

Cover page

**Title: Terrestrial Hydrothermal Fields and the Search for Life in the Solar System**

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## Preamble

The search for life on other worlds needs to consider not only whether a world is/was habitable for life (“follow the water”), but whether that world ever had the conditions necessary to *create* life (prebiotic chemistry). This is because, even though all known life on Earth exists in, or around, water, which allows for metabolism to operate, the conditions required for prebiotic chemistry differ: the formation of long-chain organic polymers (e.g., polysaccharides, oligonucleotides, and polypeptides) from their simple monomer building blocks (e.g., amino acids) is optimized under drying conditions via condensation (or dehydration) reactions in which water is a leaving group: indeed, permanent hydration causes polymers to break down – a situation referred to as “The Water Problem”<sup>1-4</sup>.

## Why terrestrial hydrothermal fields?

The multiple reactions required for life to originate require a complex variety of physico-chemical conditions, in addition to a concentration of organic molecules and various trace elements<sup>5-7</sup>. Though microorganisms appear morphologically simple, they are incredibly complex, highly structured systems with multiple ongoing reactions (e.g., long-chain organic molecules that are specific to life, pumps that control the internal chemistry of the cytoplasm, protein-based microcompartments, molecular transport and communication systems, and multi-dimensional, multi-component membranes). To generate such complexity, it is intuitive that a geologically and chemically complex system was likely required.

For this reason, the 1970s discovery of deep-sea hydrothermal vents and their primitive, chemosynthetic microbe-dependent macrofaunal communities<sup>8-10</sup> engendered the idea of life originating in the oceans via the complex interaction between heated seawater and the basaltic to ultramafic rocks of the oceanic crust<sup>11-13</sup>.

Recent studies, however, show that by far the most geologically and chemically complex systems on Earth are terrestrial (i.e. land-based) hydrothermal fields, which host hot springs, geysers, steam vents, and other manifestations of geothermal activity (Fig. 1)<sup>14-16</sup>. Indeed, there is an emerging paradigm shift towards Darwin’s insightful “Warm Little Pond” setting, *on land*, for the origin of life from almost 150 years ago<sup>17</sup>, which may in fact turn out to have been correct.

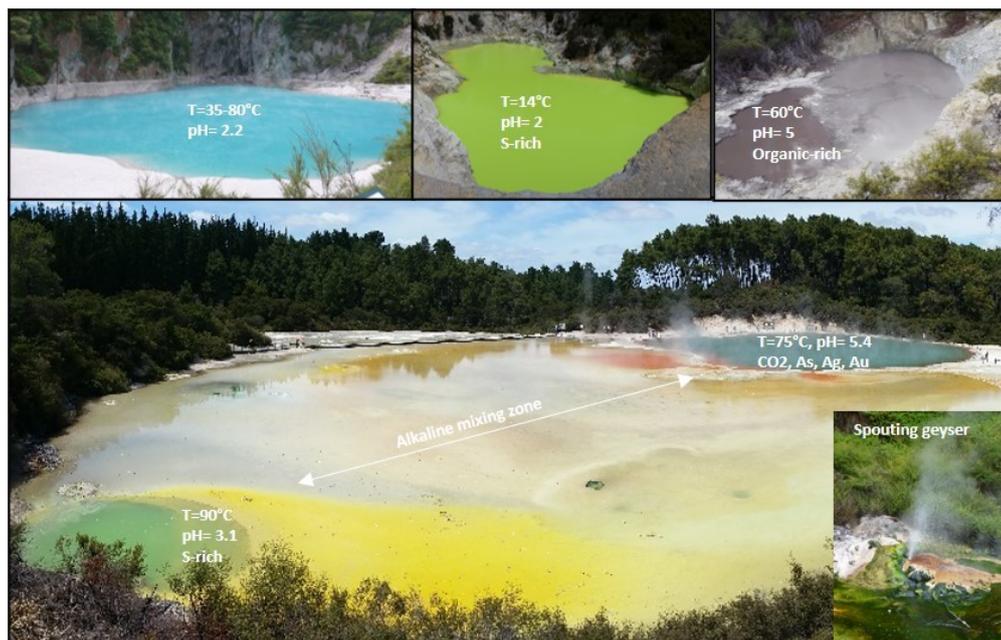


Figure 1: Example of hot spring variability, Rotorua, New Zealand.

Terrestrial hydrothermal fields not only have the hot water-rock interactions that deep sea vents have, but the following additional features that are beneficial for prebiotic chemistry.

1) Surface pools would have been able to concentrate organic molecules from in-falling meteoritic sources and interplanetary dust particles, which were many times more voluminous during Earth's earliest history<sup>18</sup> and would have contained abundant key building blocks for life including fatty acids, nucleobases, and a wide range of amino acids (including up to 96 in the Murchison meteorite alone)<sup>19-23</sup>.

2) The extreme complexity of individual terrestrial hydrothermal fields, which consist of 10s to 1000s of pools containing mixtures of meteoric water and condensates of magmatic vapors, producing a wide range in temperatures (from 10-100°C), pH (=1-12, highly acidic through highly alkaline), and ionic concentrations<sup>16,24,25</sup>, would have driven pre-biotic chemical reactions. These pools co-occur together with geysers, fumaroles, steaming ground, zoned alteration mineral assemblages of the underlying host rocks, and freshwater streams in highly varied terrain that incorporates extreme geological and geochemical diversity.

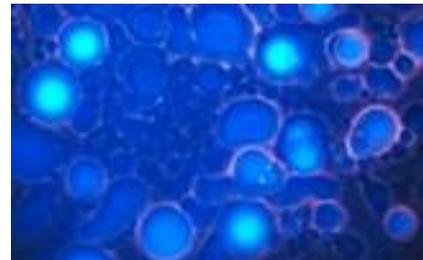
3) Terrestrial hydrothermal fields include not only the water-rock interaction of deep-sea vents, but also water-air/volcanic gas, and rock-air/volcanic gas interactions at a variety of scale, temperature, and rate, both above ground and in the subsurface<sup>26</sup>.

4) Terrestrial hot springs and geysers commonly undergo the wet-dry cycling shown to be critical in overcoming 'The Water Problem'. This can occur, in some cases many times per day (e.g., Yellowstone's Old Faithful<sup>27,28</sup>), both at pool margins and in subsurface fractures where prebiotic reactions would have been shielded from harsh UV radiation.

5) Terrestrial hot springs are concentrating environments – through drying and evaporation – that permit many cycles of complex chemical reactions. Hot spring pools also can concentrate a variety of prebiotically important elements, including not only H, N, O, P, and C, but also Fe, S, and P, as well as B, Zn, and Mn (e.g., the Fe-rich Chocolate Pots spring in Yellowstone; boratic sinters in India)<sup>6,29-33</sup>.

6) Associated hydrothermal alteration of the underlying rocks creates a variety of mineral assemblages, including clays that have been shown to catalyse the formation of long-chain organic molecules (oligomers) on the path to RNA formation<sup>34</sup>.

7) Acidic pools particularly support the formation of membranous compartments (or protocells: Fig. 2)<sup>35-38</sup>. Such protocells can encapsulate organic polymers and subject them to combinatorial selection through wetting-drying cycles that drive ever-increasing complexity and emergence of biological functions<sup>4,23,39</sup>.



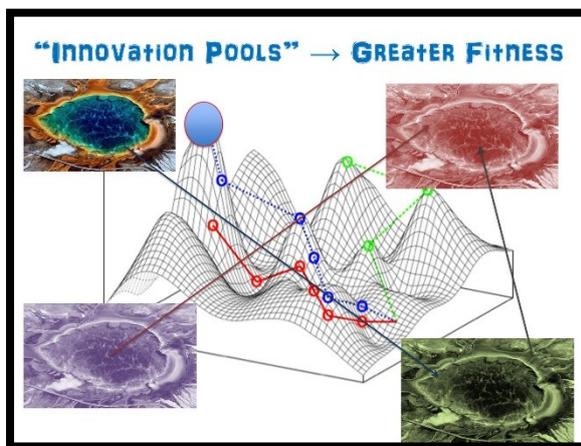
*Fig. 2: Image of a lipid-monomonucleotide mixture stained with a dye that strongly interacts with nucleic acids, which is concentrated in some (but not all) of the vesicles after being put through four wet-dry cycles, forming protocells. Scale bar is 10  $\mu$ m. Image from D. Deamer.*

8) Freshwater is key to explaining why microorganisms from all three branches of life contain an internal cytoplasm with  $K^+/Na^+$  ratios very different from seawater, or the possible compositions of ancient seawater<sup>6</sup>. Indeed, it has been shown that the high salt and total divalent cation (e.g.,  $Ca^{2+}$  and  $Mg^{2+}$ ) concentrations of seawater presents a barrier to lipid membrane assembly and protocell formation<sup>40</sup>.

9) Terrestrial hydrothermal fields receive energy from three main sources: the magmatic system, dehydration energy, and UV light, the latter shown recently to support critical prebiotic reactions, including a pathway to activated nucleotides<sup>41,42</sup>. Another energy source is abiotic photosynthesis at ZnS and  $TiO_2$  crystals<sup>43</sup>, both of which are found in an ancient Pilbara hot spring analogue site, described below<sup>44,45</sup>.

10) The most common temperature range in terrestrial hydrothermal fields, on the mid-sinter terrace, lies within the “sweet spot” for supramolecular (e.g., non-enzymatic RNA duplex formation<sup>46</sup>) assembly, at ca. 10–70°C. This is because formation temperatures need to be high enough for molecules to “search” their conformation space (become distorted). Too cold and the lack of activation energy makes it unlikely that any “function” would occur between molecules – let alone generate life. Too hot and directional intermolecular forces are weakened and associations are too short for any useful chemistry to take place.

11) Pools also have the advantage of being able to exchange contents with other pools through flows, splashing, wind, and subterranean plumbing networks that open and close on short timescales due to variable fluid/gas pressure and mineralization. This mixing of reactants, products, and energy sources results in combinations that can catalyze complex reactions creating “innovation pools” with components that become increasingly complex (Fig. 3). For example, if a component A necessary for prebiotic chemistry (such as membranes) is developed in Pool 1 and



mixed with component B (polymers) produced in pool 2, then these may mix with another component to form a composite product (protocells) that emerges in the outflow channels of pool 3, and so on. Indeed, hydrothermal fields constitute a natural system for combinatorial, or ‘messy’, chemistry, supporting serial enrichment capable of creating a continuous supply of structures, building blocks, and energy sources to drive prebiotic processes through cycles of selection.

*Fig. 3: Schematic diagram showing how variation and interaction among hot springs with different chemical/thermal properties (different colors) can lead to greater fitness of prebiotic molecules within innovation pools (blue ellipse). Inspired by Rachel Whitaker, U. Illinois. From Ref. 33.*

This combination of beneficial features, along with testing of some of the above properties both in the laboratory and in the field, has led to a new model for abiogenesis in anoxic, terrestrial hydrothermal fields (Fig. 4)<sup>6,23,38,39</sup>.

### **Terrestrial hydrothermal fields in deep time**

Fossilized terrestrial hydrothermal fields in the geological record on Earth extend back through the Cenozoic<sup>47,48</sup>, Mesozoic<sup>49,50</sup>, and Paleozoic<sup>51,52</sup>, to as far back as the 3.48 billion-year-old sinter deposits of the Dresser Formation in the Pilbara Craton, Australia<sup>44,45,53,54</sup>.

These and other examples confirm that ancient fossil hot spring deposits, just like their modern counterparts, were able to concentrate the elements required for prebiotic chemistry<sup>33</sup>, and developed similar hydrothermal alteration haloes, including clays<sup>54,55</sup>. They also: 1) preserve a fossil record of microbial life (textural biosignatures) through near-instantaneous mineralisation<sup>45,56-58</sup>, retain organic matter in life arrays (Fig. 5)<sup>50,59,60</sup>, including biomolecules<sup>61</sup>, and 3) contain a distinctive suite of trace elements—specifically Al, Cr, Mn, Fe, Ga, Zn, Ni—that are preferentially sequestered by microbial life<sup>62-64</sup>.

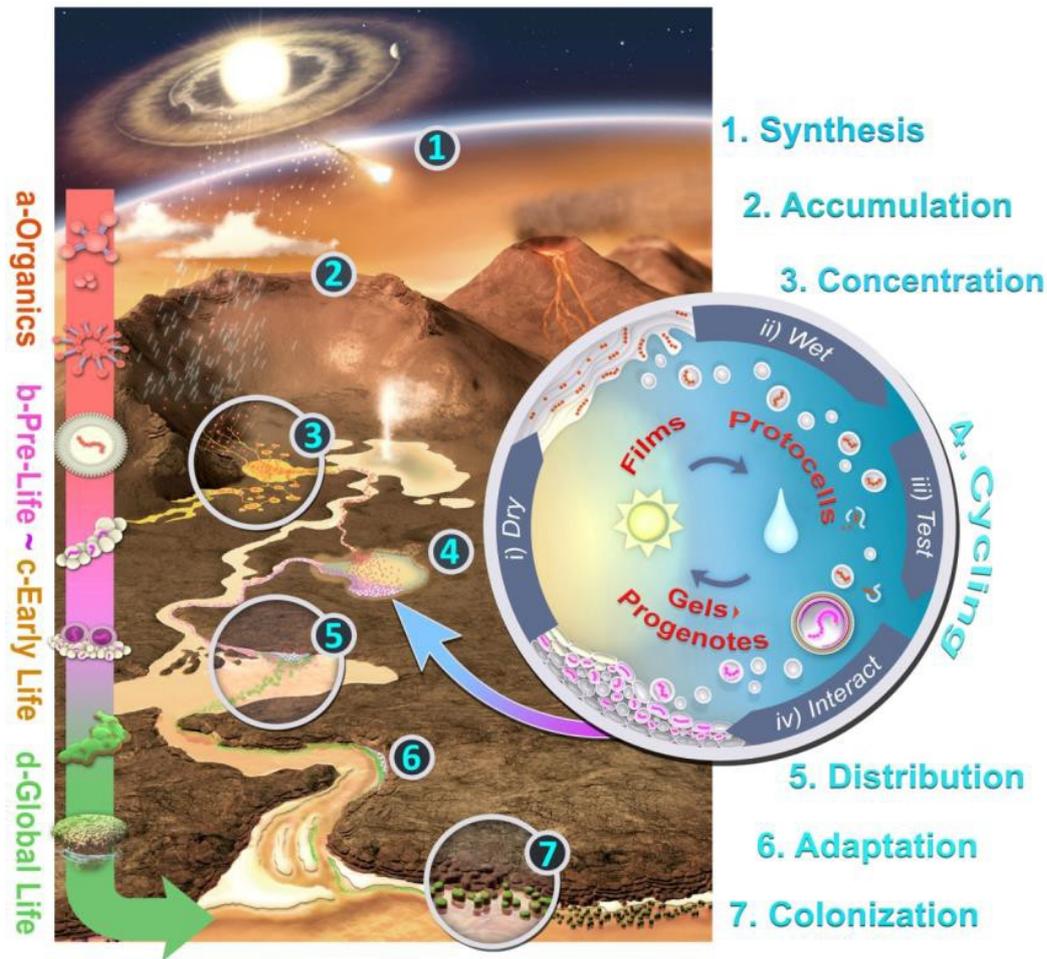


Fig. 4: A Hot Spring Hypothesis for an origin of life<sup>23,39</sup>, illustrating how simple organic compounds synthesize in space (1) and accumulate (2) within interconnected hydrothermal pools on land (3). These organics polymerize within a cycling pool and become encapsulated within protocells that undergo selection toward an origin of life (4). Life then distributes along an adaptation pathway (5,6) into the salty oceans (7).

### The search for a second genesis

From an astrobiological perspective, the consideration of an origin of life in terrestrial hot springs is important for two reasons. First, it can provide focused exploration strategies for planetary bodies where this combination of ingredients is known to have, or may have, occurred. Second, it provides us with an easily recognizable target, narrowing down the search for evidence for past life. Opaline silica deposited from hot springs is visible to orbital spectrometers<sup>66-67</sup>, as is the larger geographic footprint that surrounds hydrothermal alteration mineral zones<sup>68</sup>.

Point 1 implies that “Follow the Water” no longer suffices as a guiding paradigm in the search for a second genesis of life. This is because, although water is important for life that already exists, permanent water is an impediment to complexing organic molecules, and an exposed land surface with links to volcanic heat may be essential in generating the complexity required to make life.

This has significant implications for astrobiology. For example, Mars, which never appears to have had a fully global ocean but did have volcanism and a hydrological cycle in its early history, appears to have had the conditions necessary to generate life in hydrothermal systems<sup>69</sup>. Indeed, opaline silica deposits have already been identified on Mars by the Spirit

rover adjacent to “Home Plate” in the Columbia Hills, with robust evidence that they represent hot spring sinter<sup>66,67,70</sup>, including indications for potential biosignatures<sup>57</sup>(Fig. 6). Other candidate hot spring deposits have been observed from orbit, including one on the flanks of a volcanic cone in Nili Patera<sup>71</sup>. The combination of i) high potential for habitability, and ii) in-situ biosignature preservation of silica-depositing hot spring systems make such deposits attractive astrobiology targets for future missions to Mars.

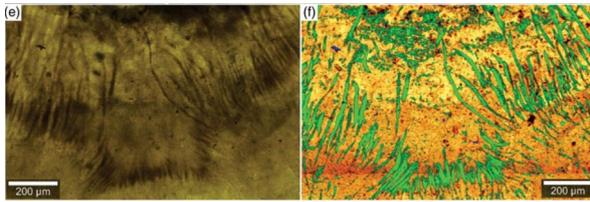


Fig. 5: Photomicrograph (left) and Raman spectroscopy image (right) of microbial filaments in Jurassic hot spring sinter: green = kerogen; orange/yellow = silica<sup>45</sup>.

Point 2 is critical because terrestrial hot spring deposits are important not only as *hosts* of life, but as *preservers of biosignatures* over billions of years<sup>39,45,51,72,73</sup>. Active hot springs on Earth today are replete with life, which includes hyperthermophiles that inhabit vent areas, as well as thermophiles that occupy most of the mid-to-low temperature region of more widely distributed hot spring discharge channels and aprons upon which thick microbial mats develop<sup>41</sup>. Representatives of early-evolved lineages of chemosynthetic life inhabit modern hot springs and have likely done so since these lineages evolved. Moreover, the organisms that inhabit high temperature transects of hot springs (>70°C) are supported by metabolisms that are dependent on chemical energy, present prior to the emergence of photosynthesis.

Most active hot spring deposits consist of opaline silica, precipitated from dissolved silica in solution in hot spring waters through biogenic and abiogenic processes such as cooling and evaporation. Entombment of microbial mats and biofilms living on opaline silica depositional surfaces in and around hot springs results in the formation and preservation of numerous microbial biosignatures that include macro-to-microscale fabrics and structures, as well as organic and inorganic chemical traces of life (Fig. 5), preserved at all temperatures, from vent to distal hot-spring aprons<sup>50,57,74</sup>. Indeed, opaline silica is the most important primary mineraloid responsible for preserving morphologically and chemically identifiable traces of life on early Earth. Its diagenetic product, quartz, is the dominant host lithology of the most ancient traces of life on Earth. Critically, it has now been established that ALL hot spring deposits identified throughout the well-established 3.5 billion-year record of life on Earth preserve traces of ancient life<sup>45,49-54,59</sup>.



Fig. 6: Comparable deposits of nodular opaline silica with digitate protrusions from Columbia Hills, Mars, and El Tatio, Chile<sup>67</sup>.

Importantly, hot springs could truly be the "first and last outpost" for life on Mars, or any rocky habitable world that becomes uninhabitable at its surface through loss of its atmosphere, desiccation and irradiation. Life, if it emerged on Mars, would have had to retreat to refuges in the saline subterranean fluids that may have hosted a deeper biosphere. The plumbing of a hydrothermal system could access that refuge and might carry such life with it through a temporary effusion of water up to a surface hot spring, where it may have temporary viability in a last surface outpost.

## Future research

### 1) Combining/synthesizing data from active and ancient hot spring sites

- Develop a catalogue of active hot spring characteristics (T, pH, Eh, trace element concentrations, microbial community composition, etc.) to define habitable conditions for chemosynthetic microbial life, and determine which parts of the system best preserve a record of microbial life (i.e. from high-, mid-, low-temperature parts of sinters);
- Develop and further define a compendium of reliable biosignatures as a function of bulk geochemistry in modern and ancient hot springs, including geochemical markers concentrated by microbes, even where organic material has been destroyed;
- Explore prebiotic chemistry, including condensation, catalysis, and self-assembly processes, in active hot springs (including surface, and near and deep subsurface);
- Investigate processes and products of active mixing zones among different hot springs, to define complexity, precipitation products, energetics, nature of chemical gradients, etc.;
- Identify the processes involved in concentration of the trace elements critical for prebiotic chemistry (e.g., B, Zn, Mn, P, S, etc.);
- Further studies of deep time hot spring analogues to better constrain early Earth conditions and preservation potential;

### 2) Experimental work

- Investigate what happens to organic matter from meteoritic in-fall in active and ancient hot springs, using laboratory simulations;
- Investigate the effects of radiation on organic biosignatures preserved in opaline silica;
- Conduct experiments to investigate retardation of “bad” far-UV under Hadean atmospheric conditions (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>) and by silica gel (and other hot spring precipitates), vs. transmittal of beneficial near-UV that promotes reaction pathways;
- Determine more precisely what ancient (anoxic) hydrothermal fields were like on a planet with a high pCO<sub>2</sub>, high temperature atmosphere;
- Grow sinters under varied field and lab conditions to try to replicate the digitate silica fabrics seen at Columbia Hills, including with and without biology.
- Identify geochemical biosignatures, and trace these from fresh opaline sinter to diagenetic quartz to determine preservation mechanisms.
- Explore prebiotic chemistry in simulated ancient conditions, with deep time mineral substrates and early Earth atmospheric conditions, heating-cooling and wet-dry cycling, and mixing to investigate membrane formation, organic compound concentration, supramolecular assembly, polymerization reactions, and combinatorial selection of protocells.

### 3) Technology development needs

- Develop and fund a sophisticated simulation anoxic chamber capable of combinatorial chemistry to investigate pathways for prebiotic chemistry. Given the complex nature of hydrothermal fields, a microfluidics system performing many experiments at once, with different early Earth inputs, substrates etc., and analyzing results with high throughput screening enabling closed loop operation (no manual operations), is required;
- Develop high throughput, high resolution methods for characterizing all other (non-single molecule) biosignatures preserved in hot springs;
- Design a biosensor for astrobiology research that can resolve and identify single molecules, based on nanopore technology.

## References Cited

- 1] Cairns-Smith AG 1982. *Genetic takeover and the mineral origins of life*. Cambridge Uni Press. 2] De Guzman V et al. 2014. *J Mol Evol* 78:251-262. 3] Hud N. et al. 2013. *Chem & Biol* 20:466-474. 4] Ross D, Deamer D 2016. *Life* doi: 10.3390/life6030028. 5] Kim HJ et al. 2011. *J Am Chem Soc* 133:9457-9468. 6] Mulkidjanian AY et al. 2012. *PNAS* 109:E821–E830. 7] Kitadai N, Maruyama S 2018. *Geosci Front* 9:1117-1153. 8] Williams DL et al. 1974. *Geophys J Royal Astron Soc* 38:587-608. 9] Corliss JB et al. 1979. *Science* 203:1073-1083. 10] Jannasch HW, Mottl MJ 1985. *Science* 229:717-725. 11] Martin W et al. 2008. *Nature Rev Microbio* 6:805-814. 12] Russell MJ, Hall AJ 2006. *Geol Soc Am, Memoir* 198:1-32. 13] Nitschke W, Russell MJ 2009. *J Mol Evol* 69:481-496. 14] Guido D et al., 2010. *J Geol Soc* 167:11-20. 15] Campbell KA et al. 2015. *Earth-Sci Rev* 148:44-64. 16] Henley RW, Ellis AJ 1983. *Earth-Sci Rev* 19:1-50. 17] Darwin C 1871. Letter to J. Hooker. 18] Pearce BK et al. 2017. *PNAS* 114:11327–11332. 19] Kvenvolden K et al. 1970. *Nature* 228:923-926. 20] Deamer DW, Pashley R 1989. *Orig Life Evol Biosph* 19:21-38. 21] Martins Z et al. 2008. *Earth Planet Sci Lett* 270:130-136. 22] Koga T, Naraoka H 2017. *Sci Reports* 7:636. 23] Damer B, Deamer D 2020. *Astrobio* 20:429-452. 24] Power JF et al. 2018. *Nat Comm* 9:2876. 25] Colman DR et al. 2019. *Astrobio* 19:1505-1522. 26] Campbell KA et al. 2019. *J Volc Geotherm Res* 370: 65-81. 27] Lynne BY et al. 2018. *J Volc Geotherm Res* 354:1-12. 28] Sanchez-Garcia et al. 2019. *Frontiers Microbio* 9 :3350. 29] Parenteau, MN, Cady SL 2010. *Palaios* 25:97-111. 30] Grew ES et al. 2011. *Origin Life Evol Biosphere* 41:307-316. 31] Ghosh W et al. 2012. *Geomicrobio J* 29, 879-885. 32] Steller LH et al. 2019. *Astrobio* 19:1459-1473. 33] Van Kranendonk MJ et al., 2020. *Astrobio*, in press. 34] Ferris JP 2005. *Elements* 1:145-149. 35] Hargreaves WW et al. 1977. *Nature* 266:78-80. 36] Deamer D et al., 2002. *Astrobio* 2:371 - 382. 37] Deamer D et al., 2006. *Philos Trans R Soc Lond B* 361:1809-18. 38] Deamer DW, Georgiou CD 2015. *Astrobio* 15:1091-1095. 39] Van Kranendonk MJ et al. 2017. *Sci Am* 317:28-35. 40] Monnard PA et al. 2002. *Astrobio* 2:139-152. 41] Mulkidjanian AY et al. 2003. *BMC Evolution Biol* 3:12. 42] Powner MW et al. 2009. *Nature* 459:239-242. 43] Mulkidjanian AY 2009. *Biol Direct* 4:26. 44] Van Kranendonk MJ et al. 2008. *Precamb Res* 167:93-124. 45] Djokic T et al. 2017. *Nat Comm* 8:15263. 46] Nelson JW, Tinoco Jr I 1982. *Biochem* 21: 5289-5295. 47] Campbell KA et al. 2019. *J Volc Geotherm Res* 370:65-81. 48] Hamilton AR et al. 2019. *J Volc Geotherm Res* 381:209-226. 49] Guido DM, Campbell KA 2018. *Geol Mag* 155:1394-1412. 50] Guido DM et al. 2019. *Geol Mag* 156:1631-1638. 51] Walter MR et al. 1996. *Palaios* 11:497-518. 52] Rice CM et al. 2002. *J Geol Soc* 159:203-214. 53] Djokic T et al. 2020. *Astrobio* in press. 54] Van Kranendonk MJ et al., 2019. In: *Earth's Oldest Rocks*, 2<sup>nd</sup> Ed., Elsevier: 985-1006. 55] Van Kranendonk MJ, Pirajno F 2004. *Geochem Explor Envir Anal* 4:253-278. 56] Trewin NH 1996. In: *Ciba Foundation Symposium*, John Wiley & Sons: 131-149. 57] Ruff SW, Farmer JD, 2016. *Nat Comm* 7: 13554. 58] Gong J et al., 2020. *Astrobio* 20:500-524. 59] Baumgartner R et al., 2019. *Geology* 47:1039-1043. 60] Nunes CI et al. 2020. *Intl J Plant Sci* 181:196-209. 61] Teece BL et al. 2020. *Astrobio* 20:537-551. 62] McKenzie EJ et al., 2001. *Geothermics* 30:483-502. 63] Baumgartner, RJ et al., 2020. *Precam Res* 337:105534. 64] Gangidine A et al. 2020. *Astrobio* 20:525-536. 65] Brown AJ et al. 2006. *Austr J Earth Sci* 52:353-364. 66] Squyres SW et al. 2007. *Science* 316:738-742. 67] Ruff SW et al. 2011. *J Geophys Res* 116:E00F23. 68] Sillitoe RH 2015. *Mineral Dep* 50:767-793. 69] Cady SL et al. 2018. Chpt 7, In *From Habitability to Life on Mars*, Elsevier. 70] Ruff SW et al. 2019. *Astrobio* 20:475-499. 71] Skok JR et al. 2010. *Nat Geosci* 3:838-841. 72] Walter MR, Desmarais D 1993. *Icarus* 101: 129-143. 73] Berelson WM et al. 2011. *Geobiol* 9:411-424. 74] Cady SL et al. 2003. *Astrobio* 3:351-368.