Molecular parameters of post impact cooling in the Boltysh impact structure

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Introduction: Impact events have the potential to generate a number of long-term sources of heat that can lead to the initiation of hydrothermal systems when the impact occurs on a water- or ice-rich target. Such hydrothermal systems have been postulated as promising locations to search for evidence of past biological processes on Mars due to the prevalence of impact cratering as a surface process in Mars’s early history [1]. In this study, we have used molecular parameters of the thermal maturity of organic matter combined with palynology and carbon isotope stratigraphy to study the post impact thermal history of crater fill sediments from the Boltysh crater, Ukraine.

Crater-fill sediments of the Boltysh crater: The Boltysh impact crater, is a 24km diameter complex structure formed on the basement rocks of the Ukrainian shield which has been dated at 65.17±0.64 Ma. The crater was drilled in the 1960s - 1980s but the cores were not curated and have been lost. A 596m cored borehole was drilled in 2008 to the W of the central uplift peak in the deepest part of the crater, and recovered a complete sequence of sedimentary rocks resting unconformably on suevite breccia. The boundary between the suevite and sediment is a 60° unconformity probably reflecting an uneven crater floor. Borehole sediments record minor weathering of the suevite prior to the formation of a shallow crater lake. The oldest sediments in this study are thin green-grey silty sands which are also present in intra-suevite fissures and as rip-up clasts in overlying coarse turbidite sandstones. These sandstones pass upsection into crudely bedded fine silty sandstones and laminated siltstones interpreted as the deposition of reworked proximal ejecta blanket material by turbidity currents in the anoxic waters of the crater lake. This dominantly laminated unit is truncated by the erosional base of the first of a thick sequence of turbidites with coarse sandstones at the base (578.75m), probably representing the establishment of an effective fluvial drainage system from the ejecta blanket into the crater via marginal deltas.

Organic, isotopic and palynologic analysis: Core samples were crushed in an agate pestle and mortar. To powdered samples (ca. 4g) internal standards were added, the samples were then solvent extracted with dichloromethane: methanol (93:7) using a soxhlet apparatus. Hydrocarbon fractions were isolated from the total extracts using Florosil and C18 solid phase extraction cartridges. Analysis of hydrocarbon fractions was performed on an Agilent Technologies 6890-5973 gas chromatograph-mass spectrometer (GC-MS), separation was performed on a DB-5 column (J&W); for biomarker quantitation the MS was run in single ion monitoring mode. For carbon isotope measurements the same samples were washed with 0.1M – 1M HCl to remove carbonate prior to the measurement of carbon abundance and isotopic composition by mass spectrometry [2]. A parallel suite of samples was subjected to standard palynological maceration techniques: for each sample, 5g of rock was processed and sieved using a 7µm mesh, aliquot stew mounts of the residue were then examined by light microscope.

Molecular parameters of thermal maturity: Biomarker distributions are sensitive to the thermal maturation of organic matter and a number of biomarker maturity parameters have been developed, in particular those based on hopanoid stereochemistry [3]. These parameters reflect the relative rates of generation and thermal degradation of different hopane isomers. In the early stages of thermal maturation relative loss of 17β-(H)-hopanes occurs so that a parameter based on the relative proportions of 17β,21β-(H)-hopanes to the sum of the other more stable isomers (17α,21β-(H) + 17β,21β-(H) + 17β,21α-(H)-hopanes) provides a useful indicator of the thermal maturity of organic matter in the early stages of maturation (plotted as β/αβ+β+α in Figure 1). Hopane data are presented in Figure 1 for depths between 545.5m and 577.25m, below this depth there is insufficient organic matter present for analysis.

The maturity parameter plotted in Figure 1 indicates that throughout most of the section
analysed (between 545m and 566m) the organic matter in Boltysk crater-fill sediments is very immature. Indeed, the $\beta/\alpha + \beta + \beta/\alpha$ ratio of around 0.3 indicates that the organic matter did not achieve sufficient thermal maturity to reach the “oil window”, the point at which organic matter has sufficient thermal maturity for catagenesis to occur. This indicates that temperatures above 585m were never in excess of 100°C as this would have significantly degraded 17β(H)-hopanes.

From 565m to 577.25m the $\beta/\alpha + \beta + \beta/\alpha$ maturity parameter progressively drops to 0. This indicates that there is both relative and absolute loss of 17β(H)-hopanes. Previous studies of hopanoid maturity parameters in organic-rich sediments proximal to igneous intrusions [4] suggest that such marked variations in the $\beta/\alpha + \beta + \beta/\alpha$ parameter result from the simultaneous destruction and generation of different isomers so that there is good evidence that a proximal heat source will cause the maturity variations observed in this study. Further evidence for heating of the crater lake itself comes from palynological data, which provides evidence for a eutrophication produced Botryococcus bloom in some of the deepest sediments that may have been thermally enhanced. However, the situation here is different from previous studies of organic maturation proximal to igneous heat sources in that the sediments were accumulating in the crater lake at the same time as they were being heated by the underlying impact crater. Given the immaturity of the organic matter observed above 565m it seems reasonable to assume that by this time there was insufficient heat emanating from the crater floor to cause the stereochemical changes observed in hopanes further down the core, i.e. the crater was no longer a significant source of heat.

**Timescales of cooling:** The crater-fill sediments and their bio- and carbon-isotope stratigraphy enable the timescale of the crater’s cooling to be estimated. A lower point in geological time for the base of the core can be established from palynological and carbon isotope data which indicates that the crater pre-dates the Cretaceous/Paleogene (K/Pg) boundary by a few hundreds to thousands of years [5]. The data in [5] indicate that a post-impact flora became established on the ejecta layer of the Boltysk crater that in turn was devastated by the Chicxulub impact. An upper point in geological time comes from evidence from palynology and carbon isotopes for the Dan-C2 hyperthermal event at around 500m. These time constraints suggest that the Boltysk crater cooled relatively rapidly after the impact, probably in significantly less than 20ka. Further data will constrain this timescale more tightly, however, it is apparent that impact craters of this size are relatively short-lived sources of heat and may therefore not be suitable environments for biological processes requiring heat to maintain liquid water.


**Figure 1** Carbon isotope stratigraphy for total organic matter and variations in the C, $\beta/\alpha + \beta$ hopenoid maturity parameter in lowermost crater fill sediments from the Boltysk impact crater, Ukraine.