CHAPTER 9

MINERAL THEORIES OF THE ORIGIN OF LIFE AND AN IRON SULFIDE EXAMPLE

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> "Oh! let us never, never doubt
> What nobody is sure about"
>
> Hilaire Belloc.

1. Introduction

If we really believe that a process of Darwinian evolution started on the Earth without the help of miracles, spacemen or whatever, then the first organisms (by which we mean the first systems able to evolve indefinitely through natural selection) must have been made of materials that were, broadly speaking, geochemicals.

The usual view has been to suppose that the critical geochemical materials were a special class of organic compounds generated by atmospheric, oceanic and other geochemical processes that were special to the early Earth. The classical picture is of life arising from an oceanic primordial soup, a vast stockpile of the right sorts of organic molecules that had been built up as a result of various energy inputs to a reducing atmosphere. Almost without discussion "the right sorts of organic molecules" for the most primitive organisms were taken to be the same as those molecules which are universal to life now. Experiments have confirmed that amino acids at least can be produced from mixtures of reducing gases subjected to artificial lightning (Miller's famous sparking experiment, 1953). Helped by the simplicity and dramatic qualities of Miller's beautiful experiment the "primordial soup" doctrine became established to the point at which most scientists seem to believe it. But there have always been doubts, particularly more recently (Hull, 1960; Hulett, 1969; Cairns-Smith, 1982; Shapiro, 1986). For one thing the idea that there was ever a strongly reducing atmosphere has little to support it, beyond a belief that such an atmosphere would have been essential for life to have started (Chang *et al.*, 1983). Even if there had been such an atmosphere it would probably not have lasted long since it would have been photochemically unstable (Wayne, 1991). Although

the matter is still being hotly debated, most current models of planet formation give the early Earth a more or less redox neutral atmosphere, an atmosphere more like that of Mars or Venus than of Jupiter, with CO_2, H_2O and perhaps N_2 rather than CH_4 and NH_3 as dominant constituents (e.g. Kerr, 1980). Large scale organic synthesis becomes progressively more difficult as conditions become less reducing. As Miller has shown more recently yields from sparking experiments with mixtures of H_2 and CO_2 become negligible as H_2:CO_2 ratios fall below unity (Chang *et al.*, 1983; Schlesinger and Miller, 1983). In any case the Isua rocks with their carbonates and banded iron formations speak of an Earth whose atmospheric and hydrospheric chemistry was not strongly reducing (Allaart, 1976).

Then again ultraviolet light, in spite of its potential for prebiotic photosynthetic activity in surface waters (Getoff, 1962; Akermark *et al.*, 1980) would actually have tended to *clear* the oceans of organic molecules through oxidation by photochemically generated ferric iron - crudely:

$$Fe^{2+} \;+\; H^+ \;+\; h\nu \;\;\rightarrow\;\; Fe^{3+} \;+ \tfrac{1}{2} H_2 \,. \tag{i}$$
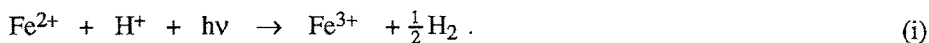
Under near neutral conditions of pH this kind of reaction is particularly efficient and leads to ferric precipitates (Braterman *et al.*, 1983; Borowska and Mauzerall, 1987). These sinking precipitates would have tended to adsorb and sediment organic materials, sooner or later oxidizing them back to CO_2 (Braterman and Cairns-Smith, 1987). So a tendency for surface waters to become slightly oxidizing under the Archaean sunlight should be set against the optimistic assessments of Mauzerall (1990) and de Duve (1991) that the atmosphere would have been more reducing than it might otherwise have been due to hydrogen production through the above kind of process. The present surface of Mars is a bleak reminder that although sunlight can produce intricate and interesting local effects - such as life now on Earth - an overall effect of, especially, its ultraviolet component on the surface of a planet is to destroy organic molecules (Armstrong *et al.*, 1966). The harder u.v. photons that can get through most ozone-free atmospheres can break many kinds of covalent bonds. In particular hydrogen atoms are broken off, and these have a net tendency to escape to space. The result is a surface oxidizing effect. If we want reducing conditions to favour the production and survival of organic molecules we should be thinking about places away from the surface, more in touch, perhaps, with the vast reservoir of reducing power in the form of, especially, iron (II), and sulfide within and beneath the crust. Hence the interest in hydrothermal systems and our emphasis later in this chapter on iron sulfide minerals.

2. Mineral Theories - Conservative and Radical

The geochemist V. M. Goldschmidt wrote a short speculative piece in 1945, two years before his death, on "Geochemical aspects of the origin of complex molecules on the

Earth, as precursors to organic life". This was published in 1952, but has received comparatively little attention. Goldschmidt suggested that carbon dioxide was probably "the main material available for the formation of primitive organic molecules, apart from subordinate hydrides of carbon, and very subordinate amounts of CO". He went on to suggest that concentrations of organic molecules would have been rather low, and that adsorption of simple organic molecules at phase boundaries, and especially on the surfaces of mineral crystals, would thus have been critical in giving rise to organized higher order aggregates. He wrote: "One most important factor for selection and arrangement of adsorbed molecules is their size and shape as related to the atomic arrangement of the inorganic substratum. Besides such two-dimensional layers of more or less loosely fixed molecules there certainly must exist some analogous linear phenomena along the edges of crystals, and this would make monodimensional strings or chains of adsorbed particles". He then went on to consider potential catalytic effects of "local fluctuations and concentrations of vibrational energy, which are possible in crystal lattices...." and pointed to the potential for quartz crystals to confer enantiomeric specificity.

Bernal had independently speculated along similar lines and in 1951 stressed the potential importance of clay minerals. Montmorillonite especially was known to have particular affinities for organic molecules, adsorbing them on and between their unit silicate layers. Bernal suggested that these minerals might have acted as heterogeneous catalysts in the building up of larger molecules. This idea has been used in many subsequent experiments and speculative theories.

Most theories of this sort have been *conservative*. By this we mean they hang on to the idea that the first forms of life, the first organisms able to evolve through natural selection, were made, broadly speaking, of the same materials as are organisms today. Minerals were environmental agents of a purely "chemical evolution" which provided an initial feedstock of, it is usually supposed, such familiar "biochemicals" as amino acids, sugars and so on.

Pirie (1959) had a more radical view. He suggested that to begin with there might have been many different biochemistries based on different elements, which settled selectively on our kind of biochemistry at a later stage. He saw the unity of biochemistry now as attesting to the effectiveness of natural selection rather than to the idea that life is only possible, or only ever happened, in one way, with one set of substances. He was particularly critical of the idea that early biological catalysts would have been made of protein: proteins are used now because the means to produce them has been evolved and because they work better, but are less plausible under primitive conditions.

It seems indeed entirely reasonable to suppose that the first organisms would have been made in a way that was particularly accessible, expecially in keeping with a current local geochemistry. Then later on initial subsystems would have been replaced by more efficient ones. This is how evolutionary and other forms of technological innovation commonly proceed - starting with what is easiest, ending with what is most efficient.

The extraordinary fixation of all life on Earth on a particular set of biochemical molecules is now generally agreed to be the result of the descent of all life now on Earth from a last common ancestor - sometimes called the universal ancestor. According to this view we all now share the same central biochemistry because the universal ancestor had this system already irreversibly built-in: DNA, RNA, proteins made from 20 amino acids, a code to translate from the nucleic acids to protein, and complex machine tools - ribosomes - to do it. The sophistication of that common ancestor has been becoming more and more apparent (Cairns-Smith, 1985). It is evidently a substantial evolutionary distance from the first organisms: the universal ancestor was surely the result of a major earlier phase of the (fully Darwinian) evolution. It seems likely that this was the phase of evolution *during which* the biochemical system of the universal ancestor was being invented - and that part of this process would have been the choice of appropriate molecules. It is out of keeping with the well understood lack of foresight in evolutionary processes (e.g. Dawkins, 1986) to insist that this choice would have been made at the outset.

So we can describe *radical* mineral theories of the origin of life as being those that would put minerals into the first organisms as part of their structure. The most radical suggestion has been that the major *control structures*, catalysts, membranes and above all genes, were all of them inorganic in nature in the first organisms, and that these were gradually replaced during the early phases of evolution as competence in the control of organic chemical reactions improved (Cairns-Smith, 1982). We will not pursue this "take over" idea in detail here except to note that given such means of updating early biochemical technologies we must be interested in the entire geochemistry of the hydrothermal systems. It is not just a matter of searching for "the right molecules". Although knowing which if any of the classes of current biochemicals can be made easily or survive well under hydrothermal conditions remains of interest, if our primary concern is with the very earliest stages of evolution we need to know without prejudice which molecules, minerals and higher order structures, are easily formed and/or reasonably stable under hydrothermal conditions. Then we can begin to assess the most likely materials for the earliest membranes, catalysts, genes and so on. So which minerals forming in hydrothermal systems look promising?

3. Layer Silicates

"Conservatives" and "radicals" can agree that clay minerals are of interest in that they interact with organic molecules, as already discussed. In general, however, simple clays have not proved to be particularly effective adsorbers of "biochemicals" from dilute aqueous solutions (Lahav and Chang, 1976) or for that matter as catalysts for making basic "biochemicals" under aqueous conditions, as commented on by Cairns-Smith (1982) and Miller and Bada (1988). They have, however, proved useful in providing surfaces to help bring about limited amino acid condensations in the laboratory through forced cycles of

wetting and drying (Lahav *et al.*, 1978) and they can adsorb nucleotides very effectively in the presence of transition metal cations (Odom *et al.*, 1979; Lawless *et al.*, 1985; Lawless, 1986).

At more sophisticated levels montmorillonite clays have been shown to exert control on the polymerization of activated amino acids - aminoacyl adenylates (e.g. Paecht-Horowitz *et al.*, 1970; Paecht -Horowitz and Eirich, 1988) and to assist in the oligomerization of various activated nucleotides (Ferris *et al.*, 1989, 1990; Ferris and Kamaluddin 1989). Then again Mortland (1984) has demonstrated selective deamination of glutamic acid with a "pesudo-enzyme" consisting of a smectite clay with bound Cu^{2+} and pyridoxal phosphate (see Pinnavaia and Mortland, 1986 for a review).

"Conservatives" tend to view such experimental results with caution: aminoacyl adenylates, pyridoxal phosphate, activated nucleotides; such molecules are now widely and properly seen as unlikely prebiotic geochemicals, whether in an ocean or a hydrothermal system. So maybe these are just model experiments, helping us to see the kinds of things that clays and other such minerals can do in the way of controlling organic reactions. (This is the attitude taken by Ferris and Kamaluddin (1989) for example.) No doubt such caution is wise, but radical theorists have reason to be more positive. If minerals were for a long time components of those early evolving systems, components that would only have been displaced once something like the modern system of genetic control had become established, then we would expect a synergy between mineral components of the old system and molecular components of the new. For a considerable time they must have had to work together.

For organisms elaborating pre-protein techniques of organic synthesis, barriers to diffusion - inert "glassware" - might have been even more important than in organisms now, and it is perhaps not too fanciful to think of montmorillonite and similar clays as standing in for lipid bilayer membranes which predominantly serve this function now. Individual silicate layers of clays are tough and flexible and, incidently, of similar thickness to lipid bilayers. Imogolite, halloysite and allophane naturally form tubes and vesicles, and clay minerals generally create complex compartmentalized microenvironments (Cairns-Smith, 1982).

Conditions in hydrothermal systems are conducive to the formation of relatively well crystallized clays and other related layer silicates such as micas. Phlogopite, for example, forms rapidly under hydrothermal conditions (*ca.* 500°C) in the laboratory as Baronnet (1972, 1980) has demonstrated. Special interest attaches here to the phenomenon of long range polytypism in connection with a possible primitive genetic system. We will now discuss this briefly.

The nanometer thick unit layers of micas have a directional structure such that each successive layer in a mica crystal can be stacked on top of the layer below it in one of three orientations. Often the stacking sequence is simple - e.g. always with the same orientation or always alternating between two orientations - but complicated more random-like sequences are common and, interestingly, some quite complicated sequences are of-

ten repeated again and again within a single stack. Apparently this arises through the operation of a screw dislocation growth mechanism (Baronnet, 1980). A random-like stacking sequence can hold "information", rather as the sequence of base pairs stacked inside a DNA molecule can, and the repetition of the same such sequence in a crystal is strongly suggestive of a replication of this "information" during crystal growth. This raises the possibility that a mica-like mineral could have been a primitive genetic material operating perhaps on surrounding organic molecules in the kind of way that Goldschmidt (1952) suggested, but through sequence dependent groove patterns that generally develop on the edge surfaces of polytype stacks (Cairns-Smith, 1988).

4. Zeolites

Zeolites can form easily under mild hydrothermal conditions. In addition to their well known size selectivity for organic molecules these minerals have the potential for information storage - especially the ABC-6 type zeolites where slabs of subtly different crystal structure can be stacked on top of each other to form an infinity of possible mixed intergrowths (Milward et al., 1985) some perhaps with distinctive adsorptive and catalytic properties. This is similar to polytypism, so the possibility of a screw replication mechanism exists here too (Cairns-Smith, 1988). Their catalytic properties and concentration in the vicinity of "black smokers" have been remarked on with respect to their possible implication in the origin of life by Nisbet (1986).

5. Oxides/Hydroxides

Of considerable interest is a large class of layer structures with adsorptive, catalytic and membrane-forming properties which have recently been studied in detail by Arrhenius and his group (Kuma et al., 1989) and discussed by them in relation to their possible significance for the origin of life. These are mixed valence hydroxides of the pyroaurite type. They can be formed in the laboratory (at pH 8-9 or above, and at temperatures ranging from 25-200°C according to type) and can be made much more quickly and easily than most clays. They can be thought of as modifications of the basic brucite structure (which consists of a stack of uncharged $M(OH)_2$ layers where M is a divalent ion such as Mg, Ca, Fe, Mn...). Substitution of some of the M^{2+} ions by trivalent ions such as Fe^{3+} or Al^{3+} creates positively charged layers between which are located anions such as Cl^- or CO_3^{2-} to balance the charges. The interlayer anions can often be exchanged - for example with CN^- or organic anions such as acetate, benzoate, dodecylsulfate, or the nucleotide adenosine monophosphate.

Oxide-hydroxides of iron and manganese are another group of minerals with anion exchange capacities, often membranous structure, and similar conditions of formation to the pyroaurite group. Arrhenius (1986, 1990) has suggested key probiotic roles for both

of these general classes of minerals - especially the iron ones - in building organic molecules from cyanide and formaldehyde.

Granick (1957) suggested a role for magnetite as part of a primitive photosynthetic device. This was never realized experimentally, but the potential of defect magnetite for reduction of carbon dioxide in the dark has recently been demonstrated (Tamaura and Tabata, 1990).

Using Inelastic Electron Tunnelling microscopy, Field and Spencer (1990) have demonstrated the production of monolayer amounts of formic acid on alumina surfaces from carbon dioxide and water; glycine from carbon dioxide, water and ammonia; and sugar-like products from carbon monoxide and water.

6. Phosphates

We should add phosphates to our list of especially interesting minerals in view of the key position of phosphate in our biochemistry. Phosphorous is often the limiting nutrient for life now on Earth (the concentrations of phosphate in bulk natural waters is of the order of 10^{-7} molar; Li, 1982). One might speculate that this now inconvenient dependence on phosphate arose because in the environment within which the first organisms evolved phosphate was relatively abundant. Certainly phosphate approaches a concentration of about 5 wt% in the iron and zinc rich layers of the most ancient of the giant exhalative-sedimentary base-metal orebodies, Broken Hill in Australia (Stanton, 1976). Stanton *et al.* (1978) speculate that the phosphorous here may have been introduced as the pentasulfide and upon hydrolysis and/or double decomposition it deposited as apatite or an iron phosphate. The requirement may have been, as now, for soluble phosphate, although there have also been speculations about the possible roles of hydroxyapatite and other phosphate mineral surfaces (see Orgel, 1986). Yamagata *et al.* (1991) have shown both from experiments at around 1300°C simulating magmatic conditions, and from volcanic gas analysis, that water-soluble polyphosphates may be produced by the partial hydrolysis of P_4O_{10}.

7. Sulfides

Sulfides too, although not as prominent as phosphates in our present biochemistry, have central roles (e.g. in ferredoxins and the thioester linkage of coenzyme A). These appear also to be ancient and sulfides may have been more important in the earliest phases of evolution (Hartman, 1975; Wächtershäuster, 1988a,b; de Duve, 1991). In relation to theories of the origin of life in hydrothermal systems they have an added interest since sulfides, especially iron sulfides, are dominant minerals here. As with other minerals the interest of these materials is not *only* that they might have been catalysts and reagents, that is to say early versions of the sulfide components of present day biochemistry, but again for possible wider roles connected with those altogether more primitive bio-

chemistries which surely preceeded ours. For example we have speculated (Russell *et al.*, 1988), that the demonstrable tendencies for iron sulfides to form tubes and botryoids (hollow pyrite hemispheres <1 cm diameter) might have provided complex reaction vessels on scales from microns to millimeters to help in the control of organic reactions. Such control is part and parcel of normal organic chemical manipulations and is in addition to catalytic control. It operates by separating solutions of different chemical composition, different pH, Eh and so on, as well as helping to arrange for solutions to be appropriately mixed - and for products to be purified through chromatographic effects. In present day organisms, maintained chemical potentials across membranes, e.g. proton potentials in mitochondria, serve as immediate power sources for redox and other reactions. Such potentials will inevitably exist within the complex plumbing of hydrothermal springs where, for example, solutions flowing within sulfide tubes have a different pH and/or Eh from the surrounding seawater - suggesting the possibility of reactions being locally driven against thermodynamic gradients.

Effects like this can be imagined from the more "conservative" point of view as having helped to provide dynamic sources of feedstock and/or niches for early organisms. On the more "radical" tack touched on earlier we should keep in mind the possibility that at some stage a geochemical evolution became a biological evolution too, that materials were being made and higher order structures were being formed under some kind(s) of genetic control - and that (for example) sulfide tubes and more especially bubbles (protobotryoids) might have become actual structural components of early organisms themselves, standing in, so to speak, for the protein-lipid membranes that constitute most of the containment, energy transducing, and other "apparatus" in organisms today.

Let us move now to a more detailed - "radical" - model of the origin of life in hydrothermal systems based on one of the most abundant kinds of minerals that are being made in them - iron sulfides.

8. A Mineral Model Based on Iron Sulfides

Corliss and his co-workers (1981), spurred on by the discovery of present day hydrothermal systems along ocean ridge spreading centers (Corliss, 1979), especially "black smokers" (Spiess *et al.*, 1980) suggested that such hot springs, which discharge ~150 liters of recycled, modified seawater a second at up to 360°C at about 250 bars, would have been ideal places to focus the chemical constituents and thermal energy required for life's origins. More recently Corliss (1990) has argued that in the hot spring environment thermal energy may be converted to high energy chemical bonds during rapid quenching and that the steep thermal and chemical gradients in this environment would encourage the formation of complex molecules. As a generality this is an attractive idea but it assumes a similar hydrothermal chemistry at the time when life was initiated, about four billion years ago. An example of evidence against this assumption is that the formation of sulfide chimneys at black smokers depends on replacement of calcium sulfate which precipitates

directly from cold ocean water as it is heated through entrainment in the hot water
(Haymon and Kastner, 1981). Calcium sulfate has an inverse solubility with respect to
temperature and therefore is physically dumped as a sleeve or chimney around the hot
plume. The chimney supplies a protective environment and is replaced by sulfides which
are precipitated as the acid hydrothermal solution mixes with alkaline seawater (Fig. 1a).
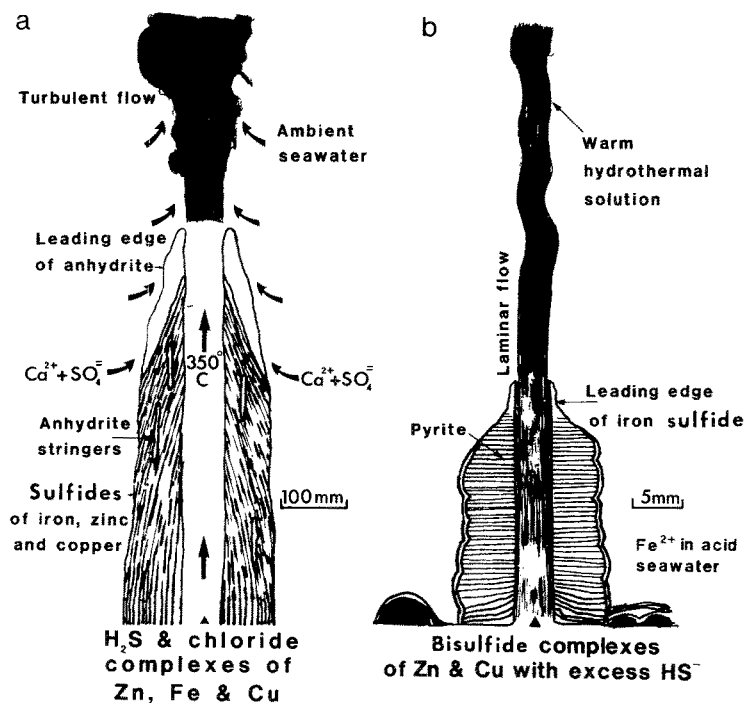

Fig. 1. Contrasting processes producing the two types of hydrothermal chimneys mentioned in the text. a)
Growth of a black smoker by preliminary precipitation of anhydrite ($CaSO_4$) from ambient cold seawater on
heating by the 350°C hydrothermal solution. Once this sleeve has been produced then sulfides are precipitated
in this protected environment as the hydrothermal solution meets cold alkaline seawater (Haymon and Kastner,
1981). b) Model for the growth of fine chemical gardens in the Hadean ocean away from ridges and volcanoes.
The fine chimney spires grow in the absence of calcium sulfate by a reaction between alkaline hydrothermal
bisulfide bearing solutions entering through fine cracks in the ocean floor into rather acid iron bearing seawater.
Such chimneys could grow in the absence of sulfate but because of the kinetics of this reaction a chimney is
only produced when the injection of the hydrothermal solution into the seawater is slow and well focused. The
fine tubes act as nucleation points for further precipitation of iron monosulfide. This monosulfide then
ozxidizes to the disulfide. Botryoids or bubbles of iron sulfide may have developed in place of chimneys or
preceded chimney growth where fluid pressures were relatively low, as sketched to the left of the diagram (cf.
Fig. 4) (Russell et al., 1989).

Although one may assume a myriad of hot springs in the earliest oceans, this particular process is unlikely in that the oceans probably contained only minor concentrations of sulfate (Walker and Brimblecombe, 1985). Also the high iron to sulfur atomic ratio in lavas would have been reflected in black smokers generated at submarine spreading centers or volcanoes associated with mantle plumes. So black smokers would have supplied Fe^{2+} and Fe^{3+} to the early oceans governed by the dissolution of magnetite. In 1979 Degens suggested that prebiotic C-H-N-O-P-S compounds would have been discharged to the sea along the same channels as vesiculating magma and he envisaged a series of organic fronts fractionating in the same way as that observed in ion exchange or gas chromatographic patterns as a function of temperature gradients within the crust. Thus he imagined a wide spectrum of new 'organic' compounds being generated and promoted by mineral catalysis to be transported to the hydrosphere. Indeed, Mg-smectites, zeolites and sepiolite (e.g. Evarts and Schiffman, 1983; Bonatti et al., 1983) in the crust might well have filtered tars and caramels from the rising organics just as they do in oil refining (Barrer, 1978).

The nature of key components of the terrestrial environment during the early Archaean when life originated remains a problem: the atmosphere, seawater, crust and mantle have all evolved and been recycled to such an extent that we have few constraints on their compositions. We can only proceed using "best estimates" but the versatility of hydrothermal processes gives us the flexibility to adapt the hydrothermal model as new evidence and constraints emerge. For example, Miller and Bada (1988) seized on another problem, arguing that far from being encouraged to form in black smokers, amino acids would, if in existence, be destroyed by the high temperature solutions.

In response to this Russell et al. (1988) pointed out that there were other submarine hot spring scenarios and recalled the discovery of 350 million year old pyrite (FeS_2) chimneys, along with botryoidal pyrite, at Silvermines in Ireland which had formed in an entirely different chemical environment and at lower temperatures to those of black smokers (Larter et al., 1981; Boyce et al., 1983). In Ireland pyritiferous lead and zinc sulfide deposits were generated at sea floor springs as a result of free convection of seawater, chemically modified as it circulated in the top twelve kilometers of the crust (Russell, 1978). Similar chimneys and botryoids have since been discovered 45 km to the north of Silvermines, at the Tynagh orebody (Banks, 1985). The chimneys at Silvermines and Tynagh had a maximum internal diameter of a millimeter or so, ranging down to micrometers, two orders of magnitude narrower than those of black smokers (Figs. 2 and 3). Millions of them formed like natural "chemical gardens" in the hydrothermal systems feeding the Silvermines and Tynagh orebodies in Ireland. This kind of system could have lasted much longer than black smokers, probably of the order of a hundred thousand years or more (Russell, 1988).

Such chemical gardens, essentially composed of iron monosulfide (Fig. 3) are formed easily in the laboratory at STP (Fig. 4) (Russell et al., 1984) much like silica gardens (Coatman et al., 1980). We made them by introducing a solution of ferrous chlo-
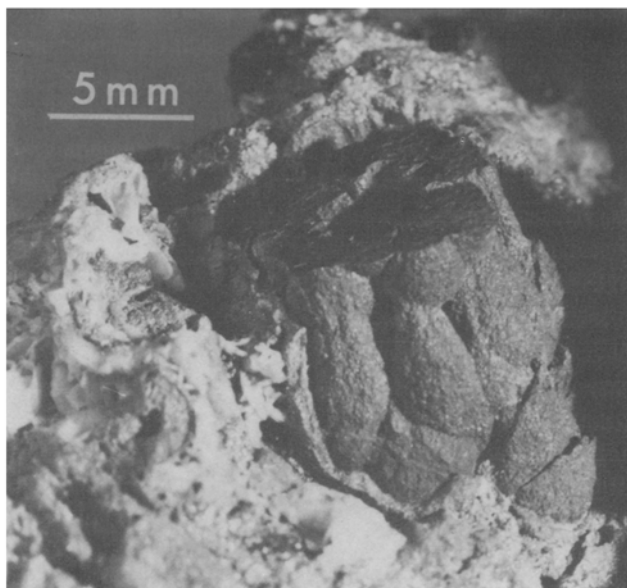
Fig. 2. Pyrite chimney formed by the egress of hydrothermal solutions at around 150°C into a brine pool 350 million years ago. Sample is from the Ballynoe Open Pit Barite Deposit, Silvermines, Ireland.

ride (made acid by hydrolysis) through an aperture 0.5 mm in diameter into a vessel containing a solution of sodium sulfide (rendered alkaline for the same reason) notionally:

$$FeCl_2 + Na_2S \quad \rightarrow \quad FeS + 2\,NaCl \ . \tag{ii}$$

Bubbles and fine chimneys composed of iron sulfide formed first with both the iron and the sulfur in reduced form probably as $Fe(SH)_2$ or mackinawite ($\sim FeS$) (Russell, 1986, 1988; and see Rickard, 1989). These oxidized to greigite (Fe_3S_4) and to pyrite (FeS_2) within a few months (cf. Kribek, 1975). Rigorous anoxic conditions which would have been necessary to prevent iron sulfide oxidation (Berner, 1967; Taylor *et al.*, 1979) were impractical in these experiments. In this analogy the iron chloride deputizes for the hydrothermal solution responsible for the Silvermines orebody which, according to our fluid inclusion analyses, ranged in temperature between $\sim$100-220°C (Samson and Russell, 1987); the sodium sulfide solution is the equivalent of a highly evaporated seawater enriched in (in the Silvermines case bacteriogenic) H_2S occupying a brine pool on the sea bottom (Boyce *et al.*, 1983). The sulfide gardens grown thus in the laboratory are remarkably similar to the fossil pyrite botryoids (hardened bubbles) and chimneys found at Silvermines and Tynagh (Russell *et al.*, 1989 and Figs. 2 and 3).
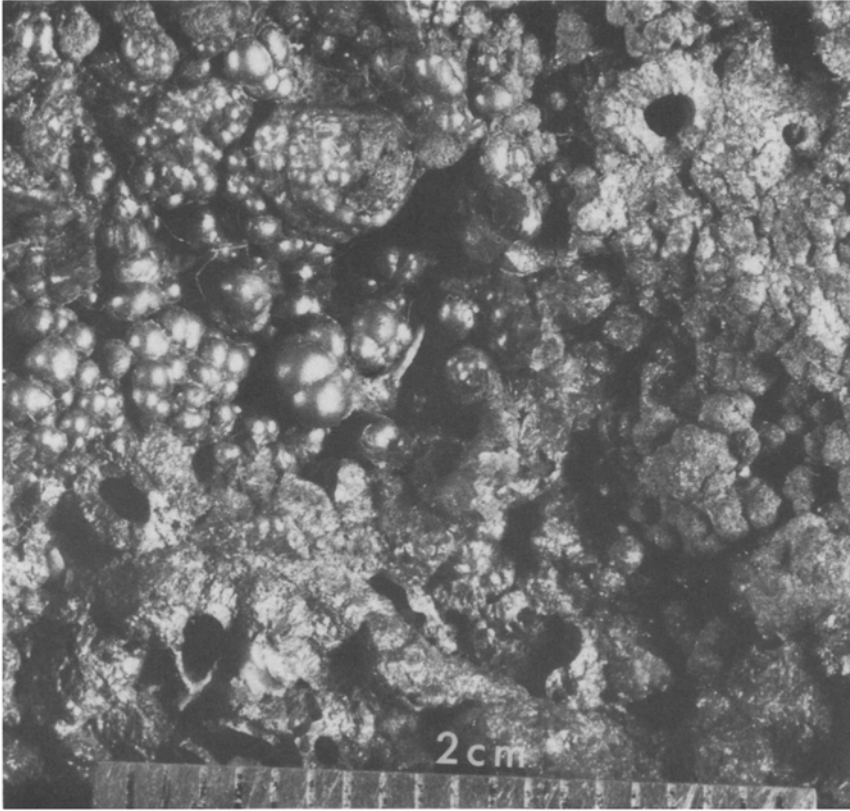
Fig. 3. View of 350 Ma-old chimneys and botryoids (hemispherical pyritic structures) from the Tynagh, ore-body, Ireland.

Conversely, exactly the same structures are produced if the alkaline sodium sulfide solution is passed through a hole 0.5mm across at the bottom of a visi jar, into a solution of acid ferrous chloride; again chimneys and bubbles of an iron sulfide gel are formed (Fig. 4). These conditions are more similar to those that we imagine pertaining four billion years ago because at that time, although much of the crust may have been basaltic (Bickle, 1986; Sleep and Windley, 1982; but see Nisbet, 1987) igneous sills would, in places, have intruded the upper oceanic crust, composed chiefly of forsterite olivine [$(Mg>Fe)_2 SiO_4$], pyroxenes [$(Mg,Fe,Ca)_2 Si_2O_6$] and minor plagioclase [$(Ca>>Na)(Si,Al)_4O_8$] or their hydrated (serpentinized) equivalents, as well as minor chrome spinels [$(Mg,Fe)(Cr,Fe,Al)_2O_4$]. Several percent of pyrrhotite ($Fe_{1-x}S$) and pentlandite (Fe, $Ni)_9S_8$ would also have been carried within the magma (Burns, 1988) along with other base metal monosulfides, and probably accessory sulfides such as rasvumite (KFe_2S_3) (Sokolova et al., 1970; Czamanske et al., 1979), djerfisherite ($K_3[Na,Cu]$
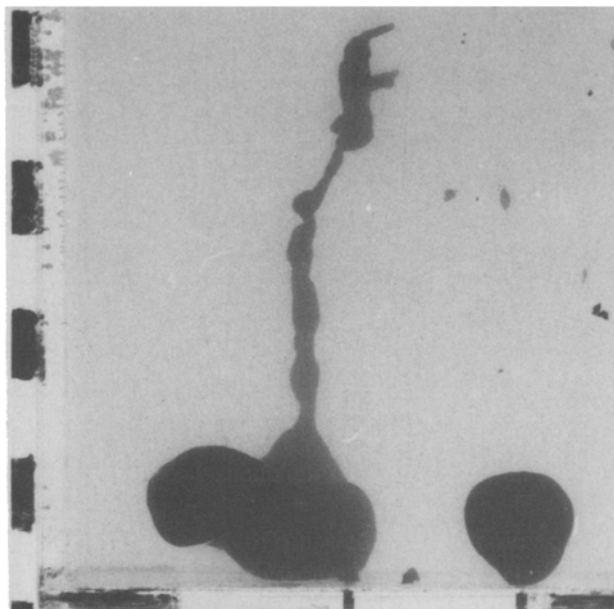
Fig. 4. Chimney-like structure of iron monosulfide formed by passing sodium sulfide solution upwards through three holes 0.5 mm in diameter in a visi jar containing ferrous chloride. Note the filled globules at the base which are compared to the pyrite botryoidals of Fig. 3. The central "proto" botryoidal bubble has "spawned" another such protobotryoid to the left before rupturing to produce the fine chimney. Further buoyant globules formed at the top of the tube, become severed, float upwards and disperse. (Vertical scale in centimeters.)

[Fe,Ni]$_{12}$S$_{14}$) (Genkin *et al.*, 1970), erdite (NaFeS$_2$•2H$_2$O) (Konnert and Evans, 1980; Czamanske *et al.*, 1980), chalcopyrite (CuFeS$_2$) and possibly molybdenite (MoS$_2$) (Fig. 5). Sulfides are especially concentrated at the base of the komatiitic lava piles where they were introduced as immiscible melts (Gresham and Loftus-Hills, 1981). We know from analysis of ground water and warm springs from modern mafic and ultramafic complexes of similar chemistry that their pH is likely to have been high (Neal and Stanger, 1984) because of the partial dissolution of magnesium and calcium oxides on hydrolysis of silicates:

$$(MO)_{\text{silicate}} + H_2O \rightarrow M^{2+} + 2OH^- \ . \tag{iii}$$

This type of hydrothermal solution would have comprised seawater convecting thermally in cracks in the oceanic crust much as today similar mass transfer of heat takes place throughout the ocean floors away from the ridges (Anderson *et al.*, 1977). The mechanism of circulation we envisage involves natural or free thermal convection driven by a
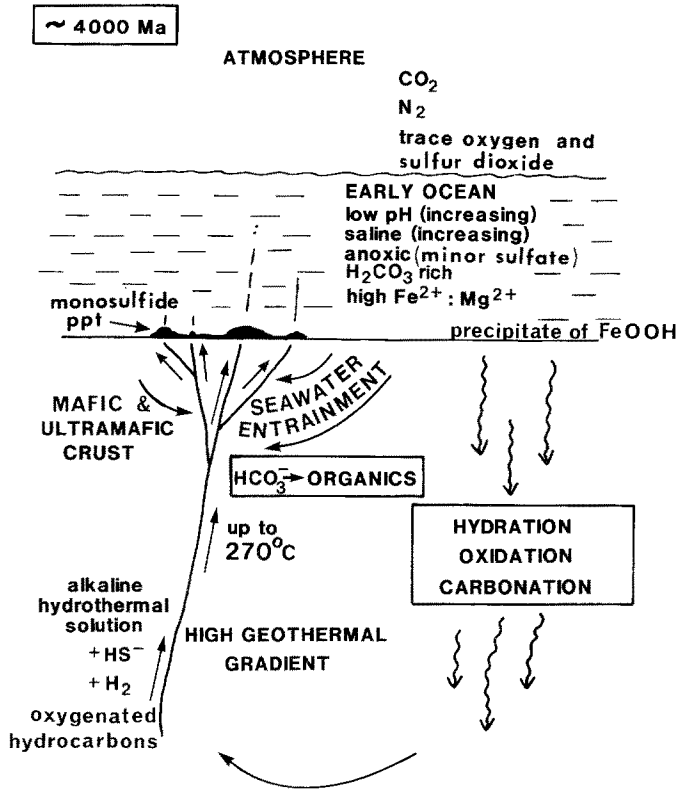
Fig. 5. Speculative sketch of the natural convection system envisaged for the Hadean Sea unrelated to hot spot volcanism oceanic ridges. The hydrothermal solution is seawater modified by interaction with the mafic and ultramafic crust and rendered alkaline by dissolution of calcium and some sodium and potassium. The early ocean itself has a relatively low pH because of the solution of atmospheric carbon dioxide and hydrogen chloride released from the mantle during massive volcanic activity.

very high regional geothermal gradient (i.e. unrelated to a magma chamber). Permeability through the top few kilometers of the crust would have been allowed by fracturing generated by differential stresses, with fracturing being further encouraged by the internal hydrostatic pressures which increased the effective stress allowing migration of joints down to depths where the temperature approached 270°C. Above this temperature porosity would have been very low indeed as a result of crack sealing. The cells would have operated to a greater depth (ultimately about 12 km) within the oceanic crust than the black smoker's convective systems, the hot water interacting with sulfide-bearing source rocks. They could have continued to operate for a million years or so in any one place at a temperature of around 150°C.

Today, seawater circulating in the crust at the oceanic ridges becomes acid (Seyfried and Dibble, 1980; Lecuyer *et al.*, 1990):

$$Mg^{2+}(\text{seawater}) + 2H_2O \rightarrow Mg(OH)_2 \text{ (silicate)} + 2H^+ \cdot \qquad\qquad\text{(iv)}$$
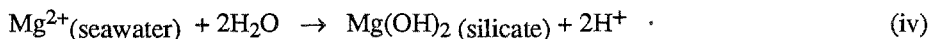
but in the early Archaean such a reaction would have been muted *off-ridge*, because of lower operating temperatures and the presence of $Ca(OH)_2$ in solution. Calculations modelling anoxic sulfate-free "Archaean seawater" with mafic to ultramafic rock using the EQ3/6 codes of Wolery *et al.* (1984) suggest a hydrothermal fluid pH about one to two units alkaline (McLeod *et al.*, 1992). Crerar *et al.* (1978) demonstrate that iron is insoluble in these conditions, though we calculate a release of ~0.001m of HS^- as pyrrhotite in the crust converts to magnetite (McLeod *et al.*, 1992).

In contrast to the ~150°C springs, the early ocean itself was probably neutral or slightly acid because of the CO_2 rich atmosphere and the precipitation of ferric hydroxide (equation i). Buffering by magnetite would have prevented large scale excursions to lower pH. Iron (II) derived from the high enthalpy springs (black smokers) would have been present to the extent of at least a few parts per million (Holland, 1973; Walker and Brimblecombe, 1985). Moreover there were no large continental masses at that time (McLennan and Taylor, 1982; Moorbath, 1985) and land would have been restricted to ephemeral volcanoes and mantle plume bulges. The reaction of the seawater with the oceanic crust would have been through further hydration, carbonation (from a portion of the dissolved carbon dioxide) and oxidation (using combined oxygen coming from the water and carbon dioxide). Hydrogen would have been released during these reactions at high temperature (Coveney *et al.*, 1987), and Fischer-Tropsch type syntheses (Storch *et al.*, 1951) could have produced "organic" molecules. French (1964) recognized this possibility following hydrothermal synthesis of siderite from ferrous oxalate dihydrate at low oxygen fugacity. His experiments resulted in the formation of complex oxygenated hydrocarbons. As the alkaline water returned to the sea floor in a convective updraft it would have cooled and mixed with acid seawater occupying the uppermost part of the crust where sulfides would have been precipitated below and at the site of exhalation (de Wit *et al.*, 1980) (Figs. 1b and 5).

An aspect of the chemistry of iron and other sulfides is made use of in mineral separation technology. Sulfides have a general affinity for dithiocarbonates and dithiophosphates and even amines (Wark and Wark, 1935; Leja, 1982). Pyrite shows a particular affinity for these surfactants which makes this mineral a nuisance during separation of zinc, lead and copper sulfide ores (Ball and Rickard, 1976).

Another aspect of mineral processing, biohydrometallurgy, exploits the propensity of *Thiobacillus ferrooxidans* to catalyze the oxidation of pyrite to ferrosulfate and sulfuric acid. Use of the energy therefrom is a further indication of the significance of redox reactions for the most primitive extant forms of life (Temple and Colmer, 1951):

$$FeS_2 + 3\frac{1}{2}O_2 + H_2O \xrightarrow[\text{ferrooxidans}]{\text{Thiobacillus}} FeSO_4 + H_2SO_4 \ . \tag{v}$$
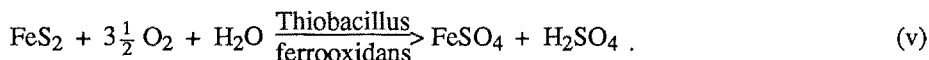
That sulfide mounds and chimneys are an attractive proposition for the site for life's early evolution gains support from the biochemical work of Woese (1987) and Lake (1988). Woese particularly has argued that the earliest known ancestor of life is an archaebacterium which is both thermophilic and sulfur metabolizing. Woese *et al.* (1990) have named such bacteria the Crenarchaeota and note that *Pyrodictium* may be related to a particularly ancient example. Intriguingly Stetter *et al.* (1983) have reported that *Pyrodictium occultum* tends to precipitate pyrite or sphalerite (ZnS) as waste around its cell walls during growth.

In thinking about the significance of iron sulfides for the origin of life we can see three intersecting lines. First the geological arguments emphasize the role of iron monosulfides and disulfides at the focal point of a medium temperature hydrothermal convection system on the primitive earth in the first oceans. This is the view forward, as it were, from conditions on the early Earth: here is a place generally suitable for the origin of life and it is a place where sulfides abound.

Then, second, there are some general properties of sulfides to consider. For example industrial experience shows that at 200°C or more, sulfide catalysts are effective in organic processing where they resist poisoning, for example in the treatment of high sulfur petroleum and oil shale (Weisser and Landa, 1973). They are semiconductors and can drive both oxidations and reductions, as well as catalyze dehydration, isomerization and cleavage reactions (Weisser and Landa, 1973), so one can imagine iron sulfides as primitive reagents ("coenzymes") and catalysts. Then again the covalent character of iron sulfide crystals and their defect structures (Ball and Rickard, 1976; Murrowchick and Barnes, 1986) make them potential information carriers as remarked earlier.

Finally there is the view backwards from current biochemistry. As we have seen earlier, this gives several indications that sulfides were important early components (Hartman, 1975; de Duve, 1991). Indeed Hall and his co-workers had suggested as early as 1971 that ferredoxins were the first enzymes and that a precursor could have been an iron monosulfide/disulfide redox catalyst. As we have seen, recent phylogenetic analyses have implicated a hot metabolism involving iron sulfides at the lowest junction of the evolutionary tree (Woese, 1987; Lake, 1988).

Taken together these three lines of exploration suggest that life may have originated in a sulfide rich environment - a hydrothermal system - and stayed in such an environment right up to the emergence of, essentially, life as we know it. Yet the gap between anything that sulfides and sulfide surfaces could do and the working of, say, the most basic protein synthetic machinery of modern organisms remains enormous. Can it really be bridged?

Wächtershäuser believes it can. In 1988 he proposed that the first energy source for reducing carbon dioxide to organic molecules was the formation of pyrite from hydrogen sulfide and ferrous ions:

$$Fe^{2+} + 2H_2S \rightarrow FeS_2 + 4H^+ + 2e^- \quad . \tag{vi}$$

Wächtershäuser (1988a, 1990b) has developed his ideas, speculating (after Hartmann, 1975) that the first autocatalytic cycle fixing carbon was the extant reductive citric acid cycle. He has further suggested (1990b) that reduction of a carboxylic acid takes place by pyrite formation via a thioacid (Fig. 6).
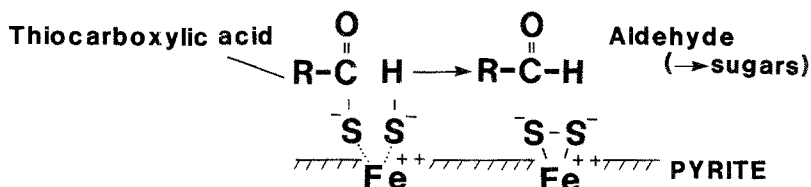
Fig. 6. Wächtershäuser's suggestion for pyrite formation. A redox reaction involving the concomitant reduction (hydrogenation) of a thiocarboxylic acid to produce an aldehyde: a route to sugars.

The thermodynamic feasibility of the reduction of CO_2 by pyrite formation is of great significance for mineral theories of the origin of life in a hydrothermal setting. It must be stressed that as yet there has been no laboratory demonstration of this process. Yet if this process is part of the metabolism of an organism we should not be discouraged by the evident existence of kinetic barriers. As Wächtershäuser (1990a) points out it is a positive *requirement* of such a chemoautotrophic redox energy source that it should not be tapped too easily or it will have been released within the general environment before the organisms can make use of it.

The reduction of carbon dioxide to organic material concomitant upon the oxidation of iron monosulfide to disulfide would only take place below about 220°C. Above that temperature carbon dioxide is stable in the iron monosulfide field. This is because of a cross-over of field boundaries at this temperature as illustrated in Fig. 7. We know from "burning the toast" that carbon is relatively stable even in oxidizing conditions.

More generally, Shock (1990b) has explained how abiotic synthesis of organic compounds of the C+H+O+N system could occur through the reduction of both CO_2 and N_2 within a seafloor hydrothermal system; the optimum temperature for high activities of "metastable" aqueous organic species is 200°C, between the oxygen fugacities of the
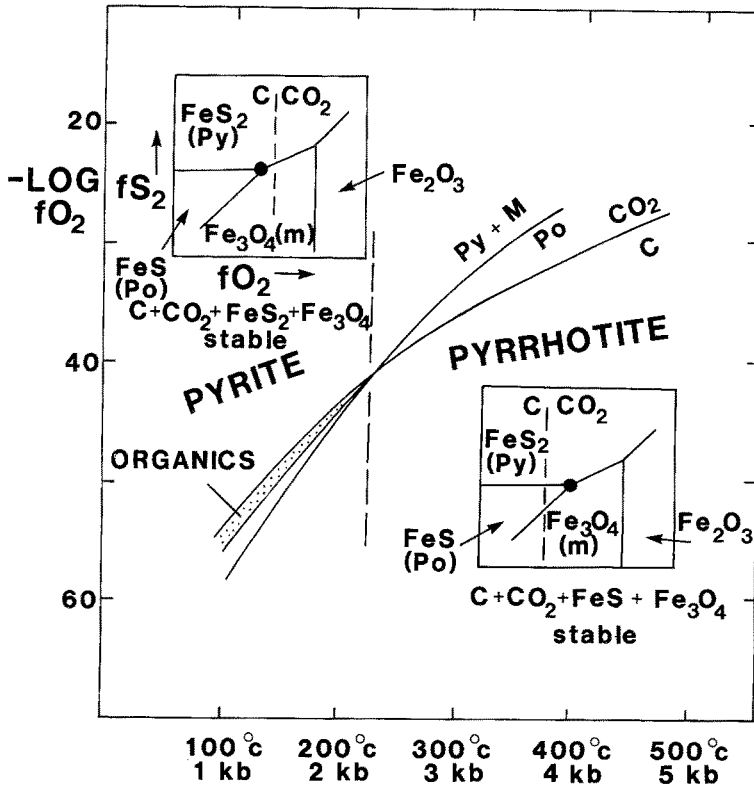
Fig. 7. With C/CO$_2$ as the control buffer, pyrrhotite is stable at high temperature and pyrite at low temperature. The insets illustrate how the C/CO$_2$ buffer migrates to lower oxygen fugacity relative to the pyrrhotite/magnetite + pyrite reaction, with increase in temperature. Curves calculated using SUPCRIT (Helgeson *et al.*, 1978) for a geothermal gradient of 100°C/Kbar. The "organics" field represents tentative phase relations at low temperature where reduction of CO$_2$ by FeS could produce organics (partly based on Hall, 1986 and Shock, 1990b).

pyrite + pyrrhotite + magnetite and the fayalite + magnetite + quartz buffers. The low temperature "field of organics" is illustrated notionally on Fig. 7.

Although no laboratory reduction of CO$_2$ by pyrite formation has been demonstrated, our geological studies of retrogressive metamorphic reactions (Hall *et al.*, 1987) have provided circumstantial evidence for such a reduction. In the Ballachulish Slates pyrrhotite clearly disappears around growing pyrite porphyroblasts (Fig. 8) and the reaction is likely to have been 'pyrite-pulled'. The C/CO$_2$ buffer becomes more reduced relative to other buffers with increase in temperature (French and Eugster, 1965) and this leads to progressive reduction on progressive regional metamorphism (Hall, 1986). On
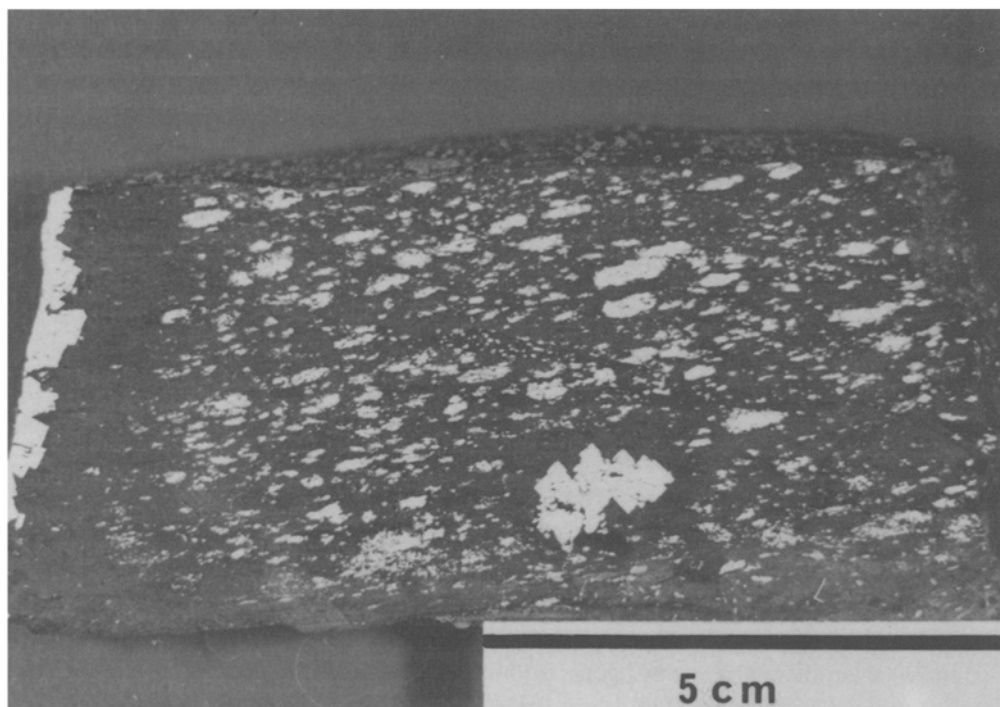
Fig. 8. Slab of Ballachulish slate cut parallel to cleavage and across a late pyrite veinlet (left). Pyrite in the veinlet and as porphyroblasts has grown at the expense of metamorphic pyrrhotite blebs. In the depletion zones around pyrite, pyrrhotite is replaced by quartz. (From Hall *et al.*, 1987, published with permission.)

cooling therefore, a C-O-H fluid buffered by C/CO_2 would become relatively oxidizing (Fig. 7). This is the process envisaged for the Ballachulish slates where near-pervasive post-metamorphic fluid has resulted in the oxidation and dissolution of pyrrhotite and the formation of pyrite. CO_2 in the fluid is the possible oxidizing agent while CH_4 is a product:

$$8FeS + 6H_2O + 9CO_2 \rightarrow 4FeS_2 + 4Fe^{2+} + 8HCO_3^- + CH_4 \ . \qquad \text{(vii)}$$
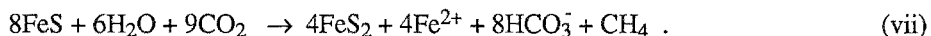
Difficulty in pyrite nucleation is evident from the relative scarcity of pyrite porphyroblasts and their similar large size. This is not surprising given the complexity of the FeS_2 structure, the stereochemistry of which is illustrated in Fig. 9 (Finklea *et al.*, 1976).

This apparent high pressure and temperature reduction of CO_2 by pyrrhotite has prompted us to speculate (Russell and Daniel, 1992) that, somewhat contrary to Wächtershäuser's view, the production of simple organic molecules took place in quite
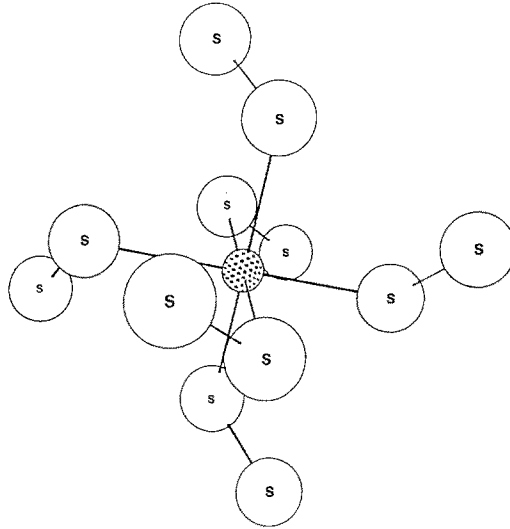
Fig. 9. Perspective drawing illustrating the stereochemistry of the $Fe(S_2{}^{2-})_6$ site in pyrite. Fe is in 6-fold octahedral coordination bonded to 6 S atoms. Each S is in 4-fold tetrahedral coordination bonded to 3 Fe and 1S.

extensive hydrothermal systems deeper within the oceanic crust, and that this provided feedstock for the cooler iron sulfide botryoidal "culture chambers". Within these further elaborations and ultimately some kind of genetically controlled metabolism became established.

Our use of an iron sulfide example for more particular speculations arose, as we discussed, from the recent interest in iron and sulfur chemistry in relation both to hydrothermal systems and to the origins of life. It is perhaps worth noting that Herrera, after more than 40 years of study into the origin of life, concluded that sulfur merited special attention because of its propensity for "cellular" development (Herrera, 1942). Little attention has been paid to Herrera's work, no doubt because of the still prevailing opinion that the first "cells" would have been made of something like lipids - or anyway that they should have been organic. But to reiterate a point made earlier, we cannot assume that the first evolving microsystems on Earth were simply simpler versions of the only evolving systems that we now know. There would, most likely, have been critical organic and inorganic components that are no longer important, or even present in our biochemistry. But perhaps iron and sulfur are among the survivors from earliest times.

Acknowledgements