The combustion characteristics and stable carbon isotopic compositions of irradiated organic matter: implications for terrestrial and extraterrestrial sample analysis

Conference or Workshop Item

THE COMBUSTION CHARACTERISTICS AND STABLE CARBON ISOTOPIC COMPOSITIONS OF IRRADIATED ORGANIC MATTER: IMPLICATIONS FOR TERRESTRIAL AND EXTRATERRESTRIAL SAMPLE ANALYSIS.

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Introduction: Ionizing radiation is the dominant creator and modifier of organic matter in space. It is capable of inducing free-radical chemistry in interstellar ice grains and the interiors of comets and asteroids, in planetary atmospheres and on the surfaces below [1,2]. Therefore, all analyses of extraterrestrial organic matter need to be aware of the nature and extent of radiolytic alteration.

This is especially true for the technique of stepped combustion-isotope ratio-mass spectrometry (stepped combustion-IRMS). Incremental heating allows the separation of carbon-bearing phases, such as kerogen, graphite, carbonate and diamond, by virtue of their different combustion temperatures [3]. The gas evolved at each temperature step is then analyzed isotopically. This technique, used extensively on terrestrial samples [4], was to have been employed by the Gas Analysis Package on the ill-fated Beagle 2 Mars Lander, and will be performed by the Ptolemy evolved gas analyzer on board the Rosetta spacecraft, upon arrival at Comet 67P/Churyumov-Gerasimenko [5,6].

The ability of stepped combustion-IRMS to separate carbon-bearing phases requires these to have significantly different combustion temperatures. Consequently, a full understanding of any process capable of causing variations in the combustion temperature of carbon-bearing phases is essential. Although thermal maturation is capable of significantly raising the combustion temperatures of organic matter and kerogen [5], this is not considered to be a significant problem on the cold and volcanically inactive surfaces of Mars and comets. Here, we show that ionizing radiation, abundant in extraterrestrial environments, can also cause significant increases in the temperature of combustion of organic matter, formed by the polymerization of simple hydrocarbons, and discuss the implications of this for extraterrestrial sample analysis.

Methods: Several naturally-occurring bitumens have been subjected to stepped combustion-carbon isotope ratio-mass spectrometry, using the MS86 machine at The Open University, UK. Three types of bitumen were analyzed: irradiated bitumen derived from the radiolytic polymerization of methane, and irradiated and nonirradiated mixtures of complex, biogenic hydrocarbons (Table 1). Irradiation was provided by uranium and thorium naturally present within the bitumens. These samples, and the effects of ionizing radiation on their organic chemistry and other properties, are described more fully elsewhere [7,8].

Results and Discussion: The results reveal the effects of ionizing radiation on the carbon isotopic composition and combustion characteristics of organic matter. There is a positive relationship between increasing radioelement concentration, and, hence, degree of irradiation, and the calculated mean combustion temperature, amongst the methane-derived bitumens. This is attributed to the progressive radiolytic formation of larger, more refractory polyaromatic hydrocarbons [8]. However, no relationship is apparent between the mean combustion temperature and radioelement concentration in the bitumens derived from complex hydrocarbon mixtures. This is probably due to the influence of other processes, such as variations in the original composition of the complex hydrocarbon mixtures, thermal maturation and oxidation.

Implications for extraterrestrial sample analysis: This data indicates that solid organic matter, formed by the radiation-induced polymerization of methane, combusts around 500 °C, and that the combustion temperature increases with increasing radiation dose Since ionizing radiation is the dominant producer and modifier of extraterrestrial organic matter [1], extraterrestrial organic matter may possess similar combustion characteristics.

Accurate predictions of the combustion characteristics of extraterrestrial organic matter would be very useful, especially for *in-situ* analyzes. It would allow the combustion profile of the experiment to be tailored in advance, enabling a greater number of smaller temperature steps to be used for the temperature range over which gas is predicted to be evolved from the material. This would provide greater analytical resolution where it is most required. This is useful in terrestrial studies, but, for extraterrestrial analyses, where the number of temperatures steps or repeat analyses possible may be strictly limited, it could be extremely important.

This data could also prevent a potential problem. Terrestrial, biogenic organic matter normally combusts at 300-450 °C. This enables stepped combustion to separate this material from carbonates, which generally decrepitate around 500-700 ºC, enabling isotopic analysis of the individual components [3]. However, the methane-derived organic polymers analyzed here combust at temperatures that not only are significantly higher that those of biogenic terrestrial organic matter, but also increase with increasing radiation dose. Hence, it is possible that certain terrestrial or extraterrestrial material might contain organic matter and carbonate with similar combustion/decrepitation temperatures. If combustion or decrepitation of two isotopically distinct phases occurred in the same temperature step, then the separate isotopic compositions of these phases are not be resolved. Instead, a value representing a mixture of the components would be returned.

This is especially significant for *in-situ* extraterrestrial analyses [5,6]. However, accurate predictions of the combustion characteristics of the target material would enable the combustion profile to be tailored so as to minimize, if not eliminate, this problem.

Conclusions: 1. Ionizing irradiation causes the mean combustion temperature of organic matter derived from the polymerization of methane to increase. This is attributed to the progressive radiolytic polymerization of small hydrocarbons into larger, more refractory and combustion-resistant PAHs.

2. This effect is not observed in bitumens derived from complex-hydrocarbon mixtures. This may be due to variations in chemical composition inherited from the source material, or to the effects of oxidation – influences that are greatly reduced in the methane-derived bitumens.

3. The methane-derived bitumens combusted at higher temperatures than the complex-hydrocarbon mixtures. This presumably reflects variations in organic chemistry.

4. Stepped combustion-IRMS results provide indications of the likely combustion behavior of extraterrestrial organic matter, on planetary surfaces or comets, which has been exposed to significant amounts of ionizing radiation. The data reported here should aid better interpretation of results of, and design and implementation of instrumentation associated with, in-situ extraterrestrial organic analyses.

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Table 1. Details and analytical results of the bitumens.

Bitumen type	Bitumen source and host rock age	Total radioelement concentration (%)	Calculated mean organic combustion temperature (ºC)	Bulk organic $\delta^{13}C$ values (‰)
Methane-derived bitumens	Boliden, Sweden; Palaeoproterozoic	7.7	458	-42.4
	Cluff Lake, Canada; Mesoproterozoic	12.3	474	-46.4
	Příbram, Czech Republic; Carboniferous	24.2	480	-59.6
Nonirradiated complex-hydrocarbon mixtures	Dingwall, Scotland; Devonian	0	350	-31.5
	Nash Scar Quarry A, Powys, Wales; Silurian	0	458	-31.0
Irradiated complex-hydrocarbon mixtures	Cerro Huemul, Argentina; Tertiary	0.21	418	-27.9
	Moonta, South Australia; Archaean	4.2	279	-21.8
	Temple Mountain, Utah; Triassic	7.0	437	-26.7
	Laxey, Isle of Man, UK; Ordovician	12.3	402	-13.6