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## LETTER TO THE EDITOR

## Is high-pressure water the cradle of life?

**Marie-Paule Bassez**

Université de Strasbourg-3, Département Chimie, 72 route du Rhin, 67400 Illkirch, France

E-mail: [marie-paule.bassez@urs.u-strasbg.fr](mailto:marie-paule.bassez@urs.u-strasbg.fr)

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### Abstract

Several theories have been proposed for the synthesis of prebiotic molecules. This letter shows that the structure of supercritical water, or high-pressure water, could trigger prebiotic synthesis and the origin of life deep in the oceans, in hydrothermal vent systems. Dimer geometries of high-pressure water may have a point of symmetry and a zero dipole moment. Consequently, simple apolar molecules found in submarine hydrothermal vent systems will dissolve in the apolar environment provided by the apolar form of the water dimer. Apolar water could be the medium which helps precursor molecules to concentrate and react more efficiently. The formation of prebiotic molecules could thus be linked to the structure of the water inside chimney nanochannels and cavities where hydrothermal piezochemistry and shock wave chemistry could occur.

(Some figures in this article are in colour only in the electronic version)

### 1. Introduction

Since experiments began in 1953, various gaseous mixtures simulating the primitive Earth atmosphere, from strongly reducing  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$  to oxidized  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$ , have been submitted to diverse energy sources [1]. These experiments led to the synthesis of biochemical molecules, including 17 of the 20 amino acids found in proteins. The two sugars and the five bases of the nucleic acids RNA and DNA were also found in the reaction products. The atmosphere which can yield the widest range of organic compounds appears to be a reducing mixture of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2$  and very little  $\text{H}_2$ , with a ratio  $\text{N}/\text{C} > 1$ . In these experiments initial formation of the two fundamental prebiotic molecules, the aldehyde  $\text{HCHO}$  and hydrogen cyanide  $\text{HCN}$ , occurs. The spark discharge yields of amino acids, of hydrogen cyanide and of formaldehyde are about the same with  $\text{CH}_4$ , with  $\text{H}_2/\text{CO} > 1$  and with  $\text{H}_2/\text{CO}_2 > 2$ . These last two ratios seem, however, highly improbable in the primitive atmosphere because of gravitational  $\text{H}_2$  escape. Thus, it has been experimentally proven [1] that a primitive Earth atmosphere rich in methane could produce the biological molecules

necessary to form the structure of living cells and the energetic processes occurring inside them.

However, with advances in geology which proposed a non-reducing primitive atmosphere rich in carbon dioxide, and with the discovery of organic compounds in meteorites, the theory of importation of extraterrestrial organic molecules [2–6] became widely favoured. The hypothesis of extraterrestrial prebiotic molecules was supported by the isotopic ratio of deuterium to hydrogen. This ratio had been found to be virtually identical in comet Halley and in terrestrial oceans. Hence, water and simple organic molecules that contributed to the origin of life could have been imported to Earth during the early cometary bombardment [7]. However, more recent studies of comet Halley [8, 9] in 1995 and of comets Hale–Bopp and Hyakutake [10, 11] in 1998 showed that oceans have significantly less deuterium than previously thought. It consequently seems quite plausible that there exists an additional origin for the organic matter that contributed to the origin of life.

The exploration of the sea-floor hot springs on the Galapagos mid-ocean rift by the American submarine *Alvin* in 1977 [12], at a depth of 2500 m, revealed that microorganisms could survive under conditions of extreme heat and pressure. Corliss [13] then suggested a submarine hot spring hypothesis for the origin of life. Life could arise from water, gas and rocks far away from the sun's rays. Wächtershäuser [14] developed a model of surface metabolism near these volcanic vents. The reaction of hydrogen sulfide ( $\text{H}_2\text{S}$ ) on iron sulfide ( $\text{FeS}$ ) could be followed by the conversion of  $\text{CO}_2$  into organic molecules. Mixing iron sulfides or iron oxides with  $\text{N}_2$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  at temperatures between 300 and 800 °C and pressures of 0.1–0.4 GPa, Brandes [15] obtained ammonia, which is a key molecule for the formation of amino acids in classical prebiotic chemistry [16].

The model proposed here for the molecular origin of life takes into account the physicochemical properties of the environment surrounding the reacting molecules, and especially the polarity of the solvent inside and outside hydrothermal vents. It is concluded that for a reduced oxygen–oxygen intermolecular distance, the structure of water could include a large number of symmetrical dimers with zero dipole moment. In such an apolar solvent, apolar molecules are soluble. They mix well and react more efficiently. Consequently, the precursor apolar molecules  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  found deep in the oceans, inside and around hydrothermal vents, may be found in higher concentrations in apolar water. Apolar water could be the privileged medium for high-pressure prebiotic chemistry, and could trigger specific prebiotic chemical processes.

## 2. The structure of supercritical water

Water in submarine hydrothermal systems found between 2000 and 3500 m is under high temperatures (350–450 °C) and pressures (20–35 MPa). These high-temperature, high-pressure values correspond to the state of water called supercritical in the thermodynamic ( $T$ ,  $P$ ) diagram:  $T_c = 374^\circ\text{C}$ ,  $P_c = 22.1\text{ MPa}$  ( $T_c \sim 402^\circ\text{C}$  for seawater). In recent years, supercritical water has attracted interest in the scientific community, and a large number of studies [17, 18] have been performed. Experiments show that some physicochemical properties are different from those of liquid water. For instance, the dielectric constant  $\epsilon$ , the viscosity  $\eta$ , the density and the ionic hydration decrease in supercritical water [19, 20]. Consequently, the solubility of ionic and polar compounds diminishes, while the solubility of apolar molecules increases. Neutron diffraction experiments [21] show that the tetrahedral structure is lost—only a small number of bonds persist, possibly due to the presence of dimers.

In previous work on supercritical water [22, 23], it was reported that, for a reduced oxygen–oxygen intermolecular distance, the inverse dimer was favoured on the electronic

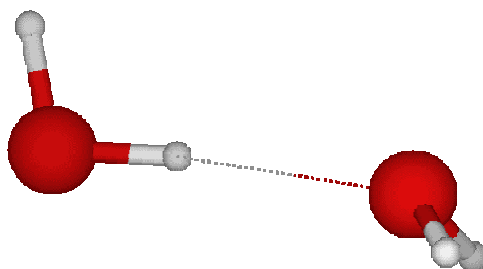


Figure 1. Linear dimer at the equilibrium O–O distance of 2.91 Å.

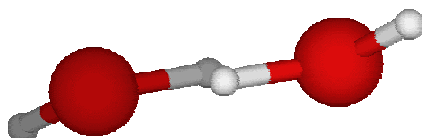
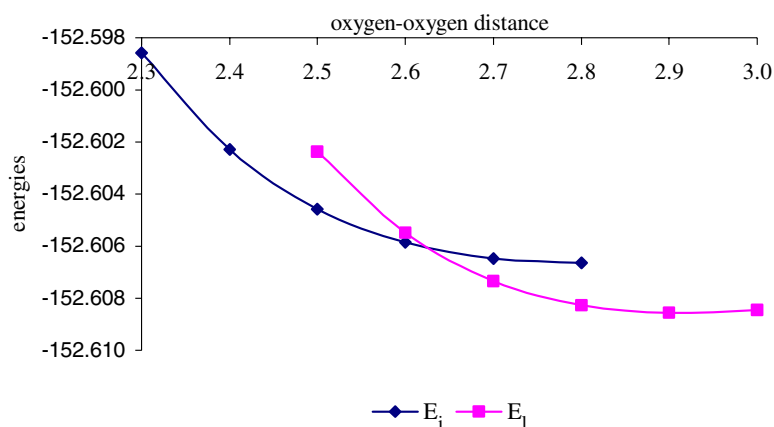


Figure 2. Inverse dimer at the equilibrium O–O distance of 2.80 Å.

potential energy surface (PES), compared with the linear structure. *Ab initio* calculations have now been performed at the Möller–Plesset level (MP2), with the GAMESS program and a 6-311 \* \* + + basis set using 74 Gaussian functions including d-type on the oxygen and p-type on the hydrogen. An energy optimization of the dimer geometry, without symmetry constraint and without constraint on the oxygen–oxygen distance, leads to a linear geometry with a plane of symmetry ( $C_s$ ) (figure 1). The oxygen–oxygen distance calculated for the energy minimum is 2.91 Å, quite near the experimental gaseous O–O distance found with microwave spectroscopy [24], namely 2.98 Å. Calculations were then performed with a value of the oxygen–oxygen distance decreasing from 3.00 to 2.50 Å in steps of 0.10 Å, starting from a distorted geometry similar to the linear one, and without any symmetry constraint (table 1). Until a distance of 2.60 Å, the optimized geometry is the linear dimer. But at 2.50 Å, the optimized geometry becomes the inverse dimer. Calculation with a  $C_s$  symmetry constraint and an O–O distance of 2.50 Å leads to the energy value of the linear geometry. Optimization of the geometry with a point of symmetry (figure 2) was then performed under a  $C_i$  symmetry constraint and without constraint on the O–O distance. The oxygen–oxygen distance calculated for the energy minimum of this inverse dimer is 2.80 Å. Optimizations, without symmetry constraint, but starting from a distorted geometry of the  $C_i$  type, were performed with O–O distances between 2.30 and 2.80 Å (table 1). Electronic energies of the linear and inverse dimers are reported as a function of the oxygen–oxygen intermolecular distances in table 1 and figure 3. These results show that at 2.63 Å, only 0.28 Å below the O–O distance of the linear dimer on its global minimum, another structure for the water dimer is energetically favoured: the symmetrical inverse dimer showing a point of symmetry. Consequently, under high pressure, for a reduced oxygen–oxygen intermolecular distance of 0.28 Å, an apolar form of water could be favoured.

It is interesting to compare the energies of the inverse and linear water dimers with their minimum geometries optimized under the  $C_i$  and  $C_s$  symmetry constraints respectively. The energy difference between the optimized linear dimer (–152.6086 hartree) and the inverse dimer (–152.6066 hartree) is –0.0020 hartree (1.25 kcal mol<sup>–1</sup>). Optimized intermolecular O–O distances are respectively 2.91 and 2.80 Å. One of the numerical uncertainties that affects all *ab initio* computations is the well-known basis set superposition error (BSSE). This error



**Figure 3.** Energies (in hartree) of the linear ( $E_l$ ) and of the inverse ( $E_i$ ) water dimers as a function of the O–O distance (in Å).

**Table 1.** Electronic potential energies (in hartree) of the linear ( $l$ ) and of the inverse ( $i$ ) water dimers as a function of the O–O distance (in Å).

$D$	$E_i$	$E_l$
3.00		–152.608 45
2.90		–152.608 55
2.80	–152.606 63	–152.608 27
2.70	–152.606 47	–152.607 34
2.60	–152.605 86	–152.605 49
2.50	–152.604 57	–152.602 37
2.40	–152.602 29	
2.30	–152.598 57	

**Table 2.** Counterpoise fragment monomer calculations: MP2, Möller–Plesset level; HF, Hartree–Fock; CP, counterpoise.

Dimer type	Level	Fragment	Monomer basis (hartree)	Dimer basis (hartree)	CP (hartree)
Linear	MP2	Donor	–76.299 411	–76.299 937	0.000 526
Linear	MP2	Acceptor	–76.299 436	–76.301 496	0.000 206
Inverted	MP2		–76.299 419	–76.300 234	0.000 815
Linear	HF	Donor	–76.052 397	–76.052 593	0.000 196
Linear	HF	Acceptor	–76.052 586	–76.053 464	0.000 878
Inverted	HF		–76.052 586	–76.052 818	0.000 232

has been corrected while using the counterpoise (CP) method [26]. The CP energy correction related to a monomer fragment is the energy of the monomer in its monomer basis minus the energy of the same monomer in the whole dimer basis set. It is a positive term. The whole dimer CP correction is the sum of the two monomer CP energy corrections. We computed the CP corrections at the monomer geometries as optimized in the dimer, since it is in these distorted geometries that a monomer ‘borrows’ Gaussian functions from its partner fragment in order to improve its own intramolecular arrangement. Results are listed in table 2.

**Table 3.** Electronic potential energies (in hartree) of the linear ( $E_l$ ) and of the inverse ( $E_i$ ) water dimers as a function of the dielectric constant.

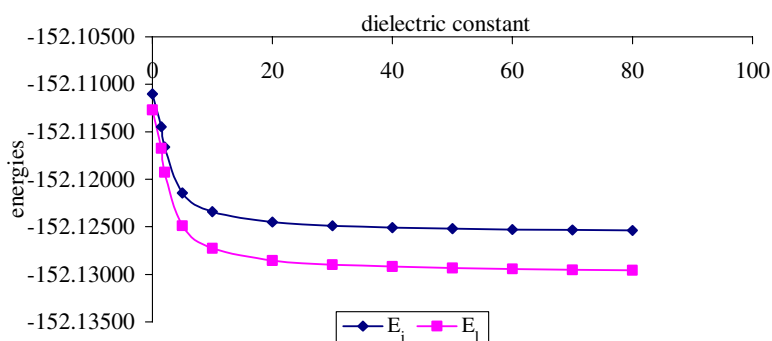
Dielectric	$E_i$	$E_l$	$E_l - E_i$
0	-152.111 00	-152.112 70	-0.001 64
1.5	-152.114 48	-152.116 75	-0.002 27
2	-152.116 60	-152.119 24	-0.002 64
5	-152.121 42	-152.124 90	-0.003 48
10	-152.123 42	-152.127 25	-0.003 83
20	-152.124 51	-152.128 53	-0.004 02
30	-152.124 89	-152.128 98	-0.004 09
40	-152.125 08	-152.129 20	-0.004 12
50	-152.125 20	-152.129 34	-0.004 14
60	-152.125 28	-152.129 43	-0.004 15
70	-152.125 33	-152.129 50	-0.004 17
80	-152.125 37	-152.129 55	-0.004 18

At the MP2 level the energy of the linear dimer before correction is  $-152.6086$ . After CP correction it becomes  $-152.6060$ . For the inverse dimer the energy is  $-152.6066$  and after CP correction  $-152.6050$ . After CP correction, the energy difference between the optimized geometries of the linear and inverse dimers becomes  $-0.0010$  hartree ( $0.63$  kcal mol $^{-1}$ ). Therefore, the energy difference is decreased by half after correction. This shows that *ab initio* computations tend to underestimate the energy of the inverse dimer in comparison to the linear dimer.

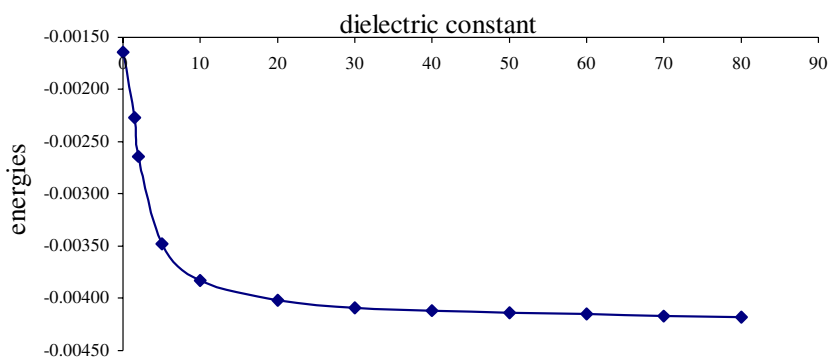
The CP correction has also been estimated at the Hartree–Fock (HF) level at the optimized MP2 geometry. The restricted Hartree–Fock (RHF) energy of the linear dimer before correction is  $-152.1127$  and after CP correction  $-152.1116$ . For the inverse dimer, the energy is  $-152.1110$  and after CP correction  $-152.1106$ . As expected the CP correction is less important at the HF level. The energy difference at the HF level is  $1.07$  kcal mol $^{-1}$  and after CP  $0.63$  kcal mol $^{-1}$ .

Solvation effects have been estimated using a conductor-like screening model. The dielectric cavity is built by the van der Waals surfaces of each atom. The size of the cavity can be adjusted using multiples of the van der Waals radius. One advantage of the COSMO approach is the possibility of a treatment at the MP2 level, the MP2-COSGMS method [27]. Unfortunately, numerical stability problems have prevented the use of this method as implemented in GAMESS. Various cavity sizes and various basis sets such as 6-311G\*\* and 6-311G\* have been tried in vain. Therefore, we studied the solvation effect on the RHF wave functions [28] but at an MP2 optimized geometry, using a wide range of dielectric constants from 1.5 to 80. The results are shown in table 2 and figures 4 and 5. The solvation effect becomes almost constant starting from a dielectric constant of 30.

For values of the dielectric constant from 0 to 10, the RHF energy difference between the inverse and linear dimers varies from  $1.03$  to  $2.40$  kcal mol $^{-1}$  respectively. Vibrational and rotational thermodynamic contributions to the free energy difference between the inverse and the linear water MP2 optimized dimers *in vacuo* have also been taken into account. Vibrational contributions, including the zero-point energy have been estimated by computing vibrational frequencies within the harmonic approximation. Rotational contributions have been estimated within the rigid rotor approximation. Such a free energy difference has been calculated, without CP correction, to be  $0.44$  kcal mol $^{-1}$  at 623 K and  $0.32$  kcal mol $^{-1}$  at 723 K.



**Figure 4.** Energies (in hartree) of the linear ( $E_l$ ) and of the inverse ( $E_i$ ) water dimers as a function of the dielectric constant.



**Figure 5.** Energy difference ( $E_l - E_i$ ) (in hartree) as a function of the dielectric constant.

### 3. Discussion

The value of 0.28 Å should be viewed with caution. Of course, better results could be obtained with larger and more costly basis sets. Moreover, comparisons with experimental diffraction results are difficult. Indeed, uncertainties in the radial distribution functions obtained from diffraction experiments have recently been discussed [25]. They led to statements about water structure above the critical point which were controversial. Consequently, it seems that improvements are still needed before an accurate estimate of the O–O distance can be safely assessed.

It is difficult to estimate precisely the average energy difference between a linear and an inverse dimer solvated in liquid water, but we have several clues. *In vacuo* the relative electronic energy difference at the MP2 level is 1.25 kcal mol<sup>-1</sup> and after CP correction it becomes 0.63 kcal mol<sup>-1</sup>, but the CP correction is not a precise tool. When taking into account vibrational and rotational energy contributions, the energy difference drops to 0.32 kcal mol<sup>-1</sup> at 723 K, but this estimation is made without CP correction and is relying on the harmonic approximation which is not very precise. Considering the effect of solvation at the HF level, the energy difference increases from 1.03 *in vacuo* to 2.40 kcal mol<sup>-1</sup> at a dielectric constant of 10. From all these values, within the range of temperature and pressure of supercritical water, it is possible to reasonably consider that the energy difference between linear and inverse dimers should be less than 1.8 kcal mol<sup>-1</sup>. This value is of the same magnitude as  $kT$  values at 623 K (1.24 kcal mol<sup>-1</sup>) and at 723 K (1.44 kcal mol<sup>-1</sup>). It is difficult to theoretically derive a more

precise estimate of dimer energy difference. It is, however, not the goal of the present study. The aim here is simply to show that the inverse water dimer population becomes a significant component of the overall dimer population in supercritical water.

Inverse dimers with zero dipole moment should contribute to the experimental physicochemical properties of supercritical water such as the decrease of the dielectric constant and the decrease in solubility of ionic and polar compounds. It is possible to conclude that in submarine hydrothermal systems water is most probably composed of a large number of these symmetrical dimers. This conclusion is also reinforced by experimental results, which provide evidence for a loss of tetrahedral coordination in supercritical water [21, 29].

This significant role played by the inverse dimers is reinforced when the zero-point energy is taken into account [30]. Indeed, the energy difference between the inverse and the linear dimers decreases substantially. Furthermore, a recent analysis [31] of the water dimer PES obtained from *ab initio* calculations confirms earlier results. The important role of the inverse dimer has also been underlined in a classical molecular dynamics study on a density functional theory (DFT) PES [32]. It seems that no zero-point energy or quantum vibrational contributions were taken into account in this last calculation. However, a significant population of inverse dimers was produced.

#### 4. High-pressure prebiotic chemistry and the origin of life

Apolar molecules found deep in the oceans in hydrothermal vent systems should dissolve in the apolar environment provided by the apolar form of the water dimers. Apolar water could be the medium which helps molecules to concentrate and react more efficiently to initiate a prebiotic chemistry. Indeed, the molecules CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> proposed for the origin of life in the primitive Earth atmosphere, are also present in hydrothermal fluids. Hydrogen sulfide, also present in hydrothermal fluids, is also in the supercritical state ( $T_c = 99^\circ\text{C}$ ,  $P_c = 9\text{ MPa}$ ). At this high pressure, H<sub>2</sub>S is known to be apolar also. These apolar molecules should be present at higher concentrations in apolar water.

Consequently, the mixture of all these apolar molecules, CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S and CO<sub>2</sub>, in the presence of minerals acting as catalysts, could lead to prebiotic synthesis. Radioactive sources concentrated in the Earth's crust [33] could activate nitrogen and enhance prebiotic chemical reactions. The nature of high-pressure water, with its apolar dimers, could be the necessary environmental condition to concentrate the elementary molecules and trigger prebiotic chemistry. Reactions could occur inside cavities acting as chemical reactors or on rock surfaces. Indeed, chimneys are formed from dissolved minerals that precipitate when superhot water meets cold ocean water. It is highly likely that this solid deposition occurring at the turbulent interface between superhot and cold water would create a spongy solid with microcavities and nanochannels of fractal dimensions as well as larger size cavities.

Furthermore, it is not only the hydrostatic pressure that must be taken into account but also the much higher effective local pressures created by the pulsed dynamics and shock waves of superheated water flowing through microchannels. Therefore, specific reactions might occur in particular cavities, while cavity walls might act as catalysts or reactants. Chimneys might consequently provide an exceptionally rich set of diverse interacting chemical reactors. As the first steps, the key molecules of hydrogen cyanide (HCN), formaldehyde (HCHO) and cyanoacetylene (HC<sub>3</sub>N) could be formed. In this apolar aqueous environment, a new kind of chemistry could occur: prebiotic chemistry in high-pressure water, or hydrothermal piezochemistry. Combined with classical prebiotic chemistry [16, 34], more complex molecules could then assemble and lead to the molecules of life such as phospholipids, amino acids, peptides, sugars and purine and pyrimidine nucleotide bases.



## 5. Conclusion

Experiments in supercritical or high-pressure water which mix variable amounts of the hydrothermal vent ingredients CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S and CO<sub>2</sub> with some metal catalysts and/or radioactive nuclides, and which simulate the microcavities and nanochannel chemical reactors of hydrothermal vents, with shock wave reactions occurring inside them and with temperature gradient around them, should lead to the chemical formation of the building blocks of life. Experiments aimed at investigating this issue have already been conducted in collaboration with Vogel [35]. However, serious corrosion problems have been encountered. A recent article [36] presents a research programme on high-pressure hydrothermal organic synthesis. A central question of this research programme is whether the unique properties of aqueous solutions at supercritical conditions might affect the synthesis and stability of important biomolecules. The model developed here could commence answering this question.

This analysis, which proposes a link between the structure of water and the synthesis of prebiotic molecules, is a continuation of earlier studies that have been conducted on the structure of water [37, 38] and on the origin of life through interstellar molecules [2–5].

The author warmly thanks Dr Francis Muguet at ENSTA, Paris, for communicating some of his results concerning linear and inverse dimers. Professor Dr Herbert Vogel, at the Institut für Chemische Technologie, Darmstadt, is gratefully acknowledged for performing preliminary experiments. The author would also like to thank Professor François Raulin, Universités Paris 12 and 7, and Professor Daniel Prieur, Institut Universitaire Européen de la Mer, Brest, for an invitation to give a talk at the meeting of the GDR EXOBIO (GDR CNRS 1877) in June 1999.

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