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Organic Analysis of Peridotite Rocks from the MAR

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Introduction

Synthesis of organic compounds inside the peridotite rock

At the bottom of the terrestrial oceans, where tectonic forces separate the lithospheric plates along mid-ocean ridges, the ultramafic rocks of the upper-mantle, the peridotites, are exposed to circulating seawater.

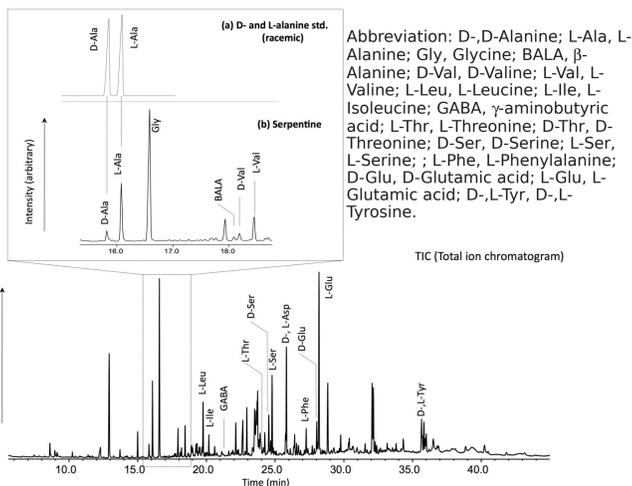
The hydrolysis of their constituents, olivine and pyroxenes minerals, into serpentine, occurs at different degrees of serpentinization with a release of H₂ depending on the characteristics of the medium such as temperature and rock composition.

It is known that H₂ with CO/CO₂ forms organic compounds and numerous calculations and experiments in the gas and liquid phases have been performed starting with simple inorganic molecules: H₂, H₂O, CH₄, NH₃, N₂, CO, CO₂.

The novelty of the hypothesis described since may 2008 [1-3] is that the organic compounds including precursors of nitrogen chiral compounds could be formed inside the rock, considering the H₂ released during the hydrolysis of the solid mineral olivine, the circulating seawater, the CO₂ embedded inside the rock, the nitrogen found in the environment and the geometrical structures of the olivine and serpentine minerals.

This synthesis could happen only where tectonic plates separate to leave the peridotite rock in contact with water.

fig. 1. GC/MS chromatogram of D- and L- amino acids extracted from the Ashadze peridotite rock



Experimental method for the analysis of the peridotite rocks

The samples have been collected during the french-russian **Ifremer Serpentine cruise in march 2007** and kindly given for analysis by Adélie Delacour and Mathide Cannat from the Institut de Physique du Globe de Paris

The analyses have been carried out in the Institute of Biogeosciences of the Japan Agency for Marine-Earth Science and Technology in Yokosuka. They are fully described in ref [8].

0.5g of sample was acid hydrolyzed with 6M HCl at 110°C during 12h.

Non-polar fraction was extracted by liquid/liquid separation in HCl solution and a hexane/dichloromethane mixture. The hexane/dichloromethane fraction was recovered.

The polar fraction, the amino acid fraction, was isolated from the hydrolysis residue with cation-exchange column chromatography. An esterification was performed with thionyl chloride/(S)-(+)-2-butanol mixture and an acylation was then performed with pivaloyl chloride/dichloromethane mixture. The *N*-pivaloyl-(S)-2-butyl esters (NP/S2Bu) of the amino acid diastereoisomers were extracted with a hexane/dichloromethane mixture and identified with gas chromatography/mass spectrometry techniques. The MS spectrum was scanned over *m/z* of 50-550.

Conclusion

This preliminary analysis of the organic composition of two peridotite rocks dredged on the ocean floor of the Logatchev and Ashadze hydrothermal sites on the Mid-Atlantic Ridge allows the identification of long-chain *n*-alkanes and of amino acids after acid hydrolysis of the rocks. Many peaks of the amino acid gas chromatograms remain unidentified. Signals of abiotically formed organic compounds may be present with negligible intensity compared to the intensities of the identified biotical signals.

Further analyses need to be made with non protein amino acids as references.

We conclude in a biotic origin for the identified amino acids but we do not exclude an abiotic origin for some amino acids which could correspond to the not yet identified peaks. This is supported by the non-confirmation of a biotic or abiotic origin for the *n*-alkanes, since carbon isotopic fractionation is inefficient in distinguishing these sources.

It could be appropriate to analyze samples which are drilled far beneath the ocean floor and which would be less exposed to biological contamination.

The analyses in organic compounds content could be identical to the analyses conducted on the Murchison meteorite. It would be also appropriate to undertake an experimental organic synthesis starting with olivine and N₂/NH₃, as described in ref [1-3].

Mars

It is to be noticed that **olivine, serpentine and carbonate** have also been discovered on Mars, in **Nili Fossae** [11]. This assemblage of minerals seems typical of serpentinized ultramafic rocks found on Earth. The same process of organic molecules synthesis could occur in this region and lead to the precursors of life.

Geological environment on the Earth

The Mid-Atlantic Ridge, MAR, is covered with several hydrothermal sites and presents black smoker activity. Logatchev (14° 45'N-43'N, 2970m) and Ashadze (12° 58'N, 4080m) are active sites, located on an ultramafic geological environment of serpentinized peridotite rocks, while Krasnov (16° 38'N) is inactive and located on a basaltic environment.

Their hydrothermal vent fluids originate from the interaction between the underlying peridotite rocks and seawater. They contain significant amounts of H₂, CH₄, N₂, CO and CO₂ and also saturated hydrocarbons, carboxylic acids and methyl esters which could have been formed during catalytic Fisher-Tropsch Type (FTT) reactions involving hydrothermal CO₂. Catalysts such as Fe-Ni alloy and Fe-Cr oxide have been proposed and laboratory serpentinization of olivine at 300°C and 500 bar have demonstrated the synthesis of hydrocarbons [4].

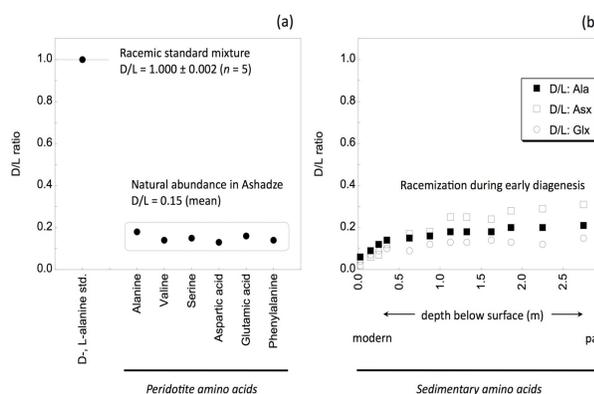
The Murchison meteorite

The mineral structure of Murchison, a CM2 chondrite, is dominated by phyllosilicates composed of minerals such as olivine, pyroxenes, calcium carbonates, iron oxides (magnetite), iron-nickel sulfides... It has been altered by water, heat, pressure shock waves, and short-lived radionuclides.

Aside from any terrestrial contamination, all the classes of organic molecules considered of biological relevance are identified within Murchison including nitrogen nucleobases and also non-terrestrial amino-acids with L- enantiomeric excesses.

Calculations using hydrogen fugacity have shown the interconnection between the mineral alterations and the organic compound synthesis within the Murchison parent body [5].

fig. 2. D/L amino acid ratios in the analysed Ashadze peridotite rock and in sedimentary rocks.



Results and Discussion Chiral amino acids

The chromatogram for the chiral separation of D- and L- amino acids (fig. 1) extracted from the Ashadze peridotite rock shows a wide variety of amino acids:

- **11 protein amino acids:** alanine, glycine, valine, leucine, isoleucine, threonine, serine, aspartic acid, phenylalanine, glutamic acid and tyrosine.
- **2 non-protein amino acids:** beta-alanine (BALA) (3-aminopropanoic acid) gamma-aminobutyric acid (GABA) (4-aminobutanoic acid)

The high intensity peak at 17,9 min could not be identified as a great number of intense peaks.

For the protein amino acids, alanine, valine, serine, aspartic acid, glutamic acid and phenylalanine, large L- enantiomeric excesses can be observed, which is an indication that:

these identified amino acids could originate from sub-seafloor biogenic processes.

Indeed, fig. 2a shows a D/L ratio for these protein amino acids of 0.18, which seems equivalent to the D/L ratio found in sedimentary rocks (fig. 2b).

Chirality

The origin of the L- enantiomeric excess of the nitrogen compounds amino acids, found in terrestrial living cells is not yet known, neither the L- excess found in the Murchison and Orgueil meteorites.

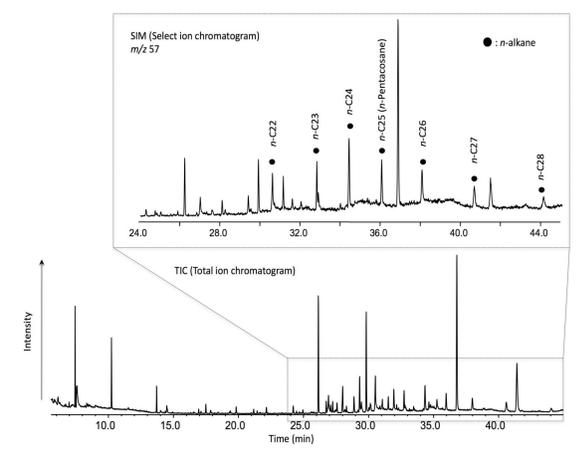
Several origins are proposed for the nitrogen element on early Earth: N₂, NH₃/NH₄⁺, NO₂/NO₃⁻, [6-7]. In the context of hydrothermal conditions, we may notice that NH₃ is synthesized from N₂ and H₂ industrially at ~500°C and ~200 bar with Fe-bearing-catalysts.

Consequently, the nitrogen element can be found in the hydrothermal geological environment and not only hydrocarbons can be formed during the serpentinization process but also nitrogen compounds such as amino acids.

In Murchison as in the terrestrial peridotites, the olivine and serpentine minerals have tetrahedral structures including octahedral sites where ions and consequently small elements, H, C, N, O, can insert. It can be imagined that an asymmetric adsorption on minerals could lead to a stereoselective synthesis of the simplest precursors of amino acids [1-3].

In order to test this hypothesis of organic compounds synthesized inside the rocks, we conducted organic analyses of two serpentinized peridotites rocks dredged on the Logatchev and Ashadze seafloors to determine their content in hydrocarbons and chiral amino acids.

fig.3. Chromatogram of hydrocarbons extracted from the Logatchev peridotite rock



Results and Discussion Hydrocarbons

We also detect a **long-chain n-alkane** compound (< n-C28H58) in the non-polar fraction (fig.3). The chromatogram of these Logatchev *n*-alkanes shows a decrease in intensity with increasing carbon number, which seems to be a characteristic of abiotic synthesis [9].

We did not intend to proceed to the analysis of the carbon-13, carbon-12 isotopic fractionation since experiments conducted at 250°C and 350 bars, have demonstrated that organic compounds synthesized abiotically in FTT reactions are depleted in ¹³C to a degree typically ascribed to biological processes [9].

Recently, an abiogenic hydrocarbon production by Fisher Tropsch type reactions has been proposed at Lost City hydrothermal field, where warm ultramafic rocks are in contact with water [10].

However we do not conclude yet in a biotic or abiotic origin for the identified n-alkanes.

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