Using stromatolites to constrain temperatures during times of biotic crisis, and comparing them to a mineralogically derived climate model of Mars

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Abstract:

Stromatolites are laminated sedimentary structures that are accretionary away from a point or surface. These structures are commonly thought to be created by cyanobacteria, either through the trapping and binding of sediment, or through metabolically-induced precipitation. Stromatolites first appear early in the fossil record (~3.8 Ga), and increase in form diversity through the Proterozoic. The occurrence of stromatolites in the fossil record decreases before the Precambrian-Cambrian boundary, and strikingly they subsequently only re-emerge in abundance at times of biotic crisis, such as the Permian-Triassic and Triassic-Jurassic extinctions. Both of these mass extinctions are coincident with large scale volcanism. Associated increases in atmospheric CO_2 caused increases in ocean acidity and increases in global temperatures, and these environmental perturbations are hypothesized to have been key drivers of mass extinction, along with anoxia and euxinia. In order to understand the role of climate change in mass extinctions, we are estimating temperatures across both boundaries using stromatolites. Specifically, we are applying the carbonate "clumped" isotope paleothermometer to well-preserved specimens that have been petrographically examined in order to ascertain their temperature of formation during extinction and recovery intervals. Samples were collected from the Cotham Marble (Triassic-Jurassic boundary interval, Bristol, United Kingdom). Subsequent to petrographic analysis, samples were micro-drilled to obtain primary phases. The resultant

carbonate powder was then analyzed for clumped isotopes using a mass spectrometer at the University of California Los Angeles. The data obtained from the stromatolites will be plotted against an absolute reference scale to calculate the stromatolite's temperature of formation to within 1-3°C accuracy. The temperature of formation for these stromatolites will be compared to current climate models to correlate trends and predict whether it would be possible to see resurgence in stromatolites with the projected climate. These climate data will be compared to a climate model derived from the mineralogical conditions of formation for the minerals found on the Martian surface. This comparison will allow a condition to be drawn about whether or not microbialite, and thus stromatolitic, life could have existed in the history of Mars.

Introduction:

Two outstanding questions in astrobiology are (1) how we could detect if there were environments on planetary bodies that have harbored microbial life, and (2) how do different forms of microbial life respond to profound changes in environmental conditions. Stromatolites have long been a target for astrobiological studies, and are a calciferous formation commonly thought to be created by cyanobacteria, either through the trapping and binding of sediment, or through metabolically-induced precipitation. Stromatolites are currently thought to be one of the earliest forms of life on Earth, dating back to approximately 3.5 billion years ago. However, stromatolites' form diversity in the fossil record decreases significantly for an extended period of time beginning slightly before the Precambrian-Cambrian boundary, only to resurface first after the Permian-Triassic (PT) extinction, and then again after the Triassic-Jurassic (TJ) extinction. These two mass extinctions are two of the biggest in Earth's history and are associated with profound environmental change. This original decrease in form diversity is attributed to many factors: including changing ocean chemistry, algal evolution and the resulting competition for sea-floor space, and exposure to grazers (Grotzinger 1999). The main theory for the resurface of these post-extinction stromatolites is the lack of competition from benthic corals as well as the lack of predation from grazing fauna (Mata and Bottjer 2012).

For this study, stromatolites from the TJ extinction were chosen for examination as they straddle one of the largest extinctions in the history of planet Earth, and allow us to examine how microbial life can respond to profound environmental change. The TJ Mass Extinction is also thought to be associated with volcanic activity, which took place at the Central Atlantic Magmatic Providence. The new crust formed from this volcanic activity caused the spread of the Earth's crust, which initiated the breakup of Pangaea. This increase in volcanic activity corresponds to an increase in atmospheric CO_2 levels as well as an increase in temperature of approximately 3-4°C. These stromatolites were chosen as they provide the distinct advantage of being relatively newer stromatolites, compared to Achaean and Proterozoic forms, and are less subject to alterations or to the diagenesis of their carbonate forms. These low levels of alteration allow for more precise measurements of temperature of formation.

Despite their astrobiologic importance, the mechanisms that govern stromatolite formation are not well understood. We plan on using stromatolites from this post-extinction era to better understand the environment of their formation, specifically temperature, by utilizing the method of multiply substituted isotopologues of CO_2 (the carbonate "clumped" isotope paleothermometer).

Using the CHEMIN data obtained from the Planetary Data System (PDS), we will calculate past Martian surface temperatures based on the mineralogical data obtained *in situ.* This temperature data will be compared to the temperature data obtained from the stromatolite samples to determine if conditions favoring stromatolite formation were present within the history of Mars.

Methods:

The TJ extinction boundary stromatolites were analyzed using clumped isotope thermometry. In clumped isotope thermometry, the mass spectrometer measures the abundance of heavy isotopes of CO_2 and compares them to an absolute reference scale. By comparison to this reference scale the temperature of formation for the carbonate samples was calculated as more heavy-isotopes clump at lower temperatures. The most common isotope of carbon dioxide is $^{12}C^{16}O^{16}O$, whereas only a small fraction of CO_2 forms the heavier isotopes of $^{13}C^{18}O^{16}O$. Measuring the abundance of such heavy isotopes allows for the calculation of the temperature of formation within a 1-3°C certainty (Huntington 2009).

Stromatolites were obtained from the appropriate extinctions boundary: the TJ stromatolites were obtained from the UK and are known as Cotham Marble. Due to the uneven distribution of the fossil record, some of these stromatolites were from places not easily accessible to researchers. These stromatolites were obtained from various other stromatolite researchers (Sarah Greene (University of Bristol) and Yadira Ibarra (USC)).

Once the stromatolites were obtained, they were drilled. This drilling is to obtain a fine powder that can be weighed out and run on a Thermo-Finnigan MAT 253 dual-inlet gas-source Isotope Ratio Mass Spectrometer. The stromatolites were drilled at the best location possible to obtain high amounts of un-altered, primary calcium carbonate. After the stromatolites were drilled, the powder was collected and stored in a desiccator until the samples were measured on the mass spectrometer.

One sample of stromatolite is approximately 8-9 mg of carbonate powder. This amount was weighed out and placed in silver capsules for delivery into the mass spectrometer. The silver capsules containing samples were individually dropped into a bath of heated phosphoric acid via a Costech autosampler. This acid bath breaks down the carbonate into carbon dioxide, which can be analyzed on the mass spectrometer. This carbon dioxide is then purified through a series of cold traps, both an ethanol and liquid nitrogen trap, which will freeze any impurities in the gas sample and evacuate them through a vacuum. In between traps the gas sample is run through a gas chromatograph (GC) which cools the sample to remove organic compounds. Once organic matter is removed, the gas is again purified before being transferred to the mass spectrometer. The mass spectrometer returns a bulk isotopic reading, which is then plotted against a line derived from bulk isotopic readings at 1000° C (a temperature with no clumping) and room temperature (a temperature with a standardized set of clumping). Based off of this line, the temperature of formation is known for the sample.

Martian surface temperature will be extrapolated using the mineralogical data obtained *in situ* from Mars by the Mars Rovers. Using known temperatures and conditions of formation for each mineral the temperature of Mars on a geological time scale can be deduced. This extrapolated data will be compared to the data obtained from isotopic analysis of the stromatolites to see if similar temperature ranges existed on Mars to allow for stromatolite formation.

Results:

The temperatures found based off of clumped isotope paleothermometry varied greatly over time as the stromatolite grew in differing climates. The different stromatolite morphologies also formed under different conditions, with laminated layers forming under hotter conditions than dendritic layers. Overall temperatures ranged from 20 °C all the way to nearly 40 °C. The lowest and oldest layer, the first laminated layer, had an average temperature of 32.3 ± 3.2 °C; the first dendritic layer, the second oldest layer, had an average temperature of 27.0 ± 3.0 °C; the second laminated layer had an average temperature of 32.2 ± 3.1 °C; the second dendritic layer had an average temperature of 33.3 ± 3.1 °C; the third laminated layer, the youngest layer, had an average temperature of 37.2 ± 3.0 °C. These average temperatures varied, however, by site with the Bristol and Lower Woods site showing a clear oscillating trend between hotter and cooler temperatures dependent on layer morphology.

Sample ID	Facies	$\delta^{13}C$ Mineral (‰VPDB)	$\delta^{18}O$ Mineral (VPDB)	Δ_{47} (v. Oz)	Δ_{47} T°C	1 se T error
TJCMBL1	Laminated 1	-0.054	-0.9	-0.472	37.1	3.3
TJCMBL1		-0.048	-0.9	-0.459	33.6	4.0
TJCMBL1		-0.087	-0.9	-0.470	36.4	3.7
TJCMBL1		-0.110	-1.0	-0.168	36.2	3.8
TJCMLWL1		0.133	-0.5	-0.234	28.8	2.8
TJCMLWL1		-0.034	-0.4	-0.256	30.7	2.1
TJCMLWL1		0.039	-0.5	-0.257	30.9	2.2
TJCMLWL1		0.034	-0.5	-0.256	30.7	2.5
TJCMLWL1		0.076	-0.5	-0.249	29.1	5.8
TJCMLWL1		0.026	-0.5	-0.252	29.8	2.0
TJCMBD1	Dendritic 1	0.120	-0.5	-0.452	28.3	2.4
TJCMBD1		-0.066	-0.8	-0.234	20.3	2.9
TJCMBD1		-0.068	-0.8	-0.233	20.0	3.6
TJCMBD1		-0.069	-0.8	-0.254	24.4	2.6
TJCMLWD1		0.350	-0.4	-0.231	28.5	2.8
TJCMLWD1		0.312	-0.4	-0.279	36.2	3.1
TJCMLWD1		0.250	-0.4	-0.225	24.2	3.0
TJCMLWD1		0.299	-0.5	-0.226	24.6	2.4
TJCMLWD1		0.301	-0.4	-0.195	18.2	2.4
TJCMLWD1		0.316	-0.5	-0.215	22.2	2.3
TJCMRD1		0.958	-3.7	-0.269	31.2	3.7
TJCMRD1		1.046	-4.0	-0.290	35.9	3.6
TJCMRD1		1.045	-3.9	-0.295	37.1	3.9
TJCMBL2	Laminated 2	-0.709	-1.9	-0.482	32.0	3.8
TJCMBL2		-0.715	-1.9	-0.431	27.1	4.2
TJCMBL2		0.342	-0.9	-0.113	24.7	3.1
TJCMLWL2		2.677	-3.9	-0.148	31.5	3.5
TJCMLWL2		0.304	-1.1	-0.265	35.9	2.4
TJCMLWL2		0.294	-1.1	-0.277	35.0	3.0
TJCMLWL2		0.305	-1.1	-0.276	34.9	3.1
TJCMRL2		1.256	-4.0	-0.280	33.6	2.5
TJCMRL2		1.286	-3.9	-0.266	30.5	2.6
TJCMRL2		1.270	-4.0	-0.293	36.6	2.7
TJCMBD2	Dendritic 2	0.435	-1.3	-0.410	22.5	2.4
TJCMBD2		0.405	-1.2	-0.410	22.5	2.3
TJCMMFD2		-2.536	-3.3	-0.327	41.7	2.9
TJCMMFD2		-2.506	-3.3	-0.301	39.2	5.1
TJCMMFD2		-2.526	-3.3	-0.323	40.7	3.0
TJCMBL3	Laminated 3	0.324	-1.0	-0.256	35.5	3.1
TJCMBL3		0.336	-1.0	-0.271	39.4	3.1
TJCMBL3		0.326	-1.0	-0.251	34.3	2.6
TJCMBL3		0.360	-1.2	-0.239	26.7	3.0
TJCMMFL3		-0.837	-2.0	-0.322	43.8	3.1
TJCMMFL3		-0.887	-2.0	-0.333	46.7	2.6
TJCMMFL3		-0.731	-2.0	-0.170	34.2	3.8

Figure 2: Temperature of formation of each sample of carbonate organized from oldest to youngest layer and by site.

CHEMIN data retrieved from the Mars Curiosity Rover revealed several minerals on the Martian surface. Among these minerals, five were of interest: anhydrite, hematite, halite, pyrite, and pyrrhotite. These minerals have been studied in Earth systems and the mechanisms under which they form are understood. These minerals were all found in relatively low abundance, however. Anhydrite composed only approximately 3.3% of soil samples, hematite composed 1.2%, halite composed 0.2%, pyrite composed 0.5%, and pyrrhotite composed 1.5%. The more abundant mineral species found in the soil samples (namely andesine and pigeonite) have not been researched as to the mechanisms of their formation. Both anhydrite and pyrite have temperature dependent formation mechanisms, with 40 °C of higher being the usual temperature required (although pyrite can form, albeit much slower, at as low as 20 °C). Anhydrite, hematite, and halite require an aqueous medium from which they precipitate. Pyrrhotite requires a high abundance of reactive iron, and low amounts of clay sediments.

MINERAL	ANDESINE	SANIDINE	ALBITE	FORSTERITE	AUGITE	PIGEONITE	ORTHOPYROXENE	MAGNETITE	ANHYDRITE	BASSANITE	QUARTZ	HEMATITE	AKAGANEITE	HALITE	PYRITE	PYRRHOTITE
PERCENT	43.8	1.7	2.7	5.1	8.5	12.7	6.8	7.0	3.3	2.0	0.6	1.2	2.4	0.2	0.4	1.5
ERROR	3.6	1.8	1.3	3.3	3.4	4.0	3.1	1.9	2.1	0.9	0.7	0.9	1.4	0.3	0.5	1.5

Figure 3: Table of minerals found on the Martian surface. Many of these minerals have not been studied in terms of the conditions of their formation.

Discussion:

The conditions of formation for the TJ stromatolites and for some of the mineral species on the Martian surface do overlap to some degree, suggesting that it is possible for stromatolitic life to have formed on Mars. When standard errors are taken into account one laminated stromatolite layer is within one standard error of the necessary 40 °C for formation of anhydrite, while all layers fall within the range of temperatures necessary for pyrite formation- 20 °C to 50 °C (MacDonald 1953; Rickard 1975). Although average temperatures do not overlap with the 40

°C threshold for anhydrite, several individual samples were found to form above or very close to this threshold, suggesting that the alga that accretes the stromatolite would be able to tolerate temperatures of this magnitude.

Anhydrite, hematite, and halite all require an aqueous medium from which to precipitate out of and new evidence suggests that running water was once present on Mars (Stiller et al. 1997; Ojha et al. 2015). Stromatolites also require water in order to grow, so these conditions are also favorable. The presence of halite suggests an environment of brackish or saltwater. Stromatolites have always been found near shore (due to their need to photosynthesize) in saltwater environments, but terrestrial inputs of freshwater could turn the water more brackish.

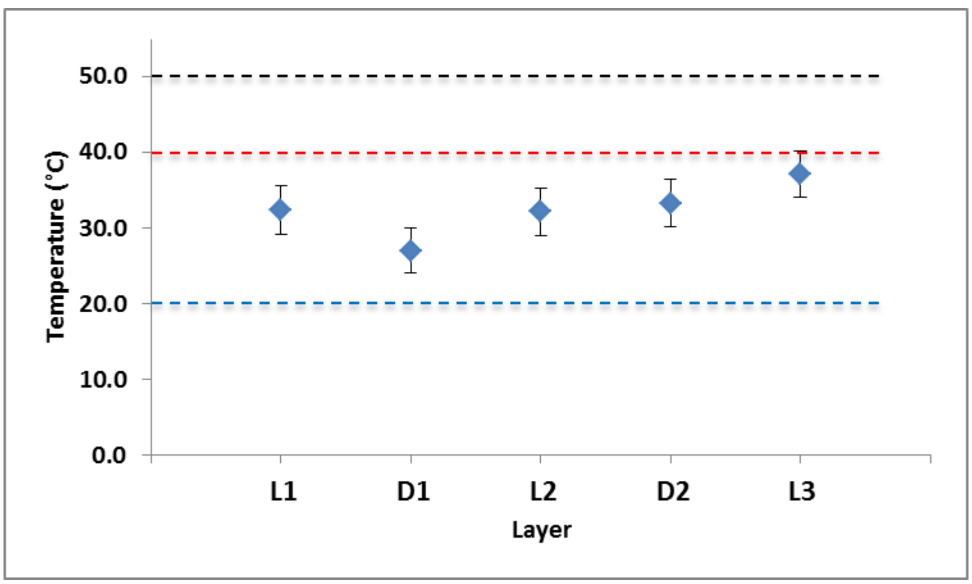

Figure 4: Average Cotham Marble temperature of formation by layer is displayed with standard errors. The dashed lines represent the main three temperatures of formation for minerals found on the Martian surface.

The ability to photosynthesize is fundamental to the growth of the algal mat that accretes calcium carbonate to create the stromatolite, meaning that high light levels would be necessary. High amounts of suspended particles could interfere with the ability of the alga to photosynthesize. Here the formation of pyrrhotite could be instrumental. Pyrrhotite requires low amounts of suspended clay particles to form (Kao 2004). Clay particles are defined by their small size and slow settlement rate. These are the particles that would be most detrimental to stromatolite growth by blocking sunlight for extended time intervals. However, with the presence of pyrrhotite, it can be understood that clay particles were relatively uncommon, allowing for more favorable conditions for stromatolite growth.

Although these are only some factors influencing stromatolite growth, the conditions on the Martian surface extrapolated from the mineralogical data suggests the possibility of stromatolitic life on Mars.

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