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Boron, lithium and methane isotope composition of hyperalkaline waters (Northern Apennines, Italy): Terrestrial serpentinization or mixing with brine?

Tiziano Boschetti^{a,*}, Giuseppe Etiope^b, Maddalena Pennisi^c, Millot Romain^d, Lorenzo Toscani^a

^a Earth Sciences Department, University of Parma, Parma, Italy

^b Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Italy and Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania ^c IGG-CNR, Istituto di Geoscienze e Georisorse, Pisa, Italy

^d BRGM, Water Department, Orléans, France

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ABSTRACT

Spring waters issuing from serpentinized ultramafic rocks of the Taro-Ceno Valleys (Northern Apennine, Emilia-Romagna region, Italy) were analyzed for major element, trace element and dissolved gas concentrations and δ^{11} B, δ^{7} Li, δ^{18} O(H₂O), δ^{2} H(H₂O), δ^{13} C(CH₄) and δ^{2} H(CH₄) isotope compositions. Similar to other springs worldwide that issue from serpentinites, the chemical composition of the waters evolves with water-rock interaction from Ca-HCO₃, through Mg-HCO₃ and ultimately to a hyperalkaline Na-(Ca)-OH composition. Most of the Ca- and Mg-HCO₃ springs have δ^{11} B ranging between +16.3% and +23.7‰, consistent with the range of low P–T serpentinites. Very high δ^{11} B in two springs from Mt. Prinzera (PR10: +39%; PR01: +43%) can be related to isotopic fractionation during secondary phase precipitation, as also inferred from δ^7 Li values. In contrast to typical abiogenic isotope signatures of CH₄ from serpentinized rocks, dissolved CH₄ from the Taro-Ceno hyperalkaline springs has an apparent biotic (thermogenic and/or mixed thermogenic-microbial) signature with $\delta^{13}C(CH_4)$ ranging from -57.5% to -40.8‰, which is similar to that of hydrocarbons from production wells and natural seeps in adjacent hydrocarbon systems. The data suggest that CH₄ in the hyperalkaline springs investigated in this study may derive from organic matter of the sedimentary (flysch and arenaceous) formations underlying the ophiolite unit. However, small amounts of H₂ were detected in one hyperalkaline spring (PR10), but for two springs with very low CH₄ concentrations (PR01 and UM15) the δ^2 H value could not be measured, so the occurrence of some abiotic CH₄ cannot be excluded. The occurrence of thermogenic CH₄ in ophiolites may be a widespread phenomenon, and thus the characterization of serpentinization-related gases requires accurate evaluation of the regional context including a careful knowledge of the relationships with surrounding sedimentary rocks and their hydrocarbon potential.

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1. Introduction

Serpentinized ultramafic rocks are currently the subject of numerous studies with implications for fluid geochemistry, the origin of life, the environment and astrobiology. Serpentinized ultramafic rocks are sites of H_2 production which may favor the development of chemolithoautotrophic microorganisms (e.g. McCollom, 2007), abiotic CH₄ probably produced by Fischer– Tropsch Type reactions (Charlou et al., 2002; Oze and Sharma, 2005; Proskurowski et al., 2008; Etiope et al., 2011), and may influence potential storage of anthropogenic CO₂ (Kelemen and Matter, 2008). Continental serpentinites have been suggested to represent environments similar to those occurring on Mars (analog sites) supporting the observation of CH₄ in the vicinity of hydrated

* Corresponding author. E-mail address: tiziano.boschetti@unipr.it (T. Boschetti).

0883-2927/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.apgeochem.2012.08.018 silicates (Blank et al., 2009; Etiope et al., 2011, 2012). In addition, they are key sites for understanding the cycling of elements with potentially harmful impact to both human health and the environment (e.g. Cr, Fantoni et al., 2002).

Oceanic serpentinization of peridotite, principally occurring under and along mid-ocean ridge crests and off-axis hydrothermal zones, leads to reduced, high pH hyperalkaline fluids with high H₂ and CH₄ concentrations. Serpentinization in the oceans is also associated with the uptake and release of many major and minor elements, such as Cl and B, which have important consequences for their global geochemical fluxes (Früh-Green et al., 2004). Present-day, low-temperature serpentinization has also been reported at convergent plate boundaries where oceanic lithosphere has been tectonically emplaced on land (ophiolite suites, e.g. Barnes et al., 1978). A characteristic feature of ophiolite outcrops are Mg-HCO₃ and hyperalkaline spring waters (e.g. Coleman and Jove, 1992). Previous studies have mainly addressed the presence of geogenic Cr(VI) in Mg-HCO₃ water (e.g. Fantoni et al., 2002), as well





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as the origin of hyperalkaline springs and of the gases related to serpentinization (Barnes et al., 1978; Neal and Stanger, 1983). In fact, whereas most natural waters have a pH from 6.5 to 8.5, hyperalkaline springs from serpentinites range from pH 10 to 12. This pH range is quite rare in nature, but it is typical of all the fluids related to oceanic and terrestrial serpentinization. Hyperalkaline waters have been reported in a wide number of countries, including Portugal, Italy, Bosnia, Greece, Cyprus, Oman, the Philippines, the USA and in the Lost-City, a hydrothermal field along the Atlantic mid-ocean-ridge (Fig. 1A, Appendix A1 for chemical comparison and references).

The present work contributes to the global geochemical dataset of ophiolitic fluids by reporting new chemical and stable isotope data on waters and dissolved gases in hyperalkaline springs from the Taro-Ceno Valleys, Northern Apennine (Italy, Fig. 1B). These springs are known for their high B concentration and high B/Cl ratio of 13 mg/L and 3 (molar ratio), respectively (Boschetti and Toscani, 2008). These values are unusual for cold and fresh



Fig. 1. (A) Geographic distribution of hyperalkaline springs from serpentinites (see Appendix A1 for data and references). (B) Simplified geologic map of the Northern Apennine, Ligurian–Emilian sector (modified from Boschetti and Toscani (2008)). Spring waters treated in this study were sampled in the Taro–Ceno Valley area, the boundaries of which are delimited by a dashed line.

waters, and rather are characteristic of hot and salty geothermal waters (Duchi et al., 1992; Garrett, 1998). The high B concentrations may be an important environmental issue because B affects plant growth and yields. It is an essential micronutrient for many plants; an overdose or an underdose of B can result in toxicity or deficiency symptoms in plants, respectively (Vengosh et al., 2004).

For this study the chemistry and B and Li isotope compositions of a suite of spring waters were determined in order to explain the origin and fate of these diagnostic elements during terrestrial serpentinization. Serpentinites may be highly enriched in B and Li because these elements are enriched in seawater and hydrothermal fluids due to their high solubility in aqueous fluids (Benton et al., 2004; Vils et al., 2011). If some of the original serpentinite B and Li can be retained in peridotites, then B and Li could be used to identify serpentinization history. However, most published studies which consider B and Li isotopes in rock and fluids during serpentinization are focused on the oceanic hydrothermal environment and successive methamorphic stages (high T and P; e.g. Benton et al., 2004; Vils et al., 2011 and reference therein), whereas no data exist on springs derived from terrestrial supergenic serpentinization (low T and P) and the related secondary minerals. In addition we analyzed the molecular composition of dissolved gases and the isotopic composition of CH₄ (δ^{13} C and δ^{2} H) to evaluate the possible presence of gas of abiotic origin, typically related to serpentinization, or gas of biologic origin (microbial or thermogenic), which may migrate from the surrounding sedimentary rocks and hydrocarbon fields and contaminate the hyperalkaline aquifers. Fluids from hydrocarbon-bearing formation brine are enriched in B and Li with a peculiar, heavy isotope composition (Vengosh et al., 1998a; Bottomley et al., 1999; Millot et al., 2011; Boschetti et al., 2011). Therefore, the potential of B, Li and CH₄ isotopes to distinguish between interaction with serpentinites and mixing with formation brine was investigated.

2. Geological and hydrological setting

The ultramafic masses of the Taro-Ceno Valley. Northern Apennine (Italy) are serpentinized lherzolitic peridotites belonging to an ophiolite sequence which represents the remnants of Mesozoic ocean floor in the South Alpine-Apennine lithospheric plate. The Northern Apennine ophiolites crop out in two palaeogeographic domains (Fig. 1B): the Internal Ligurides (IL) and External Ligurides (EL), which are identified on the basis of their current structural characteristics and their relationship with the associated sedimentary sequences. The Emilia-Romagna side of the Northern Apennines is a fold-and-thrust belt, bounded to the NE by the Po Plain that represents the filling of the present-day foredeep basin (Appendix B1 and B2). Since the Oligocene, the Apennine thrustbelt evolution caused the tectonic wedge of the allochthonous External Ligurides to move north-eastward over the folding inner margin of the autochthonous Po Plain Basin (Appendix B2). In this study, spring waters were sampled from ophiolite rocks occurring in the Middle Taro valley and Mt. Prinzera, where the Taro River enters the Po Plain (Fig. 1B). Hydration of the peridotite minerals has produced serpentine (lizardite and minor chrysotile), chlorite, and talc and bastite after olivine and orthopyroxene, respectively. Basaltic rocks, outcropping in the Middle Taro but absent in the area of Mt. Prinzera, suffered early low-grade oceanic metamorphism to varying extents, followed by orogenic metamorphism. Sedimentary rocks of the Liguride unit in contact with the ophiolites are predominantly flyschoid (marly to pelitic) and arenaceous. The geology and petrology of the ophiolites (ultramafites, basalts and cherts) and of the related Liguride Units are extensively described elsewhere (Bortolotti et al., 2001; Boschetti and Toscani, 2008, and references therein).

From a hydrological point of view, two types of ophioliterelated springs were identified in the field area (De Nardo et al., 2007): (i) springs from fracturated rocks, with an undefined permeability limit and (ii) springs from coarse detritic cover, with defined permeability limit. Some springs with high flow rate have a different origin related to DSSGD (deep-seated slope gravitational deformation) that increased permeability due to slackening of the pre-existing fractures (De Nardo et al., 2007).

3. Material and method

Nine springs from Taro-Ceno Valley ophiolites were sampled and analyzed during fall-winter 2010–2011 for their chemical and isotopic characteristics. Samples were selected on the basis of their previously detected high pH, B and Li content (Boschetti, 2003). The chemical and isotopic results obtained in this study are shown in the Appendix (A2 for dissolved constituents and A4 for dissolved gases). They will be interpreted here particularly in the context of previously published data (Venturelli et al., 1997; Boschetti, 2003; Marchiani and Venturelli, 2006; Boschetti and Toscani, 2008).

3.1. Field and laboratory methods

Field methods and analytical laboratory procedures for O and H isotope composition of water, $\delta^{18}O(H_2O)$ and $\delta^2H(H_2O)$ in % vs. V-SMOW, are those described by Boschetti and Toscani (2008). Major and trace elements of the waters including Si, Cl, Br and S were determined by inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS, respectively) at the ACME Analytical Laboratories Ltd. (Vancouver, Canada). Reported Si and Cl concentrations are the average of spectrophotometric (photometer Merck SQ300) and ICP-OES results. Boron (δ^{11} B vs. SRM951) and Li $(\delta^{7}$ Li vs. L-SVEC) isotope compositions of the collected samples were determined by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at BRGM [Orléans, France; method described in Millot et al. (2010)]. δ^{11} B and δ^{7} Li of two hyperalkaline springs (PR10 and UM15) sampled during 2001-2002 were likewise measured using preserved aliquots. The δ^{11} B of these two samples was also measured by P-TIMS at CNR-IGG isotope laboratory [Pisa, Italy; method described in Tonarini et al. (2009)]; results were statistically comparable, therefore only the data obtained with MC-ICP-MS are reported. Water samples from the hyperalkaline springs PR10, UM15 and a sample representing a Mg-HCO₃ spring (PR01) were collected following the *method* 1 described in Busenberg et al. (2006). The molecular composition of dissolved gas (N₂, Ar, O₂, H₂, CH₄, CO₂ and C₂H₆) and the stable C and H isotopic composition of CH₄, δ^{13} C(CH₄) and δ^{2} H(CH₄) in % vs. V-PDB and V-SMOW respectively, were determined at Isotech Laboratories Inc. (Illinois, USA) using a Carle AGC 100-400 TCD-FID GC and Finnigan Delta Plus XL mass spectrometer, with precision $\pm 0.1\%$ for $\delta^{13}C(CH_4)$ and $\pm 2\%$ for $\delta^2 H(CH_4)$, respectively. The spring PR10 was analyzed twice, in 2010 and 2011. Additional analyses of ${}^{13}C/{}^{12}C$ ratio of CH₄ in springs PR10, UM15 and PR1 were made at the Stable Isotope Facility at the University of California, Davis, using a SerCon Cryoprep TGII trace gas concentration system interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Two laboratory standards (CH₄ gas diluted in He) were used and calibrated against NIST 8560. Accuracy is ±1% and repeatability has a standard deviation of 0.22‰.

3.2. Thermodynamic calculation

Calculation of the dissolved water species and reactions with pure mineral phases were performed using PHREEQCI

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2.18.3 software (Parkhurst and Appelo, 1999). The original thermodynamic database *llnl.dat* was commplemented with data for datolite (Yang and Rosenberg, 1995), poorly crystalline antigorite (Gunnarsson et al., 2005) and lizardite (Blanc et al., 2007). The values of activity and saturation index S.I. = $\log (Q/K)$ (where *K* is the equilibrium constant for the reaction of dissolution of a pure solid phase, and Q the activity product referred to the dissolved species obtained by computation) are only approximate because of analytical and thermodynamic uncertainty; thus, saturation at equilibrium has been assumed conventionally to be in the range -0.2 < S.I. < 0.2 (Appendix A3).

4. Results and discussion

4.1. Update on water isotope and chemical data

New data on O and H isotope compositions of the sampled waters lie on the meteoric water lines of the north and central Italy (Longinelli and Selmo, 2003), confirming that all the waters sampled in the Taro-Ceno Valleys are of meteoric origin (Fig. 2A; Marchiani and Venturelli, 2006; Boschetti and Toscani, 2008). Ternary chemical classification plots reveal that surface waters sampled from the Taro river main stem and tributaries, and springs issuing from basalts and local sedimentary formations have a Ca-HCO₃ composition like most meteoric waters (Fig. 2B and C). In contrast, springs from the ultramafic rocks exhibit differentiation in three geochemical facies as a result of terrestrial serpentinization: they start as Ca-HCO₃ water, interact with Mg-bearing minerals resulting in Mg-HCO₃ water, then Mg precipitates in silicates such as clays, neo-formed serpentine and brucite (Ca mainly as carbonate; Boschetti and Toscani, 2008). At this latter stage, waters become Na-hyperalkaline due to the drop of (bi)carbonate alkalinity and the predominance of OH⁻ species (samples PR10 and UM15 in Fig. 2B and C). Besides the high pH, both hyperalkaline springs are characterized by greater Na, Cl, Br, I and, in sample UM15, of S, K, Rb, Cs relative to the HCO₃ springs (Appendix A2). However, because of the concurrent decrease in Mg and Ca, all springs issuing from serpentinite remain fresh having low total dissolved solids (median TDS = 128 mg/L). The most significant elemental variation concerns B which shows a concentration increase in hyperalkaline springs from one (PR10 = 2 mg/L) to two (UM15 = 13 mg/L) orders of magnitude in comparison with the average concentration in Mg-HCO₃ springs (175 μ g/L). In contrast, Li $(0.1-4 \mu g/L)$ does not show significant differences in the three water facies. During the transition from HCO₃ to hyperalkaline geochemical facies, waters experience a sharp decline of CO₂ partial pressure (and carbonate alkalinity) and redox potential, the latter as consequence of the appearance of reduced S and N. In areas of terrestrial serpentinization, the drop in (bi)carbonate alkalinity has generally been attributed to carbonate precipitation as travertine (Bruni et al., 2002) or reduction of CO₂ to CH₄ (Fritz et al., 1992). However, the decrease of redox potential is also related to oxidation of Fe(II) and reduction of H in the water molecule during hydration of Fe(II)-bearing minerals, with subsequent generation of molecular H₂ (McCollom and Back, 2009; Neal and Stanger, 1983; Palandri and Reed, 2004):

Finally, from an environmental point of view, it is also worthy to note the presence of Cr in Mg-HCO₃ water up to about $20 \mu g/L$ as total Cr, with predominance of the hexavalent species as revealed from speciation calculated using PHREEQCI software (Boschetti, 2003). This latter issue has been discussed elsewhere (Fantoni et al., 2002) and will not treated further here.

4.2. B/Cl, δ^{11} B and δ^7 Li

The B/Cl ratio of the waters increases with progressive waterophiolite interaction: B/Cl of Ca-HCO₃ water = 0.09 ± 0.02 M; B/Cl of Mg-HCO₃ water = 0.13 ± 0.07 M; B/Cl of hyperalkaline springs = 0.3-3 M (this work; Boschetti, 2003). In the hyperalkaline samples, the ratio is quite similar to that of oceanic serpentinite (Scambelluri et al., 2004; Boschetti and Toscani, 2008) so probably both B and Cl come from water-rock interaction. In fact, serpentinites have higher content of both B and Cl compared with unaltered ultramafic rocks, and most authors suggest that these elements come from seawater during oceanic serpentinization (e.g. Scambelluri et al., 2004). However, the cause of the high B/ Cl ratios of the Taro-Ceno Valley's hyperalkaline springs compared with hyperalkaline waters sampled in other locations remains unexplained (Appendix A1).

To understand the origin of B in the waters, the B isotope composition of the springs issuing from ophiolite has been examined. The δ^{11} B of the sampled springs cluster between the values of the local waterworks (+8.3%) and low P-T Liguride ophiolites (from +16% to +24%; Scambelluri and Tonarini, 2011) but springs from Mt. Prinzera (PR01 and PR10) which show heavy values up to +43‰. The difference of greater than 20‰ for δ^{11} B of the two hyperalkaline samples UM15 and PR10 that are two spring waters of the same hydrogeochemical facies is quite unusual (Appendix A2). According to thermodynamic calculation (Appendix A3), borate ion is the dominant species of B in hyperalkaline springs due to the high pH of the fluids, whereas boric acid dominates in Ca- and Mg-HCO₃ springs (e.g. Zeebe, 2010; Xiao et al., 2011). Therefore, the evolution of B isotope composition from HCO₃ to hyperalkaline UM15 sample is likely due to a pH fractionation, as suggested by the curves representing the typical trigonal(3)tetragonal(4), boric acid-borate fractionation (Fig. 3A). The greater δ^{11} B value and lower B concentration in PR10 compared to UM15 spring may be due to adsorption/scavenging of ¹⁰B (as borate) by precipitating minerals like brucite, calcite, clays and low-temperature newly formed serpentine (Xiao et al., 2011). In fact, this water sample is oversatured in all these minerals (Appendix A3).

Comparing δ^{11} B with B/Cl ratio in a binary plot provides a potential tool for identification of natural (geogenic) sources as well as of pollution (anthropogenic) sources in groundwater systems due to the wide range of δ^{11} B values from -20 to +60% and several orders of magnitude differences in the B/Cl ratio now recognized in natural waters (Vengosh et al., 1998b). The spring waters analyzed in this study fall in a new and distinct sector of the diagram, where the higher values may be caused by fractionation resulting from pH variation rather than mixing with formation brines (Fig. 3B). Exceptionally high B/Cl = 3 M in UM15 may be due to the presence of ophiolite breccias in the area which contain spilitized basalts, characterized by the presence of datolite [CaBSiO₄(OH)]. In fact, UM15 spring is undersaturated with respect to this phase (Appendix A1), indicating that water would tend to dissolve it. Spilitized basalts could also explain the presence of relatively high Na, K, Rb and Cs concentrations in UM15 in comparison with PR10 hyperalkaline spring (Wedepohl, 1988). Finally, it is noteworthy that the extended range in δ^{11} B-B/Cl space observed for the ophiolite springs of this study could help to better understand the still unexplained abnormal concentration of B found in the groundwaters of Mediterranean (Vengosh et al., 1998b) and Western USA (Farrar et al., 2006) areas, which may be related to the interaction with serpentinized ultramafic terrains.

In comparison with B/Cl, the Li/Cl molar ratio generally decreases during progressive water-ophiolite interaction: Li/Cl = 2.4×10^{-3} M in Ca-HCO₃ waters, 3.1×10^{-3} M in Mg-HCO₃ waters and 5.7×10^{-4} M in hyperalkaline waters. Local formation brines and mud volcanoes have similar ratios of 2.2×10^{-3} M

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Fig. 2. Plots of (A) δ²H vs. δ¹⁸O for waters from the Taro–Ceno Valleys. C-Italy and N-Italy are the meteoric water lines for Central and Northern Italy, respectively (Longinelli and Selmo, 2003). Monthly rain sampled at Mt Prinzera during 2005–2006 is also represented (Marchiani and Venturelli, 2006). Water chemical classification by ternary plots uses major dissolved cations (B) and anions (C). The gray dashed arrows indicate the trend during local terrestrial serpentinization. Isotope and chemical data from local spring and stream waters are showed for comparison (Boschetti and Toscani, 2008).

and 4.9×10^{-4} M, respectively (Boschetti et al., 2011); therefore, a mixing between hyperalkaline and hydrocarbon-bearing fluids may have occurred. Li isotope geochemistry may be a further tool to distinguish between serpentinization processes and the possible interaction with local sedimentary formation brine. All sampled waters are ⁷Li enriched in comparison with typical peridotites values (δ^7 Li < 10‰, Tomascak, 2004; Appendix A1), with a mean value calculated excluding hyperalkaline springs of +24.3‰, similar to the world mean river runoff (+23.5%; Tomascak, 2004). In a $\delta^{11}B-\delta^7Li$ plot (Fig. 4), the sampled Ca-HCO₃ waters trend towards the isotope composition of local ophiolites (Scambelluri and Tonarini, 2011), whereas Mg-HCO₃ waters have a more scattered distribution. The greater δ^7 Li values shown by the hyperalkaline waters is consistent with fractionation caused by Li-adsorption on precipitating secondary minerals (e.g. Lemarchand et al., 2010); however, it should be noted that the data for PR10 falls within the field of sedimentary formation brines in Fig. 4. Furthermore, the presence of relatively high concentrations of Br and I relative to Cl in hyperalkaline waters in comparison with Mg-HCO₃ waters (Appendix A2) can be another indicator of mixing with hydrocarbon-bearing fluids. However, a previous study on serpentinites reported high concentrations of halogens in these rocks (Kamineni et al., 1992). Moreover, mixing with brine is at odds with (a) the low TDS of the ophiolite springs and (b) the hypothesis stated above for an origin for B in the hyperalkaline waters from water-serpentinite interaction. In fact, the similarity between local formation brines and hyperalkaline waters is not evident if the B/Cl ratios are examined: 3.9×10^{-3} M and 3.9×10^{-2} M in formation brines and terrestrial mud volcanoes, respectively (Boschetti et al., 2011) vs. a mean of 2.1×10^{0} M in hyperalkaline springs. Finally, an average B/Cl ratio of 3.0×10^{-1} M was observed in Na-HCO₃ springs related to the hydrocarbon system of the Northern Apennine and Po plain (Boschetti, 2011), that is similar to hyperalkaline PR10 sample. However, B and Li isotope compositions in this type of water are still unknown.

4.3. Molecular composition of dissolved gases and \mbox{CH}_4 isotope composition

In the sampled springs PR01, PR10 and UM15, dissolved gas is largely composed of N₂, as typically occurs in groundwaters with a strong meteoric component (Appendix A4). Significant concentrations of CH₄ (>7 vol.%) occur in the PR10 sample, and H₂



Fig. 3. (A) Stable B isotope fractionation between dissolved B species boric acid $B[OH]_3$ and borate ion $B[OH]_4$. Curves were calculated using typical α_{3-4} values (Xiao et al., 2011) and an initial waters with pH = 7 and $\delta^{11}B = 12\%$. $\delta^{11}B$ range of the local rocks is enclosed between dashed lines (data from Scambelluri and Tonarini (2011)). See Appendix A3 for dissolved B speciation. (B) Variations of $\delta^{11}B$ and B/Cl values of potential boron sources (modified from Vengosh et al., 1998b).

(0.03 vol.%) was detected in 2011. The low H_2 concentration, however, was not sufficient to perform the $\delta^2 H(H_2)$ analysis.

The stable C isotopic composition of CH₄ (δ^{13} C) ranges from -57.5% to -40.8% which is quite different from the range typical of abiotic gas found in continental serpentinized ultramafic rocks, such as in Turkey, Oman and the Philippines (Etiope et al., 2011 and references therein; Fig. 5). For the springs PR01 and UM15, due to their low CH₄ content, it was not possible to measure the δ^2 H values (indicated in Fig. 5 by a vertical dashed line); so at present it is not possible to exclude that they may contain some abiotic CH₄ with relatively low δ^{13} C (<-30‰) and δ^2 H (<-300‰), similar to that reported for ophiolites in New Zealand (Poison Bay) and deep gas in the South Africa Precambrian Shield (Etiope et al., 2011 and references therein).

Methane in sample PR10 appears to have mixed microbial-thermogenic characteristics, similar to sedimentary CH_4 which is widespread in gas fields and surface seeps along the northern Apennine and Po Plain (Borgia et al., 1987; Mattavelli et al., 1983; Fig. 5). Although the C isotopic composition alone is not a definitive proof of the CH_4 origin, the data suggest that the analyzed spring waters are contaminated by biotic gas originating in the surrounding sedimentary rocks. In this area, the majority of microbial/diagenetic hydrocarbon gas is from shallow Pliocene and Pleistocene units, while minor thermogenic hydrocarbon contributions derive from deeper Miocene and Mesozoic units (Appendix B2). Because of the low thermal gradient within the Po Basin, gas of demonstrable microbial origin is present at depths of up to 4.5 km (Mattavelli et al., 1983). Towards the Apennine chain and its subsurface fold belt, the thermal gradient is higher and the oil window is locally as shallow as 4 km, thus thermogenic hydrocarbon accumulations are mainly restricted to the Apennine trend (Lindquist, 2001; Appendix B1). In some cases shallow gas from explorative drillings is thermogenic, having migrated from a deeper reservoir (Mattavelli et al., 1983), whereas natural seeps along the Pede-Apeninne margin posess a mixed signature (Fig. 5). The Ligurian nappe acts as a "reservoir-cap rock" on the Po Basin hydrocarbon system, promoting the thermogenic character of the Apenninic gas (Borgia et al., 1987). At the same time, it is reasonable to hypothesize that the lithostatic load of the ophiolitic masses may enhance gas escape from the autochthonous substratum, already favored by Pede-Apennine fold-and-thrust structure. Furthermore, the large volumes of marly-to-pelitic and arenaceous sediments of the allocthonous Liguride may contain degradable organic matter (Rice, 1992), perhaps sufficient to explain the presence of shallow micro-

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Fig. 4. δ^{11} B vs. δ^{7} Li for spring waters from serpentinites. Ca-HCO₃ samples plot between mean worldwide composition of surface water (Lemarchand et al., 2002; Tomascak, 2004) and the gray shaded area representing the δ^{11} B range of the local rocks (data from Scambelluri and Tonarini (2011)). However, it should be noted that Li in peridotites may be lower than δ^{7} Li < 10‰ (Vengosh et al., 1998a; Tomascak, 2004). The fields of seawater (Choi et al., 2010) and seawater-derived formation brines (Bottomley et al., 1999) are also shown for comparison. Dashed arrows show the expected B and Li isotope fractionation trends. In both figures, symbols and local serpentinites values as in Fig. 3.



Fig. 5. Plot of δ^{13} C vs. δ^2 H in CH₄. Isotopic CH₄ composition from springs PR10, PR01 and UM15 is compared with microbial-thermogenic and abiogenic sources related to serpentinization and possible Fischer–Tropsch Type (FTT) reactions (from Etiope et al. 2011), and with data from exploratory hydrocarbon wells from the Northern Apennines (black crosses, Borgia et al., 1987) and sedimentary Po plain (black X, Mattavelli et al., 1983), as well as local seeps (gray crosses, Etiope et al., 2007). C = Chimarea (Turkey); Z = Zambales (Philippines); LC = Lost City (mid-Atlantic Ocean); O = Oman; P = Poison Bay (New Zealand); K: Kloof, Witwatersrand Basin (South Africa). For PR01 and UM15 (vertical dashed lines) δ^2 H was not measured due to low CH₄ concentration; so, an abiotic origin similar to that of Poison Bay ophiolite and South Africa Precambrian Shield cannot be excluded.

bial CH₄ in the ophiolitic spring waters. However, the presence of a minor component of abiotic serpentinization gas cannot be excluded, as suggested by the occurrence of H_2 in sample PR10.

The low H_2 content detected in sample PR10 may be the result of the low water-rock interaction progress of the investigated springs. Dissolved CH_4 and H_2 were observed in the nearby hyperalkaline springs of Voltri Group (Früh-Green et al., 2009), at the boundary between Tyrrhenian versant of N-Apennine and W-Alpine domain (Fig. 1). Although isotopic results have not been published yet, the authors mention "¹³C-enriched methane" with an apparent abiotic signature (Früh-Green et al., 2009). In terms of water–rock reaction progress, the Voltri Group hyperalkaline springs appear to be more evolved in comparison with those from Taro-Ceno Valleys (Bruni et al., 2002; Boschetti and Toscani, 2008), and this can explain the presence of detectable abiogenic gases. Moreover, the different structural and geodynamic setting and the absence of sedimentary hydrocarbon fields decrease the possible role of biotic gas contamination in the interpretation of the gas source.

5. Conclusions

The Taro-Ceno Valley hyperalkaline springs have relatively heavy B and Li isotope compositions probably caused by a pH effect and formation of new mineral phases, respectively, during water-rock interactions accompanying terrestrial serpentinization. In δ^{11} B–B/Cl space, the analyzed samples describe a field that is distinct from that of other natural waters, perhaps expanding ability to identify the sources of B and Cl in other environments. Moreover, in comparison with other Taro-Ceno Valley's springs, hyperalkaline springs are also characterized by a relatively high concentration of halogens explainable by interaction with ophiolite, rather than mixing with local hydrocarbon-bearing brines from sedimentary formation.

In contrast, the gas dissolved in the waters seems to include significant biotic (microbial and thermogenic) components probably coming from the surrounding flysch and/or arenaceous units hosting hydrocarbons. However, at the local scale it is difficult to recognize the migration and the allochthonous (Liguride unit) or autochthonous (substratum) origin of the sedimentary gas. Most probably, the lithostatic load of the ophiolitic masses on the underlying sedimentary formations may enhance gas migration, already favored by Pede–Apennine fold-and-thrust structure.

Solubilization of biotic gases in ophiolite aquifers may have overwritten the initial abiotic serpentinization signature of the gas dissolved in the hyperalkaline waters. Small amounts of H₂ were however detected in the water and the occurrence of some abiotic CH₄ cannot be excluded. In this respect, further isotopic analyses, including δ^{13} C of C₂H₅ and CO₂, and δ^{2} H of CH₄ and H₂ for all hyperalkaline springs, could prove illuminating.

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Furthermore, in order to exclude definitely the hypothesis of mixing with waters from sedimentary formations, an investigation on gases, Li and B isotope composition should be undertaken in Na-HCO₃ springs related to the Northern Apennine – Po plain hydrocarbon system (Boschetti, 2011; Boschetti et al., 2011). In fact, these waters show interesting compositional similarities with hyperalkaline springs from ophiolites. Finally, thermogenic CH₄ in ophiolites could be a widespread phenomenon, thus the identification of sources of serpentinization-related gases requires careful consideration of the relationships of the ultramafic rocks with surrounding sedimentary rocks and their hydrocarbon potential.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2012. 08.018.

References

- Barnes, I., O'Neil, J.R., Trescases, J.J., 1978. Present day serpentinization in New Caledonia, Oman, and Yugoslavia. Geochim. Cosmochim. Acta 42, 144–145.
- Benton, L.D., Ryan, J.G., Savov, I.P., 2004. Lithium abundance and isotope systematics of forearc serpentinites, Conical Seamount, Mariana forearc: insights into the mechanics of slab-mantle exchange during subduction. Geochem. Geophys. Geosys. 5, Q08J12. http://dx.doi.org/10.1029/2004GC000708.
- Blanc, P., Lassin, A., Piantone, P., 2007. THERMODDEM: a database devoted to waste minerals. BRGM, Orléans, France.
- Blank, J.G., Green, S., Blake, D., Valley, J.W., Kita, N.T., Treiman, A., Dobson, P.F., 2009. An alkaline spring system within the Del Puerto Ophiolite (California, USA): a Mars analog site. Planet. Space Sci. 57, 533–540.
- Borgia, G.C., Elmi, C., Ricchiuto, T., 1987. Correlation by genetic properties of the shallow gas in the Emilian Appennine (Northern Italy). Org. Geochem. 13, 319– 324.
- Bortolotti, V., Principi, G., Treves, B., 2001. Ophiolites, Ligurides and the tectonic evolution from spreading to convergence of a Mesozoic Western Tethys segment. In: Vai, G.B., Martini, I.P. (Eds.), Anatomy of an Orogen: the Apennine and Adjacent Mediterranean Basins. Kluwer Academic Publishers, London, pp. 151–164.
- Boschetti, T., 2003. Studio geochimico e geochimico-isotopico di acque a composizione estrema e termali dell'Appennino Settentrionale. Earth Sciences Dept. Univ., Parma, Parma.
- Boschetti, T., 2011. Application of brine differentiation and Langelier–Ludwig plots to fresh-to-brine waters from sedimentary basins: diagnostic potentials and limits. J. Geochem. Explor. 108, 126–130.
- Boschetti, T., Toscani, L., 2008. Springs and streams of the Taro-Ceno Valleys (Northern Apennine, Italy): reaction path modeling of waters interacting with serpentinized ultramafic rocks. Chem. Geol. 257, 76–91.
- Boschetti, T., Toscani, L., Shouakar-Stash, O., Iacumin, P., Venturelli, G., Mucchino, C., Frape, S.K., 2011. Salt waters of the Northern Apennine Foredeep Basin (Italy): origin and evolution. Aquat. Geochem. 17, 71–108.
- Bottomley, D.J., Katz, A., Chan, L.H., Starinsky, A., Douglas, M., Clark, I.D., Raven, K.G., 1999. The origin and evolution of Canadian Shield brines: evaporation or freezing of seawater? New lithium isotope and geochemical evidence from the Slave craton. Chem. Geol. 155, 295–320.
- Bruni, J., Canepa, M., Chiodini, G., Cioni, R., Cipolli, F., Longinelli, A., Marini, L., Ottonello, G., Zuccolini, M.V., 2002. Irreversible water–rock mass transfer accompanying the generation of the neutral, Mg-HCO₃ and high-pH, Ca-OH spring waters of the Genova province, Italy. Appl. Geochem. 17, 455–474.
- Busenberg, E., Plummer, L.N., Cook, P.G., Solomon, D.K., Han, L.F., Gröning, M., Oster, H., 2006. Sampling and Analytical Methods, Use of Chlorofluorocarbons in Hydrology: A Guidebook. IAEA – International Atomic Energy Agency, Vienna, pp. 199–220.
- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., Holm, N., 2002. Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). Chem. Geol. 191, 345–359.
- Choi, M.S., Shin, H.S., Kil, Y.W., 2010. Precise determination of lithium isotopes in seawater using MC-ICP-MS. Microchem. J. 95, 274–278.
- Coleman, R.G., Jove, C., 1992. Geological origin of serpentinites. In: Baker, A.J.M., Proctor, J., Reeves, R.D. (Eds), The Vegetation of Ultramafic (serpentine) Soils. Proc. 1st Internat.l Conf. on Serpentine Ecology. Intercept, Andover, UK; University of California, Davis, pp. 1–17.

- De Nardo, M.T., Segadelli, S., Vescovi, P., 2007. Studio pilota per la caratterizzazione geologica delle sorgenti nella zona del M. Nero (alta Val Ceno e alta Val Nure – province di Parma e Piacenza). Il Geologo dell'Emilia–Romagna 25, 5–21.
- Duchi, V., Minissale, A., Manganelli, M., 1992. Chemical-composition of natural deep and shallow hydrothermal fluids in the Larderello geothermal-field. J. Volcanol. Geotherm. Res. 49, 313–328.
- Etiope, G., Schoell, M., Hosgörmez, H., 2011. Abiotic methane flux from the Chimaera seep and Tekirova ophiolites (Turkey): understanding gas exhalation from low temperature serpentinization and implications for Mars. Earth Planet. Sci. Lett. 310, 96–104.
- Etiope, G., Ehlmann, B., Schoell, M., 2012. Low temperature production and exhalation of methane from serpentinized rocks on Earth: a potential analog for methane production on Mars. Icarus. http://dx.doi.org/10.1016/j.icarus.2012.05.009, in press.
- Etiope, G., Martinelli, G., Caracausi, A., Italiano, F., 2007. Methane seeps and mud volcanoes in Italy: gas origin, fractionation and emission to the atmosphere. Geoph. Res. Lett. 34, L14303. http://dx.doi.org/10.1029/2007GL030341.
- Fantoni, D., Brozzo, G., Canepa, M., Cipolli, F., Marini, L., Ottonello, G., Zuccolini, M.V., 2002. Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks. Environ. Geol. 42, 871–882.
- Farrar, C.D., Langenheim, V.E., Sonoma County Water Agency, Geological Survey (U.S.), 2006. Geohydrologic Characterization, Water-Chemistry, and Ground-Water Flow Simulation Model of the Sonoma Valley Area, Sonoma County, California with a Section on Basement Rock Configuration Interpreted from Gravity Data by Victoria E. Langenheim, U.S. Geol. Surv. Scient. Invest. Rep. 2006–5092.
- Fritz, P., Clark, I.D., Fontes, J.C., Whiticar, M.J., Faber, E., 1992. Deuterium and 13C evidence for low-temperature production of hydrogen and methane in a highly alkaline groundwater environment in Oman. In: Kharaka, Y.K., Maest, A.S. (Eds), Proc. 7th Internat. Symp. Water–Rock Interaction: Low Temperature Environments. A.A. Balkema, Rotterdam, pp. 793–796.
- Früh-Green, G.L., Connolly, J.A.D., Plas, A., Kelley, D., Grobety, B., 2004. Serpentinization of oceanic peridotites: implications for geochemical cycles and biological activity. In: Wilcock, W.S.D., DeLong, E.F., Kelley, D.S., Baross, J.A., Cary, S.C. (Eds), The Subseafloor Biosphere at Mid-Ocean Ridges, Washington, DC, pp. 119–136.
- Früh-Green, G.L., Schwarzenbach, E.M., Méhay, S., Lilley, M.D., Bernasconi, S.M., Molinari, M., Marini, L., 2009. Alkaline Fluids and Reduced Volatiles in Modern Serpentinizing Environments. Eos Trans AGU, Fall Meeting. AGU, San Francisco, California.
- Garrett, D.E., 1998. Borates Handbook of Deposits, Processing, Properties, and Use. Academic Press, San Diego, p. 483.
- Gunnarsson, I., Arnorsson, S., Jakobsson, S., 2005. Precipitation of poorly crystalline antigorite under hydrothermal conditions. Geochim. Cosmochim. Acta 69, 2813–2828.
- Kamineni, D.C., Gascoyne, M., Melnyk, T.W., Frape, S.K., Blomqvist, R., 1992. Cl and Br in mafic and ultramafic rocks – significance for the origin of salinity in groundwater. Water–Rock Interact. 1–2, 801–804.
- Kelemen, P.B., Matter, J., 2008. In situ carbonation of peridotite for CO₂ storage. Proc. Natl. Acad. Sci. USA 105, 17295–17300.
- Lemarchand, D., Gaillardet, J., Lewin, E., Allègre, C.J., 2002. Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. Chem. Geol. 190, 123–140.
- Lemarchand, E., Chabaux, F., Vigier, N., Millot, R., Pierret, M.C., 2010. Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France). Geochim. Cosmochim. Acta 74, 4612–4628.
- Lindquist, S.J., 2001. Petroleum Systems of the Po Basin Province of Northern Italy and the Northern Adriatic Sea: Porto Garibaldi (Biogenic), Meride/Riva di Solto (Thermal), and Marnoso Arenacea (Thermal). U.S. Department of the Interior, U.S. Geological Survey.
- Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. J. Hydrol. 270, 75–88.
- Marchiani, C., Venturelli, G., 2006. Studio pilota interdisciplinare per la valutazione e la gestione delle risorse idriche della Riserva Naturale Monte Prinzera. Ricerca realizzata nell'ambito del Programma Regionale di Investimenti nelle Aree Protette 2001–2003. <http://www.parchi.parma.it/allegato.asp?ID=674960>.
- Mattavelli, L., Ricchiuto, T., Grignani, D., Schoell, M., 1983. Geochemistry and habitat of natural gases in Po Basin, Northern Italy. AAPG Bull 67, 2239–2254.
- McCollom, T.M., 2007. Geochemical constraints on sources of metabolic energy for chemolithoautotrophy in ultramafichosted deep-sea hydrothermal systems. Astrobiology 7, 933–950.
- McCollom, T.M., Back, W., 2009. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. Geochim. Cosmochim. Acta 73, 856–875.
- Millot, R., Petelet-Giraud, E., Guerrot, C., Negrel, P., 2010. Multi-isotopic composition (δ7Li-δ11B-δD-δ180) of rainwaters in France: Origin and spatio-temporal characterization. Appl. Geochem. 25, 1510–1524.
- Millot, R., Guerrot, C., Innocent, C., Négrel, P., Sanjuan, B., 2011. Chemical, multiisotopic (Li–B–Sr–U–H–O) and thermal characterization of Triassic formation waters from the Paris Basin. Chem. Geol. 283, 226–241.
- Neal, C., Stanger, G., 1983. Hydrogen generation from mantle source rocks in Oman. Earth Planet. Sci. Lett. 66, 315–320.
- Oze, C., Sharma, M., 2005. Have olivine, will gas: serpentinization and the abiogenic production of methane on Mars. Geophys. Res. Lett. 32, L10203, 4.
- Palandri, J.L., Reed, M.H., 2004. Geochemical models of metasomatism in ultramafic systems: serpentinization, rodingitization, and sea floor carbonate chimney precipitation. Geochim. Cosmochim. Acta 68, 1115–1133.

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- Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC. Version 2: A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geol. Surv.: Earth Sci. Information Center, Open-File Reports Section [Distributor].
- Proskurowski, G., Lilley, M.D., Seewald, J.S., Früh-Green, G.L., Olson, E.J., Lupton, J.E., Sylva, S.P., Kelley, D.S., 2008. Abiogenic hydrocarbon production at Lost City hydrothermal field. Science 319, 604–607.
- Rice, D.D., 1992. Controls, habitat and resource potential of ancient bacterial gas. In: Vially, R. (Ed.), Bacterial Gas. Proc Conf. Held in Milan. Editions Technip, Milan, pp. 91–118.
- Scambelluri, M., Tonarini, S., 2011. The boron isotope composition of high-pressure subducted serpentinites: constraints on tectonic setting and implications for arc magmatism. Geophys. Res. Abstr. 13, EGU2011-2710.
- Scambelluri, M., Muntener, O., Ottolini, L., Pettke, T.T., Vannucci, R., 2004. The fate of B, Cl and Li in the subducted oceanic mantle and in the antigorite breakdown fluids. Earth Planet. Sci. Lett. 222, 217–234.
- Tomascak, P.B., 2004. Developments in the understanding and application of lithium isotopes in the earth and planetary sciences. In: Johnson, C.M., Beard, B.A., Albarede, F. (Eds.), Geochemistry of Non-Traditional Stable Isotopes, pp. 153–195.
- Tonarini, S., Pennisi, M., Gonfiantini, R., 2009. Boron isotope determinations in waters and other geological materials: analytical techniques and intercalibration of measurements. Isotop. Environ. Health Stud. 45, 169–183.

- Vengosh, A., De Lange, G.J., Starinsky, A., 1998a. Boron isotope and geochemical evidence for the origin of Urania and Bannock brines at the eastern Mediterranean: effect of water–rock interactions. Geochim. Cosmochim. Acta 62, 3221–3228.
- Vengosh, A., Kolodny, Y., Spivack, A.J., 1998b. Boron Isotope Systematics of Ground– Water Pollution, Applications of Isotopic Techniques to Investigate Ground-Water Pollution. The International Atomic Energy Agency (IAEA), Vienna, pp. 17–37.
- Vengosh, A., Weinthal, E., Kloppmann, W., Team, B., 2004. Natural boron contamination. Geotimes 49, 20–25.
- Venturelli, G., Contini, S., Bonazzi, A., Mangia, A., 1997. Weathering of ultramafic rocks and element mobility at Mt. Prinzera, Northern Apennines, Italy. Mineral. Mag. 61, 765–778.
- Vils, F., Müntener, O., Kalt, A., Ludwig, T., 2011. Implications of the serpentine phase transition on the behaviour of beryllium and lithium-boron of subducted ultramafic rocks. Geochim. Cosmochim. Acta 75, 1249–1271.
- Wedepohl, K.H., 1988. Spilitization in the ocean crust and seawater balances. Fortschritte Der Mineralogie 66, 129–146.
- Xiao, J., Xiao, Y.K., Liu, C.Q., Jin, Z.D., 2011. Boron isotope fractionation during brucite deposition from artificial seawater. Clim. Past Discuss. 7, 887–920.
- Yang, W., Rosenberg, P.E., 1995. The free-energy of formation of datolite. Am. Mineral. 80, 576–584.
- Zeebe, R., 2010. Stable boron isotope fractionation between dissolved $B(OH)_3$ and $B(OH)_4^-$. Geochim. Cosmochim. Acta 69, 2753–2766.