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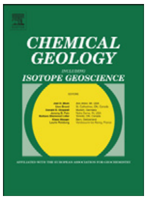

The origin of N_2-H_2-CH_4-rich natural gas seepages in ophiolitic context: A major and noble gases study of fluid seepages in New Caledonia

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ABSTRACT

The study of natural gas seepages in New Caledonia has shown the occurrence of two gas families, one is N_2-H_2-CH_4-rich, the other is N_2-rich. The N_2-H_2-CH_4-rich gases are bubbling in hyperalkaline springs (OH^--rich) known in the peridotite massif of the southern part of the island. This family of gas shows contents of N_2 between 50 and 62%, H_2 between 26 and 36%, and CH_4 between 11 and 16%. $\delta^{13}C$ values of methane are ranging from −39 to −32‰. We interpret the origin of H_2 as a product of fluid-rock interaction between basic-ultrabasic rocks and water with oxidation of Fe^{2+} and reduction of underground water in the fracture system of the peridotites nappe. Methane is interpreted as the result of a reduction of dissolved inorganic and/or organic carbon in subsurface aquifers. The second family of gas emissions was found in thermal springs in the sedimentary units located structurally below the peridotites nappe. The gas is composed mostly of N_2 (between 97 and 98%) associated with relatively high concentration of He. Both gas families show notably high N_2 vs fossil noble gas contents (^{36}Ar, ^{20}Ne, ^{84}Kr) suggesting that N_2 is not directly issued from gas dissolved in aquifers equilibrated with atmosphere but most likely finds its origin in a deep source, probably within metamorphic sediments which are tectonically buried below the ophiolitic nappe. We interpret the N_2-H_2-CH_4-rich family of gas as a result of a mixing between two end-members, (1) a H_2-CH_4-rich pole issued from the weathering of peridotite rocks and (2) a N_2-rich pole which would be issued from the metamorphosed sediments buried below the ophiolitic units. An unusual inverse correlation between the atmospheric noble gas isotopes ^{20}Ne and ^{36}Ar is interpreted as the result of a degassing of a relatively shallow confined aquifer related to a bubble flow from depth.

1. Introduction

Natural molecular hydrogen associated with methane and nitrogen has been reported several times in ophiolitic context either bubbling or simply dissolved in hyperalkaline spring water issued from serpentinized peridotites massifs, notably in Oman (Neal and Stanger, 1983; Sano et al., 1993), in the Philippine Archipelago (Abrajano et al., 1988, 1990), the Sakalin and Koryak Plateau in Russia (Smith et al., 2005), Milford Sound in New Zealand (Wood, 1970), Canada (Szponar et al., 2013), or Japan (Suda et al., 2014), and others. Also, as it is the case of the gas seeping out from ophiolitic rocks, H_2-rich fluids associated with N_2 and CH_4 contents are well-known in deep-water hydrothermal seepages of different areas of mid-oceanic ridges (Welhan and Craig, 1979; Kelley and Früh-Green, 1999; Charlou et al., 2002; Kelley et al., 2005; Proskurowski et al., 2008, and others). This type of gas seepage has always been interpreted as the result of ultrabasic rock alteration during serpentinization processes which are indeed able to generate molecular hydrogen and abiotic methane (meaning methane whose generation is not linked with organic matter thermal cracking but involves molecular hydrogen reducing any source of carbon). This interpretation well explains the nature of gas seepages discovered in ophiolitic context showing high contents in H_2 and CH_4 with high values of $\delta^{13}C$ (>−20‰), notably gas samples studied in Oman (Vacquand, 2011), the Zambales ophiolite in Luzon, in the Philippines (Abrajano et al., 1988, 1990) and in Southern Turkey (Hosgormez et al., 2008). But, so far, no publication has really attempted to explain the constant association of molecular nitrogen with these H_2-CH_4-bearing gases. One possibility is that N_2 is simply of atmospheric origin and passively taken from the aquifers or the sea water during hydrothermalism dynamics and/or bubbling processes of the H_2-CH_4-bearing gas. However this interpretation is more questionable when N_2 becomes the dominant phase in the gas seepages. We present in this paper a study of the gas composition of seepages located inside and in the vicinity of the New Caledonian ophiolite for which we tried to understand better the origin of N_2-H_2-CH_4–rich gas seepages in the ophiolitic rocks and N_2–rich gas seepages structurally below the ophiolitic rocks. This work is based on analyses on the major gases and noble gases.

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2. Geological setting of the gas seepages

The geology of New Caledonia is characterized by large outcrops of ophiolitic rocks (mainly peridotites; i.e. Fe-Mg silicates) that make one of the largest onshore massif of ultrabasic rocks preserved on Earth (Fig. 1A). The ophiolitic rocks of New Caledonia correspond to outcrops of the south-western edge of the lithospheric mantle forming the basement of the Loyalty oceanic basin (Prinzhofer et al., 1980; Cluzel et al., 2001). They are notably well exposed in the southern part of the island and they also form a series of klippes (chief mountains), in the north-western part of the island (Fig. 1A). The peridotites nappe was emplaced during Eocene times over formations of continental affinity (Paris, 1981; Cluzel et al., 2001; Fig. 1B) including (1) a basement of arc-derived formations of Pre-Cretaceous age which are overlain by basalts and formations of the Central Range that include sandstones, siltstones, grauwaches, claystones with coal of Cretaceous age and Tertiary carbonate turbidites and volcaniclastic deposits (Paris, 1981), and (2) a tectonic unit of oceanic basalts of Upper Cretaceous to Eocene age, with back-arc or fore-arc affinities which underlies the peridotites nappe (Paris, 1981; Cluzel et al., 2001). The gas seepages studied here were found within the peridotite nappe and also within grauwaches formations located structurally just under the nappe of the peridotites, in the area of La Crouen (Fig. 1A).

3. The gas-bearing springs

In the whole New Caledonia Territory, gas seepages were found in different contexts, either in the onshore, in the foreshore and in the near offshore (photo A in supplementary material). These gas seepages were sampled in two different types of springs. The first type corresponds to hyperalkaline thermal springs (with pH ranging from 10.5 to 10.9; Table 1). These hyperalkaline springs are located in the Prony area (Fig. 1). Their waters have already been studied by Barnes et al. (1978); Cox et al. (1982); Launay and Fontes (1985) and Monnin et al. (2014) in the Carenage Bay, the Kaori Bay, and offshore in the Roc Aiguille (also called needle of Prony), in all cases within the ophiolitic nappe of New Caledonia. The water is characterized mostly by the occurrence of Ca^{2+} (20–22 mg/l), Na^{2+} (11–14 mg/l), a little K^{+} (1–1.5 mg/l), Cl^{-} (10–11 mg/l), SiO$_2$ (3 mg/l), OH^{-} (21–24 mg/l) and no HCO$_3^-$ or CO$_3^{2-}$. Therefore the OH^{-} concentration is only responsible for the alkalinity of this thermal water. The springs in the foreshore (Carénage and Kaoris) and the offshore (Roc Aiguille) are associated

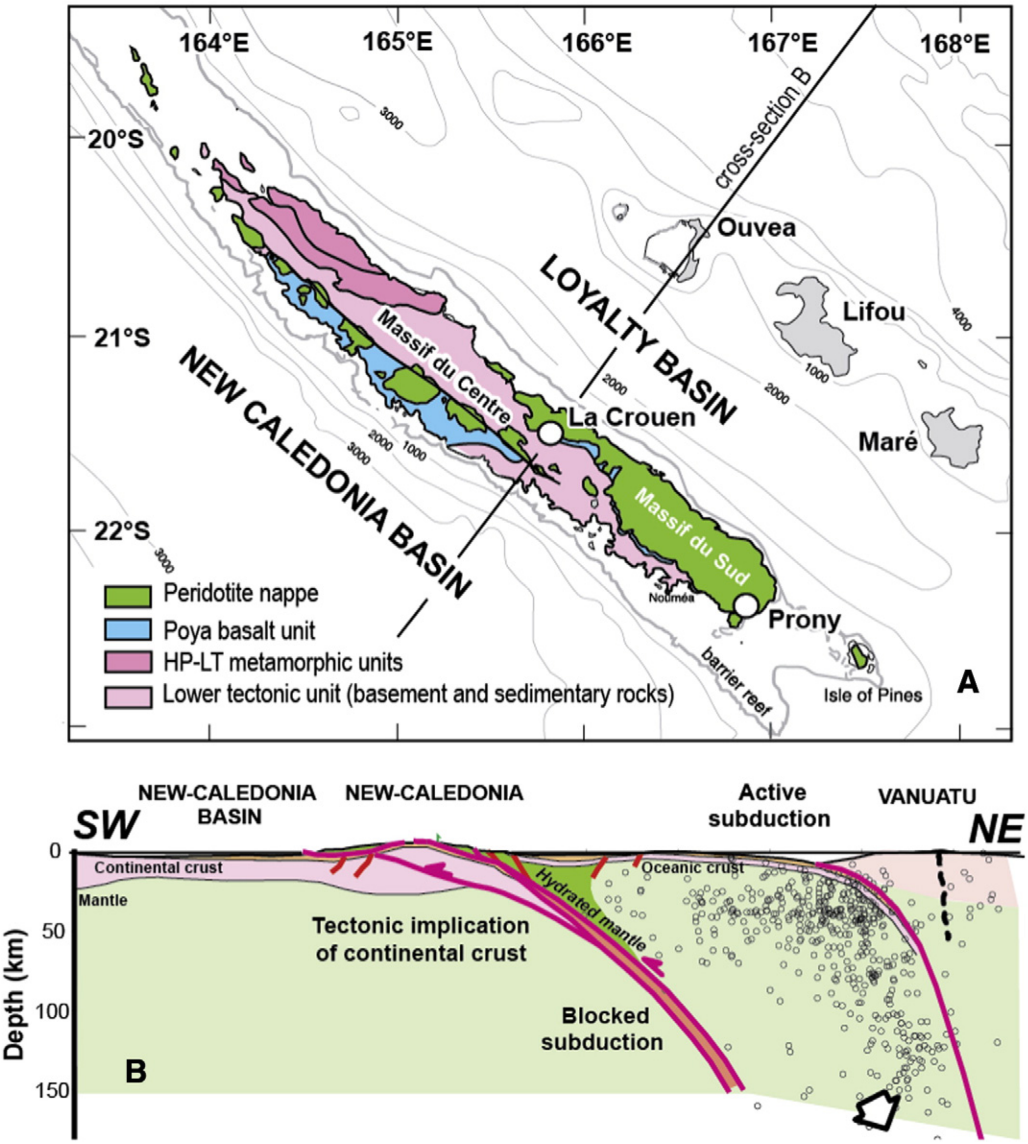

Fig. 1. Structural sketch-map (A) and simplified geological cross-section (B) of New Caledonia. Circles in B correspond to earthquake hypocenters. They well illustrate that the subduction north of New Caledonia is inactive today and that the Vanuatu subduction zone is active.