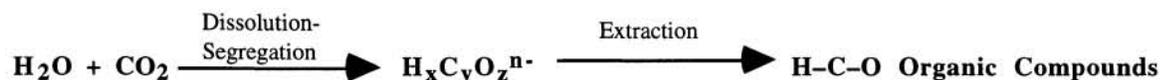


ORGANIC MATTER FROM H₂O AND CO₂ DISSOLVED IN MINERALS

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Complex organic compounds must have been available on the early Earth. However, where they came from or how they formed has remained a subject of intense discussion¹. Our work looks at the solid Earth as a possible source. We have succeeded in extracting organic molecules from inside MgO and olivine in quantities sufficient to obtain not only IR, ¹H- and ¹³C-NMR spectra but also to purify at least one of the compounds and to grow single crystals for x-ray structure determination. The MgO crystals used in these experiments had crystallized at 2860°C from a melt equilibrated with CO/CO₂/H₂O at 1 bar in a carbon arc furnace. The olivine crystals originated from the high pressure environment of the upper mantle. Thermodynamics requires that, as a melt saturates with reactive gases such as CO, CO₂ or H₂O, the crystals growing from such a melt dissolve some of these gases². During cooling, the dissolved gases undergo a redox conversion by which solute CO₂ reduces to C, and solute H₂O reduces to H₂, counterbalanced by an aliquot of O²⁻ oxidizing³ to O⁻. As the solubility decreases with decreasing temperature, C and H₂ segregate, concentrating along dislocation lines, subgrain boundaries etc.⁴ As a result, H_xC_yO_zⁿ⁻ precipitates form as predicted earlier⁵, stereochemically constrained by the surrounding lattice. When the crystals are crushed and extracted with organic solvents, the H_xC_yO_zⁿ⁻ precipitates are recouped as H-C-O molecules:



The MgO crystals were about 5-40 mm, optically clear or whitish, grown in a carbon arc fusion melt from technical purity grade MgO powder. The upper mantle olivine crystals, approximately (Mg_{0.9}Fe_{0.1})₂SiO₄, were 5-20 mm, gem-quality transparent or slightly turbid, from the San Carlos, AZ, volcanic field. Prior to crushing, 50-100 g crystals were cleaned by Soxhlet refluxing for several hours in chloroform. They were then coarsely crushed in a clean porcelain mortar and pestle, previously heated to 450°C, and Soxhlet extracted for 12-24 hrs in 100 ml solvents of increasing polarity: (i) chloroform, (ii) acetone, (iii) tetrahydrofuran (THF). Procedural controls were performed on the empty Soxhlet thimble and with crushed glass. The extracts were concentrated, yielding liquid or solid organic residues of the order of 10–20 mg. The residues were analyzed by thin-layer-chromatography (TLC), infrared (IR), nuclear magnetic resonance (¹H- and ¹³C-NMR), and gas chromatography–mass spectroscopy (GC-MS).

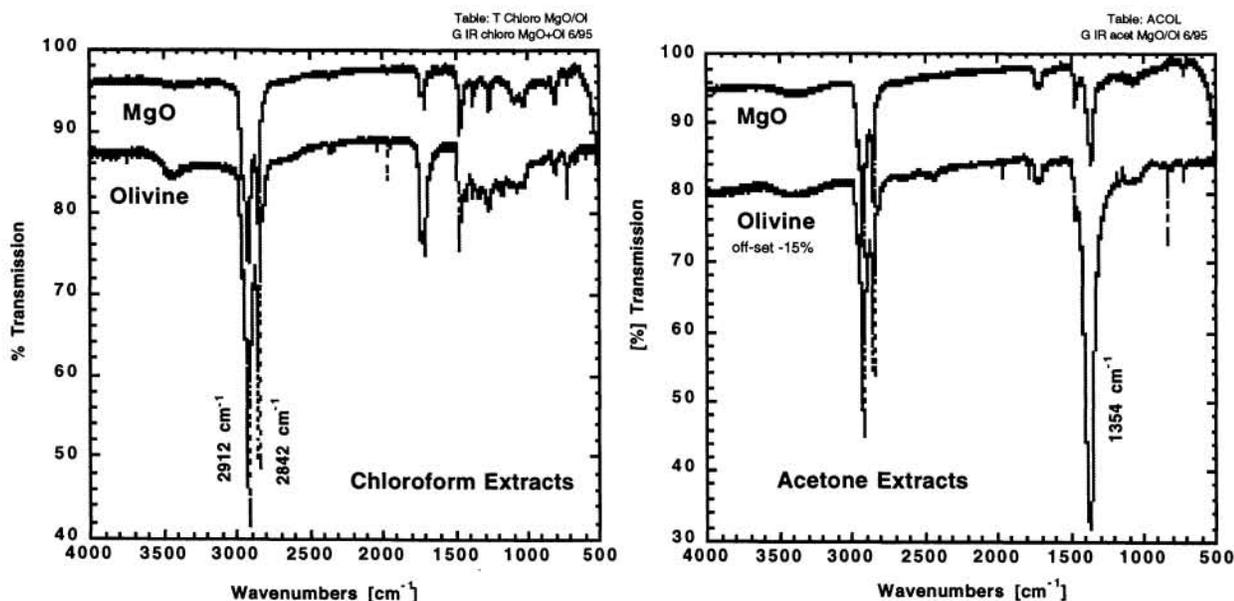


Fig. 1: IR spectra: MgO and olivine chloroform extracts. Fig. 2: IR spectra: MgO and olivine acetone extracts.

Figures 1 and 2 show IR spectra of the chloroform and acetone extract residues from olivine and MgO. The IR samples were prepared by drying a few drops of the extract on a KBr window. The spectra exhibit strong absorption bands near 2912 and 2842 cm^{-1} , indicative of C-H stretching. The acetone extracts give a strong band at 1354 cm^{-1} .

$^1\text{H-NMR}$ spectra of the chloroform extract indicate aliphatic $-\text{CH}_3$ and $-\text{CH}_2-$ groups. Hypersplitting at 4-5 ppm suggests a heteroatom or olefinic protons. No signal was observed in the aromatic region. The acetone extract indicates $-\text{CH}_3$ and $-\text{CH}_2-$ groups as singlets. The absence of coupling means that these groups are either separated by a heteroatom or a C atom carrying no protons. This suggests the presence of an oxygen-heterocyclic compound. GC-MS analyses were performed on the chloroform extract of olivine, with a Hewlett Packard 5971. The GC elution peak at 8.14 min yields an MS with 14 amu increments, characteristic of an aliphatic hydrocarbon chain. A fragment at 43 amu along with 14 amu increments indicates a series of alkyl ions $(\text{C}_n\text{H}_{2n+1})^+$. The 73 and 87 amu fragments suggest oxygen. A fragments at 41 amu, with 14 amu increments, and at 153 amu indicate a $\text{CH}_2=\text{CH}$ -terminated C-11 alkyl chain. The GC elution peak at 12.33 min shows a base peak at 71 amu, suggesting a fragment $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2^+$. These findings are supported by $^1\text{H-NMR}$ spectra showing a strong $-\text{CH}_2-$ singlet at 1.25 ppm with a less intense $-\text{CH}_3$ singlet, and by IR spectra showing C-H stretching bands at 2912 and 2842 cm^{-1} .

Figure 3 shows IR spectra of the residues of THF extracts from MgO and olivine. The band at 1723 cm^{-1} is indicative of a carbonyl group, and the broad band between $3000\text{--}3600\text{ cm}^{-1}$ indicative of a carboxylic acid group. THF extracts give a complex $^1\text{H-NMR}$ spectrum, indicating also the presence of aliphatic $-\text{CH}_3$ and $-\text{CH}_2-$ groups. The THF MgO extract was purified by extraction with immiscible solvents. A pure compound (melting point $192\text{--}194^\circ\text{C}$) was obtained which, according to ESCA data, contains only C and O. By allowing the solvent to slowly evaporate, crystals of this as yet unidentified organic compound grew up to 2 mm in size as shown in **Figure 4**.

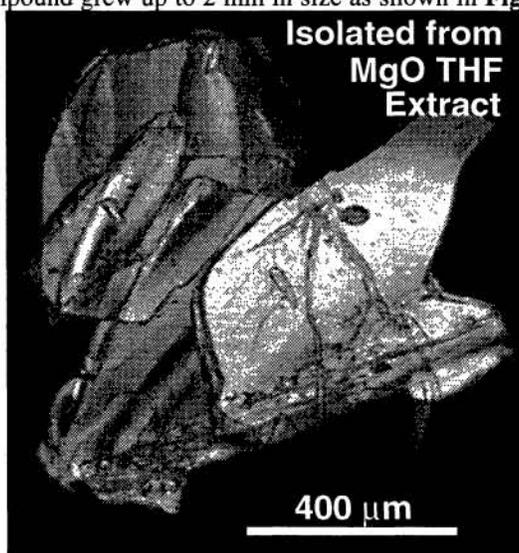
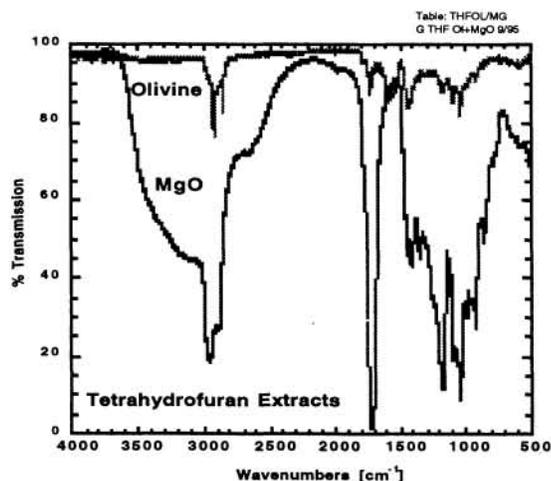


Fig. 3: IR spectra of raw THF extracts. **Fig. 4:** →

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