Abiotic methane in continental serpentinization sites: an overview

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Abstract

Until 2008 methane in land-based serpentinized peridotites (MSP) was considered to be an unusual and rare occurrence of abiotic gas. Today, reports of MSP are increasing for numerous localities worldwide in low temperature settings in ophiolites, orogenic massifs or intrusions. CH₄ emanates from focused seeps, hyperalkaline water springs or through diffuse seepage from the ground, typically along faults. MSP has a combination of stable C and H isotope composition that is different from that of biotic methane; it is likely produced by Fischer-Tropsch Type reactions between CO₂ (or other C compounds) and H₂ (from serpentinization) at low temperatures (typically <100°C) and its carbon is fossil, ¹⁴C free, which does not derive from the more recent C dissolved in the hyperalkaline waters. MPS is more common than previously assumed; it may have played a key role in the origin of life, may fuel microbial life in igneous rocks on Earth and other planets, and can be an additional source of gas in atypical petroleum systems hosting ultramafic rocks.

Keywords: Serpentinitization, abiotic methane, hyperalkaline springs

1. Introduction

Serpentinization, i.e. the hydration of olivine and pyroxene in mafic and ultramafic rocks (mainly peridotite), is today recognized as a fundamental water-rock interaction responsible for the production of secondary minerals, hyperalkaline water and gases, with implications in geophysics (changes in mantle rock rheology and seismic velocities), geochemistry (geochemical fluxes and carbon cycle), biology and astrobiology (energy and raw materials for organic compounds and chemosynthetic microbial life)¹.² Serpentinitization can produce hydrogen gas (H₂) that, with successive C reduction via Fischer-Tropsch Type (e.g. Sabatier) reactions, may lead to the generation of...
abiotic methane (CH₄) and other hydrocarbons³⁴. H₂ and CH₄ are energy sources (electron donors) in prebiotic chemistry and may have played a key role in the origin of life. Serpentinization, through H₂, can be a source of CH₄ in atypical petroleum systems where reservoir rocks are formed by or are adjacent to igneous rocks⁵⁶, and a potential source of CH₄ on other planets, such as Mars⁶⁷. In addition to submarine serpentinization, driven by seawater at mid-ocean ridges and subduction zones (see the literature on Lost City and other seafloor hydrothermal fields¹), a wide body of research has recently demonstrated the importance of active (present-day) serpentinization driven by meteoric water, occurring in peridotites already emplaced on the continents, in ophiolites, peridotite massifs or intrusions. Abiotic gas in these land-based sites has been discovered in an increasing number of countries, beginning from the 1980s with the pioneering works on springs and seeps in the Philippines, New Zealand and Oman⁸⁻¹⁰. In the last five years the list of the sites with surface manifestations of methane in serpentinized peridotites (MSP) increased considerably, including today at least 16 countries. Here is a brief but updated overview on the MSP distribution, seepage, isotopic composition and origin.

2. Surface manifestations of MSP: classification and distribution

Surface manifestations (i.e. seepage) of MSP are typically located in correspondence with faults or at the intersection of more faults, often in tectonic contact between ultramafic rocks and carbonate-rich rocks (limestone, metasedimentary rocks). Four types of MSP emissions can be distinguished:
(a) Gas bearing hyperalkaline springs (HS); (b) Gas vents, without water discharge (GV); (c) miniseepage: diffuse exhalation from the ground (peridotite outcrops and organic soil) around the springs or vents; (d) microseepage: diffuse exhalation from the ground far or independent from springs or seeps. HS and GV are a form of “macroseepage” as they refer to visible fluid manifestations⁶. Hyperalkaline waters, with pH > 9 and Ca-OH⁻ chemistry, are characteristic of active serpentinization as they result from the liberation of OH⁻ and Ca²⁺ during the hydration of olivine and pyroxenes. They reflect a relatively deep hydrologic circulation, with ages in the order of a few thousands years⁶¹¹¹². MSP has been reported in tens of HS, distributed in 16 countries (Fig. 1).

Fig. 1. Global distribution of continental MSP sites (references of the sites are in⁸ and¹⁰). Dominantly abiotic methane, determined by complete C and H isotopic analyses, is documented in countries reported in Fig. 2. All sites refer to ophiolites, except Spain, Japan (peridotite massifs) and Portugal (peridotite intrusion).
Dissolved methane concentration is generally on the order of 0.1–10 mg CH₄/L when pH is about 10–12 (normal water in equilibrium with the atmosphere has 0.00003 mg CH₄/L); between pH 8 and 9 only trace amounts of CH₄ can be detected. HS, however, seem to act simply as gas carriers, they are not necessarily place of methane origin (as discussed below) and exist only in favourable hydrogeological conditions¹². MSP can migrate and reach the surface independently from HS, in a way similar to biotic (thermogenic or microbial) gas seepage in sedimentary basins⁶. GV can be a simple “dry” emission from rock fractures, can burn producing fascinating “eternal flames” (e.g., Chimaera in Turkey, or Los Fuegos Eternos in the Philippines), or be in the form of gas bubble plumes in ponds⁶. CH₄ concentration in the gas phase is up to 86 vol.%; the rest can be H₂ (not always in significant amounts), N₂, C₂-C₆ hydrocarbons and trace amounts of CO₂. Individual “dry” vents can release several tons of CH₄ per year; bubble plumes in ponds can release 10¹⁰³ g CH₄ d⁻¹ (see¹¹). Invisible exhalations around HS or GV (miniseepage), or far from the macro-seeps (microseepage), can be detected by closed-chamber accumulation techniques or soil-gas probes⁶. They have been documented in Turkey, Greece, Italy, Spain and Portugal⁶. Microseepage and miniseepage fluxes are on the order of 10¹⁰³ mg m⁻² d⁻¹ (see¹¹). Finally, it is worth mentioning that abiotic methane likely related to serpentinization is also known to occur in deep boreholes in Precambrian crystalline shields¹³ but seepage to the surface has, thus far, not been reported.

3. MSP origin

Methane collected in MSP sites, either onshore⁴,⁶,¹¹,¹⁴ or offshore⁷, as well as that from boreholes in Precambrian shields¹³ has a stable C and H isotope composition that is clearly different from that of biotic (thermogenic and microbial) gas, as evidenced in Fig. 2.

![Fig. 2. Stable C and H isotope diagram of continental MSP (top) and updated isotopic fields of abiotic and biotic (thermogenic and microbial) gas (bottom). See text for references.](image-url)
Historically, the limited abiotic CH₄ isotope database suggested that this gas is ¹³C-enriched, with δ¹³CCH₄ values > -25‰ (VPDB). Today we know that abiotic δ¹³CCH₄ may be as low as around -40‰, and even lower values (similar to microbial gas) can be obtained in laboratory. Fig. 2 shows that MSP may have a wide range of C and H isotope composition, likely resulting from (a) the variety in the isotopic composition of the carbon feedstock involved in the production of CH₄ (CO₂ from mantle, crustal rocks or the atmosphere), (b) the temperature of the CH₄ generation mechanism, (c) isotopic fractionations in the presence of H₂O, and (d) the degree of the reaction itself. The isotopic diagram, however, is only the first step for determining the abiotic origin of gas and it cannot reveal if CH₄ is completely abiotic or mixed with some biotic components. Additional interpretative tools are necessary and may include the use of noble gases (helium isotopes), Schulz-Flory distribution tests, the molecular and isotopic composition of associated gases, and methane vs. ethane mixing plots. In any case, knowledge of the geological context is an essential precondition for final interpretations. Actually, in many cases MSP is not totally abiotic and it may have variable components of thermogenic or microbial gas. A typical condition, which is however common in all continental MSP cases, is the low temperature of the geological system. Either isotopic geothermometers or geothermal gradients suggest that the gas is produced at temperatures typically <100°C (in contrast with hydrothermal mid-ocean ridge systems that can overcome 200°C). Several laboratory Fischer-Tropsch Type (FTT) experiments demonstrated abiotic CH₄ production above 200°C by using Fe, Ni or Cr catalysts, and below 100°C using Ru (ruthenium), a Platinum Group Element common in chromitites. Geographical coincidence between Ru-rich chromitites and MSP would support the hypothesis that Ru may be a key catalyst in low T continental MSP sites. Alternatively, Fe, Ni, and Cr could have produced CH₄ in early stages of peridotite emplacement on the continent, at higher T conditions (e.g., near the metamorphic sole) and/or they are also effective at low T on longer, geological time scales, although experimentally this cannot be demonstrated. Finally, MSP has fossil, radiocarbon (¹³C) free, C (older than 50,000 y BP) whereas dissolved inorganic carbon in HS is only a few thousand years old. Therefore most, if not all, of the CH₄ is not generated from the carbon in HS. This suggests that MSP may not necessarily originate in the specific serpentinizing rocks (which produce H₂ and hyperalkaline water); CO₂ and H₂ may migrate from their environment of origin (atmosphere or any C-bearing rock and serpentinization, respectively), and mix and react where metal catalysts are more abundant, for example in fractured chromitites.

References