

GEOCHEMISTRY

Hydrocarbons and Acids of Hekla Volcanic Ash

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INTRODUCTION

Organic matter found on the surface of the earth is probably derived from once living organisms. Fatty acids and hydrocarbons occur in nature (HILDITCH and WILLIAMS, 1964) and have been identified in both recent and ancient sediments (ABELSON and PARKER, 1962; BLUMER and COOPER, 1967; COOPER, 1962). Hydrocarbons are minor but ubiquitous components of all organisms, occur extensively in older sediments, and are among the most stable organic molecules (JOHNS *et al.*, 1966 and MEINSCHEN, 1969). Freshly fallen ash taken from the erupting volcano, Hekla, southwest Iceland was examined to determine if organic matter was present. A chemical scheme designed for extraction and separation of both hydrocarbons and fatty acids was used.

EXPERIMENTAL

On June 16, 1970, 350 grams of hot, two-inch diameter pieces of volcanic ash were collected in sterile Mason jars which constituted Sample I. On June 28, 1970 ash was collected, wrapped in aluminium foil and sealed in a polyethylene bag constituting Sample II. A volcanic bomb was found, the interior of which constituted Sample III (HAUG, 1971). Carbon analysis of Hekla fine tephra and a bomb interior were reported as 144 and 72 ppm respectively (MOORE, 1971). Previously reported, a sample from Syrtlingur containing 50–100 ppm total organic carbon showed no detectable aliphatic hydrocarbons (PONNAMPERUMA *et al.*, 1967). However, aspartic acid, alanine as well as traces of glycine and serine were observed.

To ensure the removal of contamination from the outer surfaces, the samples were boiled in methanol prior to crushing. The methanol was taken to dryness and treated as a lipid extract in order to determine what hydrocarbons and fatty acids were present as surface contamination. The samples were crushed in a jaw crusher and passed through a laboratory hammer mill for finer grinding. Precautions were taken at this point to reduce possibilities for contamination by thoroughly cleaning the crushing tools before and after each sample was crushed. Sample I was extracted for eight days in a Soxhlet thimble with 500 ml of chloroform. Samples II and III were extracted with 500 ml of chloroform for one hour using ultrasonic vibrations. Each sample was thereafter treated by identical methods. The samples were filtered after extraction and the chloroform extract taken to dryness on a rotary evaporator. The lipid residue was weighed and then saponified using 0.05 N potassium hydroxide in methanol for two hours with gentle refluxing. The nonsaponifiable fraction containing the hydrocarbons was separated from the saponifiable fatty acid fraction by multiple extraction of the alkaline solution with benzene. The saponifiable alkaline fraction was then acidified with hydrochloric acid to pH 3 and extracted with benzene to remove the fatty acids from solution. The saponifiable and nonsaponifiable fractions were taken to dryness and weighed. The nonsaponifiable fraction was taken up in one ml of hexane, placed on a chromatographic column packed with prewashed silica gel and silicic acid (1:1, v/v) (Woelm, Activity I). The aliphatic hydrocarbons were eluted with 100 ml of hexane. The hexane fraction was dried on a rotary evaporator. This hydrocarbon fraction was weighed

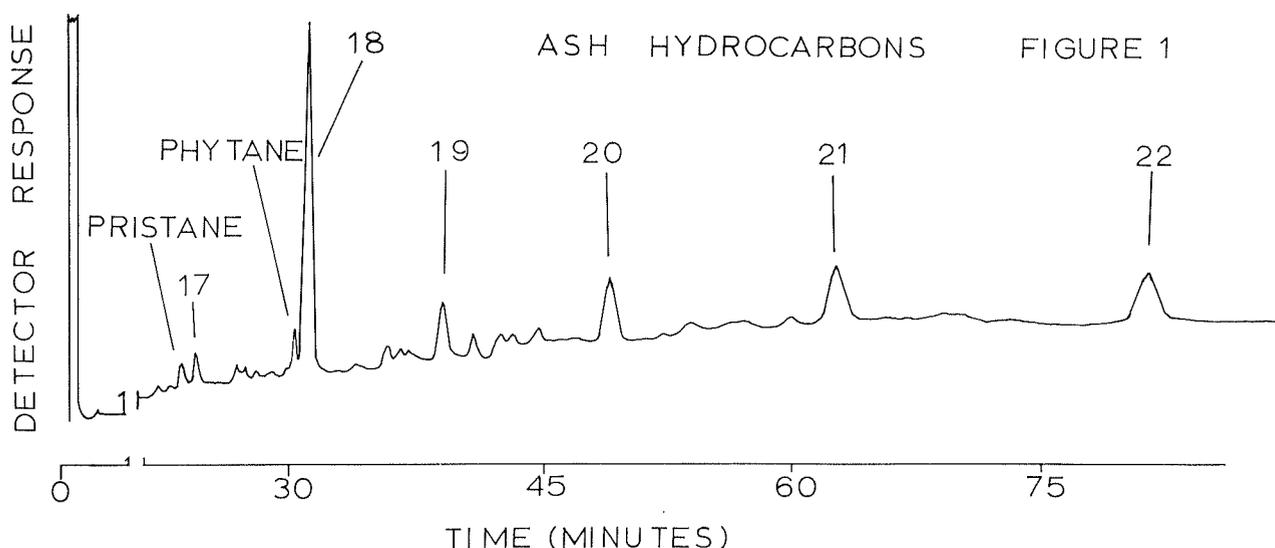


Fig. 1. Gas chromatogram of alkanes from ash. Stainless steel capillary column (150 feet \times 0.02 inches i.d.) coated with Apiezon L. Barber Coleman (Series 5000) gas chromatograph with helium flow of six ml/min using split. Temperature programmed from 150°C to 230°C at 3°C/min.

and used for identification by means of gas-liquid chromatography. The fatty acid fraction was taken to dryness and methylated using BF_3 -MeOH reagent. The fatty acid methyl ester fraction was weighed and used for identification by means of gas-liquid chromatography.

All solvents used in the chemical analyses were reagent grade and were distilled before use. Distilled water was used throughout the isolation process. As a check on contamination of samples, all solvents were treated as samples and were run through the isolation schemes for separation of hydrocarbons and fatty acids. Using the same sensitivity on the GLC at which the samples were run, the only contaminants detected were low molecular weight hydrocarbons which did not interfere with those isolated from the samples. A blank was run on the Soxhlet thimble. Detectable amounts of hydrocarbons including pristane and phytane were observed. This accounts for a large portion of the hydrocarbons identified in Sample I.

RESULTS

Normal, saturated hydrocarbons ranging from C_{16} to C_{23} having a bimodal distribution with maximums at C_{18} and C_{22} (Figure 1) were detected in each sample of ash examined. Living organisms, particularly non-marine, exhibit an odd-carbon number predominance in their hydrocarbon constituents; however, there was no odd/even predominance in the hydrocarbons in the ash. Isoprenoids, pristane and phytane were detected. Usually the presence of these hydrocarbons is cited as evidence of biological activity.

The hydrocarbon distribution of all three samples and the MeOH wash was qualitatively the same. Sample I, however, contained a much higher percentage of octadecane than did the other two samples. This was not observed in the thimble extractions. Sample III contained an anomalous peak in the C_{26} region believed to be an ester since this fraction was not saponifiable. It is interesting to note that the hydrocarbon fraction of the Diablo meteorite analyzed by Ponnampertuma also contained a prominent saturated C_{18} hydrocarbon (PONNAMPERTUMA, 1971).

The fatty acids extracted from each ash sample ranged from $\text{C}_{12:0}$ to $\text{C}_{16:0}$; $\text{C}_{18:1}$ represented 40 percent of the fatty acid fraction. Again, all samples were qualitatively the same (Figure 2). The total fatty acid fractions in Samples II and III represented less than two ppm.

One would not expect to find organic remnants in fresh volcanic ashes since the high temperatures would have destroyed any organic matter which might have been present. Since both hydrocarbon and fatty acids in all samples were just above contamination level, it cannot be said with certainty that these organic components were indigenous to the ash. The porous ash provides large surface areas for absorption of organic material from air, a possible source of contamination. This hypothesis is supported by the fact that both the acids and the hydrocarbons of each sample was qualitatively similar to the MeOH wash acids and hydrocarbons. As would be expected the hydrocarbons and acids are present in concentrations of less than two ppm.

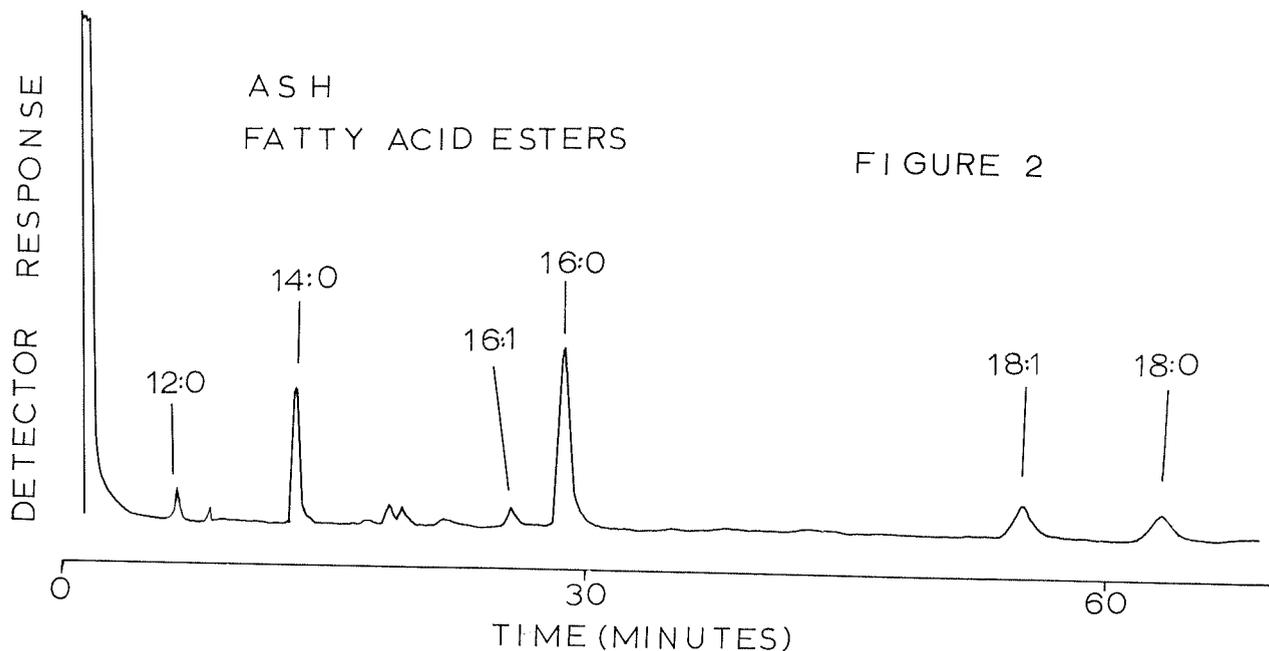


FIGURE 2

Fig. 2. Gas chromatogram of fatty acid methyl esters from ash. Copper column (8 feet \times $\frac{1}{8}$ inches o.d.) packed with 5% FFAP on Varaport 30. Barber Coleman (Series 5000) gas chromatograph with helium flow of 35 ml/min. Temperature programmed from 150°C to 225°C at 3°C/min.

TABLE I
ASH HYDROCARBON ANALYSES
SAMPLE I

Hydrocarbon	Percent Composition
n-16	trace
pristane	1.8
n-17	2.3
phytane	2.1
n-18	26.9
n-19	6.9
n-20	10.2
n-21	10.9
n-22	13.4
n-23	12.8
others	12.8

TABLE II
ASH SAMPLE I
FATTY ACID ANALYSES

Fatty Acid Methyl Ester	Percent Composition
12:0	trace
14:0	18.8
16:1	6.4
16:0	40.2
18:1	16.9
18:0	15.0
others	2.7

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