appears to be within the Matuyama epoch.

The anomalous vertical growth of the SWIR/Spiess Ridge, and its consequent rapid propagation, could be due to an unusually high rate of magma supply relative to the low (0.8 cm/year) spreading rate. When spreading cannot keep up with an overabundant magma supply, the basaltic crust tends to thicken (19). It is not clear whether the Spiess event is the surface expression of a new mantle plume, or of a branch of the Bouvet plume, or of a melting anomaly unrelated to a deep, plume-like source.

The igneous emplacement of the Spiess Ridge and its northwest propagation have disrupted the RRR geometry of TJ-2, flooding the western part of the Bouvet transform, thereby isolating the SWIR Y branch (Fig. 3). As a result, the SWIR Y segment is a dying ridge and TJ-2 has ceased to be a TJ. We conclude, therefore, that the Antarctic, South American, and African plates do not meet at present in a triple point, but in a broad zone of diffuse deformation.

If the new SWIR-Spiess segment continues its northwest propagation at the present rate, within about 1 My it will impact with the MAR at about 54°15′S, 1°15′W. This will be the site of a new TJ (TJ-3 in Fig. 3). The ~70-km-long stretch of MAR between TJ-2 and TJ-3 will probably become part of the AAR, the MAR will recede northward, and the area of the Antarctic plate will increase. Thus, we have caught the plate boundaries in the transition between two different configurations, and we have obtained a snapshot of the recent death of a TJ and the imminent birth of a new one.
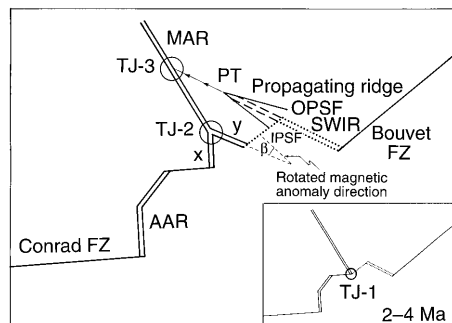

Fig. 3. Scheme outlining the evolution of the Bouvet TJ from 4 Ma to present, including a predicted configuration about 1 My in the future. The inset at lower right shows a suggested configuration valid between about 4 and 2 Ma, with a RFF-type TJ (TJ-1). The main figure illustrates a configuration valid between about 2 and 1 Ma, with a RRR-type TJ (TJ-2). The present configuration implies that TJ-2 is inactive because the SWIR-Spiess propagating ridge has disrupted the TJ-2 configuration. PT, tip of the Spiess propagating ridge; IPSF, inner pseudofault; OPSF, outer pseudofault. For significance of angle β, see text. Also shown is a predicted future configuration, with a RRR-type TJ (TJ-3) to be established within the forthcoming ~1 My.

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Activated Acetic Acid by Carbon Fixation on (Fe,Ni)S Under Primordial Conditions

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In experiments modeling the reactions of the reductive acetyl–coenzyme A pathway at hydrothermal temperatures, it was found that an aqueous slurry of coprecipitated NiS and FeS converted CO and CH_3SH into the activated thioester $CH_3\text{-}CO\text{-}SCH_3$, which hydrolyzed to acetic acid. In the presence of aniline, acetanilide was formed. When NiS-FeS was modified with catalytic amounts of selenium, acetic acid and CH_3SH were formed from CO and H_2S alone. The reaction can be considered as the primordial initiation reaction for a chemoautotrophic origin of life.

The origin of life requires the formation of carbon-carbon bonds under primordial conditions. Miller's experiments (1), in which simulating electric discharges in a reducing atmosphere of CH_4, NH_3, and H_2O produced an aqueous solution of simple carboxylic acids and amino acids, have long been considered as one of the main pillars of the theory of a heterotrophic origin of life in a prebiotic broth. Their prebiotic significance, however, is in question, because it is now thought that the primordial atmosphere consisted mostly of an unproductive mixture of CO_2, N_2, and H_2O, with only traces of molecular hydrogen (2).

An alternative theory is that life had a chemoautotrophic origin (3–6). This theory comprises several independent but complementary postulates regarding the metabolism of the primordial organisms: (i) The earliest organisms fed on CO or CO_2 at volcanic or hydrothermal sites. (ii) Their metabolism was initiated by the reductive formation of methyl mercaptan (methanethiol, CH_3SH) and its subsequent carbonylation to activated thioacetic acid (CH_3-CO-SH), akin to the reductive acetyl–coenzyme A (CoA) pathway (5). (iii) CH_3-CO-SH was fed into a carbon fixation cycle, akin to the extant reductive citric acid cycle (5). (iv) The metabolism received reducing power from the oxidative formation of pyrite from iron sulfide and hydrogen sulfide (3). (v) All chemical conversions of the primordial metabolism occurred in a ligand sphere, held together by bonding to the surfaces of iron-sulfur minerals (4), where transition metal ions such as Ni^{2+} or Co^{2+} or Se are catalytically active (5, 6). (vi) Subsequent evolutionary steps included the replacement of thioacids by thioesters and the conversion of at first wasteful branch products (like amino acids) into biocatalysts. These steps represent a dual feedback into the carbon fixation pathways

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and into their own branch pathways (6) by ligand acceleration of the transition metal sulfide catalytic centers.

Previous experiments (7–10) focused on redox reactions as chemical consequences of postulates (iii), (iv), and (v). Here we present experiments showing that the initiation pathway of postulate (ii) can be accomplished by reactions on (Fe,Ni)S.

The reductive acetyl-CoA pathway, or Wood-Ljungdahl pathway, has been considered an ancient carbon fixation pathway (11). It generates acetyl-CoA from CO_2 or CO. The key enzyme in this pathway, acetyl-CoA synthase, contains an Ni-Fe-S reaction center and forms acetyl-CoA from coenzyme A, CO, and a methyl group (12). CO, acquired from the environment or generated enzymatically from CO_2, is bonded to an Fe reaction center (13). The methyl group is transferred from an N-methyl pterin by a corrinoid-FeS protein to a Ni reaction center for acetyl formation (14). In translating this reaction into a reaction of a primordial metabolism, we considered that sulfide activity at volcanic and hydrothermal sites was high. At such sites, CH_3SH may be seen as the evolutionary precursor of N-methyl pterin (5). CH_3SH has been detected in volcanic gasses (15) and in fluid inclusions in quartz of archean origin (16). Furthermore, FeS is a ubiquitous mineral at such sites and NiS is also commonly present (17); for example, in pentlandite, FeS and NiS coexist in a weight ratio of 45–25:15–45 (18). Therefore, a mixture of NiS and FeS might be seen as the evolutionary precursor of enzymatic Ni-Fe-S clusters. Finally, CO is a regular component of hydrothermal vent waters (0.26 to 0.36 cm³/kg) (19) and of volcanic exhalations, where, for example, the gas components other than H_2O may comprise 33.5 v/v CO_2, 0.8 v/v CO, and 53.7 v/v H_2S (20) and therefore could have served as a substrate of primordial carbon fixation.

In view of these considerations, we reacted CH_3SH and CO in the presence of FeS, CoS, or NiS precipitated in situ. All reactions were carried out at 100°C in water at autogenic pressure and at various pH values (21). In the presence of NiS alone, acetic acid was formed. Acetic acid and all other products were identified by gas chromatography (GC), high-performance liquid chromatography (HPLC), and gas chromatography–mass spectroscopy (GC-MS). The yields are plotted in Fig. 1 over a broad range of pH values, as measured in the final reaction mixture. The productivity curve is high at strongly acidic and alkaline pH and low at moderately acidic to neutral pH. In the absence of CO, no acetic acid was formed. In a comparative experiment with $NiSO_4$ but without Na_2S, no reactions occurred at acidic pH; however, under alkaline conditions an $Ni(OH)_2$ precipitate (22) generated acetic acid. FeS alone or CoS alone were inactive.

We carried out additional reactions with a bimodal catalyst consisting of NiS and FeS coprecipitated in equimolar amounts (Fig. 1). The productivity curve shows a dramatic change from that for NiS alone. The formation of acetic acid was largely suppressed in the acidic and alkaline ranges, but in a narrow range around pH 6.5, the yield of acetic acid was high, up to 40 mole percent (calculated on the basis of CH_3SH). This result indicates that an FeS center interacts with the NiS reaction center. The results are in agreement with the enzymatic reaction center having a bimodal Ni-Fe-S cluster. Thus, with NiS alone the maximum activity was far outside the physiological pH range, whereas with FeS-NiS it was within this range. When benzyl mercaptan or phenethyl mercaptan were used instead of methyl mercaptan, phenylacetic acid or phenylpropionic acid was obtained (identified by HPLC and GC-MS) with a similar dependency of the reaction rates on the pH and catalytic metals. The net reaction may be summarized as follows:

$$CH_3SH + CO + H_2O \rightarrow$$
$$CH_3\text{-}COOH + H_2S$$
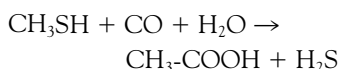
On the basis of the established mechanism of the Monsanto acetic acid process (23) and the proposed enzymatic mechanism (12–14) of the reaction of acetyl-CoA synthase, we speculate that the reaction proceeds through the intermediate formation of a metal-bonded thioacetate ligand (Fig. 2). To test for the occurrence of such an activated intermediate, we added 200 μmol of aniline as a trapping agent in addition to 100 μmol of CH_3SH and found in the presence of FeS-NiS at a final pH of 5.9 or 6.2 a yield of 4.6 or 4.8 μmol of acetanilide, respectively (24). To exclude the possibility that this acetanilide was formed by an equilibrium reaction between aniline and coproduced free acetic acid, we used 50 μmol of acetic acid in place of CH_3SH (under otherwise identical conditions), which gave 0.9 μmol of acetanilide at pH 5.8. These results are compatible with the intermediate formation of a thioacetic acid ligand of a metal center and its subsequent reaction with aniline in competition with hydrolysis (Fig. 2).

De Duve (25) proposed that thioesters formed in a prebiotic broth from carboxylic acids and mercapto (thiol) compounds and served as the energy source for the origin of life. In contrast, the theory of a chemoautotrophic origin of life postulates that thioesters may have been early evolutionary successors of thioacids (6), so we tested whether a thioester ($CH_3\text{-}CO\text{-}SCH_3$) could be detected in the reaction mixture. To bias the reaction conditions for the formation of thioester we chose a molar ratio of $NiSO_4$ to Na_2S to CH_3SH of 2:1.5:1. With this system, 7 or 9 μmol of $CH_3\text{-}CO\text{-}SCH_3$ was detected in two runs after 20 hours at pH

Fig. 2. Notional representation of a hypothetical mechanism of acetic acid formation from CO and CH_3SH on NiS-FeS. Step a: uptake of CO by an Fe center and of CH_3SH by an Ni center. Step b: formation of a methyl-Ni center. Step c: migration of methyl to a carbonyl group, forming an Fe-bonded (or Ni-bonded) acetyl group. Step d: migration of acetyl to a sulfido (or sulfhydryl) ligand, forming a thioacetate ligand of Ni (or Fe). Step e: hydrolytic formation of acetic acid. The free valences of the sulfur ligands are either bonded to another metal center or to H (or CH_3). Alternatively, in step d the acetyl group may migrate to a $CH_3\text{-}S\text{-}$ ligand to form the methylthioester $CH_3\text{-}CO\text{-}SCH_3$, which subsequently detaches.

Fig. 1. Yield of acetic acid formed from CH_3SH (100 μmol) and CO in the presence of 1 mmol of NiS (triangles), 1 mmol of NiS plus 1 mmol of FeS (crosses), 1 mmol of NiS plus 1 mmol of CoS (squares), or 2 mmol of $NiSO_4$ (circles). The acetic acid yield is plotted against the final pH of the reaction mixture. In two repetitions the curves were reproduced with deviations of up to 20%.
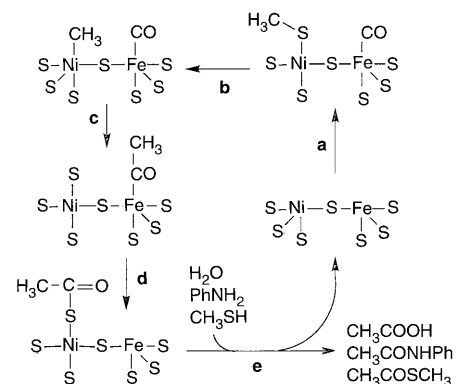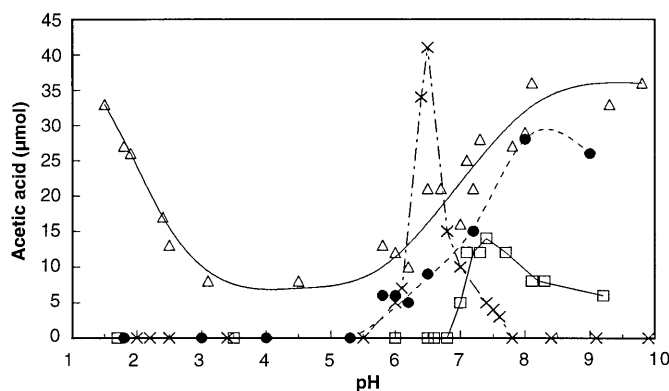
1.6 in addition to about 25 μmol of acetic acid (*26*). The thioester was not formed by a secondary equilibration between CH_3SH and free acetic acid because we failed to detect more than 0.2 μmol of CH_3-CO-SCH_3 at pH 1.7 when, under otherwise identical conditions, CO was replaced by N_2 and 30 μmol of acetic acid was added. Furthermore, 100 μmol of CH_3-CO-SCH_3 in 10 ml of H_2O at pH 1.6 and 100°C was rapidly hydrolyzed in 20 hours to less than 0.2 μmol in water or 0.4 μmol in the presence of FeS-NiS.

In the chemoautotrophic theory of the origin of life CH_3SH is thought to form as an intermediate by reduction of CO or CO_2 with FeS and H_2S. This prediction has been confirmed by the detection of small amounts of CH_3SH in the gas phase above a heated aqueous slurry of FeS reacting with H_2S and CO_2 (*27*). We found that acetic acid can be generated from CO as the sole carbon source. Throughout the acidic pH range, reaction of an aqueous slurry of 1 mmol of NiS and 1 mmol of FeS (coprecipitated in the presence of 20 μmol of Se) and 300 μmol of H_2S during 7 days at 120°C produced 0.1 to 0.3 μmol of acetic acid. The gas phase above the slurry contained traces of COS and 0.2 μmol (pH 7.8) to 1.0 μmol (pH 0.8) of CH_3SH (*28*).

Our experiments indicate that carbon fixation could happen at hydrothermal vents or volcanic settings. The rapid hydrolysis of methyl thioacetate under aqueous, hydrothermal conditions implies that accumulation of thioesters in a prebiotic broth is unlikely and that thioesters cannot serve as preexisting energy sources. In contrast, the occurrence of a metastable thioester intermediate and the speculative occurrence of a thioacetate intermediate are kinetically controlled. The thioester and thioacid intermediates have the necessary group activation for further biosynthetic reactions. The suggested mechanism (Fig. 2) of our reactions is an example for a surface metabolism (postulate v), wherein activated anionic products of carbon fixation become bonded to cationic surface valences of minerals such as transition metal sulfides in statu nascendi and react further within a ligand sphere before being hydrolyzed.

Small amounts of methane (0.1 to 0.3 μmol in the presence of NiS or 0.02 to 0.06 μmol in the presence of FeS-NiS) were found in our experiments with CH_3SH around pH 7. From the point of view of a primordial metabolism this side reaction would be a waste reaction. But at a later stage of evolution, after the emergence of chemiosmosis, it could be used for bioenergy production in conjunction with a replacement of NiS by the Ni-tetrapyrrol F_{430} (*29*). We also detected significant amounts, from 5 to 20 μmol, of CO_2 in the presence of NiS or NiS-FeS,

which may be seen as the evolutionary precursor reaction of the enzymatic CO-CO_2 interconversion at an Ni-Fe-S cluster (*30*).

In contrast to enzymatic carbonylation, industrial carbonylation requires high temperatures and pressures (*14*). The reactions reported here proceeded at 1 bar CO and at temperatures typical for hyperthermophilic microorganisms. It is of interest that methanogens and thermophilic sulfate reducers are capable of growing on CH_3SH as the sole carbon source (*31, 32*), which may be a throwback to the earliest days of life. The conditions of our reaction may be taken as a model for understanding the habitats of primitive forms of life on Earth or Mars, whereby the joint occurrence of FeS-NiS, pyrite, and CH_3SH may be interpreted as a marker for such habitats. Our results lend support for a hyperthermophilic, chemoautotrophic origin of life in an iron-sulfur world. It may strike us as ironic that nickel, one of the last biocatalytic metals to be recognized in biology (*33*), may well turn out to be among the very first in the history of life.

Note added in proof: Our result suggests a CO fixation cycle (postulate iii) from CH_3COSH through, for example, CH_2=C(SH)COSH (*34*) and HSOC-CHSH-CH_2-COSH, with cleavage into CH_3-COSH and $(HS)_2CH$-COSH as core of a primordial metabolism.

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21. For a typical experiment, a mixture of $FeSO_4 \cdot 7H_2O$ (278 mg, 1 mmol) and $NiSO_4 \cdot 6H_2O$ (262 mg, 1 mmol) was first deaerated in serum bottles (120 ml) sealed closed with Viton stoppers (Ochs, Borenden, Germany), then 2 ml of a solution of $Na_2S \cdot 9H_2O$ (240 mg, 2 mmol) in oxygen-free water (doubly distilled and boiled and cooled under a stream of nitrogen) was added for the in situ coprecipitation of FeS and NiS. Subsequently the space above the liquid was subjected to 1.05 bar (~4.5 mmol) CO (Messer Griesheim, Düsseldorf, CO 2.0), then 150 μl of 4N NaOH in oxygen-free water was added to adjust the pH to 8, and oxygen-free water was added to bring the liquid volume to 10 ml. Finally, 2.5 ml of CH_3SH (100 μmol) was added, and the reaction was carried out for 7 days at 100°C. All chemicals were purchased from Aldrich. For analysis, a sample of the liquid reaction mixture was centrifuged. The supernatant had a pH of 6.5 and contained 41 μmol of acetic acid, as determined by GC (Varian Aerograph, Series 1400; NPGS column at 140°C) and identified by GC-MS (Carlo Erba 4160/Varian MAT 112S). The gas phase was analyzed (Hewlett-Packard 5890 gas chromatograph; Chrompack carboplot P7/25m column; temperature gradient from 30° to 115°C) and found to have 19 μmol of CO_2 and 0.04 μmol of CH_4.
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26. The typical experiment (*21*) was repeated with 524 mg (2 mmol) of $NiSO_4 \cdot 6H_2O$, 180 mg (1.5 mmol) of $Na_2S \cdot 9H_2O$, and 25 ml (1 mmol) of CH_3SH, a reaction time of 20 hours, and a final pH of 1.6. In two runs, 7 or 9 μmol of CH_3-CO-SCH_3 were found, as measured by HPLC (*24*) and determined by GC-MS (*21*), in addition to ~25 μmol acetic acid.
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