crepancies reflected a significant deviation in the actual pH changes from theory because of consumption of acid by corrosion of the walls of the relatively new equipment. During the course of several months of operation the equipment passivated sufficiently that corrosion became minimal, and excellent agreement between theory and experiment was finally obtained. The small residual differences at the end of the test period probably continue to reflect small losses of acid through corrosion, some shunting of the membrane path, and some variation in the junction potential of the reference electrode with the solution in the autoclave.

An additional aspect of the membrane electrode that was examined was its stability in the presence of changes in the oxidation-reduction potential of the environment. This is one of the very real theoretical advantages of a membrane type pH sensor over sensors whose response is based on electron transfer reactions. The effect is illustrated in Fig. 3. (Also included in Fig. 3 is the potential of the autoclave wall which was monitored against the reference electrode.) It is seen that, after changing from an air to a nitrogen purge of the incoming 0.0005m H_2SO_4, a slow downward drift in potential is evident for the platinum electrode and the wall of the autoclave. This is associated with simple dilution of the oxygen concentration in the water within the autoclave. After several hours a more rapid drop in both these potentials occurred. This is attributed to loss of the passive film on the autoclave with an associated increase in corrosion rate to liberate hydrogen. The platinum electrode then clearly shows its sensitivity to this change in the oxidation-reduction environment. The zirconia membrane electrode, however, retained an essentially constant potential throughout the transients; that is, it is insensitive to changes in the oxidation-reduction potential of the environment, as expected from theory. The small transient in potential at the time of the depassivation is believed to be a response to a real change in pH.

This work demonstrates that it is possible to use an oxygen ion–conducting ceramic in a membrane type pH sensor. I believe that the structure can be developed into a device for reliable, practical measurements of pH at high temperatures and pressures.

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Phenolic Ethers in the Organic Polymer of the Murchison Meteorite

Abstract. *Seven phenolic acids and many nonphenolic organic acids, including large amounts of meta-hydroxy (3-hydroxy) benzoic acid and 3-hydroxy-1,5-benzenedicarboxylic acid, were obtained from the organic polymer of the Murchison C2 chondrite upon oxidation with alkaline cupric oxide. The phenolic acids apparently were derived from phenolic ethers in the polymer, which in turn probably were formed from carbon monoxide and hydrogen by catalytic Fischer-Tropsch type reactions in the solar nebula. In contrast, terrestrial polymers such as lignin, humic acid, and coal yield mainly para-hydroxy (4-hydroxy) benzene derivatives by the same oxidation procedure.*

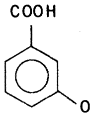
Most of the organic matter in carbonaceous meteorites (70 to 95 percent) is present as an ill-defined, insoluble macromolecular material, usually referred to as organic polymer (*1–4*). In some respects it resembles polymeric terrestrial organic matter, such as soil humic acid and coal, but its structural units have been only partially characterized (*2–4*). Recently, we have identified 15 aromatic ring systems as the corresponding carboxylic acids, upon oxidation of the Murchison polymer by aqueous $Na_2Cr_2O_7$ (*4*). This oxidation preferentially attacks aliphatic and alicyclic methylene linkages with minimum degradation of most aromatic ring systems except phenols and some heterocyclics (*5*). We now report a similar study in which we used alkaline CuO. It is a mild oxidant specific for cleaving ether linkages without destruction of phenolic rings but is not very effective for oxidizing methylene chains (*6–8*).

To remove soluble organic compounds and possible terrestrial contaminants, 36 g of finely powdered Murchison meteorite (*9*) was extracted successively with 5N HCl (refluxed for 24 hours), 0.5N NaOH (room temperature for 24 hours), and benezene-methanol (3:1, refluxed for 24 hours) before oxidation. The resulting residue (48.6 percent of the original sample weight) contains 4.1 percent carbon (*10*). An 11.5-g sample of the residue was oxidized with alkaline CuO (10.5 g of $CuSO_4 \cdot 5H_2O$, 8 g of NaOH, and 40 ml of water) at 200°C for 8 hours by the method described in (*6*). After separation of the insoluble residue, the alkaline solution was acidified with HCl, concentrated, and extracted repeatedly with benzene-ether (1:3) and finally with methanol. An alkali-soluble, solvent-insoluble fraction was recovered from the aqueous phase. The methanol extract (196 mg) and the alkali-soluble fraction (183 mg) were found by gel permeation chromatography and solid-probe mass spectrometry (*11*) to consist essentially of humic acid-like material (*12*). The benzene-ether extract (organic acids, 82 mg) was derivatized with d_6-dimethyl sulfate to yield d_3-methyl-labeled derivatives, which were analyzed by gas chromatography–mass spectrometry (GC-MS), solid-probe MS, and high-resolution MS (*13*). The results are shown in Fig. 1 and Table 1.

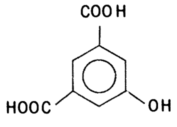
Of particular interest is the high abundance of m-hydroxybenzoic acid (**I**) and 3-hydroxy-1,5-benzenedicarboxylic acid

(**II**), (peaks A and F in Fig. 1). Both meta acids are far more abundant than their isomers. Peak A far exceeds its ortho and para isomers (peaks B and C; ratio 91/2/7), and peak F similarly dominates over its five unresolved possible isomers in peak G (ratio 87/13).

Terrestrial polymers, such as lignins (*7*), soil humic acids (*8, 14*), land-derived marine sediments (*15*), and coals (*6*), yield quite different distribution patterns upon oxidation with alkaline CuO. In general, *p*-hydroxybenzene (**III**), vanillic (**IV**) and syringic (**V**) groups, 4-hydroxy-1,2-benzenedicarboxylic acid (**VI**) and 4-hydroxy-1,3-benzenedicarboxylic acid (**VII**) are the major products,



I



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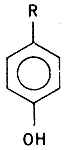

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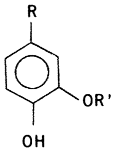

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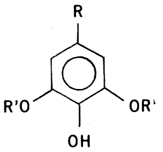

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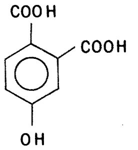

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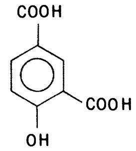
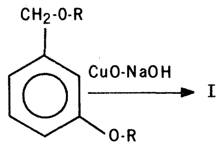


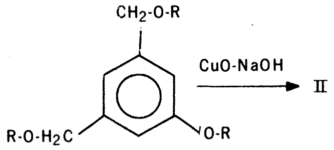
VII

where R = COOH, CHO, or $COCH_3$ and R′ = H or CH_3. Structures **IV** and **V** were not found among the oxidation products of the meteoritic polymer, a further strong indication that it is quite different in structure from lignin-like polymers of terrestrial origin. All phenolic acids identified in this study were detected as -OCD_3 derivatives in the mass spectra, and so -OCH_3 groups should have been readily observable. Although partial demethylation may have occurred during the oxidation with alkaline CuO as suggested by our control experiments (*6*), aryl methoxy groups are generally much more stable under the oxidation than any other ether groups. Therefore, the complete lack of -OCH_3 groups suggests that the meteoritic polymer has few if any aryl methoxy groups.

It is very likely that the phenolic acids identified were derived from the cleavage of ether linkages between aromatic units of the organic polymer, as shown in the examples



VIII



IX

where R = H, aryl, or aryl alkyl. The nonphenolic aromatic acids, on the other hand, may be derived from the cleavage of aryl alkyl ethers having no nuclear hydroxy group or its derivatives, or from the cleavage of C–C bonds of aliphatic and alicyclic linkages between aromatic systems, or both. However, the second case is less probable, because alkaline CuO does not effectively attack C–C bonds.

The production of phenolic acids by oxidation with alkaline CuO suggests that phenolic ethers are present in the Murchison polymer. Indeed, in 1963 Kaplan *et al.* (*16*) found several phenolic acids in $5N$ HCl extracts of meteorites, among which structure **I** was the most abundant. The predominance of the meta isomer suggests that it was indigenous to the meteorites. Since ether linkages are not cleaved under the conditions that Kaplan *et al.* used, the phenolic acids extracted with $5N$ HCl may be bonded to the meteoritic polymer by other linkages such as esters that are more readily hydrolyzed.

We have suggested (*17*) that all organic compounds in meteorites were synthesized in the solar nebula by Fischer-Tropsch type (FT) reactions of CO, H_2, and NH_3, catalyzed by clay and magnetite grains. Presumably, the observed distribution of phenolic compounds may have been produced by the same reaction, because such compounds, often with a strong predominance of certain isomers, are known to be produced in the industrial FT synthesis (*18*) along with other oxygenated species. Alkyl phenols, in particular, occur in pyrolyzates from FT reactions as well as Murchison polymers (*4, 17*).

Indeed, phenyl and benzyl ethers (ϕ-O-ϕ, ϕ-O-ϕ-CH_3, CH_3-ϕ-O-ϕ-CH_3, ϕ-CH_2-O-CH_2-ϕ, where ϕ is the phenyl group) form in the FT reaction, under the conditions suggested for the production of interstellar molecules (*11, 19*). Xylenes also form in large amounts, and the meta isomer dominates: *m*/*p*/*o* = 62/17/21 (*17*).

Phenolic acids were not seen in these syntheses. However, they were initially absent in the Murchison meteorite as well and formed only by oxidative degradation of ethers. Such ethers are produced in the FT synthesis.

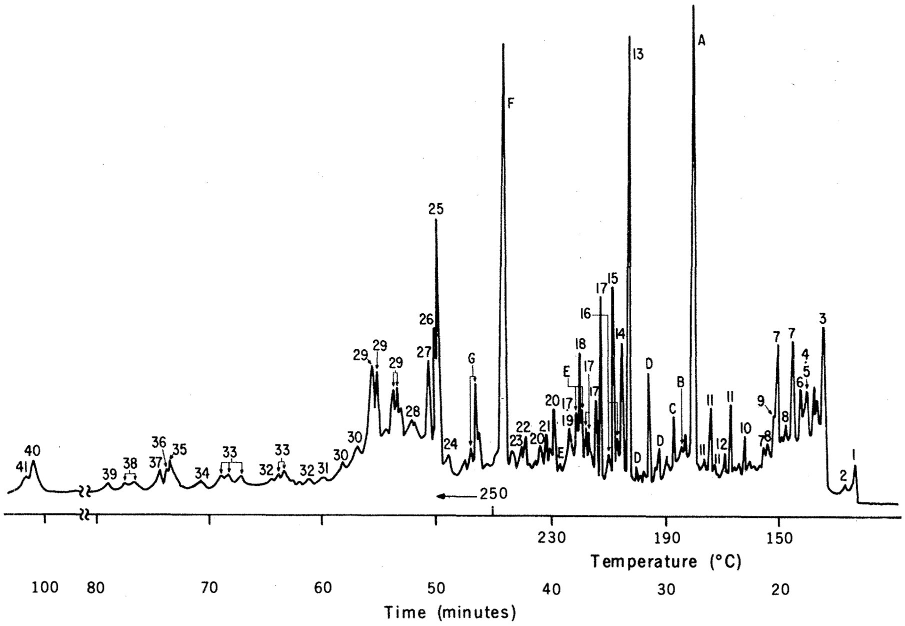


Fig. 1. Gas chromatogram of organic acids (as their d_3-methyl esters) produced by oxidation of the Murchison polymer with alkaline CuO. Peaks A and F are larger than peaks B, C, and G (their respective isomers). The analysis was carried out on a gas chromatograph (Perkin-Elmer 3920B) interfaced to a modified time-of-flight mass spectrometer (Bendix model 12) with a variable split between a flame-ionization detector and the source of the mass spectrometer. The separation was made on a glass SCOT column (45.9 m by 0.51 mm) coated with OV 17 and temperature-programmed from 70° to 250°C at 4°C per minute.

Table 1. Organic acids identified as their d_3-methyl esters by GC-MS and high-resolution MS. The percentages (by weight) of the identified organic acid groups are as follows: phenolic acids, 32.3; benzenecarboxylic acids, 47.1; biphenylcarboxylic acid, 3.5; naphthalenecarboxylic acids, 3.1; thiophenecarboxylic acids, 5.8; pyridinecarboxylic acids, 1.2; dibenzofurancarboxylic acids, 0.3; aliphatic dibasic acids, 2.4; and others, 4.3. We determined the distribution of organic acids as d_3-methyl esters by measuring the areas of GC peaks with a correction for the effective carbon number for each compound. The GC retention times and mass spectra of the phenolic and other acid esters were confirmed with authentic samples.

GC peak	Compound	GC peak	Compound
A	*m*-Hydroxybenzoic acid	17	Methylbenzenedicarboxylic acid
B	*o*-Hydroxybenzoic acid	18	Dimethylbenzenedicarboxylic acid
C	*p*-Hydroxybenzoic acid	19	Methylthiophenedicarboxylic acid
D	Methylhydroxybenzoic acid	20	Dimethylbenzenedicarboxylic acid
E	Dihydroxybenzoic acid*	21	Pyridinedicarboxylic acid
F	3-Hydroxy-1,5-benzenedicarboxylic acid	22	1-Naphthoic acid
		23	2-Naphthoic acid
G	Hydroxybenzenedicarboxylic acid*	24	Thiophenetricarboxylic acid
1	Succinic acid	25	1,2,4-Benzenetricarboxylic acid
2	Methylsuccinic acid	26	1,2,3-Benzenetricarboxylic acid
3	Benzoic acid	27	1,3,5-Benzenetricarboxylic acid
4	Glutaric acid	28	Methylthiophenetricarboxylic acid
5	Pyridinemonocarboxylic acid	29	Methylbenzenetricarboxylic acid
6	Thiophenemonocarboxylic acid	30	Methylbiphenylmonocarboxylic acid
7	Methylbenzoic acid	31	Dibenzofuranmonocarboxylic acid
8	Methylthiophenemonocarboxylic acid	32	Dimethylbenzenetricarboxylic acid
9	Adipic acid	33	Naphthalenedicarboxylic acid
10	Methyladipic acid	34	Biphenyldicarboxylic acid
11	Dimethylbenzoic acid	35	1,2,4,5-Benzenetetracarboxylic acid
12	Dimethylthiophenemonocarboxylic acid	36	1,2,3,4-Benzenetetracarboxylic acid
		37	1,2,3,5-Benzenetetracarboxylic acid
13	1,2-Benzenedicarboxylic acid	38	Methylnaphthalenedicarboxylic acid
14	1,4-Benzenedicarboxylic acid	39	Methylbenzenetetracarboxylic acid
15	1,3-Benzenedicarboxylic acid	40	Benzenepentacarboxylic acid
16	Thiophenedicarboxylic acid	41	Methylbenzenepentacarboxylic acid

*Mass spectra showed the ortho effect, which means they cannot be due to *p*-hydroxy compounds such as structures **III** through **VI**.

In any comparison, we must keep in mind the possibility that the primary distribution in the solar nebula was further modified by secondary processes, such as isomerization on catalytically active mineral grains. Natural clay minerals, silicates, and alumina act as acid catalysts (Lewis or Brønsted, or both) in isomerization, cracking, dehydration, and polymerization (*20*). For example, in the presence of such acidic catalysts at 105° to 134°C, cresols and xylenols rearrange mainly to *m*-cresol and 3,5-dimethylphenol (*21*), the thermodynamically favored isomers. (At 400°K, the equilibrium *m*/*p*/*o* ratio of isomeric cresols is 71/3/26.) The observed predominance of *m*-xylene in meteorites (*3, 22*) may reflect such rearrangement of an initial distribution rich in the ortho isomer [as expected for iron catalysts (*23*)], but it may also be a primary feature if the catalyst was clay (*11, 17*).

Phenols are not known to have been produced by the structurally nonselective Miller-Urey (free-radical) reaction (*17, 24, 25*), a mechanism originally proposed for the primitive earth that has been extended by some investigators to the solar nebula. Therefore, it is not likely that this reaction could produce the phenolic polymers that we have characterized in the meteoritic polymer. Further work, over a wider range of conditions, may show whether a precise match between the observed distribution and the primary FT distribution can be achieved or whether secondary reactions must be invoked.

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10. To avoid possible structural changes of the meteoritic polymer, the residue was not further treated with HF to remove silicates. However, for elemental analysis of the polymer, a portion of the residue was demineralized by repeated treatments with HCl-HF. The resulting sample gave the following composition (in percentages) on a dry, ash-free basis: C, 76.48; H, 4.46; N, 2.41; S, 4.28; and O, 12.37 (by difference). If all carbon (4.1 percent) in the residue is due to organic polymer and if the polymer is 76.8 percent carbon, then the concentration of polymer in the residue is about 53 mg/g.
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