

Hydropyrolysis: A new technique for the analysis of macromolecular material in meteorites

Mark A. Sephton^{a,*}, Gordon D. Love^b, Will Meredith^c, Colin E. Snape^c,
Cheng-Gong Sun^c, Jonathan S. Watson^d

^a*Impacts and Astromaterials Research Centre, Department of Earth Science and Engineering, South Kensington Campus, Imperial College London, SW7 2AZ, UK*

^b*Department of Earth, Atmospheric and Planetary Sciences, E34-550, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

^c*School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

^d*Centre for Earth, Planetary, Space and Astronomical Research, Open University, Milton Keynes, MK7 6AA, UK*

Received 27 July 2004; received in revised form 27 June 2005; accepted 29 June 2005

Available online 10 August 2005

Abstract

The carbonaceous chondrite meteorites are fragments of asteroids that have remained relatively unprocessed since the formation of the Solar System 4.56 billion years ago. The major organic component in these meteorites is a macromolecular phase that is resistant to solvent extraction. The information contained within macromolecular material can be accessed by degradative techniques such as pyrolysis. Hydropyrolysis refers to pyrolysis assisted by high hydrogen gas pressures and a dispersed sulphided molybdenum catalyst. Hydropyrolysis of the Murchison macromolecular material successfully releases much greater quantities of hydrocarbons than traditional pyrolysis techniques (twofold greater than hydrous pyrolysis) including significant amounts of high molecular weight polyaromatic hydrocarbons (PAH) such as phenanthrene, carbazole, fluoranthene, pyrene, chrysene, perylene, benzoperylene and coronene units with varying degrees of alkylation. When hydropyrolysis products are collected using a silica trap immersed in liquid nitrogen, the technique enables the solubilisation and retention of compounds with a wide range of volatilities (i.e. benzene to coronene). This report describes the hydropyrolysis method and the information it can provide about meteorite macromolecular material constitution.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Meteorite; Murchison; Organic; Pyrolysis; Hydropyrolysis; Polyaromatic hydrocarbons

1. Introduction

Meteorites are overwhelmingly dominated by fragments of asteroids coerced into Earth-crossing orbits by relatively recent collisions in the asteroid belt and the perturbing effect of gravitational interactions with Jupiter (Wetherill and Chapman, 1988). Meteorites have escaped many of the geological processes experienced on the planets and as a result preserve some of the

most primitive materials in the Solar System. In particular, the low petrographic type carbonaceous chondrites have elemental abundances similar to those of the Sun and contain substantial amounts (up to ca. 5%) of H, C and N in the form of organic matter (Sephton, 2002). Meteoritic organic matter is, at present, our only available record of natural pre-biotic chemical evolution and, based on deuterium enrichments appears to contain some exceedingly ancient matter which is only partially transformed from pre-solar materials (Kolodny et al., 1980; Robert and Epstein, 1982). The organic matter in meteorites is present as three solubility classes; around 25% is present as solvent-soluble or free organic matter but the majority is in the form of a

*Corresponding author at: Department of Earth Science and Engineering, South Kensington Campus Imperial College London, SW7 2AZ, UK. Tel.: +44 (0)20 7594 6542; fax: +44 (0)20 7594 7444.

E-mail address: m.a.sephton@imperial.ac.uk (M.A. Sephton).

complex solvent-insoluble macromolecular material (Sephton, 2002 and refs therein). The macromolecular material itself can be operationally defined into pyrolysable (i.e. breaks down under thermal stress) and non-pyrolysable (i.e. does not break down under thermal stress) fractions. These two macromolecular fractions are termed labile organic matter and refractory organic matter, respectively (Sephton et al., 2003). As the dominant organic entity, the macromolecular material is key to understanding the origin of meteoritic organic matter as a whole.

The macromolecular material in Murchison has been investigated using non-destructive techniques such as infra-red spectroscopy (Hayatsu et al., 1977) and nuclear magnetic resonance spectroscopy (NMR) (Croin et al., 1987; Gardinier et al., 2000; Cody et al., 2002). More commonly, the macromolecular material has been studied using destructive techniques, such as stepwise heating and pyrolysis. Stepwise heating experiments distinguish between different carbon phases in the meteoritic macromolecular material by their susceptibility to combustion or pyrolysis (thermal decomposition) and have revealed significant isotopic heterogeneity (e.g. Robert and Epstein, 1982; Kerridge et al., 1987). However, stepwise heating experiments provide little or no structural information.

Pyrolysis thermally decomposes macromolecular organic material and the products (the pyrolysate) are then identified, usually with a mass spectrometer, and carefully studied to reveal the constitution of the parent material. Initially, this approach entailed introducing the pyrolysate directly into the mass spectrometer (e.g. Studier et al., 1972). Subsequently, to achieve higher resolution, the pyrolysis products were separated with gas chromatography (GC) prior to analysis by mass spectrometry (e.g. Levy et al., 1973).

Recently, the meteoritic macromolecular material has been fragmented using hydrous pyrolysis where the sample remains in contact with water for the duration of the experiment (Sephton et al., 1999). In the case of terrestrial macromolecular materials (kerogens), hydrous pyrolysis converts more than 55% of the macromolecular phase to solvent-soluble products that are amenable to further analysis by GC-based systems (e.g. Lewan, 1997). A comprehensive review of the information gleaned from the pyrolysis of meteoritic macromolecular materials is presented in Sephton (2002).

Most recently, hydrolysis has been applied to the study of meteorites (Sephton et al., 2004). Hydrolysis refers to open-system pyrolysis assisted by high hydrogen gas pressures (>10 MPa). When applied to terrestrial kerogens, fixed-bed hydrolysis in the presence of a dispersed sulphided molybdenum catalyst commonly converts more than 85% of the macromolecule to solvent-soluble hydrocarbons (e.g. Roberts et al.,

1995). A continually replenished supply of high-speed hydrogen ensures that product rearrangements are minimal, thereby suppressing the recombination of pyrolysis products into a solvent-insoluble char and avoiding alteration of the organic structures and stereochemistries (e.g. Love et al., 1995). Indeed for petroleum source rocks and coals, char yields are less than 20%; for coals the char is dominated by intractable intertinite macerals (Snape et al., 1994; Roberts et al., 1995). In this paper, we describe in detail the highly efficient hydrolysis method and the information it reveals about the constitution of meteoritic macromolecular materials.

2. Experimental

2.1. Hydrolysis

Crushed whole meteorite was prepared for hydrolysis treatment by performing solvent-extraction (ultrasonication with a solvent mixture of 93:7 dichloromethane(DCM)/methanol followed by removal of the supernatant, $\times 3$), a process which removes any free organic matter (Sephton et al., 1998, 2000). Subsequently, the sample was impregnated with an aqueous solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$ to give a nominal loading of molybdenum of 2 wt%. $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ reductively decomposes in situ under hydrolysis conditions above 250 °C to form a catalytically active sulphided molybdenum phase. Hydrolysis runs were performed in an open-system, temperature-programmed reactor configuration, which has been described in detail previously (Love et al., 1995) (Fig. 1). In this investigation, catalyst-loaded samples (50–300 mg of solvent-extracted sample) were initially heated in a stainless-steel (316 grade) reactor tube from ambient temperature to 220 °C at 300 °C min⁻¹, then to 520 °C at 8 °C min⁻¹, using a hydrogen pressure of 15 MPa. A constant hydrogen sweep gas flow of 6 dm³ min⁻¹, measured at ambient temperature and pressure, through the reactor bed ensured that the residence times of volatiles generated from pyrolysis was extremely short, of the order of a few seconds.

The hydrolysis products (the hydrolysisate) were collected in a trap cooled with dry ice and recovered in DCM. In an attempt to retain volatile products more efficiently, a second analysis was performed using silica as a trap adsorbent and liquid nitrogen as a coolant. This procedure has been shown to improve the recovery of volatile molecules such as benzene and heptane from 0% to over 40%, while molecules with higher molecular masses than decane are almost completely retained (Meredith et al., 2004). The silica trap was washed ($\times 3$) with DCM and the extracts

Download English Version:

<https://daneshyari.com/en/article/10705444>

Download Persian Version:

<https://daneshyari.com/article/10705444>

[Daneshyari.com](https://daneshyari.com)