Thermal alteration of organic matter in an impact crater and the duration of postimpact heating

John Parnell
Department of Geology and Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK
Gordon R. Osinski
Department of Planetary Sciences, University of Arizona, 1040 East 4th Street, Tucson, Arizona 85721-0077, USA
Pascal Lee
Search for Extraterrestrial Intelligence (SETI) Institute, National Aeronautics and Space Administration (NASA) Ames Research Center, Moffett Field, California 94035-1000, USA
Paul F. Green
Geotrack International Pty Ltd., 37 Melville Road, Brunswick West, Victoria 3055, Australia
Martin J. Baron
Department of Geology and Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK

ABSTRACT

The 24-km-diameter Tertiary Haughton impact structure formed in rocks that contained preexisting liquid hydrocarbons. Biomarker ratios in the hydrocarbons show a consistent pattern of variation in degree of heating across the structure. The heating reached a maximum at the crater center and is attributed to hydrothermal activity following impact. Kinetic modeling suggests a time scale of ~5 k.y. for the heating, at a maximum temperature of 210 °C. The short time scale suggests that in moderate-sized craters, which are abundant on Mars, heating is not so extensive that fossil or extant organic matter would be obliterated.

Keywords: Haughton impact structure, impact craters, biomarkers, thermal maturity, thermal alteration, Mars.

INTRODUCTION

Numerous impact craters contain organic matter, sometimes abundantly, suggesting that impact events can have a significant role in hydrocarbon generation and concentration (Grieve and Masaitis, 1994; Grieve, 1997). The survival of organic matter following hypervelocity impacts is also of interest because impact craters are viewed as possible sites for the establishment and evolution of primitive life on Earth and other planets such as Mars (Holm, 1992; Farmer, 2000; Kring, 2000; Newsom et al., 2001). Our understanding of the alteration of organic matter by impacts is severely limited because most occurrences are in old (early Paleozoic and Precambrian) craters where much biomolecular information has been degraded, subsequent geologic events have overprinted and obscured impact-related data patterns, and exposure can be very limited. Measurement of the degree of alteration requires a relatively young, well-exposed crater that has no significant postimpact history. These requirements are met by the mid-Tertiary Haughton impact structure, Devon Island, Nunavut, Canada, which crops out in a polar desert. The 24-km-diameter structure developed in Ordovician–Silurian sedimentary rocks, with an uplifted central part. Following impact-related hydrothermal activity, the crater has undergone only minor Tertiary lacustrine sedimentation (Robertson and Sweeney, 1983; Osinski et al., 2001). The Haughton impact occurred in dolomite-rich rocks that already contained liquid hydrocarbons. The hydrocarbons occur as widely distributed micrometer-scale fluid inclusions that had been entrapped during mineral crystallization when the dolomites were deeply buried in Silurian–Devonian time (Parnell et al., 2003). The hydrocarbon-bearing inclusions occur both within and outside the crater. This occurrence of hydrocarbons sealed within minerals is highly advantageous, as the inclusions can survive considerable heating without rupturing and so preserve the biomolecular data that reflect the degree of heating.

The fate of organic matter is dependent upon the degree and duration of heating, but to date the duration has been deduced from theoretical models for cooling behavior (e.g., Daubar and Kring, 2001; Rathbun and Squyres, 2002). Here we show that organic geochemical biomarker data derived from transects across the Haughton impact structure can be used to constrain the heating time. Biomarker data can provide information on heating because different organic molecules are formed or destroyed at different rates with temperature increase, and their relative abundances can be used to provide reliable parameters (Peters and Moldowan, 1993). This approach is widely used in oil and gas exploration, to deduce thermal histories of rocks, and also correlation between them (Hunt, 1996). Consequently, their use is very well understood, particularly over a temperature range up to ~250 °C.

METHODOLOGY

Biomolecular data (Fig. 1) were obtained by mass spectrometry on hydrocarbon extracts from samples of dolomite along two transects through and around the impact structure. Sampling sites (Fig. 2) from the central uplift of the crater, as located by rock stratigraphy and fracture density, are assessed to have been subject to shock pressures to 10 GPa or higher, in comparison to pressures of well below 1 GPa in the surrounding region. The high pressures are represented by an abundance of shatter cones and planar deformation features within quartz. Samples were extracted by using dichloromethane, then separated by using thin-layer chromatography, and hydrocarbon and aromatic fractions were analyzed by gas chromatography–mass spectrometry for *n*-alkanes ($m/z = 85$), hopanes ($m/z = 191$), steranes ($m/z = 217$), phenanthrene ($m/z = 178$), and methylphenanthrenes ($m/z = 192$).

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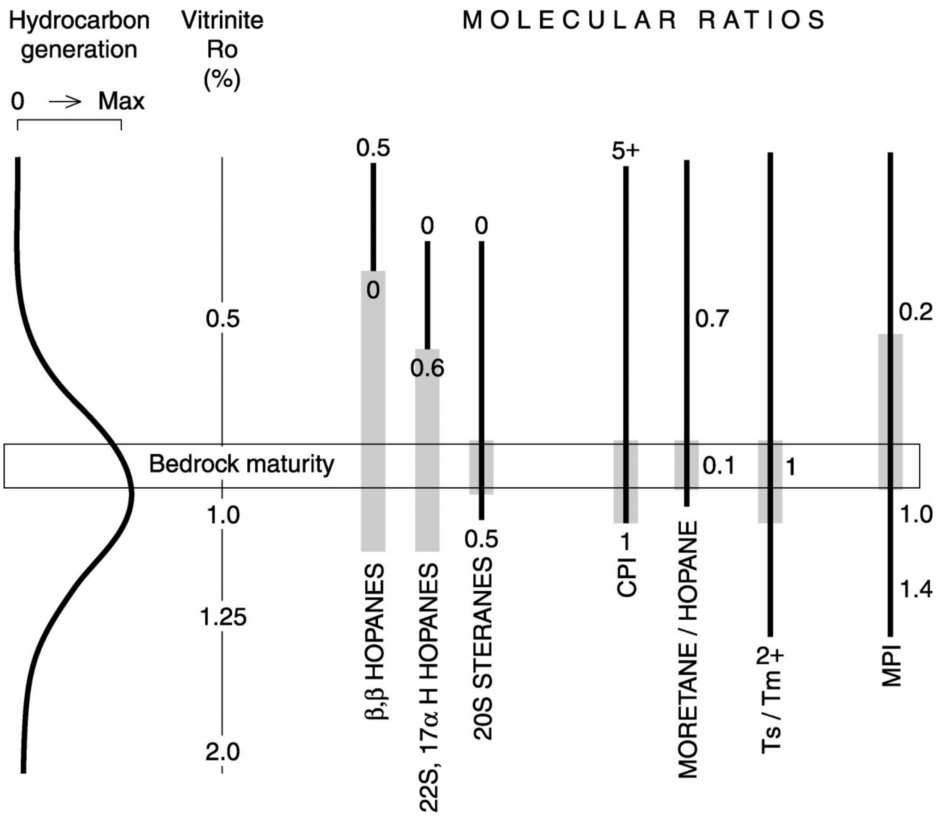

Figure 1. Biomarker data for Haughton impact structure samples. Thermal maturities allowed by data (shaded) are all consistent with window of peak oil generation. CPI—carbon preference index; MPI—methylphenanthrene index.

THERMAL MATURITY

Thermal maturity parameters based on hydrocarbon biomarkers are recorded in Figure 1. Carbon preference index (CPI) values close to 1.0, C_{32} αβ 22S/(22S + 22R) hopane ratios close to equilibrium at 0.6, Ts/Tm rearranged hopanoid ratios close to 1.0 [Ts/(Ts + Tm) of 0.5], C_{29} ααα 20S/(20S + 20R) sterane ratios up to 0.48, C_{30} moretane/hopane ratios close to 0.1, and a lack of ββ hopanes are all consistent with the window of peak oil generation (Fig. 1). This level of maturity is also indicated by regional graptolite reflectance data (Gentzis et al., 1996). As the 20S/(20S + 20R) sterane ratios have not reached their equilibrium values of ~0.5, there is potential to use this parameter to map variations in thermal maturity. The sterane ratio is particularly sensitive to variations in maturity from pre–oil window to peak–oil window (Peters and Moldowan, 1993). The transects across the crater (Fig. 2) show that lower ratios are attained at locations outside and at the crater margin, compared to locations farther inside the crater and a maximum in the crater center, indicating that hydrocarbons inside the crater have undergone additional heating. All samples that are within the central uplift exhibit ratios of 0.44 or greater. The Ts/Tm ratio extends the maturity scale beyond the oil window (van Graas, 1990) and thus is a valuable complement to the sterane ratio (Waples and Machihara, 1991). It is less sensitive to maturity variations within the oil window, as reflected by similar values from samples in the outer part of the crater, although these values are clearly higher than those from outside the crater. However, the parameter is more sensitive at higher maturities and accordingly shows a large increase at the crater center to a maximum value of 7.08.

DISCUSSION

Heat Sources

The main heat sources contributing to thermal anomalies at impact sites are the shock pressure wave, including the generation of melts during the impact event, and heat from the central uplifted part of a crater where the geothermal gradient is raised (Boer et al., 1996; O'Keefe and Ahrens, 1999). The relative importance of these sources is still a topic of debate. For example, some studies suggest that the melt sheet contributes more energy, including residual heat after the shock wave passes, although the uplifted center is calculated to have a longer cooling time in <100-km-diameter craters, such as that at Haughton (Daubar and Kring, 2001). However, when shock heating from the passage of the shock wave is considered, heat contribution from the central uplift appears to be comparable with that from impact melt rocks (Thorsos et al., 2001). Our determination of a thermal anomaly focused in samples from the central uplift is consistent with a model in which the crater center retains an elevated temperature over a longer period. Consequently, we assume that the heat represented by the elevated biomarker ratios was a result of the subsequent hydrothermal system and residual heat from the shock wave. Evidence for hydrothermal activity, in the form of crosscutting mineral veining, is found widely distributed across the crater (Osinski et al., 2005). Although several samples are from the vicinity of the impact melt breccias, representing temperatures of at least 700 °C, the biomarker data indicate that only the crater center sample has been subject to the maximum increase in maturation (i.e., heat), suggesting that contact metamorphic temperatures from the impact melt breccias are not reflected by the samples. The initial shock wave would impart thermal energy, but the accompanying high pressure at that stage is likely to retard, rather than promote, organic maturation reactions (Carr, 1999), and cancel the effect of enhanced temperature at this early stage. Also, clasts of dolomite within the impact melt breccias preserve their liquid hydrocarbon inclusions within millimeters of the clast surface, showing that heat transmission into the bedrock during the initial shock heating, and from residual heat after the shock wave, was extremely limited.

Duration of Heating

Biomarker ratios are kinetically dependent, i.e., they change in response to heat to a degree controlled by the time scale of heating (van Duin et al., 1997). In cases where anomalous heating has only been applied for a limited period of time, kinetic maturity parameters have not reached their equilibrium values. By using an independent measurement of temperature that is not kinetically dependent, it is possible to use the kinetic parameter to determine the heating time. Absolute measurements of temperature can be determined from phase transitions and from fluid-inclusion data (inclusions trap fluid instantaneously; thus this process is not kinetically controlled). The melting of carbonates within the melt breccias records a temperature of at least 700 °C (Osinski and Spray, 2001; Osinski et al., 2001), but the dolomite samples from which the sterane data shown in Figure 2 were collected are unmelted and reached a maximum proven temperature of ~210 °C (determined from fluid-inclusion homogenization temperatures in impact-related hydrothermal calcite veins; Osinski et al., 2005). These inclusions are distinct from the preimpact oil-filled inclusions. The veining occurred near the contemporary land surface, so a pressure correction to this temperature is not required.

The 20S/(20S + 20R) sterane ratio is the

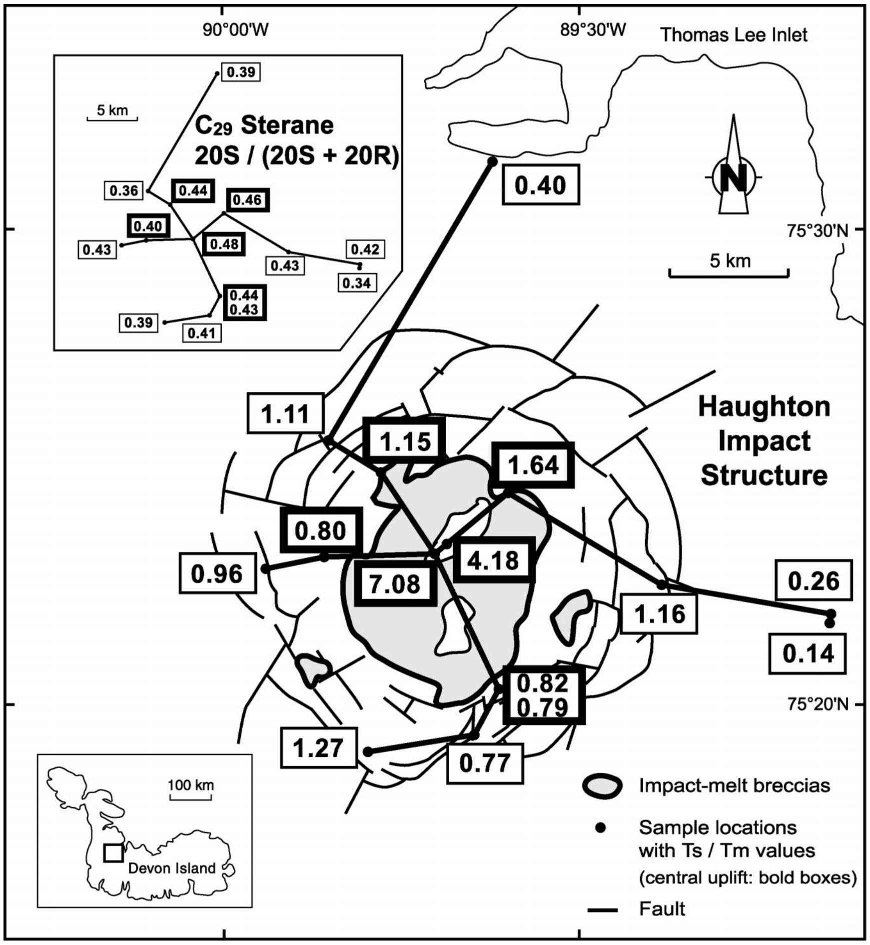

Figure 2. Transects of rearranged hopane (Ts/Tm) and sterane (inset) biomarker ratio data across Haughton impact structure, showing increasing values toward crater center.

most reliable hydrocarbon biomarker for correlation with vitrinite reflectance (Ro), the most widely used measurement of thermal maturity in rocks, which is also kinetically dependent (Waples and Machihara, 1991). The correlation allows the Ro equivalent to be determined in the maturity range up to the oil window (Bein and Sofer, 1987; Waples and Machihara, 1991). However, at higher maturity levels, including post–oil window conditions, aromatic indices are more effective measures of maturity. The methylphenanthrene index (MPI) provides a good correlation with vitrinite reflectance (Radke et al., 1982; Radke, 1988). MPI values of 0.42 and 0.87, from outside the crater and the maximum level inside the crater, equate to vitrinite reflectance values of 0.65% and 0.92%, respectively, by using the relationship $Ro = 0.6MPI + 0.4$ (Radke, 1988). Adopting these values as the ambient maturity level and the time-dependent response to heating, respectively, kinetic modeling (Burnham and Sweeney, 1989) yields a time scale of ~5 k.y. for the maximum hydrothermal temperature of 210 °C (Fig. 3).

The variations in thermal maturity cannot be attributed to differences in burial depth. A comparison can be made of rocks at the same stratigraphic level from the easternmost localities (Ts/Tm = 0.14, 0.26) and from the edge of the central uplift region (Ts/Tm = 1.64), where the difference can only be attributed to impact-related heating. The crater center sample is structurally uplifted from a deeper stratigraphic level by ~480 m (Frisch and Thorsteinsson, 1978), which under a normal geothermal gradient of 30 °C/km could account for a difference in vitrinite reflectance of as much as 0.15% (Hunt, 1996), i.e., only about half the difference measured.

The sources for error in this calculation are in measurement of biomarker ratio and adoption of an absolute maximum temperature. The background sterane ratio and methylphenanthrene index could both be ±0.03 (standard deviation), which equates to variations in vitrinite reflectance of only ~0.02%. The maximum values of these parameters at the crater center are necessarily based on a single sample, but if the same standard deviations are applied, the maximum reflectance value could similarly vary by 0.02%, which represents an uncertainty in the heating time of ~±1 k.y. The modeling is much more sensitive to the value used for absolute temperature, as reaction rate is exponentially dependent upon temperature, and a general guide is that a 10 °C rise in temperature could double the rate. Therefore the greatest source of error is the fluid-inclusion temperature. In accord with common practice in inclusion studies, the 210 °C fluid-inclusion temperature is assumed to be the maximum temperature achieved by the hydrothermal system. If any higher temperature was achieved, the duration of heating could have been shorter. Similarly, if we attribute the maximum component of the elevated reflectance that could be due to difference in stratigraphic level, the duration is reduced to 1 k.y. The approach assumes that we are measuring the duration of a heat pulse of constant magnitude, rather than a progressively cooling system. This is also common practice (O'Brien et al., 1996; Middleton et al., 2001) and reflects the fact that, at cooler temperatures, reactions are exponentially

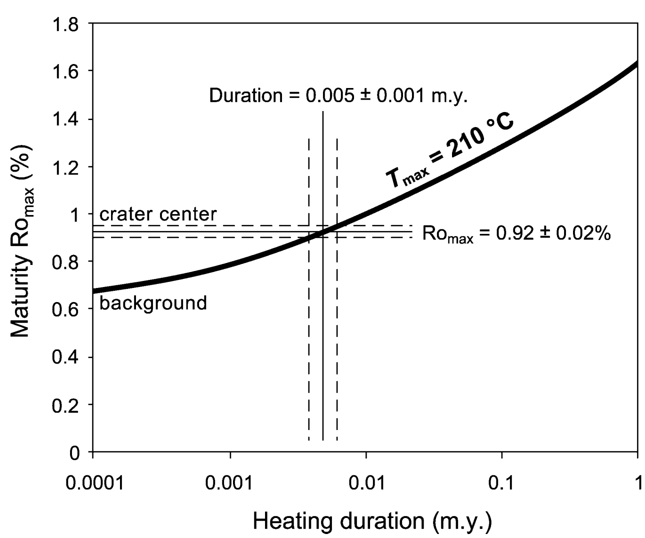

Figure 3. Time vs. maturity curve for maximum temperature of 210 °C (maximum fluid-inclusion temperature). Curve shows maturity achieved from background level of Ro (vitrinite reflectance) = 0.65 for possible durations of heating. Crater center value of 0.92% ± 0.2% represents heating for ~5 k.y. ± 1 k.y.

slower and contribute relatively little to the measured maturity. However, we emphasize that fluid circulation would continue, albeit at lower temperatures, after the measured heat pulse.

CONCLUSIONS

Existing estimates of the time scale of hydrothermal heating in impact craters are indirectly inferred from the modeled cooling time of heat sources. These estimates are for larger craters, including Manson (McCarville and Crossey, 1996), Sudbury (Ames et al., 1998; Abramov and Kring, 2004), Chicxulub (Daubar and Kring, 2001), Chesapeake Bay (Sanford, 2003), and a 180-km-diameter model (Rathbun and Squyres, 2002), and are in the range 10^4–10^6 yr. Our much shorter determination for a crater of <30 km diameter implies that heating in such craters may have been short-lived in terms of organic evolution, but concomitantly did not present such an extensive source of heat that existing organic matter was obliterated. It is widely believed that frequent impact events on the early Earth destroyed organic matter and inhibited evolution (Maher and Stevenson, 1988); however, the Haughton data suggest that in moderate-sized craters, biomolecules, fossilized remains, and even extant microbial life may have survived. Similarly, as the great majority of craters on Mars are <30 km diameter (Barlow, 1990; Rodionova and Khramchikhin, 1996), any organic matter that may have been present in the craters is unlikely to have been completely destroyed, and could have left a record.

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