CHAPTER 2

HYDROTHERMAL SYSTEMS: THEIR VARIETIES, DYNAMICS, AND SUITABILITY FOR PREBIOTIC CHEMISTRY

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William Fyfe (1978) once remarked that the dominant cooling process of the Earth involves convective circulation of cold seawater. He added that it could hardly be otherwise when magmas are introduced at 1200°C under a thin layer of their own volcanic cover - the oceanic basalts. Convecting water acts as a cooling fluid, carrying thermal energy away from the hot areas of the Earth's crust toward the relatively cold surface. Convective processes dramatically increase the transfer of heat in the Earth's crust towards the surface in comparison with purely diffusive processes. Fluid movement occurs at relatively high velocities within the solid crustal matrix, and the more heat there is to be transferred the faster and more intense circulation has to be. Hydrothermal circulation is likely to have been more intense in the distant past of Earth's history. Probably the best argument for this assumption is that the total heat production of the Earth, based on concentrations of heat-producing radioactive elements, had to be much higher in the Hadean and the Archean than it is at present (see Chapter 1, Table I for the ages of the Earth). For example, assuming the Earth at steady state, the current radioactive heat production for the bulk of the planet corresponds to approximately one half of the observed heat flux (McKenzie and Richter, 1981). In the Hadean and the Archean, heat production by radioactive elements would have been more than 4 times higher (extrapolation based on present concentrations and radioactive decay rates), and therefore the heat flux must have been significantly higher (Davies, 1980; O'Connell and Hager, 1980) and the associated hydrothermal circulation more intense. In addition, other sources may also have contributed significantly to heat production on the early Earth. Among these are accretional energy resulting from planetesimal and meteoritic fragment impacts, and differentiation energy resulting from exothermic chemical reactions, partitioning and fractionation in the interior of the planet (Jeanloz and Morris, 1986). The discovery of Archean komatiites (Viljoen and Viljoen, 1969) is in agreement with a hotter Earth's upper mantle and lower crust, but the existence of high pressure mineral assemblages in Archean metamorphic rocks (Boak and Dymek, 1982) also indicates that horizontal variations of temperature existed in the Archean crust and that temperature anomalies in the mantle

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might have been higher than today (Jeanloz and Morris, 1986). The global tectonic style of the Archean Earth was probably much different than that observed today. Several models have been proposed, some including a large amount of scattered hotspots (Fyfe, 1978), numerous micro-plates (van Andel, 1985), larger plates subjected to modern plate motion and tectonics (Card, 1990), etc. However, the types of hydrothermal environments in the crust of the Archean Earth must have been quite similar to the ones observed today since the cooling processes were roughly identical (circulation of aqueous fluid in a solid matrix), the big difference being that more hydrothermal activity probably occurred globally, and that the proportions of the different types of environments varied. In this chapter we will discuss briefly the dynamic chemical and physical processes occurring in crustal hydrothermal systems, and the different types of contemporary submarine hydrothermal systems, comparing whenever possible with evidence of fossil ancient systems.

1. Dynamic Processes in Hydrothermal Systems

The primary role of submarine hydrothermal systems can be seen as to allow a smooth transition between masses at different temperatures (molten magma at more than 1000°C and seawater at approximately 0°C). This heat dissipating system works by circulating an aqueous fluid rapidly through fracture and pore pathways within the crustal rock matrix, transporting heat from the hot areas towards the colder ocean water. Recharge by seawater provides the bulk of the cooling mass in motion, and permeable oceanic crust provides the solid matrix supporting and directing the flow of the cooling fluid. The result is complex temperature and flow distributions within the oceanic crust and the existence of sharp physical gradients.

Fluids are released from magmatic intrusions as the crust cools down. Among the components released are H_2O, H_2S, HCl, HF, CO_2, CH_4, SO_2, and H_2 (Burnham, 1979). The release of these volatile components acts as an additional physical force for hydrothermal convection; it might also play a role in the fracturing of the crustal rock above the intrusion producing preferential transport pathways for the cooling fluid (Brimhall and Crerar, 1987). The magmatic components released combine by mixing with the circulating fluids, therefore changing their chemical composition along the flow paths. Water/rock interaction takes place and results in additional chemical variation along the paths. Associated with fluid mixing and water/rock interaction are variations of pH, ionic strength, and redox potentials (see Chapter 5). Therefore, in addition to sharp and complex physical gradients there are no less sharp and complex chemical gradients. Other parameters can influence chemistry independently of temperature or flow patterns (degassing, mixing, mineral precipitation or dissolution, etc.).

Mineral and rock composition gradients also exist along the flow paths. Freshly fractured rock surfaces and recrystallized rock material is found where magmatic melt has been injected. Different mineral assemblages represent different equilibrium conditions along the fluid circulation paths. The pH conditions can be buffered by silicate mineral assemblages (for instance, K-feldspar/muscovite/quartz), and oxygen fugacity (redox conditions) can be buffered by the assemblage pyrite/ pyrrhotite/magnetite in presence of sulfur species, or by magnetite/hematite when no sulfur is present (see Chapter 5). Mineral precipitation or dissolution can occur everywhere in the hydrothermal system in response to chemical disequilibrium. Chemical disequilibrium at a given location in the oceanic crust can be the result of fluid mixing, degassing, change in redox conditions or pH, cooling, high velocity fluid movements, etc.

The pressure and temperature gradients existing in hydrothermal systems have a dramatic effect on the properties of water. This is perhaps best illustrated in Figs. 1 and 2 (for discussion see Brimhall and Crerar, 1987). Fig. 1 illustrates the degree of variation of selected physical properties of water (thermal expansion, compressibility, heat capacity, and viscosity) as a function of temperature. Fig. 2 shows the variation of the dielectric constant of water versus temperature. A decrease of one order of magnitude in the dielectric constant of water between 0 and 374°C (critical temperature of water) can be simply interpreted as meaning that water is a good solvent for charged ions at low temperature and a poor solvent at high temperature. This implies that aqueous chemistry at high temperature is quite different than usually thought; for example, water at 200°C would be expected to have solvation properties more similar to methanol or nitrobenzene than to water at room temperature. This is, however, an over-simplification. It does not take into consideration the changes in chemical speciation of dissolved compounds. It also ignores the effects of higher pressure, which will tend to force the dielectric constant of water towards higher values. Furthermore, high temperature and pressure conditions affect other factors that control the chemical behavior of water and any dissolved molecules (molecular vibration, ligand field stabilization, electron spin-pairing, etc.). For more detailed discussion compare with, for example, Helgeson and coworkers (1981), Brimhall and Crerar (1987) and references listed therein. For our purpose it is important to consider that gradients in the physical and chemical properties exist for water and any dissolved chemical species circulating in hydrothermal systems, and that the changes of these properties under the extreme conditions found in the Earth's crust can be dramatic and are very often ignored in the study of chemical evolution and the origin of life.

Depending on the dimension scale considered for hydrothermal activity, hydrothermal processes appear to be active for periods of millions of years (100 km scale ridge segments), thousands of years (100 m scale hydrothermal vent fields), years (individual hydrothermal chimneys or seeps), days (episodic formation of large hydrothermal plumes), or even minutes (violent hydrothermal discharges). Considering the range of velocities at which the circulating fluids travel through the different parts of an hydrothermal system (m/s where venting, cm/yr or less where recharging), one has to take into account periods of time ranging from seconds to years for studying chemical and physical processes involving contact between mobile and immobile phases. Depending on the time scale considered, a chemical or physical reaction might not have enough time to be carried out to

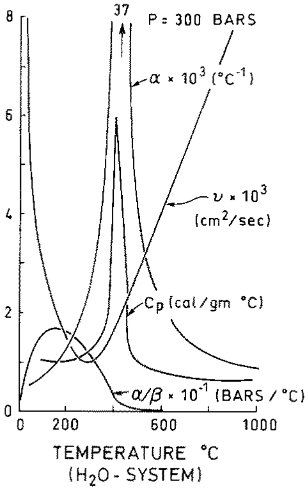

Fig. 1. Physical properties of pure water at 300 bar versus temperature; y-axis gives values in units shown adjacent to each curve in figure. The symbols α, β, Cp, and ν refer to coefficients of thermal expansion and compressibility, heat capacity and viscosity, respectively. From Norton (1984). Reproduced, with permission, from the Annual Review of Earth and Planetary Sciences Vol. 12. Copyright 1984 by Annual Reviews Inc.

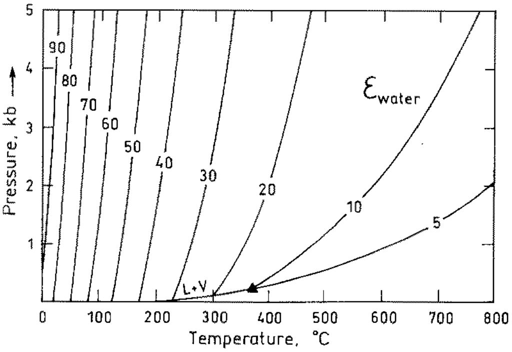

Fig. 2. The dielectric constant of water as a function of temperature and pressure. The triangular spot marks the critical point of water. From Brimhall and Crerar (1987). Copyright 1987 by the Mineralogical Society of America.

completion or equilibrium in hydrothermal systems. This implies that slow chemical and physical processes are expected to take place mostly out of equilibrium, moderately fast chemical and physical processes might only be able to reach equilibrium in some parts of the system, depending on fluid velocity and temperature conditions, and that only very fast chemical and physical reactions are expected to be carried to completion everywhere. The definition of fast and slow reactions varies depending on where a reaction is considered to take place. Thousands of years are available for reactions to approach equilibrium in the recharge zone, whereas minutes or seconds only may be available in a hydrothermal vent. The importance of the kinetics of reaction for chemical and physical processes cannot be overemphasized. In submarine hydrothermal systems a large range of chemical and physical reactions will never have the opportunity to approach equilibrium.

Fluids in submarine hydrothermal systems circulate through pores and fractures in the oceanic crust and its overlying sediments. The entire system can be considered as saturated with water with the exception of localized zones where degassing, boiling, or non-aqueous phases might exist (for example, supercritical CO_2). The porosity (defined as the part of the crustal rock matrix which can be occupied by a fluid, expressed in volume percent) of fresh unaltered oceanic crust is in the order of 10 percent (Davis, 1969; Johnson and Morris, 1962). Chemical and physical hydrothermal alteration, including mineral dissolution and fracture development, can increase porosity to more than 30 or 40 percent, depending on the intensity of the alteration processes. Sediments deposited on the oceanic crust have porosities from as high as 80 percent prior to being compacted through diagenesis, to porosity values of 30 to 50 percent deeper in the sedimentary column. A porosity gradient is therefore in place, and porosity increases towards the surface and within the most hydrothermally altered zones. Therefore, in submarine environments, large amounts of aqueous fluids are integral parts of the oceanic crust and sediments, and exchanges between fluid and solid phases can take place virtually everywhere. The sizes of pore and fracture features can vary by several orders of magnitude, from micrometer-size (interstitial spaces) to meter-size (large open fractures, for example).

For fluids to flow through a block of rock or sediments, pores and fractures have to be opened and connected enough to permit fluid circulation. Tectonic and thermal stresses, which are characteristics of hydrothermal systems, enhance connected porosity through fracturing and weathering of portions of the oceanic crust. Therefore permeability (defined as the ease with which fluids can move through a solid matrix) of the crust can be locally very large, for example, within the most hydrothermally altered and fractured zones connecting deep areas of the hydrothermal system to the seafloor. Away from zones where fluid circulation is facilitated by the presence of open fractures and hydrothermal weathering, anomalies in the temperature distributions are much less pronounced. Slight negative temperature anomalies occur, however, in the areas of the crust where recharge by cooling fluids takes place, and slight positive temperature anomalies occur where returning cooling fluids migrate towards the seafloor (Fig. 3). The main rea-

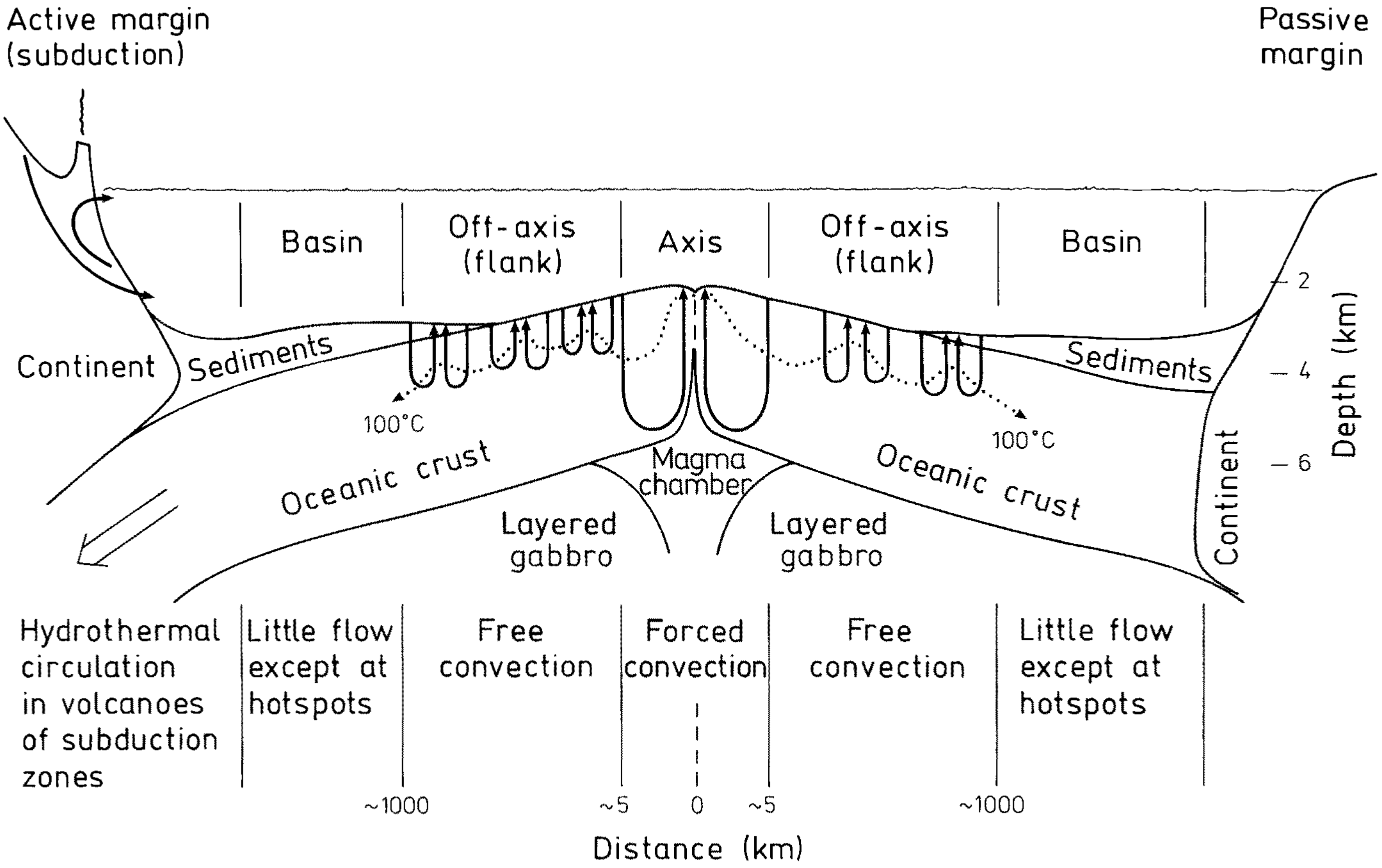

Fig. 3. Cartoon of diverging oceanic plates showing the spreading-center with a sediment-free on-axis hydrothermal system. Some off-axis hydrothermal systems in flank position to the spreading-axis are illustrated, with negative temperature anomalies where the fluids are recharged and positive anomalies where the hydrothermal fluids migrate towards the seafloor. Also included in the picture are both a passive continental margin and an active margin where the oceanic plate is subducted underneath a continent and volcanoes with hydrothermal circulation are formed.

son for the small size of the temperature anomalies away from the center of hydrothermal activity can be explained by a different transport process being dominant. In this case, fluid transport is dominated by the permeability of the porous media, the circulating fluids tend to be dispersed in the solid matrix, rather than channelled in fractures and weathered zones, and the velocity of fluid migration is slower. The interaction between the solid crustal matrix and the fluids is high, and the rate of heat diffusion is significant relative to the rate of circulating fluid migration. Some significant effects associated with fluid transport in porous media (relative to fluid transport in fractured media) are: first, the time available for any chemical reactions to proceed is much longer; second, the amount of interaction between the solid phase and the fluid phase is much more intense; and third, the volume of crust affected by fluid circulation is much larger. It is important to keep in mind that the two fluid flow systems described (fracture flow versus porous flow media) are not separated in the real oceanic crust, but are interconnected. An area dominated by one type of flow regime can be transformed, with time, into a system characterized by the other type of flow regime, with every combination in between.

During transport, the circulating aqueous fluid carries dissolved chemicals and gases within the intricate flow paths of the oceanic crust mineral matrix. Chemical reactions are expected to occur within the circulating fluid (see Chapters 4, 5 and 6), and because of transport, phases with different specific chemistry are juxtaposed and can interact along the flow paths. This results in the possibility for chemical mass transfer between phases to occur. Mass transfer can occur through diffusion, dissolution, precipitation, or volatilization processes. In addition, surface sorption processes can lead to the accumulation of selected chemical species onto the surface of minerals by preferential stripping of chemicals having an affinity for these specific surfaces (cf. Hochella and White, 1990; Holm *et al.*, 1992). This mechanism can lead to relatively high localized concentrations of chemicals which would not be otherwise expected to be found at such levels in the oceanic crust.

The above discussion is only meant to introduce the concept of dynamic processes into the mind of the reader. Dynamic phenomena of potential importance for our understanding of the origin of life on Earth are numerous, among the ones not mentioned in the discussion above are: the formation of fluid inclusions; the formation and transport of colloid-size particulates; the dynamics of chemical exchange and partitioning between the aqueous phase and non-aqueous fluid phases such as supercritical carbon dioxide; and the dynamics of selective chemical stripping in the structure of clay minerals.

2. Classification of Marine Hydrothermal Systems

On the present Earth most of the new oceanic crust is created by basalt production at ocean ridge spreading centers (Fig. 3). Basalt is also produced at oceanic hotspots. Ridge basalts are estimated to make up about 99% of new crust formation (Burke and Wilson, 1976). In both types of geological setting we will, however, expect hydrothermal circulation to exist. Geologists classify hydrothermal systems according to their tectonic setting. Thus, in the marine environment six general classes of hydrothermal systems can be distinguished (cf. Figs. 3 and 4):

1. Sediment-'starved' or sediment-free on-axis systems on plate tectonic spreading centers (mid-ocean ridges).
2. Sediment-covered on-axis systems on plate tectonic spreading centers.
3. Off-axis systems on the flanks of spreading centers and into the ocean basins.
4. Systems associated with backarc basins and backarc spreading centers.
5. Systems at hotspots.
6. Systems associated with subduction zones.

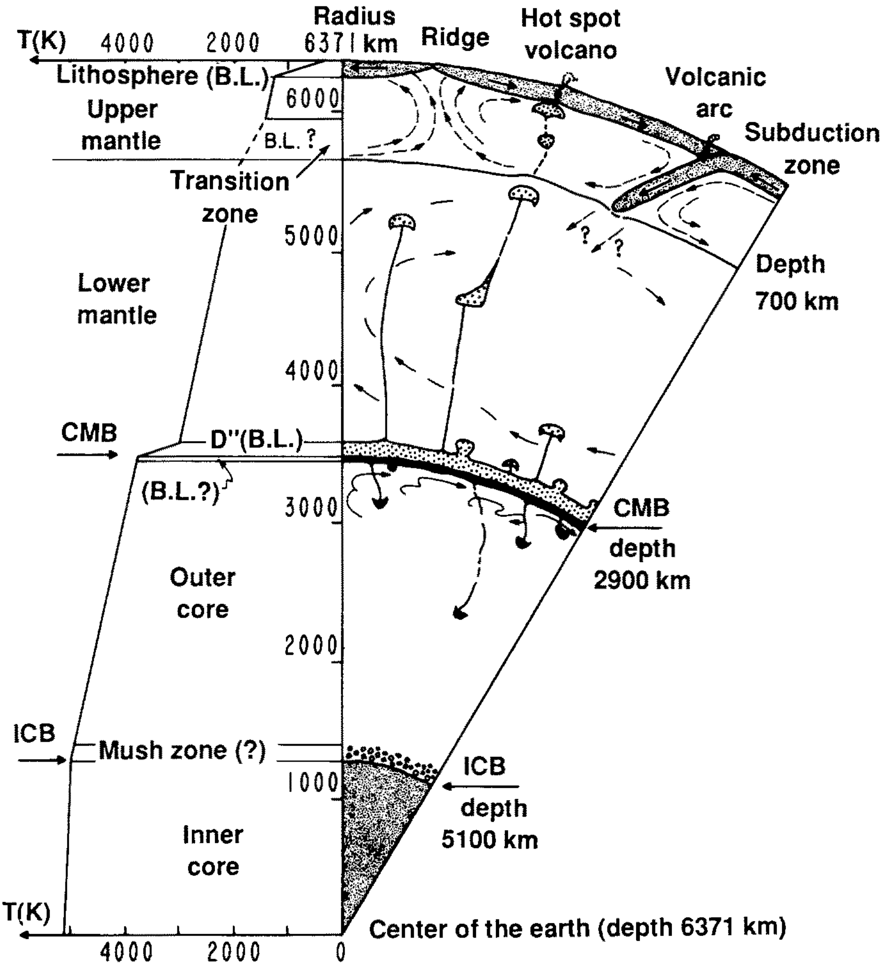

Fig. 4. Schematic diagram of core-mantle coupling. Heat from the outer core thickens the lowermost layer of the mantle. Eventually this layer breaks up into huge, rising plumes leading to hot-spot volcanism. Abbreviations: CMB, core-mantle boundary; ICB, inner-outer core boundary; B.L., boundary layer. From Courtillot and Besse (1987). Copyright 1987 by AAAS.

In addition to the marine systems there also exist continental hydrothermal systems (see below).

During the Second Conference on Scientific Ocean Drilling in Strasbourg in 1987 the different components of fluid circulation in the Earth's crust were thoroughly evaluated (COSOD II Report, 1987). The main contributors to the hydrodynamic flux through the crust appear to be: a) hydrothermal flow at spreading centers and their flanks (points 1, 2 and 3 above), b) upward flow of pore water at active margins due to sediment compaction and other diagenetic processes during subduction, and c) hydrologic flow from continents at passive and active margins (Fig. 3). Hydrothermal activity at subduction zones is probably a minor contributor to the total hydrodynamic flux and should not be confused with the expulsion of cold pore water to the deep sea due to tectonic compaction of subducted sediments.

3. Sediment-Free On-Axis Systems at Spreading Centers

Since the major portion of oceanic basalts is formed at plate tectonic spreading axes, it is not surprising that most hydrothermal systems today are found along the mid-ocean ridges (Fig. 5). Features that most people probably come to think of when the term 'hydrothermal system' is used were first studied on the East Pacific Rise at 21°N (Spiess *et al.*, 1980). This vent field is a typical example of sediment-free on-axis hydrothermal systems at the spreading centers with the black and white 'smokers' and water that is injected into the deep-sea at temperatures of about 350°C. The hydrothermal activity is driven by 'forced convection' due to steep temperature gradients in the crust surrounding the ridge axis (Fig. 3). They were at first believed to exist only in conjunction with fast- and intermediate-spreading ridges (6-12 cm/yr), mainly in the Pacific Ocean. However, such systems have now been found along both the fast- and intermediate- as well as the slow-spreading ridges. They extend all the way from the Pacific through the Indian Ocean into the Atlantic and, most likely, the Arctic Ocean (Campbell *et al.*, 1988). The COSOD II Report (1987) estimated the flow of hydrothermal water at an average temperature of 350°C through on-axis systems to 24 km^3/yr. The time estimated to cool an on-axis hydrothermal system ranges between 10^2 and 10^4 years (Fehn and Cathles, 1986). By definition the spreading centers are very young; the newly formed rock is often referred to as 'zero-age' crust. Therefore, in open settings, normally no sediment cover exists around the vents. The geochemistry and the dynamics of the hydrothermal waters will differ from the fluids of sediment-covered systems in several ways, the two major ones being that pH will stay at a low level (pH 3-4, protons are primarily released to solution through deposition of Mg compounds, cf. Von Damm *et al.*, 1985; Fouquet *et al.*, 1991) and that smooth temperature gradients above the hydrothermal system are less common (often a sudden quenching of 350°C water of their vents to the ambient temperature of about 2°C).

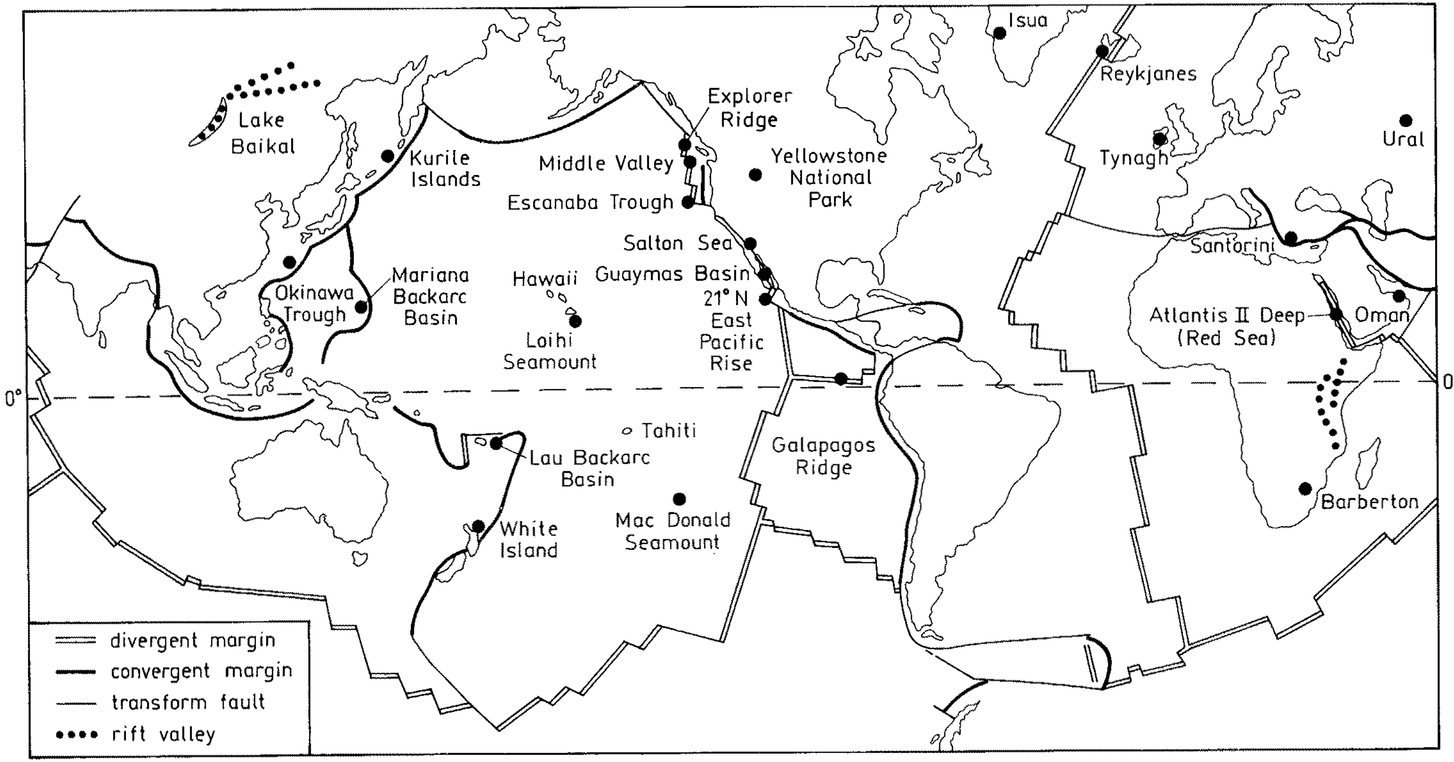

Fig. 5. Outline map of the major plate tectonic boundaries of the Earth and locations mentioned in the text.

4. Sediment-Covered On-Axis Systems at Spreading Centers

Only when spreading zones approach continents may the on-axis type of hydrothermal system be sediment-covered (Fig. 6). Such settings exist, for instance, in the Red Sea (Degens and Ross, 1969), which represents an early stage of opening of an ocean basin, and in the Guaymas Basin of the Gulf of California (Lonsdale *et al.*, 1980), where the East Pacific Rise starts a set of 'transform faults' through western Mexico and southern California. Sediment-covered hydrothermal systems also exist in the NE Pacific Ocean where the extensions of the East Pacific Rise, i.e. the Gorda, Juan de Fuca and Explorer Ridges, run close to the NW parts of the North American continent. Accordingly there exist on the Gorda and Juan de Fuca Ridges the sedimented Escanaba Trough and Middle Valley, respectively (SRDPG, 1990). The Guaymas Basin, as an example, is covered by about 400 m of diatomaceous mud and terrigenous plagioclase-rich sediments (Curray *et al.*, 1979, 1982; Einsele *et al.*, 1980). Conductive heat flow results in hydrothermal circulation and extensive thermal alteration of both organic (2% org. C) and mineral matter (Simoneit, 1983, 1984). Compared with sediment-free on-axis hydrothermal systems the sediment-covered ones may have much more extended thermal gradients, higher pH (about pH 6; Simoneit, 1984) due to buffering by sedimentary $CaCO_3$ (8%) particles and, of course, contain a much more diverse array of potential catalysts for abiotic organic reactions in the form of mineral matter. Since sediment-covered on-axis hydrothermal systems are situated relatively close to continents they are severely 'contaminated' by both terrigenous and autochthonous organic matter (due to rich nutrient supply) of biological origin. Thermal alteration of the biogenic matter leads to formation of petroleum compounds. This has, of course, little to do with abiotic synthesis. However, an understanding of the chemical behaviour of organic compounds in such systems will provide clues for possible abiotic reactions.

5. Off-Axis Systems at Spreading Centers

Off-axis hydrothermal systems in the spreading ridge flanks have maximum temperatures of about 200°C and are driven by 'free convection' due to cooling of the oceanic crust (Fehn, 1986, Fehn and Cathles, 1986, COSOD II Report, 1987). This zone continues between a few kilometers and as much as 1000 km away from the ridge axis (Fig. 3) with a hydrothermal activity that remains over long periods ($>10^5$ years, Fehn, 1986). Free convection cells may under special circumstances migrate laterally through the oceanic crust as separate entities but will mainly move with the plates as if attached. Because the oceanic crust increases in age at a regular rate away from the spreading axis, the sedimentary cover will have accumulated pelagic sediments in direct proportion to the distance from the ridge and in inverse proportion to the spreading-rate. Thus off-axis systems will always be more or less covered by sediments and share the properties of smooth thermal gradients and the presence of an abundance of mineral catalysts with the sedimented on-

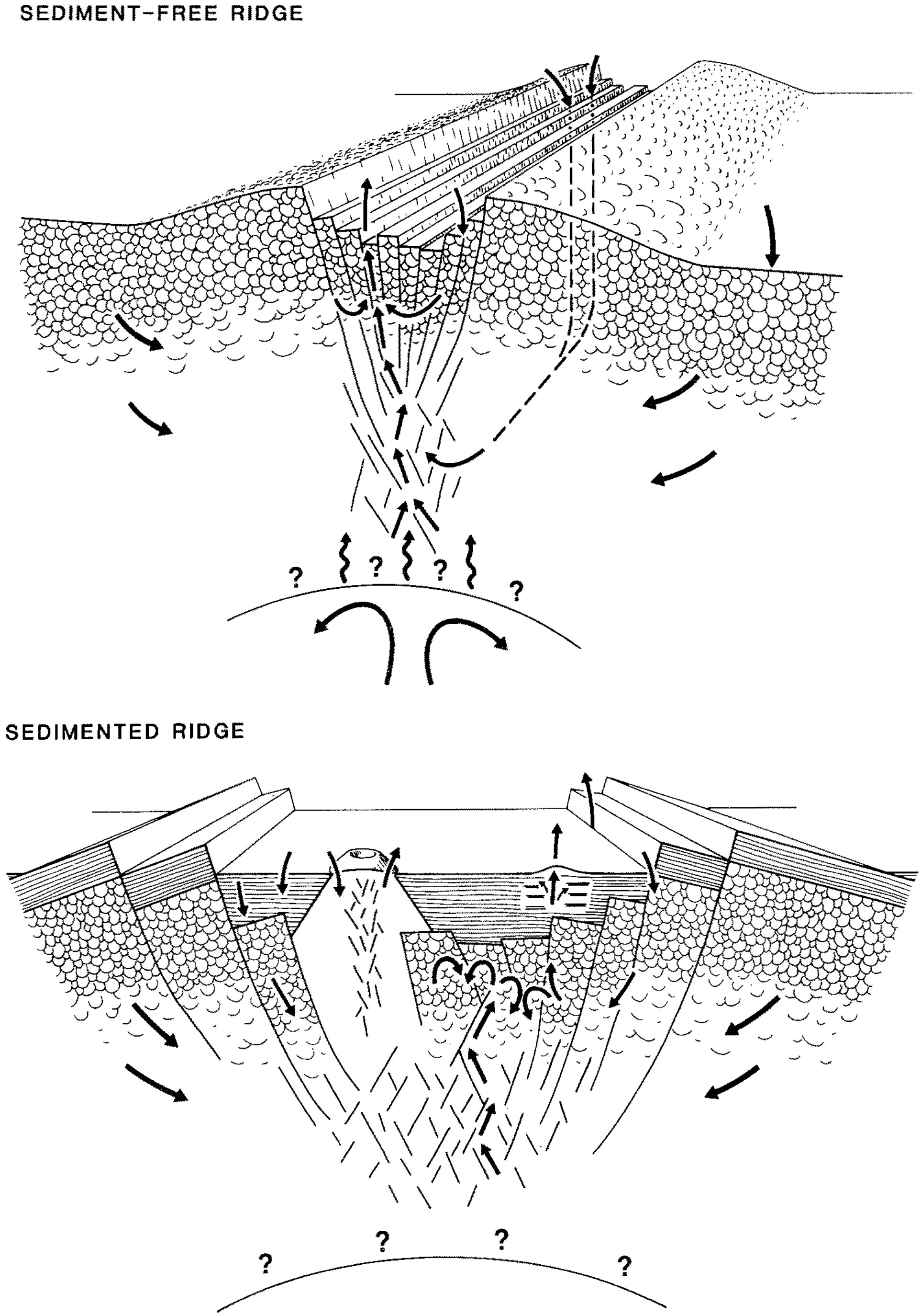

Fig. 6. Schematic illustrations of hydrothermal circulation at sediment-free and sedimented ridges. From COSOD II Report (1987).

axis systems. In general the contamination by biogenic matter is likely to be much lower in the pelagic sediments of deep-sea off-axis hydrothermal systems. Few survey efforts have been directed towards off-axis hydrothermal systems. Fehn (1986), however, reported that the frequency of some hydrothermal low-temperature fields south of the Galapagos spreading center and the distances between them correspond to model calculations of off-axis hydrothermal systems. In its long term plans the Ocean Drilling Program (ODP) recommends a cross-axis flank site array on the East Pacific Rise (EPRDPG, 1991) in order to study off-axis circulation. The volume of water at an average temperature of 150°C that circulates through off-axis systems was estimated by the COSOD II Report (1987) to be more than twenty times greater (560 km^3/yr) than the volume that is circulated through the hot on-axis vents (24 km^3/yr). Sea-floor convection involves large areas of diffuse input of fluids, especially at the off-axis type, and small areas of intense discharge. Fyfe (1978) thus remarked that there is more chance of local chemical equilibrium along paths of input and disequilibrium during discharge. This may have important consequences for the dynamics of both the inorganic and organic geochemistry of hydrothermal systems.

6. Systems Associated with Backarc Basins and Backarc Spreading Centers

Hydrothermal systems associated with backarc basins and backarc spreading centers were not discovered until quite recently. This type of fluid circulation in the Earth's crust was thus never included in the calculations of the COSOD II Report (1987). The type of geological setting is, however, from studies of the Kuroko type of sulfide ores deposits, known to be associated with (reducing) hydrothermal activity. Horibe and coworkers (1986) reported the occurrence of giant plumes of hydrothermal methane-enriched water at 3000 m depth at the Mariana backarc spreading center in the western Pacific Ocean. The great rise height (600-700 m above the sea floor) of the Mariana plume was interpreted to be due to higher effluent temperature, perhaps more than 400°C, than those of mid-ocean spreading centers. Sakai and coworkers (1990) studied hydrothermal chimneys and mounds by submersible at 1300-1500 m depth in the Okinawa backarc basin south of Japan. The highest temperature measured in the vent fields was 320°C. One of their most spectacular findings was the observation of the release of bubbles of liquid CO_2 from the sea floor of active hydrothermal sites and the formation of CO_2 hydrates. The approximate composition of the bubbles was 86% CO_2, 3% H_2S and 11% residual gas, mostly CH_4 and H_2. The isotope ratios of C and S, as well as the He, indicate that the CO_2-rich fluid has a magmatic origin. Fouquet and coworkers (1991) recently reported the occurrence of hydrothermal fields at the spreading center of the Lau backarc basin west of the Tonga Islands in the Pacific Ocean. The main divergences from the hydrothermal fluids of mid-ocean ridges are the acidity (pH 2) and the high temperature (400°C) of the Lau hydrothermal solutions. Increased temperatures in the bottom water are registered several meters away from the vents, something which is not observed with the on-axis hydrothermal systems. Some of the transition elements, such as Mn, Zn and Cd, are also much more abundant in the Lau systems.

7. Hydrothermal Systems at Hotspots

It was mentioned in the beginning of this chapter that ridge basalts make up about 99% of the crust of the modern ocean floor. The remaining percent originates from hotspot basalt production. Hotspots are believed to have their roots deep in the Earth's mantle, maybe in the core-mantle boundary (Fig. 4) (cf. Courtillot, 1990). The magma that forms ridge basalts, on the other hand, is believed to circulate almost entirely in the upper mantle. Some hotspots, like the one heating the Yellowstone National Park, are situated underneath continents. Others, like Iceland and the Axial Volcano of the Juan de Fuca Ridge (Massoth *et al.*, 1989), are integral components of the mid-ocean ridge system. In the Pacific Ocean, as an example, there are three known active hotpots at intraplate positions (Karl *et al.*, 1989). Those are the Loihi Seamount south of the Hawaiian Island group, the Macdonald Seamount of the Austral Island chain and the Mehetia volcano group near Tahiti. Hydrothermal activity has thus far only been observed at low-temperature vents (30°C) of the Loihi Seamount (Karl *et al.*, 1988, 1989), although its existence is postulated at other hotspots as well. Analysis data of the hydrothermal fluids that were sampled from the Loihi vents have been compared with data of other low-temperature vent fields (Karl *et al.*, 1989), such as those of the Galapagos Rift spreading center (Edmond *et al.*, 1979) and the Juan De Fuca Axial Volcano hotspot (Chase *et al.*, 1985). Compared to the the other low-temperature vents the Loihi hotspot systems are especially rich in CO_2 (300 mM) and Fe (1 mM), but the concentrations of NH_4^+ (5.2 μM), PO_4^{3-} (3.5 μM) and CH_4 (7.3 μM) are also elevated. The measured pH was about 5.5.

8. Systems Associated with Subduction Zones

Compared to the marine hydrothermal activity at mid-ocean ridges, backarc spreading centers and hotspots, the circulation and geothermal heating of sea water through the lithosphere at subduction zones is probably of minor importance (Fig. 3). Some well documented systems do exist in the literature, like, for instance, the Santorini caldera in Greece (cf. Holm, 1987) and the systems at the volcanoes of the Kurile Islands off the Pacific Coast of Asian Russia (Mukhin, 1974). For the purpose of studying abiotic organic processes and chemical evolution the subduction zone hydrothermal systems would probably be less suitable than most others because of biotic contamination due to the occurrence of much more organic material. An advantage, on the other hand, would be that they often are easily accessible and require relatively less sophisticated technical equipment.

9. Continental Hydrothermal Systems

Continental hydrothermal systems could be defined by different sets of criteria in addition to their position on continents. Hydrothermal activity in association with continental hotspots was mentioned earlier, but such activity does occur in other geological settings as well. In Chapter 1 the hydrothermal systems of the East African Great Rift Valley was described as a dormant part of the global rift suture system. Tiercelin and coworkers (1989) reported the occurrence of hydrocarbons associated with hydrothermal systems of Lake Tanganyika in the East African Rift. The hydrothermal activity that exists at depth of the Lake Baikal in Siberia, on the other hand, is a result of the opening up of a rift due to the collision between India and the Eurasian continent (Ballard, 1983). The hydrothermal fields of the Salton Sea area in southern California are localized on a transform fault of the spreading center between the Pacific Plate and the North American Plate, but must still be regarded as continental systems. Also the type of activity that occurs intimately associated with subduction in, for instance, southern Europe and New Zealand may be labelled as 'continental' in character. One way of distinguishing the continental systems from the marine ones would be the type of associated petrology. Continental systems are normally characterized by andesitic ('acidic') volcanism, although they may share this criterion with marine systems of the subduction zone type and even some marine hotspots. Several hydrothermal systems on the Icelandic hotspot, for example, occur in relatively andesitic terrain (e.g. Landmannalaugar). Another criterion that could be used is the type of water that circulates through the lithosphere. Continental systems are normally fed by meteoric water, but, again, most hydrothermal areas of Iceland except for those of the Reykjanes Peninsula, are percolated by meteoric water. This criterion would, on the other hand, classify the hydrothermal aquifer of the White Island Volcano off the northern coast of New Zealand as marine even though the volcanism is andesitic and the saline water is isolated from exchange with ocean water. Nisbet (1989) favored continental subaerial hydrothermal systems as likely sites for the origin of life because of their claimed moderate temperatures and fluctuating pH, which is often even mildly alkaline. For chemical evolution purposes it is not clear, however, that there is an advantage in modelling continental hydrothermal systems instead of marine ones. This has yet to be settled. One of the main tasks of this special volume is to inspire the pursuit of such research.

10. Fossil Evidence of Hydrothermal Activity

Fossil evidence of hydrothermal activity through Earth's history is widespread in the sense that hydrothermally altered rocks are common in the geological record. Distinct hydrothermal cells, on the other hand, are perhaps not as easily distinguished due to ageing of unstable mineral phases, at least not in rocks older than the Phanerozoic Eon. Much of the knowledge that we have of the record of ancient hydrothermal activity in the lithosphere is to be found in studies of ore deposits. Hodgson and Lydon (1977) have published a condensed description of the characteristics of different types hydrothermal systems and the geological setting of volcanogenic massive sulfide deposits. When ore geologists talk of 'exhalative sedimentary' ores (Oftedahl, 1958), they are likely to mean metal deposits that have precipitated from hydrothermal solutions. The most obvious evidence for ancient plate tectonics and hydrothermal circulation in oceanic crust is to be found in ophiolites, i.e. slabs of oceanic crust that have not been subducted but have been accreted onto the continents. Oudin and Constantinou (1984) reported the occurrence of hydrothermal vent fragments in ore deposits of Late Cretaceous age of the Troodos ophiolite complex on Cyprus. They also observed fossil worm tubes and other organic remains identical to the modern ones in on-axis deposits of, for instance, the East Pacific Rise and the Juan de Fuca Ridge. Simultaneously with the report by Oudin and Constantinou from Cyprus, Haymon and coworkers (1984, 1989) published their first article on the occurrence of hydrothermal vent worm tubes from 'early Late' Cretaceous (95 million years ago-Ma) sulfide ores of ophiolites in Oman on the Arabian Peninsula. Such worm tubes appeared for a while to be the first preserved hydrothermal eucaryotic fossils of the geologic record. Previously Larter and coworkers (1981) had found Lower Carboniferous (about 350 Ma) hydrothermal pyrite tubes at Silvermines in Ireland but excluded a biological origin, although the 'exhalative sedimentary' deposits were clearly associated with ancient hydrothermal feeder channels. However, Banks (1985) later reported the occurrence of a fossil hydrothermal worm assemblage of about the same age in the Tynagh lead-zinc deposit in Ireland. Kuznetsov and coworkers (1988) found the most ancient and complete fossil hydrothermal benthic fauna reported thus far in the literature. Not only did they find modern type fossil tube worms in Devonian (410-360 Ma) ophiolite formations of the Ural area of Russia, they also recovered fossils of the giant clams that are so intimately associated with present hydrothermal activity. These observations indicate that hydrothermal processes are active also during convergence of continental plates, at least in the final stages.

The oldest (about 3.8 Ga) sedimentary rocks on Earth have been found at Isua on Greenland. The rocks are relatively metamorphosed, but Appel (1979) proposed an 'exhalative sedimentary' origin of the sulfides in the iron-formation of Isua. At the other end of the Atlantic Ocean de Wit and coworkers (1982) described 3.3-3.5 Ga old 'pods' of ironstone (preferred term for 'iron-formation' on the southern hemisphere) in the Archean Barberton greenstone belt of Southern Africa. They interpreted the pods as representing buried, mineralized hydrothermal channels and chimneys. de Wit and coworkers also reported structures that resemble modern subaerial hydrothermal mud pools associated with ferruginous shales, banded iron-formation and stromatolites. Their interpretation of the 'mud pool' structures was, however, later claimed to have been refuted due to the lack of feeder zones (Lowe, pers. comm.). It is probably not so much the specific fossil phenomena but the geological environments as a whole that give us most of the information about the hydrothermal conditions on the young Earth. Thus MacGeehan and MacLean (1980) considered the genesis of all Noranda-type massive sulfide ores of Archean greenstone terrains to be intimately related to sub-seafloor geothermal activity. Similar types of 'exhalative sedimentary' sulfide ores deposited as chemical sediments on the ancient seafloor are also common in the Proterozoic Eon (cf. Rickard *et al.*, 1979). Fripp (1976) pointed to the well known worldwide association of gold deposits with Archean banded iron-formation and the fact that a hydrothermal origin is favored by most geologists for the Archean banded iron-formations (cf. Holm, 1987), although the mere oxidation of some Fe(II) to Fe(III) may have been due to photochemical processes (Braterman *et al.*, 1983). Fripp (1976) proposed that deposition of iron, sulfur, silica, arsenic, carbonate, and trace metals, including gold, took place from hydrothermal solutions on the seafloor as stratiform beds of iron-formation. It must be mentioned in this context that banded iron-formations are probably much more common in the geological record from the Archean than previously believed (Gole and Klein, 1981). Nisbet (1987) noted concerning the information available in Archean terrains: 'The greenstone terrains tell us about the surface of the Earth, the environment in the shallow seas and the beginnings of life'. Many Archean greenstone belts contain mineral deposits in what are probably extinct hydrothermal systems. Characteristically such deposits consist of veins of sulfide minerals, often closely associated with 'graphite' that probably originates from 'cracked' organic residues. There is little proof as yet that the Archean graphite is biogenic, but Nisbet (1987) remarked that the analogy to modern ocean ridges is indeed fascinating.