Thermal transformations in modified calcium carbonates: when geology meets biology

Stephen Thompson

Diamond Light Source, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire. OX11 0DE

Observed differences in thermal behaviour between calcium carbonates of biogenic and abiogenic origin – capable of being analysed remotely by surface landers – are widely cited as potential biomarkers for determining whether life once existed on Mars. Notably, differences appear to exist in both phase transformation and breakdown temperatures: firstly from aragonite to calcite between 400 and 500 °C and then between 700 and 900 °C as calcite breaks down to CaO and CO₂; and in both cases occur at significantly lower temperatures in carbonates of biogenic origin.¹⁻³ However, though seemingly compelling as a potential marker of past life, there has been no investigation into the physical mechanism behind these differences and as such, no direct proof that they are uniquely diagnostic of a biogenic versus abiogenic origin for any carbonates found on the Martian surface.

To address this problem, the structural and morphological modification in synthetic biomimetic carbonate formed in the presence of amino acid has been investigated.^{4,5} The aragonite-to-calcite phase transition and calcite-to-oxide breakdown temperatures are found to be significantly lower compared to carbonate synthesised in the absence amino acid. The observed temperature differences in the biomimetic carbonate closely follow the reported differences for naturally occurring biogenic and abiogenic carbonates. The biomimetic carbonates exhibit modified crystal morphologies, with a correspondingly highly strained crystal lattice, similar to that observed in biogenic carbonates.⁶ The induced microstrain adds an additional energy term to the carbonate lattice energy, lowering the activation energy required for structural transformation or decomposition. Although produced via biomimetic means, the carbonate investigated in these experiments is nevertheless abiogenic in origin and given suitable localised conditions such as pooled water within impact craters and a supply of organic molecules, delivered to the planet by meteorites, could result in the formation of naturally occurring biomimetic carbonates on the Martian surface and would exhibit the same thermal characteristics as biogenic carbonate. As a limiting case, therefore, the thermal behaviour of any apparently biogenic Martian calcium carbonate may in fact only be a marker for a prebiotic organic chemistry having once been present on the Mars, rather than living organisms.

References

- 1. Cabane, M., *et al.* Did life exist on Mars? Search for organic and inorganic signatures, one of the goals for SAM (Sample Analysis at Mars). *Adv. Space Res.* **33**, 2240 (2004).
- 2. Stalport, F., Coll, P., Cabane, M., *et al.* Search for past life on Mars: Physical and chemical characterisation of minerals of biogenic and abiogenic origin. 1. Calcite. *Geophys. Res. Lett.* **32**, L23205 (2005).
- 3. Stalport, F., Coll, P., Szopa, C., *et al.* Search for past life on Mars: Physical and chemical characterization of minerals of biotic and abiotic origin: 2. Aragonite. *Geophys. Res. Lett.* **34**, L24102 (2007).
- 4. Thompson, S. P., Parker, J. E., *et al.* Thermal breakdown of calcium carbonate and constraints on its use as a biomarker. *Icarus.* **229**, 1 (2014).
- 5. Thompson, S. P., Parker, J. E., *et al.* Morphological templating of metastable calcium carbonates by the amino acid leucine. *J. Phys. Conf. Ser* 286, 012030 (2011).
- 6. Parker, J. E., Thompson, S. P. *et al.* A study of the aragonite-calcite transformation using Raman spectroscopy, synchrotron powder diffraction and scanning electron microscopy. *CrystEngComm* **12**, 1590 (2010).

Email corresponding author: Stephen.thompson@diamond.ac.uk