of ore formation played a role at ‘HYC’, the water chemistry of the restricted basin as well as the organisms that inhabited the water column and bottom sediments must have played an important role in mineral precipitation (Logan et al., 2001). These phenomena can be studied particularly well for HYC as the OM of the BCF distal to the ore bodies is exquisitely preserved and biomarkers have yielded unprecedented details about its microbiology. The best preserved biomarkers were detected in the Glyde River region in the south of the Batten Trough (Jackson et al., 1986). The dominant lithologies are thinly bedded or planar laminated, dolomitic, carbonaceous and pyritic siltstones and shales. The dolomitic facies typically contain 0.2 to 2% organic carbon, and locally up to 7% (Powell et al., 1987). The OM occurs in discrete bedding-parallel stringers or in continuous, sub-millimeter planar laminated layers that likely represent microbial mat facies. The OM is only marginally mature and exceptionally well preserved for its age with H/C > 1.6 and R-E T_{max} as low as 435 °C (Powell et al., 1987).

The biomarkers extracted from dolostones of the Glyde River area describe an unusual, purely microbial biota distinct from ecologies observed later in Earth’s history (Brocks et al., 2005; Summons et al., 1988). In Phanerozoic bitumens, fossil steroids derived from eukaryotic organisms such as algae are usually very common. In the BCF, however, diagnostic eukaryotic steroids, that possess alkylation in position 24 (e.g. *XIb-c*), were beneath detection limits (Brocks et al., 2008). In contrast, aromatic steroids without side chain alkylation but with a methyl group at C-4 were very abundant. These 4-methyl steroids (*XIId*), in conjunction with abundant 3 β -methylhopanes (*XIIIc*), suggest that aerobic methane oxidising bacteria played an important ecological role. Such aerobic methanotrophs thrive best in

sulfate-starved environments (<0.5 mM; Hoehler et al., 1998), suggesting that sulfate concentrations in the Glyde River sub-basin were significantly beneath the present marine level of 28 mM.

The bitumens also include a large variety of isoprenoids such as unique oligoprenyl-curcumanes (XXVIII) of likely bacterial origin (Brocks et al., 2009), intact carotenes (Lee and Brocks, 2011) and very high abundances of the aromatic carotenoid derivatives isorenieratane (XIX), chlorobactane and okenane (XXIX; Brocks and Schaeffer, 2008). The likely biological precursors of isorenieratane and chlorobactane are the carotenoids isorenieratene and chlorobactene, accessory pigments in the light harvesting system of brown-pigmented and green-pigmented green sulfur bacteria (Chlorobiaceae) respectively. Chlorobiaceae are strictly anaerobic, obligate phototrophic organisms that exclusively utilize photosystem I. They require reduced sulfur species such as sulfide (e.g. H_2S) and sulfur as electron donors and thrive in anoxic waters beneath a shallow chemocline within the light-penetrated zone. Thus, isorenieratane and chlorobactane suggest that the basin was at least episodically anoxic and sulfidic up into the photic zone of the water column (photic zone euxinia).

Photic zone euxinia as an episodic or permanent chemical state of the McArthur Basin is also substantiated by very high relative concentrations of the otherwise uncommon biomarker okenane (XXIX). The likely biological precursor of okenane is okenone, a purple-coloured pigment produced by planktonic purple sulfur bacteria of the family Chromatiaceae (Brocks et al., 2005). Like green sulfur bacteria, Chromatiaceae are anoxygenic phototrophs that predominantly utilize sulfide and sulfur as their electron source. In stratified waters, they commonly inhabit a layer just above green sulfur bacteria within the light penetrated zone directly beneath the oxic-anoxic interface. Particularly informative is the relative abundance of the three aromatic carotenoids. In some BCF sediments, okenane derived from Chromatiaceae and chlorobactane from green-pigmented Chlorobiaceae are the most abundant molecules, while isorenieratane (XIX), indicative of brown-pigmented strains, is relatively minor. Based on modern ecosystems with similar pigment distributions, this pattern may indicate a basin state with a very shallow thermocline at ~12 m (Brocks and Schaeffer, 2008). In modern ecosystems, this strong activity of Chromatiaceae and green-pigmented Chlorobiaceae is often also associated with low abundances of oxygenic phototrophs in the overlying water column, and this is confirmed by the paucity of steroid biomarkers of eukaryotic algae. The full spatial and temporal extent of photic zone euxinia during deposition of the BCF remains to be investigated. However, extensive euxinia in the basin would support sedimentary exhalative models of sulfide formation at HYC.

4.1.2. McArthur basin mineralised HYC deposit

The HYC deposit within the Barney Creek Formation is the largest of the Palaeoproterozoic Pb–Zn–Ag ore deposits of north eastern Australia. The HYC Pyritic Shale Member was deposited within the Batten Trough, with its eastern boundary located along the syndepositional Emu Fault Zone along which the thickest sections of the Barney Creek Formation are preserved (Fig. 4). The host sediments of the HYC ore horizons consist of dark, carbonaceous, and pyritic dolomitic siltstones, with abundant graded breccias (Croxford and Jephcott, 1972; Ireland et al., 2004; Logan, 1979). Eight separate ore bodies have been identified in the HYC deposit (Large et al., 1998; Williford et al., 2011), as well as several different sulfide phases distinguished by $\delta^{34}\text{S}$ analysis (Eldridge et al., 1993). An early diagenetic pyrite phase (Py 1) had $\delta^{34}\text{S}$ values (–13 to +15‰) consistent with formation by bacterial sulfate reduction (BSR) in a system open to sulfate, and probably formed at, or close to, the sediment water interface (Fig. 4). A later and more massive pyrite phase (Py 2) which was more enriched in ^{34}S ($\delta^{34}\text{S}$ values of –5 to +45‰) could be indicative of closed-system reduction within the sediment pile (Eldridge et al., 1993) or by the incorporation of excess heavy sulfate, within a BSR pyrite zone immediately beneath the sediment

water interface, in the outer zone of the sub-surface mineralising system (Hinman, 1996). The unmetamorphosed nature of the HYC host sediments is reflected by fine grained sulfides, and thermal maturity of organic sediments in the broader McArthur Basin range from early mature to overmature (Logan et al., 2001).

Mineralisation was thought to have involved the interaction of hot, metal and sulphate rich brine with Barney Creek Formation sediments and OM during or after deposition (Fig. 4), the exact timing of which remains contentious (Williford et al., 2011). The moderately hot (150–250 °C) ore-forming fluid was identified as oxidised brine, rich in sulfate and metals at the point where it entered the basin (Hinman, 1996; Large et al., 1998).

Many of the aliphatic and aromatic hydrocarbons described in Section 2.1 have been detected in the OM of the HYC deposit (e.g., Chen et al., 2003; Logan et al., 2001; Williford et al., 2011). The total ion chromatogram from GC–MS analysis of the saturate and aromatic fractions of a Pit 1 HYC sediment is shown in Fig. 3. Logan et al., 2001 reported even numbered methyl-alkanes with branching at odd Cs (e.g., XII) in the bitumen of the ‘two-orebody’ through which hot hydrothermal fluid flowed (R_0 values of 2.0–2.5, being lower than other ore bodies). These are aliphatic biomarkers of sulfide-oxidising bacteria, consistent with communities of these organisms at the sediment water interface at the top of Py 1. Significantly, this molecular evidence – also supported by morphological characteristics – re-dated sulfide-oxidising organisms back another 800 million years to 1640 Ma (Logan et al., 2001).

The PAH distribution of HYC sediments is characterised by high abundances of parent aromatics (e.g., XI, XXIV–XXVI) and negligible abundances of alkyl aromatics, typical of sediments exposed to relatively high thermal maturities (Chen et al., 2003). PAH abundances were observed to increase with solubility and brine temperature gradients away from the Emu Fault, caused by hydrothermal fluid movement. Most of the PAHs in the HYC may have migrated from deeper depths where temperatures were higher. Nevertheless, transportation of certain PAHs suggests the hydrothermal fluids were at temperatures higher than 250 °C (Chen et al., 2003), although catalytic effects by metals may have reduced solubility temperatures. Previous models had ore-forming brine at temperatures of between 150 and 250 °C (Large et al., 1998). Temperatures of 250 °C greatly increase the metal-carrying capacity of the brine and would allow sulfide to be present in the ore fluids. Brines > 250 °C would have been generated in deeper areas of the McArthur basin, in which case evaporites would not be required as a source of sulfate (Chen et al., 2003).

The HYC PAHs had very similar $\delta^{13}\text{C}$ values to kerogen of the Wollgorang Formation, a dolomitic, pyritic black shale (6% TOC; Donnelly and Jackson, 1988) at the top ~20 m of the ~1700 Ma Tawallah Group (Bull and Rawlings, 1999), which underlies the Barney Creek Formation (Williford et al., 2011; Fig. 4). This stable isotopic correlation pointed to the reaction of basinal fluid with OM of the Wollgorang Fm to form PAHs at temperatures of 250 °C and depths of ~6 km. These data are supportive of Logan et al.'s (2001) model of ore genesis, which has metals and OM carrying fluids originating in an evaporitic deposit lower in the basin, then migrating upward with the ore fluid via conductive structures within the Emu Fault (Fig. 4), dropping in temperature to ~200 °C before reaching Barney Creek sediments (Logan et al., 2001; Williford et al., 2011).

Stable hydrogen (δD) isotopic values of *n*-alkanes (III) were also considered by Williford et al. (2011). *n*-Alkanes across the thermal maturity range covered by HYC sediments showed an enrichment in D by up to 50–60‰ (Sessions et al., 2004; Williford et al., 2011). This is consistent with the δD -maturity relationship of other studies (Dawson et al., 2007; Radke et al., 2005) where it was attributed to hydrogen exchange with a highly D-enriched brine fluid during ore genesis. A detailed model of HYC mineralisation showing hydrothermal fluid movement and metal sulfide precipitation as well as some of the key organic geochemical data which contributed to this scheme is shown in Fig. 4.

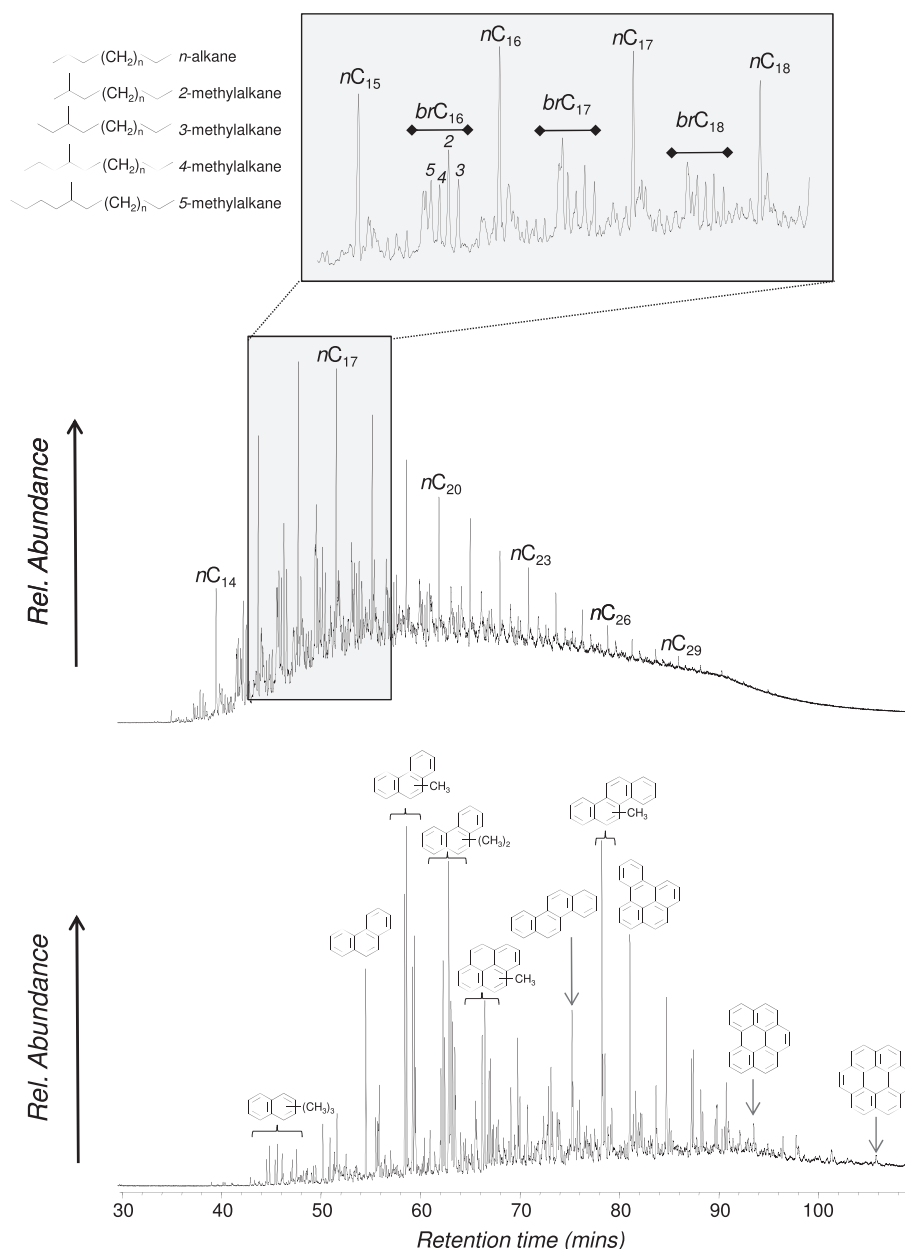


Fig. 3. Gas chromatograms of complex mixtures of aliphatic (top) and aromatic (bottom) hydrocarbons extracted from the HYC deposit (Williford et al., 2011). Products are resolved according to molecular weight and polarity, or molecular shape for separation of components of equal mass. Compounds of higher mass and boiling point elute at higher temperatures.

4.2. Kupferschiefer formation

The Kupferschiefer – commonly called the English Marl Slate – traditionally has been considered as an example of syngenetic strata-bound metal deposit associated with OM enrichment (Brongersma-Sanders, 1966; Wedepohl, 1964). The sediment was formed as a basal layer in a large intracratonic basin following an ingress upon sea-level increase. Establishment of reducing conditions and downward migration of a redox front into underlying strata leached oxidised metals from the latter and allowed their precipitation as sulfides in the Kupferschiefer marl or the basal conglomerate layer (Wedepohl, 1964). This syngenetic metal association characterised by Pb, Zn, and pyrite enrichment dominates the extended basinal facies of the Kupferschiefer and can be explained by scavenging of these metals from seawater and co-precipitation in pyrite. Exceptional concentration of Cu, Ag, Au, PGE, and barite is restricted to sub-basins in the margin of

the Zechstein Basin in Germany (East of the Rhenish Massif in the Hessian Depression and Sangershausen district of the Thuringian Basin; west of the Rhenish Massif in the Lower Rhine Embayment) and in Poland (Lower Silesia), where it has been attributed to epigenetic processes (Jowett, 1986; Kucha, 1983, 1985; Vaughan et al., 1989).

These processes are favoured by a specific basin architecture where thick terrestrial red beds are covered by a transgressive marine shale. The red beds serve as a source for the metals whereas the overlying shale serves as cap rock leading to hydrodynamic closure of the system and establishment of long-lasting convective flow cells (Hitzman et al., 2010; Jowett, 1986). The OM in the shale will then be oxidised by the advective metal-bearing brines from which base metal sulfides will be precipitated (Gize, 1999b; Vaughan et al., 1989). Temperature and salinity of the brines and thus their metal solution properties will be variable and depend on their depth of origin. Focusing of brines into the basin margins due to pinch-out of

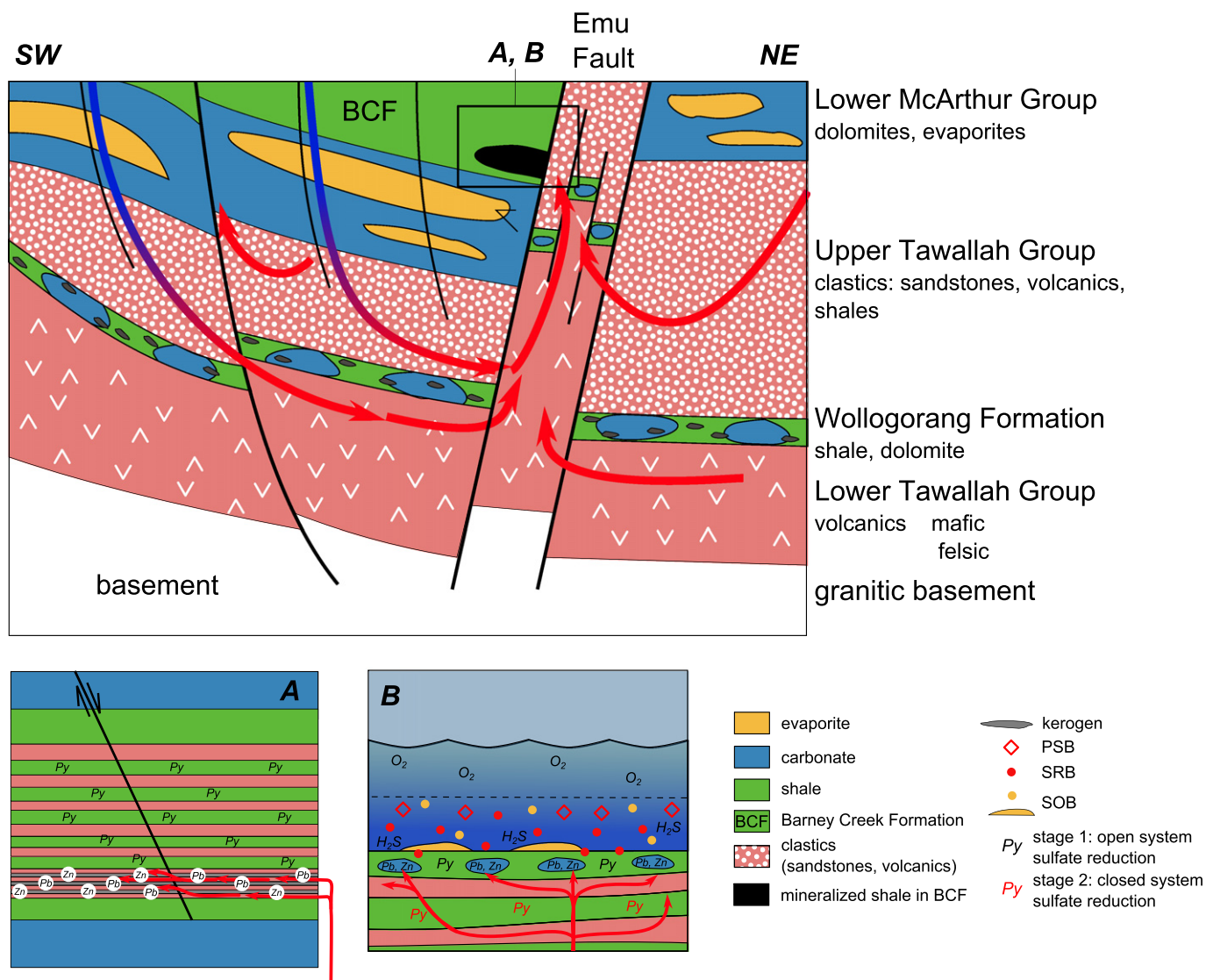


Fig. 4. Ore genesis model for the Barney Creek Formation in the HYC mine illustrating the source of metals in the Tawallah group clastics, the source of organics in the Wollongorang Fm., and the fluid flow pathways along the Emu Fault system to access the BCF. The inserts depict (A) postdepositional mineralization via metalliferous brines using the Emu Fault system to accessing the base of the BCF, where they spread laterally along permeable clastic intercalations within the BCF. The brines then interact with OM-rich BCF shales to precipitate metal ores. Syngenetic metal enrichment (B) in the BCF was stimulated by a highly reducing and sulphidic environment, colonised by sulfate reducing, sulfur oxidizing, and purple sulfur bacteria, as evidenced by their respective organic and inorganic biomarkers. These promoted redox reactions involving dissolved metal species provided by brines ascending via the syndepositional Emu fault system. Early and late pyrite formation in open and semi-closed systems are revealed by characteristic $\delta^{34}\text{S}$ signatures of pyrites. For further details see text.

permeable strata is influenced by the tectonic regime at the basin margin with faults acting as preferred fluid conduits.

The effect of syngenetic metal enrichment on the OM composition of the Kupferschiefer is negligible but difficult to study in marginal areas, where epigenetic alteration is common and problematic to study in the central basin due to deep burial and thermal maturation.

4.2.1. Non-mineralised Kupferschiefer

Non-mineralised Kupferschiefer, mainly studied in the Lower Rhine Embayment, from base to top reveals a tripartite lithological and geochemical evolution (Grice et al., 1996a, 1996b, 1997). The basal T1-I subunit is richest in organic matter (TOC 3–7%), clay content, pyrite and base metals. It is followed by a carbonate enriched T1-II subunit with reduced organic matter (TOC 1 to 3.5%), pyrite and base metal content. The uppermost T1-III subunit passes into the bioturbated Zechstein Carbonate (Ca-1) and exhibits an increase on dolomite vs. calcite, indicative of increased salinity, low OM (TOC < 1.5%) and metal contents. This is due to a high degree of oxidation under lower sea

level and sediment deposition close to storm wave base. A comparable lithological evolution, with a gradual change from basal calcitic to dolomitic marls at the top of the formation has been described for the English Marl Slate (Sweeney et al., 1987).

The molecular composition of the extractable low maturity bitumen reveals an *n*-alkane (III) distribution dominated by short-chain homologues maximising at *n*-C₁₅ to *n*-C₁₇ derived from algal sources in the basal section (Grice et al., 1997; Schwark and Püttmann, 1990). Lowering of sea-level led to a relative increase of long-chain homologues (*n*-C₂₅ to *n*-C₃₇) with a pronounced odd-even predominance indicative of a terrestrial plant wax origin in subunit T1-III (Grice et al., 1997). Enhancement in salinity and bottom water oxygenation from subunit T1-I to T1-III is evident from increasing Pristane (XIV)/Phytane (XV) and trimethylated chroman (XXII) concentrations (Schwark and Püttmann, 1990). A major shift in primary producer association and preservation conditions is revealed by a high hopane (e.g., XIII)/sterane (e.g., XII) ratio of about 4 in the T1-I subunit shifting to a ratio of about 1 in T1-II and then increasing

again to about 2 in T1-III subunits (Grice et al., 1997). A high proportion of chlorophyll and bacteriochlorophyll derived biomarkers is represented by intact porphyrins (e.g., IX, X) and their degradation products, the maleimides (e.g., XXI, XXXVII), and by C₁₅, C₁₉ (XIV) and C₂₀ (XV) isoprenoids (Grice et al., 1996a, 1996b; Schwark and Püttmann, 1990) dominating over neighbouring *n*-alkanes by factors of 2 to 10 (Grice et al., 1996a). Porphyrins in the non-mineralised Kupferschiefer are dominated by Ni-porphyrins (Eckardt et al., 1989) with ratios of Ni- vs. V=O-porphyrins varying between 0.95 in the basal subunit and 0.8 in the central subunit (Schwark and Püttmann, 1990).

The non-mineralised Kupferschiefer is rich in biomarkers derived from Chlorobiaceae (Grice et al., 1996a, 1996b, 1997; Schwark and Püttmann, 1990). Key indicator molecules for Chlorobiaceae comprise isorenieratane and diagenetic di- (e.g. isorenieratane, XIX) and triaromatic isoprenoids, aryl isoprenoids and isobutyl maleimides (e.g., XXI; Grice et al., 1996a, 1996b, 1997; Schwark and Püttmann, 1990). These components were also detected in samples from the Yorkshire Basin, Great Britain (Pancost et al., 2002), indicating that photic zone euxinia occurred as a basin-wide phenomenon. The widespread presence of Chlorobiaceae points to an extremely high sulfuration potential in the entire Kupferschiefer Sea that initiated intensive pyritisation associated with co-precipitation of base metals, leading to the primary syngenetic metal enrichment *sensu* Wedepohl (1964) and Brongersma-Sanders (1966).

The carbon isotopic composition of bulk OM from non-mineralised Kupferschiefer shows values between −27 and −30‰ (Bechtel and Püttmann, 1997) and only minor variation over the sediment profile. CSIA of biomarkers (Grice et al., 1996a, 1996b, 1997) reveals slightly enriched $\delta^{13}\text{C}$ -values for all compound classes (*n*-alkanes, isoprenoids, steranes, hopanes) in the T1-I subunit indicative of high primary productivity followed by a 2‰ shift to lighter $\delta^{13}\text{C}$ -values in the T1-II and T1-III subunits due to a decline in productivity in agreement with lower TOC values in these sections. The biosynthetically induced isotopic difference between the $\delta^{13}\text{C}$ values of C₁₅ and C₁₇ *n*-alkanes as well as hopanoids (−28.5‰ in subunit T1-I) primarily derived from algae versus acyclic isoprenoids and steroids depleted to −30.5‰ indicates an algal bloom in subunit T1-I. Due to the different carbon assimilation pathway the Chlorobiaceae derived components including methyl-isobutyl maleimides exhibited much enriched $\delta^{13}\text{C}$ -values of about −17‰. The relative high abundance of methyl isobutyl maleimide (XXI) to methyl ethyl maleimide (XXVII; expressed as a ratio) supports the limited light availability in subunit T1-I due to the high algal productivity.

A recent review of organic facies of the Kupferschiefer in Poland for the non-mineralised sediments gave similar results to the Lower Rhine Embayment (Bechtel et al., 2000; Kotarba et al., 2006), though no facies evolution over the Kupferschiefer interval is discussed in any detail. Deposition took place under reducing conditions though no molecular indication of photic zone euxinia has been reported. Salinity variations determined by methylated chromane abundances or composition presumably could not be conducted due to the lack of these components even in immature samples. The composition of the organic matter based on R-E hydrogen indices is equivalent to a type II kerogen. Molecular analysis yielded thermal maturity controlled Pr/Ph values to between 0.4 and 2.0. The pristane/*n*-C₁₇ or phytane/*n*-C₁₈ ratios even for immature samples were lower than those reported for the Lower Rhine Embayment. A nearshore depositional environment is reflected by CPI values ranging between 0.88 and 1.48, indicative of a moderate terrigenous plant wax input. As a consequence the organic facies in the Polish part of the Zechstein Sea differs slightly from that in the Lower Rhine Embayment, most likely to more restricted paleoceanographic conditions in the latter.

In summary the molecular and bulk geochemical composition of the Kupferschiefer sediment indicates a high productivity, restricted and oxygen-depleted environment with excellent preservation potential

for OM and high enrichment of pyrite and sulfurised base metals in the basal T1-I subunits. Conditions of sedimentation in the central and uppermost subunits then gradually decrease to lower productivity, higher salinity, higher water column oxygenation and low accumulation potential for OM and base metals.

4.2.2. Mineralised Kupferschiefer

Within the area of the Lower Rhine Embayment only very minor mineralisation of Kupferschiefer occurs, mainly noticeable in the form of barite enrichment in basal Kupferschiefer, along deep-reaching faults into the Carboniferous basement. Mineralisation is restricted to the area of the Krefeld High (Püttmann et al., 1990), where a deep-seated magmatic pluton has been postulated. Even for a barite enrichment of up to 14% in basal Kupferschiefer of the Lower Rhine embayment, the effect on the organic matter composition is minimal and not distinguishable from facies or maturity induced variability.

For the Hessian Depression, the Sangershausen District of the Thuringian Basin and the adjacent Fore-Sudetic Monocline in Lower Silesia, Poland, enrichment of base metals, PGE, Au and Ag to economic levels are known (Hitzman et al., 2010; Kucha, 1983, 2003; Kucha and Przybyłowicz, 1999) and several mining districts have been in operation for centuries, though exploitation has ceased in most areas. All of these deposits sit on the margin of the Kupferschiefer Sea, or respectively close to the pinch out of underlying clastic sediments of the North German Basin, in a tectonic regime that has been affected by the Variscan Orogeny leading to the establishment of fault systems that have been reactivated and enable fluid flow from deeper basin parts into the Kupferschiefer (Hitzman et al., 2010).

Access of hydrothermal oxidising fluids into the basal Kupferschiefer in the Hessian Depression and the Thuringian Basin in Germany or the Fore-Sudetic Depression in Poland led to similar alteration of OM, as demonstrated in various studies (e.g. Bechtel et al., 2000; Heppenheimer et al., 1995; Kotarba et al., 2006; Püttmann et al., 1989). Epigenetic effects are strongest in areas affected by 'Rote Fäule' (equivalent to 'Red Alteration'), where pyrite is entirely replaced by hematite and OM is severely reduced to <0.2% TOC (non-mineralised TOC values of generally between 3 and 10%, depending on carbonate dilution) and summed concentrations of Pb, Zn, and Cu are <1500 ppm. In the direct vicinity of such Rote Fäule alterations the Kupferschiefer can be significantly mineralised, mainly by Cu, Pb, Zn but also PGE, Au, and in particular Ag. Oxidising fluids in the Rote Fäule zones lead to the loss of OM. The degradation was accompanied by HI-indices falling to about 50 from around 300 to 400 (mgHC/gTOC) in non-mineralised strata. Despite the significant loss of total organic matter the TOC-normalised extract yields only declined from around 50 to 80 mg/gTOC to 30 to 35 mg/gTOC, leaving sufficient bitumen for molecular characterisation (e.g. Bechtel et al., 2000; Heppenheimer et al., 1995; Kotarba et al., 2006; Püttmann et al., 1989, and references therein).

Molecular composition of the samples affected by Rote Fäule oxidation is characterised by a predominance of short chain *n*-alkanes (III; <*n*-C₁₇) at the expense of mid- and long chain homologues (Bechtel et al., 2000; Kotarba et al., 2006; Püttmann et al., 1989). In contrast the isoprenoids pristine (XIV) and phytane (XV) are less affected by the oxidation and increase in relation to neighbouring *n*-C₁₇ and *n*-C₁₈ alkanes, respectively. The Pr/Ph ratio increases with intensity of Rote Fäule mineralisation but intensive oxidation may lead to a complete loss of these isoprenoids (Bechtel et al., 2000). The aromatic fraction of samples from the Rote Fäule oxidation zone is characterised by a severe loss of methylated analogues and preservation of phenanthrene (XI), fluoranthene (XXX), pyrene (XXXI), benz(a)anthracene (XXXII), chrysene (XXIV), benzofluoranthenes (XXXIII) and benzopyrenes (XXXIV), whereby the aromatic fraction contributes 40 to 50% by weight of the total extract (Bechtel et al., 2000). The relative distribution of parent aromatics dominated by the 4-ring aromatics and 5-ring analogues were pronounced in non-oxidised samples (Bechtel et al., 2000; Heppenheimer et al., 1995). The

ratio of phenanthrene (XI) vs. the sum of methylphenanthrenes (e.g. XIa) for Rote Fäule samples thus on average is between 2 and 3, whereas mineralised but unoxidised and non-mineralised Kupferschiefer gives values around 0.7 to 1.5 and <0.6, respectively (Bechtel et al., 2000). In a previous study Püttmann et al. (1990) reported even higher phenanthrene enrichment values between 0.65 and 5.3 for mineralised samples close to but not within Rote Fäule zones, where a value of 8.3 was reached. The methylphenanthrene index (MPI-1) is similarly affected by epigenetic oxidation and declines to values <0.5 within the Rote Fäule zone. A decrease in MPI-1 could be caused by the relative decrease of methylated versus parent phenanthrene or by a shift in the methylphenanthrene isomer distribution. As these data are not reported the question remains open for further investigation. The degradation scheme for methylated phenanthrenes to phenanthrene and further to biphenyl (XXIII, $n=0$) as proposed by Püttmann et al. (1989) is supported by the increase in biphenyl at the expense of phenanthrene (XI) in the Rote Fäule zone (Püttmann et al., 1990). Thioaromatic (e.g., dibenzothiophene, VI) compounds and to a lesser degree oxoaromatics (e.g., benzofuran, XXXV) known to occur in variable concentrations and compositions in the Kupferschiefer (Rospondek et al., 1994, 2007) dramatically decline in their abundance in the Rote Fäule zones, indicating that epigenetic oxidation affected the heteroaromatics to a larger degree than the aromatics (Bechtel et al., 2000).

The mineralised zones directly adjacent to the epigenetically oxidised Rote Fäule show economically significant enrichment in various base metals, PGE, REE, Au, and Ag (summarised in Vaughan et al., 1989). Base metal concentrations (preferably Cu, Pb, Zn) can exceed 15% by weight and are accompanied by severe changes in primary OM composition as well. These changes are, however, different to those noted for the Rote Fäule.

In general, the distribution of *n*-alkanes shifts to longer chain homologues, the ratios of *n*-alkanes vs. isoprenoids declines in mineralised shales/marls and the Pr/Ph ratio increases (e.g. Bechtel et al., 2000; Kotarba et al., 2006; Large and Gize, 1996; Püttmann et al., 1989, 1990). The degree of methylation declines for aromatics but not as severe as with Rote Fäule oxidation. Concentrations of thio- and oxoaromatics, in particular dibenzothiophene (VI) and dibenzofuran (XXXV), increase to maximum values in mineralised zones close to but not with the Rote Fäule facies (Bechtel et al., 2000; Püttmann et al., 1990). The methylation of dibenzothiophenes in mineralised compared to non-mineralised samples declines comparable to the degree of methylation of phenanthrene.

Based on geochemical as well as mineralogical and sedimentological investigations, the following synthesis of mineralisation in the Kupferschiefer was developed. Ascending metalliferous and oxidising brines derived from a semi-closed hydrological system in the North German/Saxonian Basin, buried to sufficient depth (>5000 m) to generate hydrothermal fluids. Red Beds from within the basin sourced the base metals into the fluids and these utilised the high permeability clastic lithologies to advect to the basin margins. Here the low permeability marls and mudstones of the Kupferschiefer acted as barrier to the advected fluids, which after reacting with the bituminous and particulate OM in the cap-rock cooled down to get downvected again. Thus a circulation system was initiated that over several millions of years continuously provided dissolved metals to the basal Kupferschiefer leading to the local economic metal enrichment. In areas, where a pinch-out of

Kupferschiefer strata on e.g. paleohighs occurred, the regional seal was healed by cementation of permeable lithologies via mixing of cold descending brines from overlying evaporitic Zechstein strata with hot ascending metalliferous brines, leading to further metal precipitations unrelated to presence of organic matter (Kucha and Pawlikowski, 1986). A further process of unquantified magnitude is associated to late postdepositional faulting and fracturing of Kupferschiefer, allowing ascending metal-bearing solutions to penetrate deep into Kupferschiefer and even breaching it to accumulate copper ores in overlying Zechstein Limestone (Blundell et al., 2003).

The main metal precipitation mechanism is based on a redox reaction between oxidising fluids and reducing organic matter. Transfer of hydrogen from solid OM is recognised in declining R-E HI values and in bitumen by an increase in the degree of demethylation and aromatisation. The precipitation of base metals occurred preferably as metal sulfides, whereby sulfur to some degree was also partitioned into epigenetic thioaromatic hydrocarbons (e.g., IV–VII). Besides these oxo-aromatic hydrocarbons (e.g., XXXV, XXXVI) were formed upon bitumen oxidation. It may be envisaged that preferential reaction occurred between brines and bitumen that was expelled from the Kupferschiefer with onset of thermal catagenesis. Despite the low intrinsic permeability of the Kupferschiefer, brines must have been able to impregnate the sediment, in order to facilitate hydrogen transfer reactions with solid kerogen.

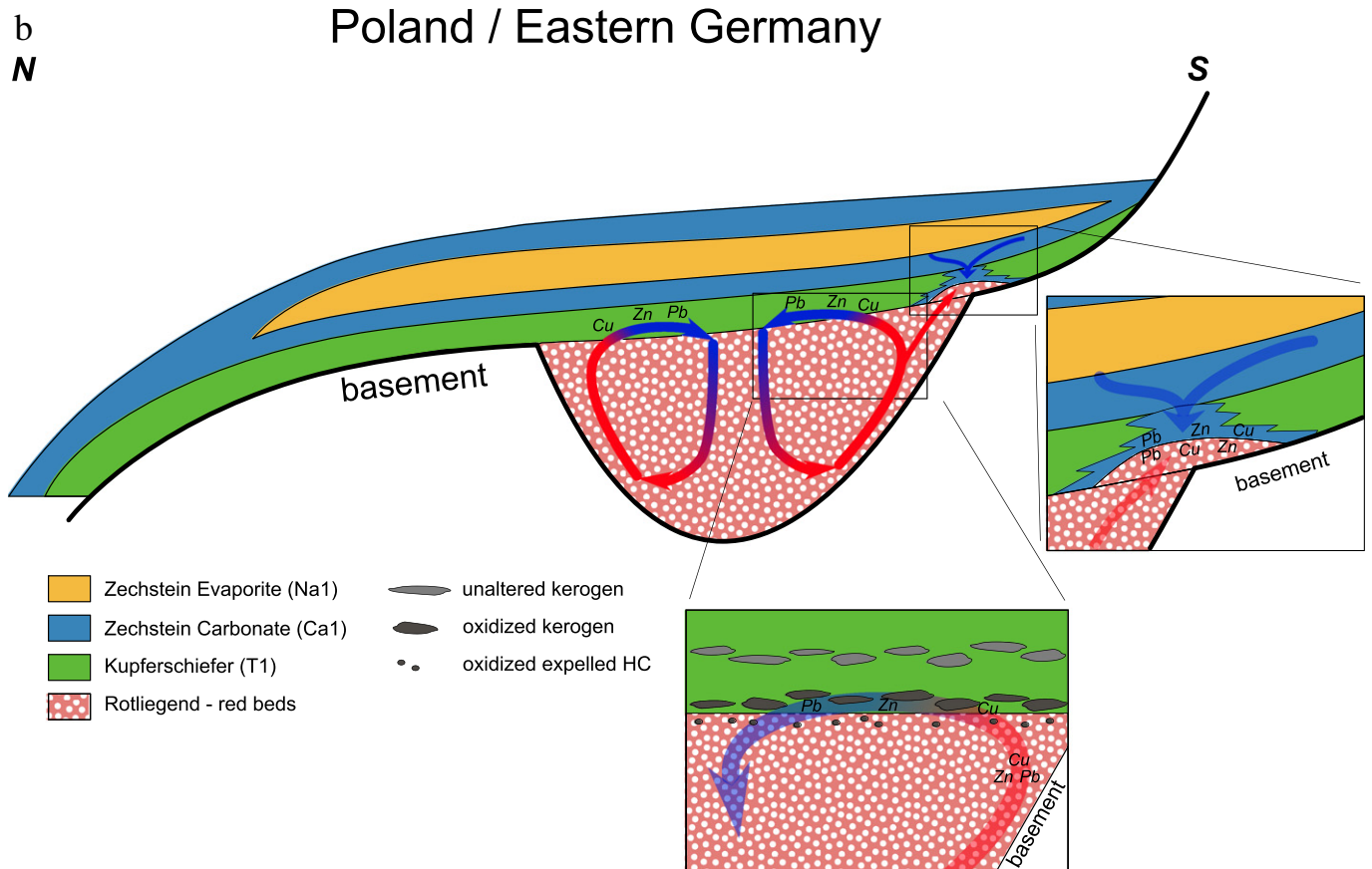
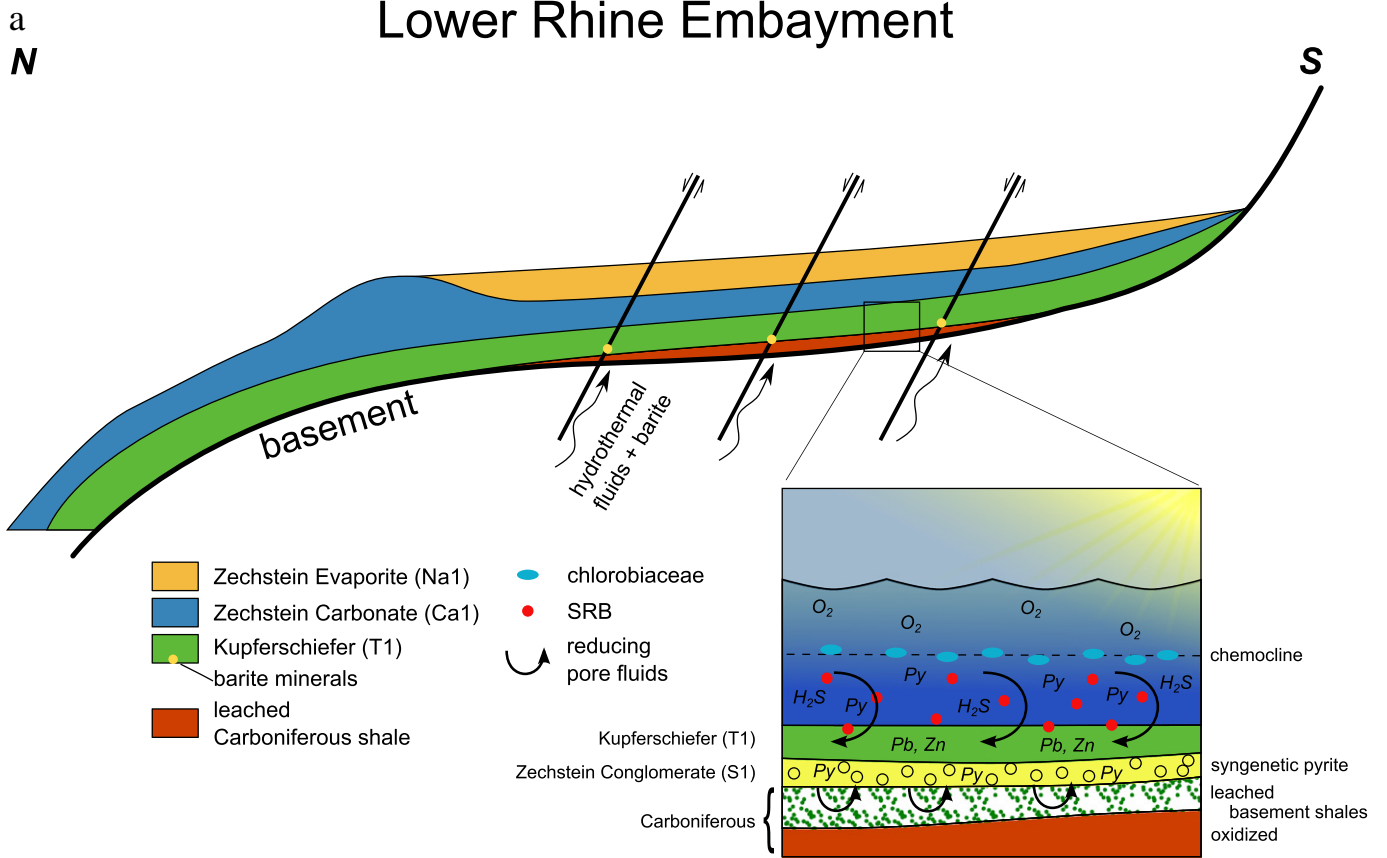
Two separate models for hydrothermal fluid movement and mineralisation in the Lower Rhine Embayment (top) and Poland-East German (bottom) regions of the 'Kupferschiefer' formation are displayed in Fig. 5.

5. Fluid inclusions

Fluid inclusions (FIs) are ubiquitous throughout sedimentary environments and may provide valuable information about the fluids responsible for mineral precipitation or host rock alteration (Fairmaid et al., 2011; Gize, 1999b; Polito, 1999; Robb and Meyer, 1991). FI data can also indicate the temperature and pressures at the time of mineralisation and the composition and density of the fluid that transport solutes to the site of deposition (Polito, 1999).

Importantly, the hydrocarbons sequestered within FI are protected from biodegradation and other subsequent alterations (Hulen and Collister, 1999) and represent an important geological record of pristine fluids. Most FIs in mineral deposits contain simple gases such as CH₄, CO₂ and H₂O (of different salinities). CH₄ and trace concentrations of other hydrocarbon gases have been detected in FIs in nearly all metamorphic and igneous hosted ore deposits (Gize, 1999b; Polito, 1999). Microthermometry or Laser Raman spectroscopy has been traditionally used to analyse the gas content of FIs. Microthermometry measures the fluid phase changes over a large temperature range (≥ -190 °C) and also provides a measure of the temperature of homogenisation or FI entrapment. Laser Raman is a non destructive analytical technique which measures spectral signals indicative of specific inorganic complexes. This analysis allows identification of stoichiometric hydrates, gases (comprised of C, O, H, N or S) and certain daughter minerals and can confirm compound phases identified by microthermometry (Polito, 1999; Rosasco and Roedder, 1979; Seitz et al., 1996).

Fig. 5. Ore genesis model for (a) Lower Rhine Embayment and (b) Poland-East German regions of the 'Kupferschiefer Formation'. In the Lower Rhine Embayment the Kupferschiefer transgressed directly on the Carboniferous bedrock, with only very thin Rotliegend sediments suitable as source for metal leaching. Syngenetic pyrite mineralisation initiated by bacterial sulfate reduction is most intensive in the coarse grained transgressive conglomerate layer below the Kupferschiefer. Base metal enrichments is dominated by Pb and Zn, with slightly elevated concentrations of Cu and Barite restricted to fault zones reaching deep into Carboniferous strata around the Krefeld High pluton. In the East German/Polish mineralization districts subbasin filled with thick Rotliegend Red Bed deposits are overlain by a Kupferschiefer cap-rock. Convective flow-cells transport sulfate and metal bearing oxidising brines to the basin margins, where these oxidize organic matter present in the Kupferschiefer as kerogen or expelled bitumen, in particular in underlying coarser clastics. Both types of organic matter, solid kerogen and liquid bitumen, were affected by redox processes. Kerogen served as H-donor as revealed by lower HI-values, and bitumen experienced intensive demethylation and aromatization. Metal sulfide precipitation favored Cu over Pb and Zn on the hotter basin fringes and Pb or Zn in the cooler central basin areas. In areas where the Kupferschiefer cap-rock is missing, e.g. above paleo-highs colonised by biotherms, descending cold brines from overlying evaporites mixed with ascending hot basin brines to precipitate metal ores and seal the regional cap-rock by cementation.



FIs containing hydrocarbons larger than gaseous condensates ($>C_{10}$) have occasionally been detected in various styles of mineralisation, e.g. Cu, Au and U (George et al., 2009; Landais and Gize, 1997) although oil bearing FIs are more common in petroliferous rocks. Microthermometry and Laser Raman analysis can generally also be applied to these oil-bearing inclusions (Cisternas and Hermosilla, 2006) however, the more complex hydrocarbon composition of these FIs is more adequately analysed by GC–MS.

5.1. GC–MS analysis of the hydrocarbon composition of FIs

FIs can be opened for subsequent GC–MS analysis of their chemical content by a range of methods including mechanical crushing (e.g., George et al., 1996, 2004, 2007; Karlsen et al., 1993), thermal decrepitation (e.g. Hoffmann et al., 1988; Horsfield and McLimans, 1984), laser drilling (e.g., Greenwood et al., 1998; Volk et al., 2010; Zhang et al., 2012) or carbonate dissolution with ethyl diamine tetra-acetic acid (EDTA; Ferguson, 1987; Polito, 1999). Thermal methods may distort the concentrations of gaseous constituents by the production of CO_2 , CH_4 and other molecules through thermal decomposition of minerals and interstitial carbonaceous material (Andrawes et al., 1984; Polito, 1999; Potter and Longstaffe, 2007). Moreover, CO_2 and some other gases released by crushing methods are also prone to adsorption to newly generated surfaces (Bray et al., 1991), although this problem can be minimised by crushing in a helium flow at low temperatures ($\leq 120^\circ C$; Polito, 1999). EDTA dissolution is not subject to such analytical bias, and gas volumes produced are typically similar to crushing methods, and higher than obtained with the application of heating methods. GC separation of gaseous range hydrocarbons traditionally required the cryogenic cooling of GC ovens to very low temperatures (e.g., Horsfield and McLimans, 1984; Muscio et al., 1994), but specialised gas GC columns able to resolve gaseous constituents at ambient temperatures have also been used to analyse the gas content of fluid inclusions (e.g., Mycke et al., 1994).

The higher MW (C_7 – C_{35}) liquid hydrocarbons in FIs do not appear to be affected by either crushing (George et al., 1996, 2004, 2007, 2009) or thermal decrepitation (e.g., Greenwood et al., 1998; Hoffmann et al., 1988; Horsfield and McLimans, 1984). Crushing and heating devices can be retrofitted to most types of GCs to support online analysis, although crushing procedures are usually conducted off-line and often in combination with solvent extraction (e.g., George et al., 1996, 2004, 2007).

With the advancement of new techniques, analyses of oil-bearing FIs from ore deposits have become more common. FIs in oil-bearing Carlin-type Au deposits of the Yankee Basin (Alligator Ridge, Nevada) were released and solvent extracted after crushing of vein matter to <100 mesh (Hulen and Collister, 1999). GC–MS analysis of the saturate and aromatic fractions of this FI oil showed hydrocarbon ratios consistent with a thermal maturity within the oil window (R_o equiv of 0.75–0.95). This was consistent with microthermometry homogenisation temperatures that were generally $<150^\circ C$, with most at $\sim 120^\circ C$. Using the conversion of Barker and Pawlewicz (1994), this corresponds to geological temperatures of 113–132 $^\circ C$, which is low for Carlin-type Au mineralisation but ideal for oil preservation. The FI hydrocarbons were also related to Yankee Basin oil and the Pilot shale, excluding two other source options that had been previously suggested. Significantly, this implied that free oil in the Yankee Basin participated in Au mineralising hydrothermal systems. Based on FI data, Hulen and Collister (1999) further speculated that 1) OM may provide the reducing power for the formation of Au sulfides; 2) reaction between Au species and asphaltenes could produce organic-metallic compounds, either in transit or at the point of accumulation; and 3) high concentrations of carbonic acids could have intensified rock porosity (e.g. decalcification) to accommodate greater entrapment of oil and metal brine rich hydrothermal fluids. Furthermore, the organic concentration of hydrothermal fluids could increase

with migration and additional oil may be generated by the interaction of hot fluids with sub-mature hydrocarbon source rocks (Hulen and Collister, 1999).

In a novel approach, Polito (1999) used SPME–GC–MS to analyse the aliphatic and aromatic hydrocarbons from carbonate hosted FIs of the Junction Au deposit (Kambalda, WA). The analysis was outsourced to a commercial laboratory (Actlabs, Ancaster, Ontario, Canada), however, and very few analytical details were provided. The results included trace amounts of $\leq C_{17}$ aliphatic (e.g., *n*-alkanes, *III*; branched alkanes, e.g., *XVI*, *XVII*; cycloalkanes) and alkyl-aromatics (e.g., benzenes, *I*; naphthalenes *II*; and anthracenes, *XXXVII*) which were largely indicative of anthropogenic sources and not indigenous to the ore body. This result further highlights the careful analytical approaches required for uncompromised analysis of trace hydrocarbons such as present in FIs. Reliable FI analysis can only be conducted following complete removal of all younger fluids from interstitial space (e.g., George et al., 2009).

Bulk analysis of FIs cannot distinguish between charges of hydrocarbons trapped at different periods of basin evolution. However, the high spatial resolution of lasers can be used to separately open and analyse selected oil FIs (Greenwood et al., 1998; Volk et al., 2010; Zhang et al., 2012).

A novel technology to evaluate minute quantities of hydrocarbons in individual FIs is the combination of a secondary ion microprobe (SIMS) that can drill into a single inclusion and a fast Time of Flight mass spectrometer (TOF) to detect the released molecules. This technology has, for example, been used to explore for the presence of hopane and sterane biomarkers in single oil-bearing inclusions trapped in hydrothermal veins of fluorite and calcite and containing oil from Ordovician source rocks (Siljeström et al., 2010). However, as TOF-SIMS simultaneously measures the bulk of all molecules and molecular fragments released from the inclusion without prior separation by gas chromatography, the identification of molecular structures remains equivocal. Yet, TOF-SIMS promises to yield a wealth of new information about the content of individual FIs, and new technologies that may include MS/MS capability, could significantly strengthen the resolution of exact chemical structures.

5.2. Stable isotope analysis of FIs

Stable isotopic analysis can provide important insights into the origin, phase and interaction of the gaseous and organic compounds trapped within FIs. A vacuum line is typically used to isolate the different gas components released by thermal or mechanical procedures followed by isotopic measurement using EA-IRMS (Dutkiewicz et al., 2003). The complete isolation of CO_2 from methane and other hydrocarbon gases for direct $\delta^{13}C$ measurement can be challenging, but its $\delta^{13}C$ value can be inferred from mass balance of volumes and $\delta^{13}C$ values of the hydrocarbons present and bulk material (Dutkiewicz et al., 2003).

Several researchers have developed sophisticated analytical systems in which crushing devices have been directly interfaced with isotope ratio mass spectrometers to support on-line $\delta^{13}C$ measurement of FI gases. Ueno et al. (2006) separately measured the $\delta^{13}C$ composition of methane and CO_2 isolated from gas-rich FIs in 3.5 Ga hydrothermal precipitates from the Pilbara craton in Western Australia. Several preparative steps were implemented in a rigorous effort to avoid co-measurement of background CH_4 . The CH_4 had a very light $\delta^{13}C$ value of -56‰ indicative of a microbial source and inconsistent with thermogenic CH_4 that is typically $>-30\text{‰}$ (e.g., Welhan et al., 1988). This discovery extended the known origin of methanogens back in time by ~ 700 million years.

A new on-line continuous flow method for analysis of the $\delta^{13}C$ of C_1 – C_5 gases and δD of $\leq C_2$ gases from FIs was reported by Potter and Longstaffe (2007) with the impressive detection sensitivity of

20 nmol for $\delta^{13}\text{C}$ and 100 nmol for δD – improving upon previous detection limits for trace gases in Fls. The capacity to identify gas sources at these detection thresholds was demonstrated on gas Fls from the Khibina alkaline igneous complex (NW Russia) and the south Wales coalfields. The methane $\delta^{13}\text{C}$ (–13 to –8‰) and δD (–120 to –50‰) values were attributed to a juvenile magmatic gas phase, whereas the $\delta^{13}\text{C}$ of the C_2 – C_5 hydrocarbons (12‰ more depleted than CH_4) was consistent with an abiogenic origin. Furthermore, the $\delta^{13}\text{C}$ values of CO_2 were consistently lower than CH_4 (by up to 9‰) and the δD values of C_2H_6 70–100‰ beneath $\delta\text{D}_{\text{CH}_4}$, consistent with generation of the CO_2 and higher hydrocarbons during sub-solidus, kinetic CH_4 -oxidation, fractionation and polymerisation reactions. Abiogenic origins of organic matter in ore deposits may be similarly recognised by similar CSIA of gas Fls.

$\delta^{13}\text{C}$ values were measured for CO_2 and CH_4 and the $\delta^{15}\text{N}$ value of N_2 in Fls within a fracture fill mineralisation from the Lower Saxony Basin (Germany), a major oil and gas province, with Cadomian and Variscan age crystalline rocks filled with Paleozoic–Cenozoic sediments (Lüders et al., 2012). The isotopic measurement of the Fl gases was simultaneously obtained on samples as small as 0.1–0.5 g. The data revealed that the CH_4 trapped in Fls were from a different kerogen to the host rocks. The rock setting showed $\delta^{13}\text{C}_{\text{CH}_4}$ values of –25 and –19‰, typical of high-maturity coals, whilst $\delta^{13}\text{C}_{\text{CH}_4}$ values of –45 to –31‰ for the Mesozoic mineral Fls was more consistent with the primary cracking of type II kerogens (Lüders et al., 2012). The $\delta^{13}\text{C}_{\text{CO}_2}$ values of the Fls were consistently close to zero indicative of an inorganic source (Lüders et al., 2012). In addition to information about biogenic or abiogenic origin of the fluids, the isotopic composition of these Fl gases helped indicate the thermal maturity and extent of migration of the fluids (Lüders et al., 2012). The fluid source, type and maturity information provided by the Fl isotope values was consistent with corresponding bitumen hydrocarbon data.

A great advance that will help to assess the provenance of gases in Fls in ore systems is now also afforded by specialty gas phase GC columns that can be used to separate and measure the isotopic values of the different components of gas mixtures at ambient GC oven temperatures, but these have not yet been widely utilised for on-line GC/MS analysis of Fl gases. Boreham and Edwards (2008) did use such a gas column to separately measure the $\delta^{13}\text{C}$ value of pentane isomers in natural gases which showed a wide carbon isotopic variability due to the interplay between decomposition, isomerisation and methylation mechanisms.

6. Organic–inorganic synergies

6.1. The catalytic effect of metals on hydrocarbon processes

Many of the chemical reactions which occur during the thermal maturation of organic materials – e.g., defunctionalisation, rearrangement, disproportionation, C–C bond cracking, condensation, oxidation, and reduction – can be catalysed by minerals. This effect may be further promoted by the high adsorption capacity of clays (e.g. montmorillonite) and other minerals with high surface areas and exposed cations (e.g., Collins et al., 1995; Eltantawy and Arnold, 1973; Espitalié et al., 1984; Johns, 1979; Johns and McKallip, 1989; Kennedy et al., 2002; Seewald, 2003). Many studies have investigated the effect of selected metals (Au, U, Cu, Pb, Zn), minerals or metallo-porphyrins (IX, X) on the hydrocarbon behaviour of kerogen and organic compounds (Eglinton et al., 1986; Goldstein, 1983; Hart and Brown, 2004; Heller-Kallai et al., 1996; Höld et al., 1998; Johns, 1979; Lewan et al., 2008; Mango, 1996; Raimondo et al., 1998; Wei et al., 2006). Outcomes from a selection of these studies follow.

Ni- and Vanadyl-porphyrins showed no obvious effect on the generation of CH_4 from alkenes (Mango, 1996). Their catalytic ineffectiveness may be the result of the metals occurring as cations

strongly bound to the central regions of large tetrapyrrole molecules (Lewan et al., 2008). Laboratory simulated thermal maturation of marginally mature black shales of the Permian-Kupferschiefer spiked with selected transition-metals (Cu, Pb, Zn) also showed the transition metals had little effect on CH_4 yields (Lewan et al., 2008). Again, however, this outcome may have been dictated by the limitations of the experimental procedure including 1) the metals not occurring in the proper form; or 2) the poisoning of potential catalytic microcosms by polar-rich bitumen, which impregnates the rock matrix during the early stages of petroleum formation (Lewan et al., 2008).

The effect of several minerals (montmorillonite K10, acidic aluminosilicate, kaolinite, illite, CaCO_3 , CaSO_4) and elemental sulfur on the formation of diamondoids was the focus of another study (Wei et al., 2006). Diamondoids are well known pyrolysis products of kerogen (Tissot and Welte, 1984) and are readily produced on the oxidation of simple organic compounds such as cholesterol, cyclohexane, and cedrene (Fort and Schleyer, 1964). Samples representative of all four kerogen types (I, II, II-S, and III) were separately spiked with the minerals and artificially matured. The catalytic effect of the minerals on the formation of diamondoids ranged from high for montmorillonite K10 and acidic aluminosilicate (both strong Lewis acids/oxidation agents) to one of inhibition with CaCO_3 (Wei et al., 2006). These contrasting effects suggest the formation of diamondoids follows a carbonium ion mechanism rather than an electron transfer mechanism. The availability of water had negligible effect, but sulfur appeared to poison the catalytic activity of montmorillonite K10 (Wei et al., 2006).

6.2. Metal–carboxylic acid interactions

Several researchers have investigated the effect metal species have on the thermodynamic generation of organic acids from maturing kerogens. Organic acids can increase reservoir porosity by increasing the solubility of minerals (via metal–organic acid anion complexation) or by increasing their dissolution rates (Knauss et al., 1997; Surdam et al., 1984). They are strongly water soluble so will be rapidly transported in the water phase which means their encounter with mineral phases must occur close to their source kerogen (Barth and Bjorlykke, 1993). Consequently, there has been considerable interest in understanding the major sources (e.g. source rocks, oils) of the organic acids potentially impacting metal rich ores (Andresen et al., 1994; Barth et al., 1989; Borgund and Barth, 1994; Curiale et al., 1992; Kharaka et al., 1993; Lundegard and Senftle, 1987; Lundegard et al., 1992; Stalker et al., 1994).

The production kinetics for carboxylic acids and light hydrocarbons from thermally treated kerogen were investigated to evaluate the potential importance of carboxylic acids on the aqueous speciation of rock-forming metals (Knauss et al., 1997). This study used a novel experimental approach in which the organic samples and other reactants were located in gold bags allowing both temperature and pressure to be regulated throughout the pyrolysis experiment. In this way the sample remained in the single fluid phase, with no, potentially interfering, headspace gases. Samples were withdrawn by syringe without having to cool the reaction/pyrolysis vessel. This strategy differs from traditional hydrous pyrolysis requiring many separate experiments to be conducted at different temperatures and the quenching of the thermally treated samples to ambient temperatures and pressure when subsequent reactions and phase changes can occur (Knauss et al., 1997). High temperature metal–organic aqueous speciation had never been directly determined by experiments of this nature (i.e. measured *in situ* during the hydrous pyrolysis of an oil source rock), so the thermodynamic calculations were made with high temperature thermodynamic data and speciation/solubility geochemical modeling. This is a database of approximately 1000 inorganic and organic aqueous species, 1000 minerals and 100 gases and

included reference thermodynamic data for acetic acid (Shock and Helgeson, 1990) and metal–acetate complexes (Shock and Koretsky, 1993) with data extrapolated to high temperature and pressure using the SUPCRT92 code (Johnson et al., 1992). Chemical thermodynamic speciation modeling suggested that the organic acids produced by these pyrolysis experiments will influence the solubility of alkaline earths, but have little impact on the solubility of aluminum species (Knauss et al., 1997).

In a similar study investigating the role of carboxylic acid complexes in the formation of MVT deposits (Giordano, 2002), the organic acids were determined to have a minor effect on metal transport compared to inorganic complexes.

6.3. Increasing the thermodynamic relevance of organic geochemical studies

The inclusion of organic characterisation data in thermodynamic models should provide a better understanding of the nature and role of the organics in ore system fluids. However, questions about the role of organic compounds in metal transport and deposition have not been fully addressed by the organic geochemical studies described in this review. The quantities of metal carried by ore fluids containing only inorganic metal species may be insufficient to account for the formation of base-metal deposits (Giordano and Barnes, 1981); therefore, some models for ore fluids invoke organic acids and other polar organic compounds as potential complexing agents (see review by Giordano, 1994 and cited research including Saxby, 1976). In other scenarios, metal–organic complexation makes minor contributions to metal transport (Giordano, 2002; Sicree and Barnes, 1996). The organic geochemical characterisation of ore systems is, by necessity, directed towards OM that can be sampled in and around modern systems. The OM that is found in proximity to the ore is hydrocarbon-rich with only a very small polar fraction (Rospondek et al., 1994), as would be expected from diagenetic or metagenetic conditions (Tissot and Welte, 1984), compared to the acid-rich organics likely to be within the ore fluid. The largely non-polar hydrocarbon component of sedimentary environments, while likely to be involved in depositional processes such as thermochemical sulfate reduction, is not a primary candidate for enhancing the transport of metals. Characterisation of the polar component of the bitumen would yield clues about the types of polar organic species involved in metal transport. Given the non-polar nature of GC analysis, other sensitive analytical techniques able to resolve the highly complex polar fractions of sedimentary OM will be required. Electrospray ionisation (ESI) is one such method. ESI coupled with high-resolution Fourier transform ion cyclotron resonance mass spectrometry has been shown to be a viable technique for detection of polar compounds, revealing trends in the compositions of nitrogen-, sulfur- and oxygen compounds in crude oils of differing maturity (Hughey et al., 2004). To our knowledge, a similar type of ESI based MS analysis has not been performed on bitumen sourced from ore deposits. A potential further application of ESI-MS related to ore metal transport is the characterisation of metal–organic ligand binding equilibria (Di Marco and Bombi, 2006).

In models for metal transport, the composition of organic species, particularly carboxylic acids, in ore fluids is often partially derived from analogous systems such as oil-field waters, and certain thermal and chemical features of fluid inclusions including CO₂, H₂O and even at times trace metal concentrations (Giordano and Barnes, 1981). The metal-carrying capacity of model ore fluids is then assessed using these compositional data combined with thermodynamic calculations (Giordano, 2002; Sicree and Barnes, 1996). The contributions by traditional analytical characterisation of present-day organics to these models can be augmented by increasing attention to 1) extraction and analysis of polar fractions; 2) solubility and complexation of metals in organic-rich fluids (Emsbo et al., 2010); and 3) maturation of organic

matter at hydrothermal (>150 °C; Simoneit et al., 1992) and even metamorphic conditions (George, 1992; Schwab et al., 2005) which for the lowest metamorphic grades can start at 200–300 °C (Brocks et al., 2003a) extending up to the ~550 °C (Schwab et al., 2005).

The calibration of molecular maturity parameters and isotopic effects at high temperatures (to at least 550 °C is possible; Schwab et al., 2005) would help to constrain conceptual and mathematical models for hydrothermally derived ore fluids and alteration of organic matter in deposits exposed to early stages of metamorphism. A better understanding of the role of organic species in mobilisation, transport and deposition of ore metals requires these types of observations as well as thermodynamic data (enthalpy, entropy, volume and heat capacity) for the organic and metal–organic species of interest. Carefully planned laboratory experiments can help provide individual thermodynamic values, such as the thermal and pressure treatment of metal species in aqueous environments to provide solubility and speciation data (e.g., Rempel et al., 2006).

7. Conclusions

The hydrocarbon compositional data provided by traditional organic geochemical procedures can help identify the origin of the major regional organic inputs as well as the subsurface operation of significant biogeochemical processes on the organic matter (OM). Antiquated biochemical signatures sequestered within sulfide and other minerals over long geological periods have also helped illuminate the evolution of organisms reflecting early life forms. The abundance and stable isotopic values of OM at bulk and compound specific levels, including even the organic components of mineral entrapped fluid inclusions (usually gases such as CO₂, H₂O and sometimes CH₄ and higher MW HCs), can also aid source and deposition reconstructions. The gas or fluid composition of FIs can provide important information about the character and pathways of hydrothermal fluids. Furthermore $\delta^{34}\text{S}$ analysis of sulfides is able to distinguish between thermochemical and bacterial reduction of sulfates – from which thermal ranges can also be inferred.

Organic geochemical data has also occasionally revealed information relating to the interaction of quantitatively significant organic and inorganic substances in mineral rich regions. Aside from the dedicated organic geochemical appraisal of several deposits including the HYC and Kupferschiefer deposits discussed here, studies of mineral associated OM have been underwhelming in the respects of both frequency and sophistication. The sporadic and often divergent information provided by organic geochemical studies of different mineral types and regions has not yet convincingly revealed the extent to which metal–organic complexes or other organic properties are crucial to ore genesis. Most previous reports describe the use of organics as records of conditions, with little that really relates to mobilisation, transport or deposition of metals. Questions remain about whether coexistences of organics and metals are simply the product of a common process or, at least in some cases, identifiable, unambiguous, causal mechanisms.

Effective integration of organic and inorganic systems knowledge is essential for a proper treatment of ore formation in the organic-rich environments which characterise many valuable mineral deposits. Thermodynamic modeling of ore deposits requires physical measurements – or estimates based on geological observations – of pressure, temperature, fluid composition, fluid source, fluid history, metal source, mechanisms of metal transportation and deposition and subsequent history. Classical organic geochemical characterisation of the OM in mineral settings need to be extended to include the measurement and interpretation of such data, which can then be integrated with organic data relevant to the nature, migration and interactions of hydrothermal fluids, the precipitation of metal rich inorganic substances and mineral accumulations. This should include targeted characterisation of the polar organic compounds thought to be important to the complexation and mobilization of

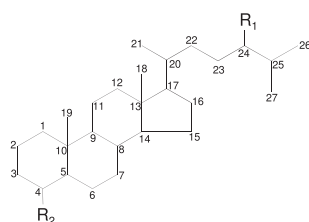
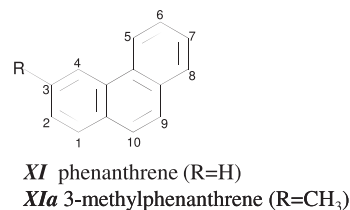
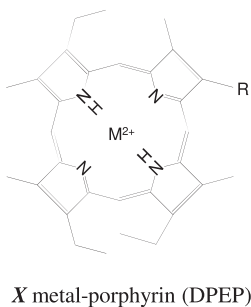
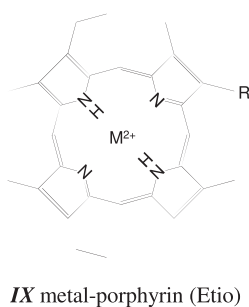
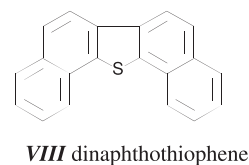
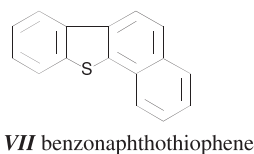
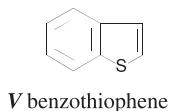
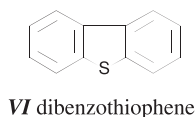
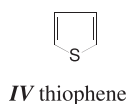
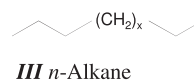
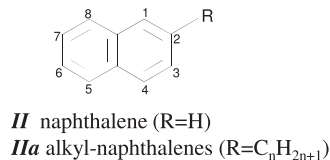
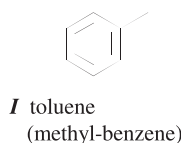
metal species analysis and identification of the metal species in organic-rich fluids; and the formation of metal–organic complexes and measurement of specific thermodynamic properties (e.g., solubility and complex/speciation data) which relate to metals in organic-rich fluids. Establishment of further relationships between molecular biomarkers and ancient microbial sources, via correlations with modern analogues, will also extend knowledge of the microbes active in mineralization processes.

Acknowledgements

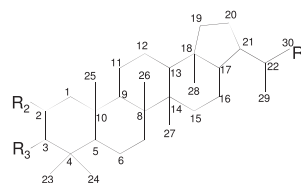
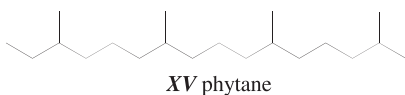
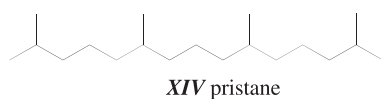
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Appendix A

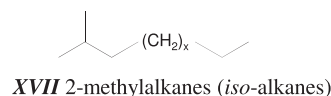
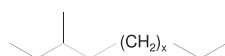
Molecular structures of common aliphatic and aromatic hydrocarbons detected in mineral deposits.

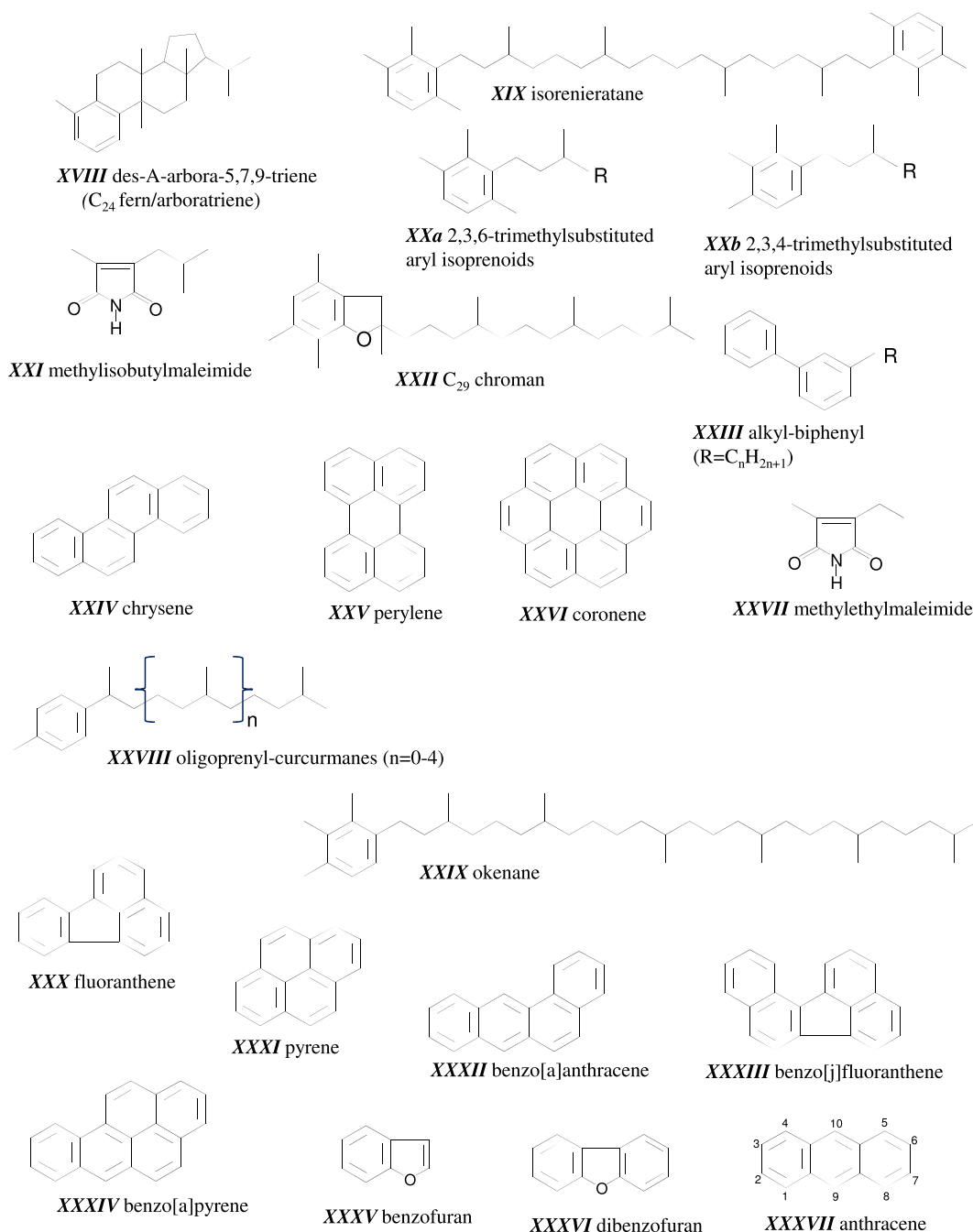


R₁ = H (cholestane, **XIIa**), CH₃, CH₂CH₃
(stigmastane, **XIIb**), C₃H₇ (**XIIc**)
R₂ = CH₃ for 4-methylsteranes (**XIId**)



- R₁ = C_nH_{2n+1}, n = 1–5 for C₃₁–C₃₅ homohopanes (**XIIIa**) with 22R and 22S diastereomers
- R₂ = CH₃ for the 2α-methylhopanes (**XIIIb**)
- R₃ = CH₃ for the 3β-methylhopanes (**XIIIc**)





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- Asphaltenes:** The fraction of oils or bitumen which is insoluble in non-polar organic solvents (e.g. *n*-pentane)
- Biomarker:** Molecular fossils of biological compounds such as membrane lipids and pigments. During sedimentary diagenesis the biomarkers commonly lose their chemical functional groups and turn into hydrocarbon skeletons - stable over hundreds of millions of years - that can often still be linked to a particular biosynthetic origin and may yield information about ancient microbial ecosystems and environmental conditions
- Bitumen:** Solvent extractable fraction of organic matter in sediments
- BSR:** Bacterial sulfate reduction (conducted by specific bacteria converting SO_4^{2-} into reduced and reactive sulphur species, including H_2S , HS^- , S^{2-})
- Catagenesis:** Temperature-pressure-time driven cracking process that results in the conversion of organic kerogen into bitumen
- CPI:** Carbon Preference Index, the predominance of even carbon-numbered or odd carbon-numbered molecules. A typical example is plant waxes that have strongly elevated concentrations of *n*-alkanes with 29, 31, and 33 carbon atoms over those with 28, 30 and 32
- CSIA:** Compound specific isotope analysis
- $\delta^{13}\text{C}$ (‰): Stable carbon isotope value = $[(\text{R sample})/(\text{R standard}) - 1] \times 1000$ where $\text{R} = {}^{13}\text{C}/{}^{12}\text{C}$ (‰ units = per mill)
- δD (‰): Stable hydrogen isotope value = $[(\text{R sample})/(\text{R standard}) - 1] \times 1000$ where $\text{R} = \text{D}/\text{H}$ (‰ units = per mill)
- Diagenesis:** initial change (chemical, physical or biological) to OM after its initial deposition and prior to exposures of relatively high temperatures and pressures
- EA:** Elemental analysis
- EDTA:** Ethylenediaminetetraacetic acid; used to dissolve carbonate and release sequestered FIs.
- ESI:** Electrospray Ionisation
- FI:** Fluid Inclusion
- GC–MS:** Gas chromatography coupled to mass spectrometry
- HI:** Hydrogen Index (Rock-Eval pyrolysis parameter), indicating hydrogen content of OM normalised to carbon
- HYC:** “Here’s Your Chance” Pb–Zn–Ag Mine (Paleoproterozoic Barney Creek Formation, McArthur Basin, Australia).
- ICP–MS:** Inductively coupled plasma mass spectrometry
- irMS:** Isotope ratio mass spectrometry
- Kerogen:** Fraction of primary organic matter in sediments that can not be extracted using organic solvents
- Kupferschiefer:** Transition metal-rich Late Permian Kupferschiefer Formation (Germany–Poland) or Marl Slate (U.K.)
- MPI-1:** Methyl (M) phenanthrene (P) index $1 = 1.5 \times (3\text{MP} + 2\text{MP}) / (\text{P} + 1\text{MP} + 9\text{MP})$
- MVT:** Mississippi Valley Type
- MW:** Molecular weight
- OM:** Organic matter
- OSC:** Organic sulphur compounds
- PGE:** Platinum Group Elements (platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), osmium (Os), and ruthenium, (Ru) often occurring in the same deposits
- Pristane (Pr):** C_{19} regularly branched isoprenoid
- Phytane (Ph):** C_{20} regularly branched isoprenoid
- Porphyry:** Diagenetic product of chlorophyll found in kerogen and bitumen. N-bearing aromatic heterocycle
- Pyrobitumen:** Solid hydrocarbon mineraloid formed by thermal maturation of petroleum
- R-E:** Rock Eval pyrolysis
- REE:** Rare earth elements – 15 consecutive elements of the periodic table starting with lanthanum (La), plus the elements yttrium (Y) and scandium (Sc), which have similar properties and occur in the same mineral deposits
- SOB:** Sulfide-oxidising bacteria – group of bacteria involved in the oxidation of sulfides
- SRB:** Sulfate reducing bacteria utilizing SO_4^{2-} as a electron acceptor and release reduced sulfur species such as sulfides
- T_{max} :** Rock-Eval parameter – temperature of maximum pyrolyzate yield, indicator of thermal maturity
- TOC:** Total organic carbon content
- TSR:** Thermochemical sulfate reduction
- Vitrinite Reflectance (R_o):** Petrographic indicator of the thermal maturity of kerogen in sedimentary rocks; the reflectivity of >30 individual grains of vitrinite measured under a microscope, given in units of reflectance, % R_o

Glossary

Aliphatic Hydrocarbons: Compounds composed of H and C exclusively (hydrocarbons) that may be cyclic or acyclic and contain double bonds but not an aromatic ring

Aromatic Hydrocarbons: Hydrocarbons with conjugated (alternating double and single) bonds between carbon atoms forming rings. The simplest aromatic hydrocarbon is benzene. Aromatic hydrocarbons also known as arene or aryl hydrocarbons