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# Temperature and salinity history of the Precambrian ocean: implications for the course of microbial evolution

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#### **Abstract**

The temperature and salinity histories of the oceans are major environmental variables relevant to the course of microbial evolution in the Precambrian, the "age of microbes". Oxygen isotope data for early diagenetic cherts indicate surface temperatures on the order of 55-85 °C throughout the Archean, so early thermophilic microbes (as deduced from the rRNA tree) could have been global and not just huddled around hydrothermal vents as often assumed. Initial salinity of the oceans was  $1.5-2\times$  the modern value and remained high throughout the Archean in the absence of long-lived continental cratons required to sequester giant halite beds and brine derived from evaporating seawater. Marine life was limited to microbes (including cyanobacteria) that could tolerate the hot, saline early ocean. Because  $O_2$  solubility decreases strongly with increasing temperature and salinity, the Archean ocean was anoxic and dominated by anaerobic microbes even if atmospheric  $O_2$  were somehow as high as 70% of the modern level.

Temperatures declined dramatically in the Paleoproterozoic as long-lived continental cratons developed. Values similar to those of the Phanerozoic were reached by 1.2 Ga. The first great lowering of oceanic salinity probably occurred in latest Precambrian when enormous amounts of salt and brine were sequestered in giant Neoproterozoic evaporite basins. The lowering of salinity at this time, together with major cooling associated with the Neoproterozoic glaciations, allowed dissolved  $O_2$  in the ocean for the first time. This terminated a vast habitat for anaerobes and produced threshold levels of  $O_2$  required for metazoan respiration. Non-marine environments could have been oxygenated earlier, so the possibility arises that metazoans developed in such environments and moved into a calcite and silica saturated sea to produce the Cambrian explosion of shelled organisms that ended exclusive microbial occupation of the ocean.

Inasmuch as chlorine is a common element throughout the galaxy and follows the water during atmospheric outgassing, it is likely that early oceans on other worlds are also probably so saline that evolution beyond the microbial stage is inhibited unless long-lived continental cratons develop.

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#### 1. Introduction

The Precambrian represents the first 3.5 billion years of Earth history and is the age of the microbes. Isotopic evidence (Mojzsis et al., 1996; Rosing, 1999; Rosing and Frei, 2004) and possible microfossil evidence (Schopf, 1993) hint that prokaryotic microbial life was already established at the time of the earliest preserved rock record at 3.5-3.8 Ga (billion years before present). Eukaryotes did not appear until about 2.7 Ga (Brocks et al., 1999) and metazoans until about 0.55 Ga. Considering the rapidity with which life can evolve, these delays in the appearance of more complex varieties pose outstanding challenges for understanding the course of evolution on Earth and for exploring the probable nature of life or past life elsewhere in the solar system and cosmos. As often noted, the Precambrian is an enormous interval of time in which evolutionary advances could have been made via internal advances in biological mechanisms, so it seems likely that environmental conditions rather than internal factors were responsible for the delay in the appearance of more complex life. The most popular current explanation for the end of microbial dominance is that atmospheric oxygen levels rose throughout the Precambrian until some critical threshold necessary for metazoan respiration was achieved (Runnegar, 1982 and references cited therein). Clearly, a minimum amount of atmospheric oxygen is needed, but the level of oxygen dissolved in water is the real issue. Temperature and salinity strongly govern oxygen solubility, and these are largely unconstrained variables which have probably varied significantly over geologic time.

In this paper, I explore aspects of the Precambrian ocean environment in which earliest microbial life evolved and explore the possibility that high temperature and salinity were major factors affecting microbial evolution, that the "Cambrian explosion" may represent movement of already evolved metazoans from non-marine environments into the sea after a major salinity decline resulting from deposition of enormous salt deposits in the Neoproterozoic, and that early hydrospheres on planets, rather than being "cradles of life", are probably so saline that early evolution is actually inhibited until, or unless, long-lived continental cratons with non-marine aqueous environments develop.

# 2. Analytical methods

Oxygen isotope data for cherts were measured using the conventional fluorine extraction method on 20-mg samples.  $CO_2$  derived from this procedure was isotopically analyzed with a 15-cm isotope ratio mass spectrometer.  $\delta$ -values were first determined relative to  $CO_2$  derived from a carbonate working standard and then referred to the SMOW standard using  $\alpha_{CO_2}$ – $H_2O=1.0412$  (O'Neil et al., 1975). Data for Precambrian cherts from the PPRG collection (Schopf and Klein, 1992) are given in Table 1. Other new data are given in Table 2.

# 3. Climatic temperature history

Inasmuch as different types of microbes have greatly different temperature ranges in which they thrive, major changes in climatic temperature over geologic time would certainly have affected the course of their evolution. The common occurrence of pillow lavas, cross-beds and other sedimentary structures indicative of liquid water throughout the Precambrian clearly indicate past temperatures in the approximate range 0-100 °C. The silicate weathering "thermostat" of Walker et al. (1981) is often invoked as a constraint on temperature variations. In this model, increases in atmospheric CO<sub>2</sub> from volcanic emissions are consumed during silicate weathering which then causes greenhouse heating to decline. This reduces the rate of weathering and allows CO<sub>2</sub> emitted from volcanoes to increase. A steady state is reached and the CO2 level is thus regulated to keep climatic temperatures in the 0–100 °C range. The time interval in which this feedback cycle works and the actual temperature range of the "thermostat" cannot be specified. While useful for understanding why the Earth has been hospitable to life for so long, this feedback model cannot be used to constrain major temperature changes that may have occurred in the Precambrian within the broader temperature range of 0–100 °C.

 $^{18}\mathrm{O}/^{16}\mathrm{O}$  ratios provide an approach for measuring past temperatures, but the method is not straightforward and varies depending upon the age of the materials. Measurements of  $\delta^{18}\mathrm{O}$  for unrecrystallized, original carbonate precipitates such as sea shells or fibrous aragonitic marine cements can yield the actual

Table 1
PPRG chert samples

PPRG che	Age	$\delta^{18}$ O	PPRG #	Age	$\delta^{18}$ O	PPRG #	Age	$\delta^{18}$ O	PPRG #	Age	$\delta^{18}$ O	PPRG #	Age	$\delta^{18}$ O
TTRO #	rige	(‰)	TTRO #	rige	(‰)	TTRO II	rige	(‰)	TTRO II	rige	(‰)	TTRO //	rige	(%)
1475	550	26.8	1282	770	19.1	1309	1700	17.4	2027	2735	16.3	1409	3000	12.8
1475	550	26.4	1283	770	20.6	1261	1885	20.0	2027	2735	16.0	1633	3000	10.6
1476	550	27.1	1340	770	17.2	1261	1885	19.7	2028	2735	16.8	1436	3300	18.9
1477	550	26.4	1342	770	20.7	1261	1885	19.3	2029	2735	15.6	1444	3300	16.4
1477	550	26.2	1229	775	20.5	1587	1925	17.7	2031	2735	15.6	1465	3330	13.6
1318	610	24.3	1280	780	21.3	1845	2250	26.4	2031	2735	16.0	1466	3330	14.6
2245	640	23.5	1222	785	18.6	1415	2325	21.0	2031	2735	15.5	2718	3330	14.2
2245	640	22.9	1424	800	27.1	1415	2325	21.7	2032	2735	16.5	2718	3330	15.3
1473	650	20.3	1424	800	28.4	2526	2325	23.4	2033	2735	16.2	1458	3400	15.2
1474	650	22.7	1635	800	26.2	1417	2400	23.3	2033	2735	16.1	2002	3400	17.1
2333	680	24.4	1676	800	23.3	1412	2450	20.4	2035	2735	16.1	2002	3400	16.9
2332	685	29.3	2364	800	23.6	2515	2450	24.3	2038	2735	15.1	2002	3400	17.4
2332	685	30.3	1245	850	28.0	2519	2450	17.7	2039	2735	14.9	1440	3400	12.5
1478	740	27.5	1246	850	29.6	2520	2450	19.8	2040	2735	14.2	1440	3400	12.8
1479	740	27.4	1253	850	19.6	2520	2450	22.7	2041	2735	14.6	1441	3400	12.8
1480	740	27.2	1243	850	22.6	1293	2500	17.1	2041	2735	14.8	1998	3400	15.3
1481	740	27.2	1249	850	26.1	1293	2500	15.8	2044	2735	14.9	1999	3400	15.2
1481	740	23.6	1251	850	20.1	1294	2500	20.1	2044	2735	15.0	2001	3400	17.5
1481	740	24.7	1251	850	21.9	1372	2650	16.6	2044	2735	15.4	2644	3400	15.1
1482	740	27.3	1251	850	23.2	1372	2650	17.1	2045	2735	14.3	1447	3435	14.1
1483	740	26.8	1252	850	27.4	1416	2650	12.1	2046	2735	15.2	2010	3435	13.2
1248	760	29.2	1256	850	20.1	1907	2650	18.6	2048	2735	16.2	2010	3435	11.9
1255	760	24.3	1313	850	24.7	1907	2650	18.4	1354	2750	8.7	2010	3435	13.9
1257	760	23.5	1313	850	24.6	1921	2650	18.2	1354	2750	9.1	1448	3435	18.5
1258	760	25.6	1314	850	27.0	2435	2650	16.3	1354	2750	11.6	1438	3435	13.7
1259	760	25.9	1315	850	24.9	1467	2690	17.4	1354	2750	11.8	1439	3435	14.5
1322	760	22.6	1317	850	27.8	1467	2690	18.0	1355	2750	10.9	1439	3435	15.0
1322	760	21.8	1317	850	27.9	1467	2690	14.8	1355	2750	11.1	1439	3435	18.7
1325	760	31.3	1319	850	28.3	1467	2690	14.6	1355	2750	13.0	1439	3435	14.7
1230	770	27.8	1321	850	26.7	2690	2690	16.4	1356	2750	7.8	1442	3435	13.1
1230	770	26.9	1328	850	26.7	2690	2690	14.8	1356	2750	8.2	1451	3435	6.3
1230	770	24.2	1332	850	20.8	2690	2690	14.5	1356	2750	11.1	1451	3435	6.0
1231	770	26.4	1333	850	22.7	2019	2735	16.5	1356	2750	10.9	1453	3435	14.4
1232	770	22.2	1333	850	23.3	2020	2735	15.8	1455	2750	15.5	1453	3435	14.3
1232	770	22.3	1333	850	22.1	2021	2735	14.9	1457	2750	16.3	2637	3435	6.6
1233	770	25.4	1359	900	22.2	2021	2735	16.4	1461	2750	13.6	2638	3435	14.8
1233	770	24.9	1360	1050	24.7	2021	2735	14.6	1469	2750	11.2	2645	3435	15.4
1281	770	19.9	2242	1364	27.3	2022	2735	15.6	1469	2750	13.2	2646	3435	14.7
1281	770	20.3	1308	1700	16.6	2024	2735	16.6	1464	2768	12.8	1449	3450	10.0
1281	770	21.2	1309	1700	17.4	2025	2735	15.9	1464	2768	12.9	1449	3450	9.3
1281	770	22.2	1309	1700	17.5	2025	2735	16.0	1408	3000	11.0	1450	3525	12.7
1281	770	21.9	1309	1700	17.2	2026	2735	15.7	1408	3000	11.2			

temperature of the sea water, and measurements across a single shell can even record seasonal variations during the life of the organism (Urey et al., 1951). Thousands of paleotemperatures have now been measured for Cenozoic sediments with this method, but it is rare to find actual original precipitates in strata much older. All marine precip-

itates eventually go through a period of mineralogical "stabilization" where the originally deposited microcrystalline high-Mg calcite, aragonite and calcite dissolve and reprecipitate into interlocking crystals of calcite and/or dolomite. In platform deposits, stabilization usually occurs within a few million years because meteoric waters enter the system along

Table 2 Miscellaneous chert data

Unit/age	Lab #	$\delta^{18}{ m O}$	Unit/age	Lab #	$\delta^{18}{ m O}$	Unit/age	Lab #	$\delta^{18}{ m O}$	Unit/age	Lab #	$\delta^{18}$ O
		(%0)			(%0)			(‰)			(%0)
Edwards Fm.	415	32.4	Edwards Fm.	447b	33.2	Belt Supergroup	700	20.7	Gunflint Fm.	547	19.9
Texas	413	31.8	Texas	446	31.3	Montana	701	20.4	Ontario, Canada	563	18.2
100 Ma	412	32.2	100 Ma.	431c	27.9	1350 Ma.	703	20.1	2090 Ma.	513	19.1
	428	33.0		431a	29.5		706	19.5		550	21.6
	406	33.2		432	30.5		707	18.9		549	22.2
	418	31.9		424	32.2		710	19.2		553	18.9
	409	32.9		425	31.2		717	19.9		507	25.9
	401	32.7		470	31.9		736	20.5		555	23.7
	466a	33.3		457	29.1	Gunflint Fm. Ontario, Canada	527	22.6		542	15.1
	466b	32.2		469	32.0		525	22.3		541	20.7
	463	32.0		452	33.5	2090 Ma.	524	23.4		536	23.1
	404	34.7		465	30.5		519	23.6		545	22.9
	461	30.4		462	31.3		523	24.1		538	17.4
	421	33.1		458	31.5		522	21.8		526	22.7
	408	33.4		468	32.3		518	20.6		566	21.7
	422	33.7		449	33.0		516	23.7		544	23.1
	423	32.7		450	33.3		507	26.1		548	23.1
	424	30.8		467	32.2		515	21.7		565	25.2
	410	33.2		472	32.8		509	24.0		564	18.7
	407	34.0	Chuar Group	907	30.2		507	26.0			
	400	33.0	Arizona	901	26.8		501	23.1			
	434	33.6	750 Ma.	902	26.3		500	23.3			
	439	34.2		903	26.6		514	23.0			
	431b	34.9		906	25.2		517	22.2			
	433	32.5		906	26.1		517	22.9			
	431c	27.8		904	27.1		514	21.6			
	430	32.3		905	26.8		514	23.4			
	427	32.1		900	31.2		509	24.4			
	421	33.1		910	26.2		507	26.2			
	401	32.4		911	29.8		502	23.9			
	425	30.6		915	31.0		508	23.6			
	441	33.0	Bass Limestone	912	28.5		506	21.8			
	442	32.4	Arizona	913	26.4		504	23.2			
	443	33.4	1200 Ma.	916	30.3		505	22.7			
	445	33.5		909	20.4		541	21.1			
	435	32.6		917	26.5		543	24.3			
	451	33.3		914	23.0		507	25.6			
	447a	30.6					546	23.1			
	448	32.6					532	21.5			

coastal margins and vigorously promote solution/recrystallization. Original marine precipitates of Precambrian carbonates have never been documented; all have been stabilized into limestone or dolostones. Inasmuch as most Precambrian carbonates are platform carbonates (deep sea varieties having been long since scraped into subduction zones), the parent water for present crystals probably had a low  $^{18}{\rm O}$  meteoric water component, and O isotope variations thus reflect both temperature and also variable  $\delta^{18}{\rm O}$  of the

stabilizing fluids (see James and Choquette, 1990 for an excellent review). An additional problem is that carbonates undergo recrystallization rather easily in response to heating during deep burial and low grade metamorphism. For all these reasons, oxygen isotope paleothermometry of carbonates as practiced on Cenozoic material usually cannot be used in the Precambrian.

Cherts composed of microcrystalline quartz are very common in sedimentary rocks of all ages and typically form during stabilization of carbonates (see review by Knauth, 1994). The primary silica precipitate is usually opal and this metastable amorphous material is dissolved and reprecipitated into the intergrown microcrystalline quartz masses sampled as chert. In Phanerozoic examples, the initial opal is usually precipitated by diatoms, radiolarians, and sponges. In Precambrian examples, the silica may have been biologically produced by microorganisms, introduced as an inorganic precipitate from a silicasaturated ocean, released during stabilization of clay minerals, or derived from volcanic glasses in the flow path of the stabilizing pore fluids. Archean strata contain cherts representing wholesale silicification of sediments on a scale not present in younger rocks (Knauth and Lowe, 2003). Opal was apparently precipitated on a colossal scale in the Archean ocean and all materials deposited, whether volcanic or sedimentary, were subjected to silicification and conversion to chert during early diagenesis. Quartz itself is one of the most resistant minerals to later isotopic alteration (Taylor, 1974). Masses of chert have essentially no measurable permeability and strongly resist the later dissolution/reprecipitation episodes so common in carbonates. Recrystallization can occur during metamorphic heating but water/rock ratios at that point are usually so low that  $\delta^{18}$ O is largely unchanged (Knauth and Lowe, 2003). The isotopic composition of cherts thus provides a possible approach for determining past stabilization temperatures. If stabilization occurs during shallow burial (as is generally the case for shallow water deposits), such temperatures approximate the climatic temperature during stabilization. An explanation of the method and early results were presented by Knauth and Epstein (1976) and Knauth and Lowe (1978).

Knauth and Lowe (2003) showed that Archean cherts of the Onverwacht Group, S. Africa have  $\delta^{18}$ O values about 10% lower than those of Phanerozoic cherts. They argued from this that climatic temperatures at 3.5 Ga were on the order of 40 °C warmer than those of the Phanerozoic. Fig. 1 shows their data along with previously published data from the Precambrian and new data. The approximate 10% variation of  $\delta^{18}$ O for cherts of a given age is not data scatter, but is caused by variable amounts of low  $\delta^{18}$ O meteoric water in the initial stabilization to form chert

or by later stabilization during deep burial at elevated temperatures (often millions of years later, but not resolvable on the time axis of Fig. 1).

Data plotted in Fig. 1 are nearly all for platform cherts where field evidence indicates stabilization to quartz during shallow burial (e.g. synsedimentary brecciation of chert nodules, host-rock laminae compacted around nodules, slumped nodules, preservation of organic-walled microfossils, etc.). The samples were further screened petrographically to eliminate cherts metamorphically recrystallized to mosaic quartz. The 3.8 Ga data (Perry et al., 1978) are for amphibolite-grade metamorphic rocks but are included here because they are the only known data for the oldest cherts and because the authors argued that the maximum values represent early diagenetic values. Because of the large amount of field work at vastly different localities required to sample and screen appropriate samples from the whole of geologic time, the data are necessarily still very limited in number. There is clearly an overall trend of cherts getting more <sup>18</sup>O-rich with time as initially proposed by Perry (1967), and this has been attributed to an overall climatic cooling of the Earth with time (Knauth and Epstein, 1976; Knauth and Lowe, 1978). Alternative explanations include increasing  $\delta^{18}$ O of the ocean with time and later alteration due to metamorphism and/or long-term isotopic exchange with low <sup>18</sup>O ground waters. Knauth and Lowe (2003) evaluated these alternative explanations and argued that they were incompatible with the data for the 3.5 Ga Onverwacht cherts and thus not likely explanations for the younger data. Unless the arguments of Knauth and Lowe (2003) can be refuted, the overall trend of the data in Fig. 1 must be due primarily to an Earth that has cooled down over the past 3.5 Ga.

Deducing an actual temperature for a given data point in Fig. 1 is generally not possible from  $\delta^{18}{\rm O}$  values alone.  $\delta^{18}{\rm O}$  of a chert depends only upon  $\delta^{18}{\rm O}$  of the parent water and the temperature, but it is rarely possible to specify  $\delta^{18}{\rm O}$  of ancient early diagenetic waters. An additional problem is that there are several quartz-water isotopic fractionation with temperature expressions proposed for temperatures <200 °C (Matheney and Knauth, 1989). What can be said is that there has been a general increase of about 10% in  $\delta^{18}{\rm O}$  of cherts between the Archean and the Phanerozoic with possible rises and falls in the maximum

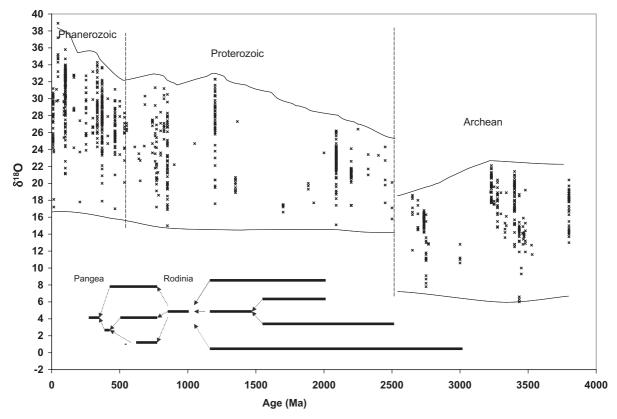


Fig. 1. Compilation of new and previously published oxygen isotope data for screened chert samples over geologic time. All samples except the 3800 Ma examples are for unmetamorphosed cherts or cherts metamorphosed no higher than Greenschist Facies. The history of long-lived continental cratons is taken from Rogers (1996) and the horizontal lines represent periods of stability of specific cratonic masses identified by him. The 10% variation in  $\delta^{18}$ O for cherts at any given time is caused by the presence of low  $^{18}$ O meteoric waters present during diagenetic chert formation and/or formation of cherts during deeper burial at elevated temperatures. The overall increase in  $\delta^{18}$ O with time is interpreted as global cooling over the past 3500 Ma. New data are given in Tables 1 and 2. Published data are from Knauth and Lowe (1978, 2003), Force et al. (1986), Gao and Land (1991), Suchecki and Hubert (1984), Kenny and Knauth (1992), Beeunas and Knauth (1985), Winter and Knauth (1992) and references cited therein.

values along the way, as suggested from the overall pattern in Fig. 1. Regardless of which quartz-water fractionation expression is used, this 10% increase corresponds to an overall decrease in temperature of about 40 °C (Knauth and Lowe, 2003). If global temperatures in the Tertiary (extreme left side of Fig. 1) were on the order of 10–20 °C, then the lower  $\delta^{18}$ O values at approximately 3.5 Ga corresponds to temperatures on the order of 55–85 °C (see Knauth and Lowe, 2003 for a detailed discussion of this). The cause of such large climatic temperature variations is unknown, but variations in the amount of greenhouse gases such as water vapor,  $CO_2$  and  $CH_4$  are commonly invoked (e.g. Kasting and Siefert, 2002).

Although possibly premature, there is strong suggestion of a major jump of about 3–5‰ to higher  $\delta^{18}{\rm O}$  somewhere around 2.5 Ga (Fig. 1). Upper Archean cherts from several localities are strongly depleted in  $^{18}{\rm O}$  relative to those of the Paleoproterozoic. Most of these are from the Fortesque Group, Western Australia, and are likely non-marine deposits (Walter, 1983) that formed in lower  $^{18}{\rm O}$  waters. Existing values at 2.65 Ga are below +18.4 and are more  $^{18}{\rm O}$  depleted than almost all younger cherts. Going forward in time, values jump to as high as +24.5 by 2.45 Ga and never return to values similar to those of the Archean. This change in  $\delta^{18}{\rm O}$  is one of the striking aspects of the data in Fig. 1 and

corresponds to an approximate general temperature decrease on the order of 20  $^{\circ}$ C, suggesting Paleoproterozoic temperatures on the order of 40  $^{\circ}$ C. The change toward lower climatic temperatures suggested by these data could be related to drawdown of  $CO_2$  during weathering of the first truly extensive, long-lived continental cratons thought to have developed at this time (Goodwin, 1996; Rogers, 1996) and/or by the decay of a methane greenhouse (Kasting and Siefert, 2002).

 $\delta^{18}$ O values appear to generally rise throughout the Proterozoic and become more similar to Phanerozoic values by 1.2 Ga. The interval between 1.2 and 0.685 Ga yields values >+30, similar to post-Ordovician cherts. Data are frustratingly scarce during the important Neoproterozoic-Lower Paleozoic transition period. For time intervals where there are too few data to establish the approximately 10% spread in  $\delta^{18}$ O inherent in cherts as they form, there is always a possibility that significantly more positive or negative values will be found as new data are obtained. However, the combined  $\delta D$ - $\delta^{18}O$ approach (e.g. Knauth and Epstein, 1976; Kenny and Knauth, 1992; Fallick et al., 1985; Sharp et al., 2002) allows a rough assessment of temperature or temperature changes without knowledge of  $\delta^{18}$ O of the parent water, something not possible with only one isotope. The combined  $\delta D$ ,  $\delta^{18}O$  data for Cambrian strata indicate that the low  $\delta^{18}$ O values of the lower Paleozoic are not due simply to the inadequacy of sampling (Knauth and Epstein, 1976). There is thus a tantalizing suggestion in Fig. 1 that climatic temperatures were not much different from most of the lower Paleozoic in the Mesoproterozoic and Neoproterozoic, but "jumped" on the order of 10–15 °C (the value necessary to increase  $\delta^{18}$ O about 2‰) sometime between about 685 and 550 Ma, possibly associated with termination of late Proterozoic glaciation events. This is roughly coincident with the advent of metazoans in the ocean, but the isotope data are presently far too few to clarify climatic temperature changes during this important interval. Platform cherts probably do not form during glaciations when carbonate production drops, and the time between deposition and diagenetic fixing of the isotopic signal in stable microcrystalline quartz may be too great to detect short intervals of glaciation and the possible sudden

post-glacial warmings proposed by Hoffman et al. (1998). The same considerations apply to the likely early Paleoproterozoic glaciations. So far, no chert of any kind that is known to have actually formed as microquartz during a glacial time has been identified or isotopically analyzed.

If the isotopic data for cherts are related to overall climatic temperatures, then there were very hot conditions throughout most of the Archean, an overall decline to cooler temperatures throughout the Proterozoic, and a possible major warming somewhere near the Precambrian/Cambrian boundary. Although still sparse, the data are perhaps sufficient enough to consider implications for the history of microbial life.

Thermophilic and hyperthermophilic microbes are deeply rooted in the rRNA phylogenetic tree suggesting that the earliest organisms on Earth were high temperature forms. This has supported speculation that earliest life originated at sea floor hydrothermal vents (e.g. Baross and Hoffman, 1985). However, recent results suggest that the most deeply rooted bacteria are thermophilic but not hyperthermophilic (Gaucher et al., 2003). The optimal temperature is about 65 °C, essentially that deduced from the O isotope record for the time of the earliest sedimentary rock record (Knauth and Lowe, 2003). Earliest thermophilic life could have thus been global in extent rather than a phenomenon localized only around hydrothermal vents.

As first noted by Hoyle (1972), the fossil record suggests that organisms appeared on Earth sequentially in order of tolerance to high temperatures. Schwartzman (1999) has independently explored this concept in detail and argues that the overall declining temperatures over geologic time have largely determined the course of evolution. In this view, the Precambrian was the age of microbes because of overall higher temperatures and the ability of microbes to thrive under such conditions. It follows that metazoans and more complex forms had to await the cooling of the Earth. However, additional factors are likely because the emerging data (Fig. 1) suggest that only the Archean was at temperatures typically greater than about 40 °C.  $\delta^{18}$ O of the limited data from the Proterozoic are similar to those of the Phanerozoic, hinting that Phanerozoic-like temperatures were already present in much of the upper Proterozoic. There is no evidence for sudden increase in  $\delta^{18}$ O (indicating cooling) at the Precambrian/

Cambrian boundary; the available data indicate a lowering of  $\delta^{18}$ O values suggesting a major *warming* around this time. While temperature was likely a major factor in affecting the course of evolution in the Precambrian as argued by Schwartzman (1999), it appears unlikely as the sole explanation for the overall late arrival of the metazoans.

# 4. Ocean salinity

Although life has now adapted to a wide range of salinities, the salt concentration is clearly an important environmental variable that controls and limits the nature of biologic activity. For example, restricted lagoons of the Persian Gulf turn into "faunal deserts" when salinities approach 2× the open ocean values (Hughes Clarke and Keij, 1973). Although certain bacteria can thrive at higher salinities, populations of marine bacteria generally decrease with increasing salinity and diversity is exceptionally low in hypersaline water masses (Larsen, 1980). Salinity can also have a strong effect on the solubility of atmospheric gases, especially oxygen. The salinity history of sea water is thus a crucial parameter that has received very little attention.

Although significant progress has been made on determining cation ratios in Phanerozoic sea water from fluid inclusions in halite (e.g. Lowenstein et al., 2001), Cl<sup>-</sup> variations over time cannot presently be determined from the rock record. DeRonde et al. (1997) and Channer et al. (1997) attempted to do so by analyzing fluid inclusions 3.5 Ga quartz/goethite deposits interpreted as Archean sea-floor hydrothermal chimneys. However, these goethite deposits have now been reinterpreted as Cenozoic spring deposits (Lowe and Byerly, 2003). At present, there are no compelling examples of inclusion-bearing crystals that grew in Precambrian sea water and remained unaltered with time.

Enormous salt beds, the so-called "saline giants" are observed in the geologic record, and these were deposited at specific times rather than continuously (Fig. 2). The episodic nature of the deposition and subsequent episodic erosion of these units during tectonic uplift has surely led to major salinity variations in the oceans over time. Salinity of the ocean is thus an unconstrained variable that depends

upon the frequency of deposition and erosion of these giant salt beds.

Cl<sup>-</sup> is an incompatible element and was probably initially outgassed as HCl along with water during the earliest history of the Earth (Holland, 1984). The entire Cl inventory would have been in the ocean and could not have been reduced until evaporitic salt deposits began to form. This could not have happened until long-lived continental cratons developed in the Paleoproterozoic. Salt deposited in coastal environments is eventually recycled to the sea via dissolution and runoff. At any given time, some amount of salt is stored in supratidal deposits causing ocean salinity to be lower than its initially high, pre-continent value. However, the issue of whether a steady state for the removal-return cycle of evaporites has ever been achieved is overshadowed by the larger issue of the saline giants, the enormous deposits of salt that occur at specific times in Earth history.

There appear to be two large time intervals in which most of the known salt deposits were deposited (Fig. 2). About 40% of the Phanerozoic inventory was sequestered in the interval 180-250 Ma. Much of the rest was deposited in the Neoproterozoic and Cambrian. The Neoproterozoic inventory has never been estimated, but the enormous accumulations in Australia, Oman, Saudi Arabia, Iran and Pakistan clearly rival the Luann Salt (USA, 180 Ma) in geographic extent and thickness and are therefore shown in Fig. 2 as approximately equal to, or greater than, the Luann inventory. Holser et al. (1980) and Hay et al. (2001) have argued that major salinity changes occurred in the Phanerozoic in response to the imbalance between deposition and erosion that allowed the net deposition of salt at certain times as clearly illustrated by the figure.

Assuming that the Earth's hydrosphere was outgassed early (rather than continuously), Holland (1978) estimated the initial salinity by adding back the halite that has been removed by deposition and is currently stored in sedimentary basins on the continents. Using an early estimate by Zharkov (1981) for the amount of halite, the salinity would have been only about 1.2× the modern value. An ocean this saline would have been a problem for most metazoans today, but its effect on bacteria cannot be considered significant. Cyanobacteria, for example, have little problem with this enhanced salinity. However, this estimate did not take into account many huge new

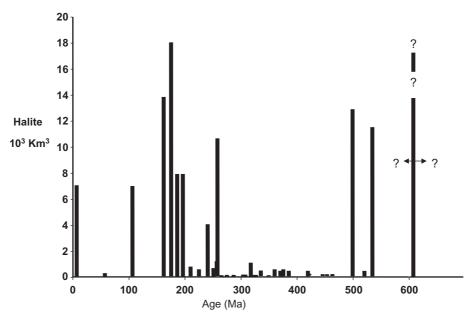


Fig. 2. Halite accumulations in the Phanerozoic. Data were originally listed by geologic time period (Zharkov, 1981; Land et al., 1988) and are centered here on the absolute age of these designated periods. Precambrian halite has never been inventoried. The Neoproterozoic value estimated here is based on the assumption that the enormous accumulations in Australia, Oman, Iran and Pakistan are spread over basins larger in extent than that hosting the Luann salt, USA (180 Ma). Most of the known salt was clearly deposited in two large pulses, one in the interval 180–250 Ma and one in the interval 500–700 (?) Ma. Sequestration of these "saline giants" requires a rare combination of geographic, geologic, climatic, oceanographic and depositional conditions.

subsurface salt deposits that have been subsequently discovered or were not inventoried by Zharkov (1981). These include all Precambrian examples, all African and South American occurrences, and the Gulf Coast Luann salt. More importantly, there is possibly an equal or even much greater amount of NaCl that was previously in sea water but is now present in the ubiquitous deep basin brines (Land, 1995). The salinity of ground water almost everywhere increases with depth (with notable exception when shales dewater to form overpressured reservoirs) and many large sedimentary basins have vast amounts of hypersaline brine with Cl<sup>-</sup> concentrations in excess of 100,000 mg/l. The brines are remnants of evaporite fluids that deposited the salts (Carpenter, 1978) and also develop when subsurface salt is dissolved by groundwater. Once lodged in sedimentary basins, brines are exceedingly difficult to flush out with meteoric waters (Domenico and Robbins, 1985) and persist for hundreds of millions of years (Knauth, 1988; Rose and Dresel, 1990). The amount of brine currently sequestered within continents has never been estimated, but it likely contains at least as much

NaCl as the halite deposits, and this must be added to the solid salt inventory when estimating how much NaCl has been removed from sea water. Land (1995) recognized this problem and suggested an amount of NaCl in subsurface brine possibly two times greater than the halite value. It is thus possible that ocean salinity could rise to values of 1.6–2× the modern value, or even higher, if all the salt and brine currently sequestered on the continents were returned to the ocean from which it was extracted by sedimentation on continents (Knauth, 1998). The value is certainly much higher than the previously proposed value of 1.2× (Holland, 1978), which was considered inconsequential. It seems likely that the early ocean was significantly more saline and significantly warmer than previously thought.

# 5. Consequences of a hot, super-saline early ocean

A hot, super-saline early ocean puts significant environmental constraints on the nature and diversity of early marine life. Cyanobacteria can tolerate both the high temperatures and high salinities suggested here, so there is no environmental objection to interpretations of early Archean microfossils as possible cyanobacteria (Schopf, 1993). The salinity tolerance of thermophilic and hyperthermophilic organisms deep in the phylogenetic tree is not known, so it is presently not clear if their inferred antiquity contradicts the salinity scenario suggested here. Halophilic bacteria can thrive in salinities  $>10\times$  sea water, but most of these aerobic microbes are clearly recent adaptations that could only have appeared after the rise of atmospheric oxygen. One variety, Halobacterium species NRC-1, surprisingly, appears to be one of the most ancient archeans (Ng et al., 2000). Halophiles therefore may have existed in marine or non-marine evaporitic settings on the early Earth, but they could not have thrived in the lower salinities of the open ocean. The high temperature and salinity proposed here therefore do not preclude microbial life in marine environments, but these environmental variables could have limited its diversity.

Estuaries and coastal environments diluted by meteoric water runoff as well as non-marine environments would all have the high temperatures, but salinity there could range from fresh water in lakes and rivers to hypersaline in evaporitic environments. Diversity and evolutionary adaptation should have been enhanced in these ever changing, diverse environments although the small amounts of emergent continental crust and lack of long-lived cratons would have limited the environments available. Targeted searches for a microfossil record in these types of environments are highly warranted, but such environments are difficult to identify in the oldest sedimentary rocks. One possible example is where the uppermost strata of the 3.5 Ga Onverwacht Formation, S. Africa, culminate in a shallow water sequence complete with conglomerates and O isotope evidence suggesting progressive input of meteoric water (Knauth and Lowe, 1975). Possible coastal or lacustrine strata in the even older Warawoona cherts in Australia have been suggested (Lowe, 1983). Unfortunately, low grade, extensive metamorphism lowered  $\delta^{18}$ O of most Australian cherts (Richards et al., 2001), and areas of best preservation of microquartz have not yet been identified as has been done for the African examples (Knauth and Lowe, 2003). Considering the rarity of preserved cherts that formed in coastal or non-marine environments at this time together with the low probability of finding microfossils in any rock, the lack of a fossil record from these environments is therefore not surprising. However, the extraordinary rarity of claimed microfossils in any of the marine 3.5 Ga rocks despite relentless searches is consistent with the idea that life in the hot, salty Archean ocean was a very limited affair.

The effect of high salt on the origin of life itself is a crucial issue that has received little attention. Most origin of life experiments and considerations have been done assuming normal sea water as the medium. However, experiments by Apel et al. (2002) suggest that fresh water was more conducive to the origin of life and Ricardo et al. (2004) have argued that evaporitic borate-rich environments are favorable for formation and preservation of ribose in an "RNA world". It is clear that consideration of early molecular and biologic evolution in the "primordial soup" should at least consider the possibility that marine fluids were hot and saline and ask whether this matters in the various origin of life scenarios.

## 6. Oxygen solubility

A hot ocean at  $1.5-2\times$  modern salinity is a significantly different fluid from the modern ocean with respect to many physical and chemical properties. Geochemical models of the early Earth usually use the dilute solution chemistry of the textbooks at temperatures of 25 °C, but dilute solution chemistry is only an approximation even for solutions as saline as modern sea water. It is even more inappropriate for the much higher salinities that must have existed on the early Earth. There have been no attempts to geochemically model such an Archean ocean and the task is not within the scope of this paper. However, one chemical aspect of the decline in salinity with time merits consideration and that is the effect of salinity on  $O_2$  solubility in sea water.

Fig. 3 shows the solubility of oxygen in sea water as a function of salinity and temperature under the present atmospheric level (PAL) of oxygen (data from Weiss, 1970). At the present salinity value of 35% and temperatures less than 25 °C, dissolved  $O_2$  is >5 ml/l. At Archean temperatures of >55 °C and  $2\times$  modern salinity (70‰) dissolved  $O_2$  would be less than 3 ml/l

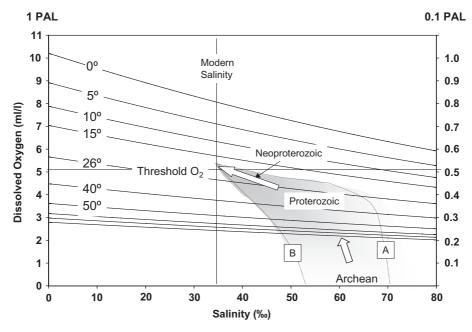


Fig. 3. Dissolved oxygen in seawater as a function of salinity and temperature for the present atmosphere (1 PAL  $O_2$ ) and an ancient one with 10% of the present atmospheric level of  $O_2$  (0.1 PAL) using experimentally determined algorithms by Weiss (1970). An example threshold level of 0.5 ml/l for dissolved  $O_2$  required for Neoproterozoic metazoans is shown together with example trajectories for the evolution of dissolved  $O_2$  in seawater with time. Curve B invokes a minimum salinity in the Archean and a relatively steady decrease throughout the Precambrian. Curve A is for high initial salinity with little decline until deposition of the great Neoproterozoic saline giants. Under an atmosphere of 0.1 PAL  $O_2$  and temperatures of 15–25 °C, reduction of ocean salinity by deposition of these salt deposits could shift dissolved  $O_2$  to values above that required for metazoan respiration, as shown by the arrow labeled "Neoproterozoic".

even if atmospheric  $O_2$  were at the modern value. If the Archean atmosphere had just 30% less oxygen than the modern value, the oceans would have been anaerobic due to the high temperature and salinity alone, even if these values were somewhat less than the 55 °C, 70% example values used here. In today's ocean, sinking organic matter gets respired and an oxygen minimum zone with dissolved O<sub>2</sub> often <1 ml/l forms at several hundred meters depth before deep, oxygenated polar waters mix back into the system at the deeper depths. A hot, saline early ocean would not have the cold, oxygenated deep waters even if atmospheric O<sub>2</sub> levels were high. In other words, the high salinity and high temperatures alone guarantee a basically anaerobic ocean environment as long as atmospheric O2 levels were below about 0.7 PAL.

It has long been argued that atmospheric  $O_2$  was very low in the Archean although alternative interpretations involving significant  $O_2$  levels have persisted up to Ohmoto's (2003) recent advocacy. The debate has been temporarily settled with the discovery

of mass independent fractionation of S isotopes in Archean sedimentary rocks (Farquhar et al., 2000) that can currently only be explained in terms of UV fluxes sufficient to make ozone from top to bottom of the atmosphere that would keep  $O_2$  levels  $<10^{-5}$  PAL (Pavlov and Kasting, 2002). The already low atmospheric O<sub>2</sub> level inferred in this way for the Archean atmosphere would be over three times lower in the ocean because of the reduced solubility from high temperature and salinity (Fig. 3). The cause of precipitation of oxidized iron or partially oxidized iron in iron formations and jasper (chert with fine red hematite) in such anoxic fluids remains problematic. An intriguing possibility is that estuaries and coastal waters were diluted enough with meteoric waters to reduce salinity enough to allow longer retention of oxygen generated by photosynthesizers than in the open ocean. Oxidation in such environments would help certain cases of iron clearly oxidized in the Archean, such as the hematitic clasts in the Onverwacht conglomerates (Lowe and Knauth, 1977).  $\delta^{18}$ O

of the associated cherts in this example decreases going up-section suggesting progressively increasing amounts of low <sup>18</sup>O non-marine waters in this depositional and diagenetic environment.

## 7. The Proterozoic salinity decline

The only natural mechanism for getting salt out of sea water is evaporation. The initially high salinity of the ocean must have declined in parallel with the development of sedimentary basins and climatic conditions capable of forming and preserving the great saline giants. The conditions necessary to do this actually occur only rarely and require vast inland shallow seas on continents mainly centered on the equator as well as possible special coastline geometries, ocean currents and other variables that converge to produce these improbable deposits (Sonnenfeld, 1984). The history of stable cratons is a different question from the history of when and how continental crust formed in the geochemical sense. Continental crust, per se, may have segregated early in Earth history (Armstrong, 1991) or may have developed largely after 2.5 Ga (e.g. Goodwin, 1996). The history of stable cratons, however, is something that cannot be investigated geochemically but must be reconstructed from the geology and age-dates of ancient terrane remnants still preserved, as done by Rogers (1996). When compared with this history of continental platforms (Fig. 1), there is strong suggestion that the two great episodes of salt deposition in the late Precambrian and in the Phanerozoic occurred during and after the breakup of the two great supercontinents in Earth history, Rodinia and Pangea. Numerous enclosed arid equatorial basins associated with these supercontinents apparently developed during their breakup to account for the deposition of these salt (and associated brine) deposits.

Large salt deposits older than Neoproterozoic are not known in the geologic record. One interpretation of this is that such deposits existed but have been dissolved away by younger ground waters and/or squeezed out of the older sequences by deformation, the so-called "vanished evaporites" (Garrels and MacKenzie, 1981). Salt is certainly highly soluble and physically mobile; deep burial usually induces diapirs such as the thousands of examples in the Gulf

Coast region of the United States. Salt is so soluble that it is incredible that any remains at all in pre-Tertiary sequences and much of the deep brine in sedimentary basins is undoubtedly derived from the "vanished evaporites". However, the inventory shown in Fig. 2 does not show a progressive decrease in the amount of subsurface salt with increasing age of the sediments. Certainly, the older Precambrian strata have had ample time and exposure to deformation to insure that vast amounts of salt were removed and recycled into the sea. However, the continental history of Rogers (Fig. 1) suggests that the amount of longlived craton was less prior to 1.0 Ga and essentially absent prior to 2.0 Ga. This, together with the absence of any inferred supercontinents suggests that the amount of salt sequestered on continents in the Meso/Paleoproterozoic was vastly less than in later times and exceptionally low in the Archean. The inference is that significant lowering of the ocean's initially high salinity did not begin until about 2.5 Ga and probably did not undergo its first really big decline until the Neoproterozoic, the time of the oldest strata bearing any evidence of saline giants.

A remarkable aspect of the microbial record in the Precambrian is the limited diversity of the eukaryotes throughout the Proterozoic (Schopf, 1992). High salinity could be an additional factor to others proposed for this limited diversity such as the scavenging of nutrients in a stratified, sulfidic ocean (Anbar and Knoll, 2002). Basically, only salt tolerant organisms could have been present in the open ocean.

Metazoan life is impeded not only because of the direct effects of salt on cell functions, but also because of the decreased solubility of oxygen with increased temperature and salinity. Threshold values have been proposed for a number of primitive animals based on biochemical considerations, diffusion rates and empirical size/weight requirements. Runnegar (1982) reviewed these efforts and derived a probable minimum oxygen requirement for *Dickinsonia*, a probable Neoproterozoic metazoan, on the order of 0.5 ml/l. This threshold value is shown as an example in Fig. 3 together with calculated curves for dissolved O2 in sea water as a function of temperature and salinity in an atmosphere with O2 levels of 0.1 PAL, a lower estimate for the Neoproterozoic (Canfield, 1998). Several scenarios are shown in this figure for the evolution of dissolved O2 in the Precambrian. All start with an essentially anoxic Archean ocean with high salinity in the range 50–70‰. Curve A is for an extreme case where the first major reduction in ocean salinity occurs in the Neoproterozoic. Temperatures are allowed to decline in the Mesoproterozoic to about 25 °C, possibly somewhat lower than suggested by the existing (but still inadequate) O isotope data. The salinity decline then follows the oxygen solubility curve for 25 °C to higher dissolved O<sub>2</sub> levels until the threshold for *Dickinsonia* is reached. In this case, a major salinity decline alone associated with Neoproterozoic salt deposition is a major factor in allowing metazoans to occupy the ocean.

Curve B is similar to A, but allows for a less salty Archean ocean and a less episodic sequestration of salt over time. Salinity decline could still be a major factor in oxygenating the ocean, but it would have to be coupled with a dramatic late Proterozoic temperature decrease not apparent in the existing O isotope data (Fig. 1). There are many variables that have to be estimated to construct these example curves and the threshold level for Dickinsonia is only one rather uncertain example. The important point is that, if the great salt deposits of the Neoproterozoic produced the first great salinity decline in the ocean, then dissolved O<sub>2</sub> could have moved up one of the temperature curves as shown to cross whatever threshold level was required for oceanic metazoans. Lower temperatures associated with the late Precambrian glaciations would deflect example curves A and B strongly upward in addition to the slide to the left (Fig. 3). The combined effects of Neoproterozoic salt deposition and glaciation cannot be ignored when considering a rise in oxygen as the cause of the rise of metazoans.

# 8. End of the age of microbes—the Cambrian explosion of metazoan life

The cause of the Cambrian explosion of organisms with mineralized hard parts is a long-standing puzzle with many proposed explanations. Molecular clocks suggest metazoan evolution was well under way in the upper Precambrian (Wray et al., 1996; Lynch, 1999; Benton and Ayala, 2003), but the marine strata are essentially barren of such organisms. One unexplored resolution to this contradiction is the possibility that animals evolved in the upper Precambrian and have

not been found yet as fossils because they thrived in environments that have a low preservation potential. The deep sea and the non-marine are the two depositional environments with the least preservation potential relative to the marine shallow water platform environments where fossils are most favorably preserved. Deep sea sediments are usually carried to subduction zones in less than 200 Ma and become severely metamorphosed. Non-marine environments are high on continents and most are eroded away in short order. However, some, such as the Neoproterozoic Bitter Springs Formation and the 2.7 Ga Fortesque Group in Australia, have survived and do contain microfossils (Schopf and Klein, 1992). Geochemical evidence suggests microbial occupation of soil environments as far back as 2.6 Ga (Watanabe et al., 2000). Microfossils have been found in paleokarst as far back as 1.2 Ga (Horodyski and Knauth, 1994) and Kenny and Knauth (2001) presented isotopic evidence indicating extensive photosynthesizing communities in humid karst terranes in the Neoproterozoic. Lakes, soils and karst pits appear to have been the site of microbial activity throughout much of the Precambrian. Hedges (2003) has even argued that the Neoproterozoic ice ages were brought on by a greening of the land surface so extensive that biotically enhanced weathering brought the CO<sub>2</sub> level of the atmosphere down so low that glaciation set in. Very few deposits from these non-marine environments have been identified and explored for a fossil record in the uppermost Precambrian. The possibility remains that these are the stealth environments where metazoan evolution could have progressed before an explosion into the sea.

As argued above, salinity and temperature of the ocean may not have achieved Phanerozoic-like values until deposition of the great Neoproterozoic salt deposits. There is an interval of 100 million years, or more, prior to the Cambrian explosion during which metazoans could have evolved in lakes, rivers, streams and soils. Non-marine environments have an enormous range of salinities, from very low values in lakes and rivers to hypersaline values in playas, which would have allowed ample opportunity for experimentation at optimal salinity levels. With oxygenation of the atmosphere, the more dilute waters could oxygenate well ahead of the ocean. With deposition of the Neoproterozoic salt deposits, ocean salinity

declined enough to allow adaptation of non-marine organisms to this vast new niche. The appearance of shells may thus be simply the result of soft bodies moving into fluids saturated with respect to calcite, silica and phosphate (?). This is the reverse direction of the conventionally assumed sea to land migration of life, but it is equally plausible and perhaps more so if the salinity issue (as well as its effect on dissolved O<sub>2</sub>) is considered.

The test of this heterodox idea is a thorough exploration of Neoproterozoic non-marine environments wherever they can be identified. Floodplain deposits and lake deposits need to be identified and explored for possible bioturbation. Paleokarst on the 1.2 Ga Mescal Limestone has been exhaustively searched for disruption to karst pit and cave deposit laminae, and none has been found. If metazoans were in that non-marine setting that deep in the Proterozoic, they did not leave their calling cards. Similar searches in younger paleokarst or any non-marine deposits in the upper Precambrian may prove more fruitful, especially considering molecular clock indications that metazoans were *somewhere* in the upper Precambrian.

## 9. Implications for astrobiology

"Follow the water" is the current slogan for the new science of astrobiology. Inasmuch as the only form of life we know requires water to exist, the logical first step in astrobiological prospecting in the solar system and elsewhere in the galaxy is to identify targets that have, or had, oceans of water. There is even hope of someday imaging a planet around a distant star that appears as a "pale blue dot" indicating a water-covered planet similar to Earth. Such an image would be an encouraging sign that life is possible throughout the cosmos and would provide justification for research efforts in astrobiology. However, Cl also "follows the water" because it does not fit into silicate mineral structures and would outgas as HCl along with water to produce very saline early hydrospheres.

One initial astrobiology target is Mars because there is considerable geomorphic evidence (e.g. tributary networks, outflow channels) that a significant hydrosphere existed early in the planet's history (Baker, 2001 and references cited therein). As much as 90% of the early hydrosphere was lost, probably

due in large part to photodissociation of water vapor followed by hydrogen loss (Jakosky and Philips, 2001). This water loss would have effectively evapoconcentrated any early martian hydrosphere into a brine which would have evolved into a concentrated Ca-Na-Mg-Cl brine after reaction with the basaltic megaregolith and become enormously more concentrated during eutectic freezing when the climate turned cold (Knauth and Burt, 2002). Any early large bodies of water on Mars would have started salty and become vastly more salty with time. Although rare forms of life eventually adapted to rather salty water masses on Earth (as in the Dead Sea), it is not known whether concentrated brines are conducive to the formation and early evolution of living systems. Considering that such brines are generally lethal to most known forms of life, the prospect of evolution of life in early martian oceans seems unlikely. Abundant geomorphic evidence (Baker, 2001) suggests rains in the higher elevations with probable formation of short-lived lakes, rivers and other less saline water masses. Caliche would have formed on the ubiquitous martian basalts and could have trapped any early microbes that somehow developed in these upland, less salty water masses (Knauth et al., 2003).

Europa, a satellite of Jupiter, is another major astrobiology target because there is evidence of an ocean below its icy crust. If Europa assembled out of materials with a Cl/H<sub>2</sub>0 ratio similar to that of the Earth, then this putative ocean would have had a similarly salty early ocean. Eutectic freezing of salty water bodies produces H<sub>2</sub>O ice (see Knauth and Burt, 2002 for a discussion of eutectic freezing), which moves outward in the gravity field and leaves a more concentrated solution behind. The thick icy crust of Europa thus suggests extensive removal of water from the initially salty solution and further suggests that the subsurface ocean is probably a very concentrated brine. Some of the subsurface fluid is interpreted as having debouched along "spreading centers" where the icy crust is thought to have split, and remote sensing suggests the presence of large amounts of sulfates in these areas (McCord et al., 1998). Clbearing phases to be expected there at these low temperatures are hydrohalite (NaCl·2H2O) and antarctictite (CaCl<sub>2</sub>·6H<sub>2</sub>O). There is no indication that such phases have been considered in the remote sensing techniques and there are no know laboratory

calibration curves to test the obvious prediction of Cl phases along with the sulfates. As in the case of early Mars, the issue is whether an early hydrosphere that starts salty and becomes even more salty with time is good or bad for the origin of life.

Cl is produced during oxygen burning in stars just prior to supernova explosions (Wallerstein et al., 1997) and is strewn into space during the subsequent explosion along with other "metals" (anything heavier than He in astronomical parlance) created in stars. There is therefore every reason to expect that Cl follows the water throughout the galaxy and that there are no regions basically free of this element. Early hydrospheres throughout the cosmos are thus likely to have been initially salty. On Earth, the evolution of life beyond the microbial stage was retarded for 3.5 Ga, possibly in large part due to high temperatures and high salinity. The development of continents was crucial to regulating temperatures to life-tolerant values and to the sequestration of salt and brine, the only known natural mechanism that can significantly reduce salinity in oceans. The discovery of a "pale blue dot" elsewhere in our galaxy would be encouraging for astrobiology, but finding a "pale blue dot" with brown (or green) spots would significantly enhance the prospects of metazoan evolution somewhere else than on Earth.

Ward and Brownlee (2000) recently argued that microbial life could be widespread elsewhere, but that more complex life forms are probably exceptionally rare. Certainly on Earth, something retarded evolution of metazoans for over 3.5 billion years. The thesis presented here is that high oceanic Cl and high temperature were major factors and that the development of large stable continental platforms as well as chance geographic configurations during their drift histories to allow huge evaporite deposits were necessary factors for oxygenation of the ocean and the breakthrough to metazoan life. Inasmuch as the Earth is the only planet in the solar system with continents and plate tectonics, it is likely that similar planets are equally scarce in other solar systems, even if they are within the "habitable zone" with regard to stability of water. Microbiology was the paleontology of the Precambrian, and the simple considerations presented here support the idea that microbial life dominates the history of any water-based life elsewhere in the cosmos.

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