



Detection of Molecular Biosignatures inside Rocks



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Introduction

Organic compounds inside or nearby peridotite rocks

At the bottom of 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. They evolve.

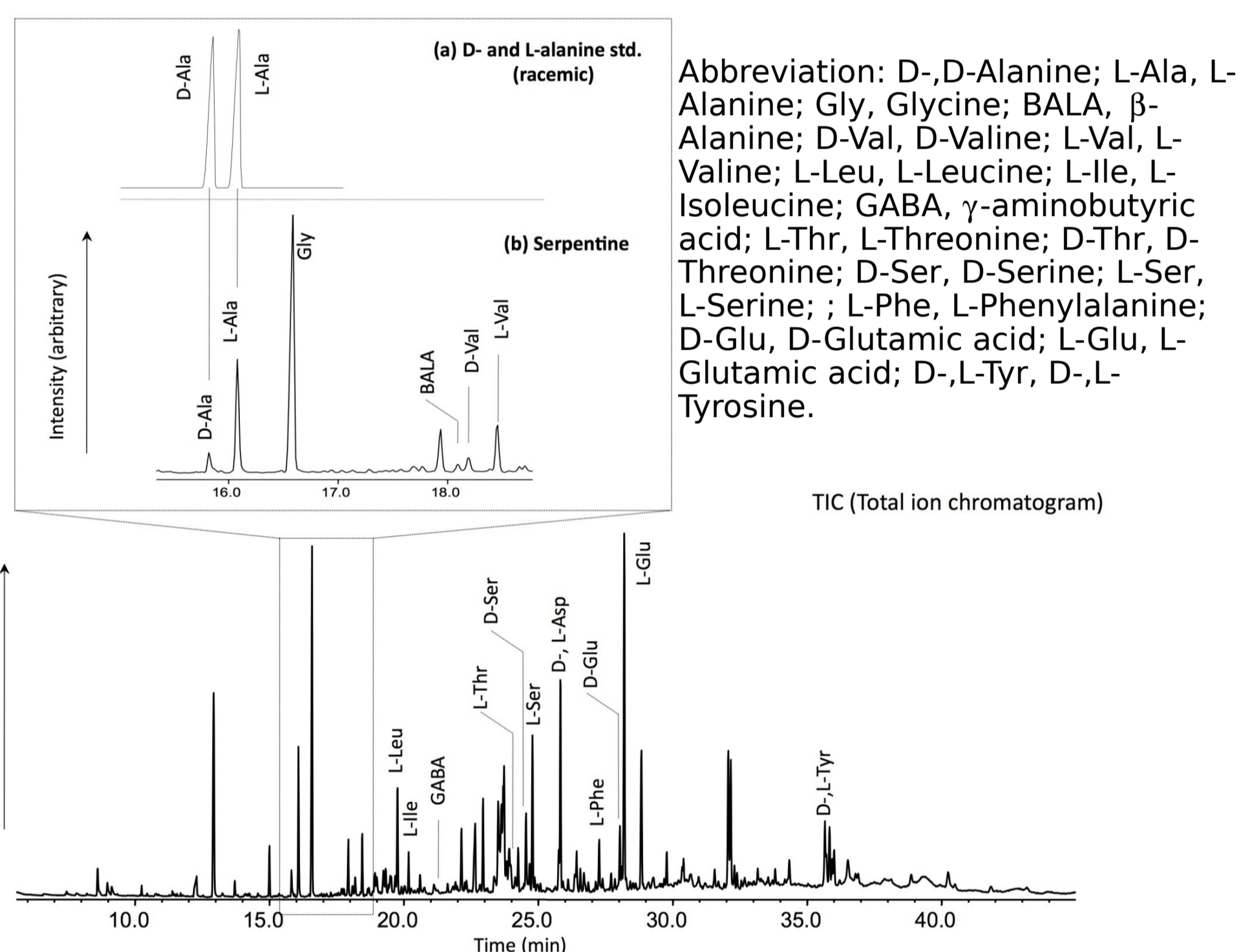
The hydrolysis of their silicate constituents, olivine and pyroxenes minerals, into serpentine, occurs at different degrees of serpentinization with a release of H₂ depending on the characteristics of the medium such as temperature and rock composition.

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, CO₂, CO, CH₄, NH₃, N₂.

The novelty of the hypothesis described since may 2008 [1-4] is that the organic compounds including precursors of nitrogen chiral compounds could be formed inside the rock, or just nearby, considering H₂ released during serpentinization of the peridotite rock, the circulating seawater, the CO₂ embedded inside the rock or dissolved in seawater, and its hydrothermal transformation into CO, the nitrogen of the environment and the geometrical structures of the minerals.

This synthesis could happen only where peridotite rocks are in contact with water.

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



Geological environment on Earth

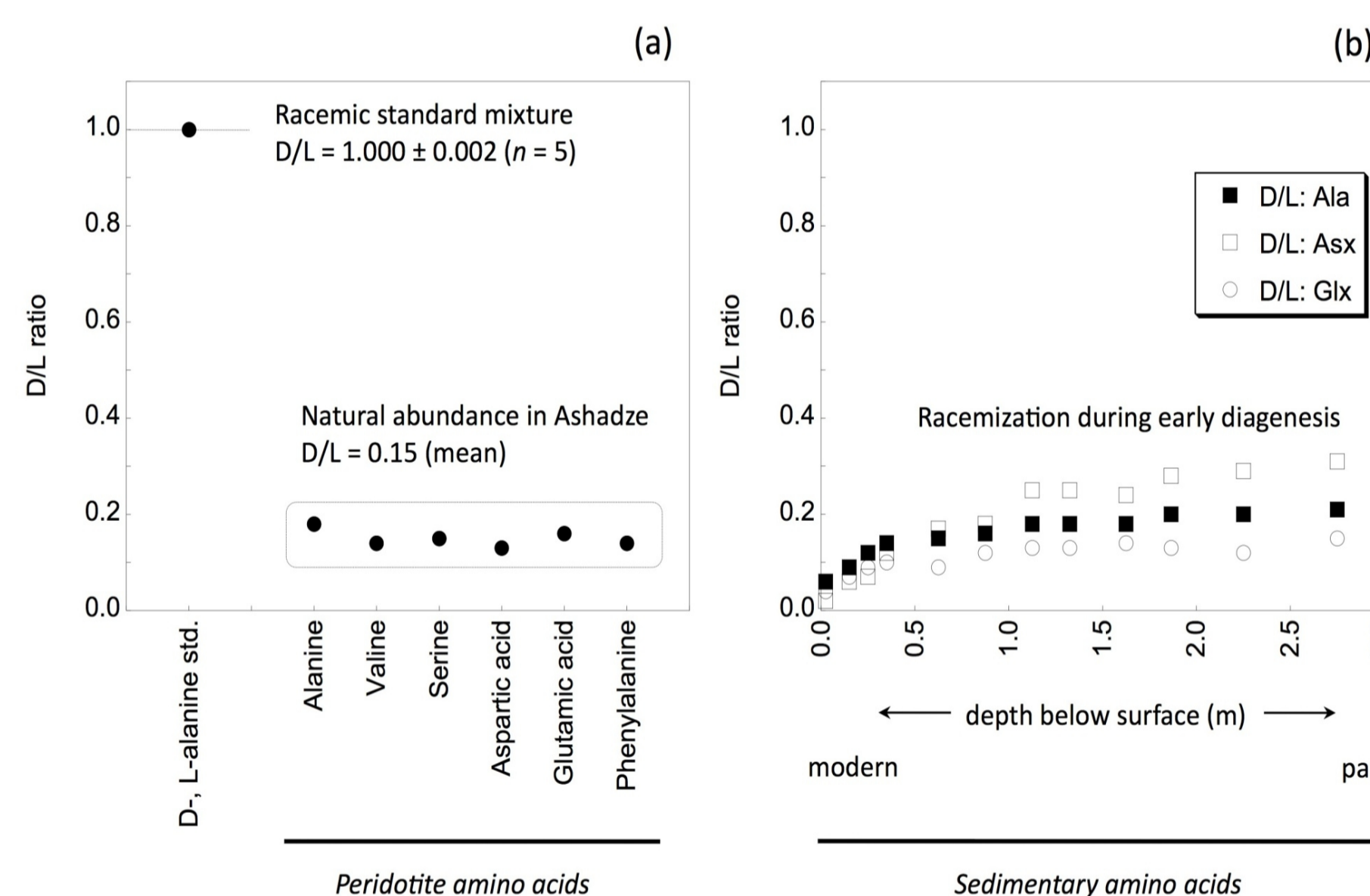
The Mid-Atlantic Ridge, MAR, is covered with several hydrothermal sites and presents black smoker activity. Logatchev (14° 45'N-43'N, 2970m) and Ashadze (12° 58'N, 4080m) are active sites, located on an ultramafic geological environment of serpentinized peridotite rocks, while Krasnov (16° 38'N) is inactive 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 [5].

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. Since nitrogen may be found in hydrothermal geological environments, nitrogen compounds such as amino acids, not only hydrocarbons, may form during serpentinization processes.

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].

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



Geological environment on Mars

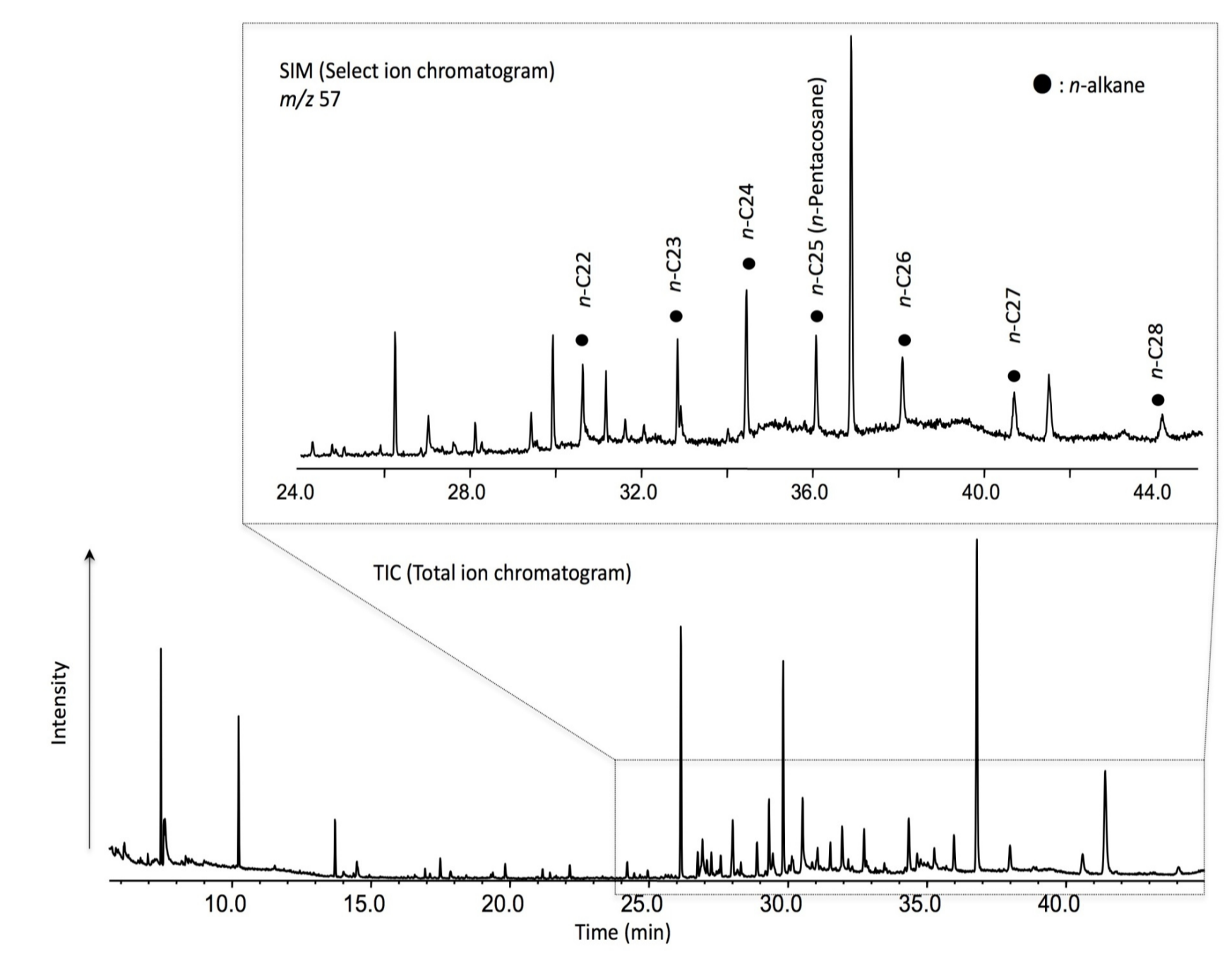
Olivine, serpentine and carbonate have been discovered in Nili Fossae on Mars [8]. This assemblage of minerals seems typical of serpentinized ultramafic rocks found on Earth. Organic molecules synthesis might occur in this geological site and lead to precursors of life.

A knowledge of the terrestrial serpentinized peridotite rocks would bring information on the organic content of martian rocks.

We conducted organic analyses of two serpentinized peridotite rocks dredged on the Logatchev and Ashadze seafloors to determine their content in hydrocarbons and chiral amino acids.

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fig.3. Chromatogram of hydrocarbons extracted from the Logatchev 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 were conducted in the Institute of Biogeosciences of the Japan Agency for Marine-Earth Science and Technology in Yokosuka. They are fully described in ref [9].

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. MS spectrum was scanned over m/z 50-550.

Conclusion

This 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 HCl 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.

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.

We analyzed terrestrial rocks which contain carbonate, olivine and serpentine minerals and we found organic compounds: long chain n-alkanes and amino-acids. Martian rocks dredged in the region where olivine and serpentine have been observed could be analyzed with the same methods and instruments.

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 are observed, which is an indication that:

these identified amino acids might 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).

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 [10].

We did not intend to proceed to the analysis of carbon-13, carbon-12 isotopic fractionation, since experiments conducted at 250°C and 350 bars, demonstrated that organic compounds synthesized abiotically in FTT reactions are depleted in ¹³C to a degree typically ascribed to biological processes [10].

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 [11].

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

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