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 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.

REFERENCES AND NOTES

1. Data provided by C. T. Sandwell and W. H. F. Smith, The Geodetic Data Center, Scripps Institute of Oceanography, La Jolla, CA 92033, USA.
10. The data were obtained during two Italian-Russian expeditions with the research vessels N. Strakhov in 1994, and Gledenzhik in 1996. In addition to multibeam morphobathymetry and magnetometry, gravimetric and seismic reflection data were also collected. Extensive sea-floor rock sampling was also achieved.
20. Sponsored by the Italian Antarctic Program (PNRA). We thank the officers and crews of RV N. Strakhov and RV Gledenzhik; N. Zitellini, who was co-chief scientist in cruise S-18, as well as D. Brunelli, A. Ciprioni, L. Gasperini, F. Sciuto, and M. Terrenzoni for their cooperation at sea; and L. Casoni for help with the illustrations. Contribution No. 5628 from L-DEO and No. 1075 from IGM.

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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 CH₃SH into the activated thioester CH₃-CO-SCH₃, 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 CH₃SH were formed from CO and H₂S alone. The reaction can be considered as the primordial initiation reaction for a chemosynthetic origin of life.

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

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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 CH₄, NH₃, and H₂O 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 cycle (2).

An alternative theory is that life had a chemosynthetic 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 CO₂ at volcanic or hydrothermal sites. (ii) Their metabolism was initiated by the reductive formation of methyl mercaptan (methanethiol, CH₂SH) and its subsequent carbonation to activated thioacetic acid (CH₃-CO-SH), 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 CH₃SH were formed from CO and H₂S alone. The reaction can be considered as the primordial initiation reaction for a chemosynthetic origin of life.

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http://www.sciencemag.org • SCIENCE • VOL. 276 • 11 APRIL 1997
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 CO₂ 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, CO₂, and a methyl group (12). CO, acquired from the environment or generated enzymatically from CO₂, is bonded to an Fe reaction center (13). The methyl group is transferred from an N-methyl pterin by a corrinoid-Fe₃S 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, CH₃SH may be seen as the evolutionary precursor of methyl-CH₃ pterin (5). CH₃SH has been detected in volcanic gases (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 H₂O may comprise 33.3 v/v CO₂, 0.8 v/v CO, and 53.7 v/v H₂S (20) and therefore could have served as a substrate of primordial carbon fixation.

In view of these considerations, we reacted CH₃SH 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 NiSO₄ but without Na₂S, 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 CH₃SH). 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:

\[ \text{CH}_3\text{SH} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{S} \]

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 CH₃SH 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 CH₃SH (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 chemosynthetic origin of life postulates that thioesters may have been early evolutionary successors of thiocicids (6), so we tested whether a thioester (CH₃-CO-SCH₃) could be detected in the reaction mixture. To bias the reaction conditions for the formation of thioester we chose a molar ratio of NiSO₄ to Na₂S to CH₃SH of 2:1:5:1. With this system, 7 or 9 µmol of CH₃-CO-SCH₃ was detected in two runs after 20 hours at pH 6.5.
1.6 in addition to about 25 μmol of acetic acid (26). The thioester was not formed by a secondary equilibration between CH₃.SH and free acetic acid because we failed to detect more than 0.2 μmol of CH₃.CO-SCH₃ at pH 1.7 when, under otherwise identical conditions, CO was replaced by N₂ and 30 μmol of acetic acid was added. Furthermore, 100 μmol of CH₃.CO-SCH₃ in 10 ml of H₂O 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 chemoeautothetic theory of the origin of life CH₃.SH is thought to form as an intermediate by reduction of CO or CO₂ with FeS and H₂S. This prediction has been confirmed by the detection of small amounts of CH₃.SH in the gas phase above a heated aqueous slurry of FeS reacting with H₂S and CO₂ (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 H₂S 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 CH₃.SH (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 a natural setting and react further within a liquid 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 CH₃.SH 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 Fe₃₃₀ (29). We also detected significant amounts, from 5 to 20 μmol, of CO₂ in the presence of NiS or NiS-FeS, which may be seen as the evolutionary precursor reaction of the enzymatic CO₂-CO₃ interconversion at an Ni-Fe-S cluster (30).

In contrast to enzymatic carboxylation, industrial carboxylation 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 CH₃.SH 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 CH₃.SH may be interpreted as a marker for such habitats. Our results lend support for a hyperthermophilic, chemoeautothetic origin of life in an iron-sulfur world. It may strike us ironic that nickel, one of the last biocatalysts to have emerged (after the emergence of chemiosmosis, it could be used for bioenergy production in conjunction with a replacement of NiS by the Ni-tetrapyrrol Fe₃₃₀ (29). We also detected significant amounts, from 5 to 20 μmol, of CO₂ in the presence of NiS or NiS-FeS, which may be seen as the evolutionary precursor reaction of the enzymatic CO₂-CO₃ interconversion at an Ni-Fe-S cluster (30).

During the reaction, after the emergence of chemiosmosis, it could be used for bioenergy production in conjunction with a replacement of NiS by the Ni-tetrapyrrol Fe₃₃₀ (29). We also detected significant amounts, from 5 to 20 μmol, of CO₂ in the presence of NiS or NiS-FeS,