

PETROLOGICAL IMPLICATIONS FOR THE PRODUCTION OF METHANE AND HYDROGEN IN HYPERALKALINE SPRINGS FROM THE OTHRYS OPHIOLITE, GREECE

Tsikouras B.^{1,2}, Etiope G.^{3,4}, Ifandi E.¹, Kordella S.⁵, Papatheodorou G.⁵ and Hatzipanagiotou K.

¹University of Patras, Department of Geology, Section of Earth Materials, 265 00 Patras, Greece
v.tsikouras@upatras.gr, selenia.21@windowslive.com, k.hatzipanagiotou@upatras.gr,

²University of Brunei Darussalam, Department of Petroleum Geoscience, Jalan Tungku Link,
Gadong BE1410, Bandar Seri Begawan, Brunei Darussalam

³Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Italy,
Giuseppe.etiope@ingv.it

⁴Faculty of Environmental Science and Engineering, Babes-Bolyai University Cluj-Napoca,
Romania

⁵University of Patras, Department of Geology, Laboratory of Marine Geology and Physical Oceanography, 265 00 Patras, Greece, stacato77@hotmail.com, gpapathe@upatras.gr

Abstract

Altered mafic and ultramafic rocks were studied in correspondence with hyperalkaline, CH₄-bearing and very low-hydrogen spring waters in the Othrys ophiolite, whose chemical features are typical of present day serpentinisation. The H₂ paucity is interpreted as the result of the incorporation of high-silica, aqueous fluids, probably derived from mafic rocks. The vein assemblage of serpentine + magnetite is related to circulation of low-silica fluids whereas serpentine + talc, tremolite after garnet and Fe-rich serpentine in the interior of serpentine veins reflect a late circulation of low-temperature (likely below 120 °C), high silica activity fluids. The high-silica conditions might have limited or interrupted the production of H₂, which was subsequently consumed by CO₂ hydrogenation to produce CH₄. The lack of H₂ could also be due to peridotite alteration by CO₂-rich fluids. This would imply that the Othrys peridotites, among similar methane-bearing peridotites, may be considered as terrestrial analogues of Martian ultramafic rocks, which are thought to contribute to methane emission in the atmosphere of Mars. Understanding the mechanism of methane abiotic production will likely shed light to the details of some crucial aspects as the greenhouse-gas budget, the production of hydrocarbons and the origin of life on Earth.

Key words: Abiotic methane, Othrys ophiolite, serpentinisation, methane seepage.

Περίληψη

Μελετήθηκαν εξαιλιωμένα βασικά και υπερβασικά πετρώματα, από το οφιολιθικό σύμπλεγμα της Όθρυς, σχετιζόμενα με υπεραλκαλικές πηγές, πολύ χαμηλής περιεκτικότητας σε υδρογόνο, από τις οποίες ανακαλύφθηκε ότι εκπέμπεται CH₄, ο χημισμός των οποίων υποδεικνύει ότι προέρχονται από τρέχουσα σερπεντινίωση. Η απουσία H₂ οφείλεται πιθανά στη συμμετοχή υδατικών διαλυμάτων υψηλής

ενεργότητας SiO_2 , προερχόμενα από βασικά πετρώματα. Η παραγένεση σερπεντίνης + μαγνητίτης σε φλεβίδια, σχετίζεται με κυκλοφορία ρευστών χαμηλής ενεργότητας SiO_2 ενώ η παραγένεση σερπεντίνης + τάλκης, ο σχηματισμός τρεμολίτη σε βάρος γρανάτη και η παρουσία σερπεντίνη πλούσιου σε Fe, στο εσωτερικό φλεβιδίων σερπεντίνη, αντανακλούν μεταγενέστερη κυκλοφορία ρευστών χαμηλής θερμοκρασίας (πιθανά $< 120^\circ\text{C}$) με υψηλή ενεργότητα SiO_2 . Αυτά, πιθανά περιόρισαν ή διέκοψαν την παραγωγή H_2 , που εξαντλήθηκε λόγω αντίδρασης με το CO_2 για να παράγουν CH_4 . Η απουσία H_2 πιθανά οφείλεται ακόμα στην εξαλλοίωση των περιδοτιτών από ρευστά πλούσια σε CO_2 . Οι περιδοτίτες της Όθρυς, μεταξύ άλλων περιδοτιτών που περιέχουν μεθάνιο, μπορούν να θεωρηθούν ως τα γήινα ανάλογα υπερβασικών πετρωμάτων του πλανήτη Άρη, τα οποία θεωρούνται ότι συμβάλλουν στην εκπομπή μεθανίου στην ατμόσφαιρα του. Η κατανόηση του μηχανισμού παραγωγής αβιοτικού μεθανίου είναι πιθανό να δια φωτίσει τις λεπτομέρειες κρίσιμων θεμάτων, όπως το ισοζύγιο των αερίων του φαινομένου του θερμοκηπίου, το σχηματισμό ανώτερων υδρογονανθράκων καθώς και το μυστήριο της προέλευσης της ζωής στη Γη.

Λέξεις κλειδιά: Αβιοτικό μεθάνιο, οφιόλιθοι Όθρυς, σερπεντινίωση, διαφυγές μεθανίου.

1. Introduction

Present-day serpentinisation (i.e. hydration by meteoric water) of ultramafic rocks on continents is a widespread process documented in many countries (Barnes *et al.*, 1978; Marques *et al.*, 2008 and references therein). It is typically revealed by the occurrence of hyperalkaline waters ($\text{pH} > 10$) of Ca-OH type, depleted in magnesium and CO_2 , but with abundant methane (CH_4) and hydrogen (H_2). Hydrogen is produced by the olivine hydration, and methane is assumed to derive by subsequent Fischer-Tropsch Type (FTT) reactions, like the Sabatier reaction, $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$, which may be catalysed by metallic minerals typically occurring in ultramafic lithologies, such as magnetite, chromite and awaruite (see review by Etiope and Sherwood Lollar, 2013). Present-day serpentinisation typically occurs at temperatures below 100°C , which would imply that also abiotic methane synthesis takes place at such low temperatures (Etiope *et al.*, 2011, 2013). Accordingly, origin and exhalation of methane in serpentinised ultramafic rocks have attracted the interest of many scientists for its implication in planetary geology, astrobiology and energy resource exploration. In particular, serpentinites are considered as terrestrial analogues of hydrated olivine-bearing rocks on Mars, thus representing a possible source of methane observed in the Martian atmosphere (e.g., Oze and Sharma, 2005; Etiope *et al.*, 2011, 2012). Moreover, understanding the exact mechanism for abiotic methane production will have significant implications to our knowledge on the origin of life (e.g., Holm *et al.*, 2006; Russell *et al.*, 2010), as well as on hydrocarbon formation (Etiope and Sherwood Lollar, 2013).

While complete molecular and isotopic analyses of the gases represent the first fundamental step to understand their origin and, indirectly, the links with the serpentinisation process, petrological analyses of the serpentinised ultramafic rocks is an essential task to directly show the low temperature mineralogical changes which drive gas production, and in some cases, gas consumption. With this aim, we present a preliminary petrological study on serpentinised ultramafic rocks in association with altered mafic sequences of the Othrys ophiolite, in central Greece. At this site hyperalkaline springs, characteristic of present-day serpentinisation, show significant amounts of methane, with isotopic composition similar to that observed in other serpentinisation sites and crystalline environment (Etiope *et al.*, 2013). Unlike the gas in the Philippines, Turkey, New Zealand, Canada, Oman and Japan but similar to that found in peridotite inclusions in India and Oman, and in hyperalkaline springs in Italy and Portugal (Sachan *et al.*, 2007; Miura *et al.*, 2011; Boschetti *et al.*, 2013; Etiope *et al.*, 2013 and references therein), the Othrys springs release extremely low amounts of H_2 . Our petrological analysis was specifically

aimed at investigating mineralogical processes and features that may explain this H₂ depletion and the low temperature serpentinisation.

2. Geological Setting of the Othrys Ophiolite

The Othrys ophiolite comprises part of the eastern ophiolite belt in Greece, which is obducted to the west on the Pelagonian carbonate platform (e.g., Robertson, 2002; Papanikolaou, 2009; Robertson *et al.*, 2009). It is a dismembered and inverted suite composing of three structural units: The lowermost Sipetorrema Pillow Lava unit (after Smith *et al.*, 1975) includes pillow lavas, rare lava flows and interbedded siltstone and chert. The intermediate Kournovon Dolerite unit consists of minor cumulate gabbro cut by vertical sheeted dolerite dykes and local rhyolitic outcrops. The uppermost Mirna Group includes a series of inverted thrust sheets revealing lateral transition from continental material (clastic sediments and shallow water carbonates) to pelagic carbonates of the Mesozoic Pelagonian Zone (Smith *et al.*, 1975; Smith, 1993). The higher structural members comprise dismembered oceanic mantle rocks dominated by serpentinised harzburgite with minor lherzolite, plagioclase lherzolite and dunite (e.g., Dijkstra *et al.*, 2001; Barth *et al.*, 2003; Barth and Gluhak, 2009; Tsikouras *et al.*, 2009). In several places, massive chromitites predominate as podiform, lenticular or irregular ore bodies in serpentinised dunites within harzburgites, hosting platinum group elements and sulfides (Garuti *et al.*, 1999). The peridotites are in tectonic contact with an ophiolitic, tectonic mélange consisting of fragments of dolerite, basalt, red chert and serpentinised peridotite incorporated in a tectonised, multi-coloured, pelitic matrix (Dijkstra *et al.*, 2001; Tsikouras *et al.*, 2009).

The area of interest extends between Archani and Ekkara, at the southwestern part of the Othrys ophiolite and includes mantle exposures of medium- to coarse-grained serpentinised harzburgite with lesser plagioclase-bearing lherzolite, as well as dunite forming thin layers few cm to few meters thick, intercalated in the harzburgite (Figure 1). A remnant doleritic sheeted-dyke complex is overthrust by the peridotites. Locally, whitish rodingite dykes are found in serpentinised harzburgites very close to the Archani spring (Tsikouras *et al.*, 2009). The peridotites are in tectonic contact with an ophiolitic mélange, which in turn tectonically overlies a Late Cretaceous-Tertiary flysch. An active fault zone, the Leontari-Anavra line, extends immediately north of Ekkara, at the south border of the Thessaly Plain (Papathanassiou *et al.*, 2007).

3. Petrography

3.1. Serpentinised Peridotites

The ultramafic samples collected from the study area include variably serpentinised (20 – 80%) harzburgites and lesser dunites and lherzolites. The most intensely serpentinised harzburgites display mainly mesh and lesser ribbon and bastitic textures; local interlocking, interpenetrating and hourglass textures occur as replacements on older serpentines. The less altered harzburgite contains relics of orthopyroxene porphyroclasts, clinopyroxene, olivine and Cr-spinel. Rare plagioclase occupies interstices of the porphyroclastic grains and along with neoblastic clinopyroxene and olivine are typical indicators for melt impregnation in the peridotite. The serpentinised dunite shows porphyroclastic to cataclastic textures with the predominance of fragmented olivine; fewer, disseminated Cr-spinel and traces of clinopyroxene participate in its primary assemblage, too. The serpentinised lherzolite samples have protogranular, porphyroclastic and cataclastic textures. Primary phases include strained olivine, orthopyroxene, clinopyroxene and Al-spinel.

Besides serpentine, the secondary assemblage includes variable percentages of actinolite, magnetite and scarce talc, brucite, chlorite and calcite. The presence of the low temperature lizardite and chrysotile polytypes of serpentine is suggested from X-ray diffraction patterns (not given). Magnetite is regularly found in mesh cores, formed typically after olivine breakdown or in veins associated with serpentine (Figure 2a); it frequently rims spinel grains, too. Local garnet ± tremolite

pseudomorphically replaces orthopyroxene (Figure 2b), while talc appears along cleavage planes or at the rims of orthopyroxene occasionally with magnetite (Figure 2c). Actinolite in the altered lherzolites is associated to diopside. Calcite is also present either within mesh cores or filling veins traversing the samples (Figure 2d).

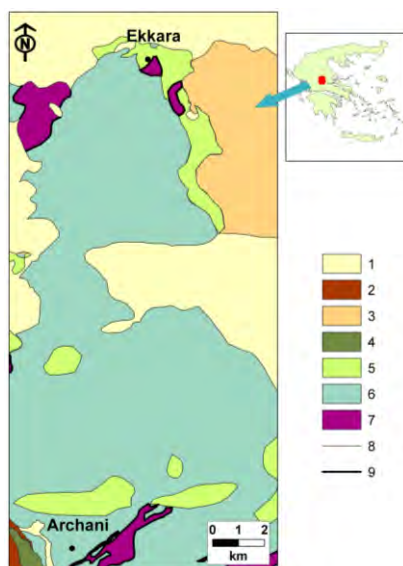


Figure 1 – Simplified geological map of the investigated area (modified after IGME, 1962, 1970; 1: Neogene – Quaternary deposits, 2: Eocene East Pindos flysch, 3: Upper Cretaceous transgressive limestone, 4: Lower Cretaceous sandstone, 5: Dolerite, 6: Serpentinised peridotite, 7: Ophiolite mélange, 8: normal contact, 9: tectonic contact).

Three vein assemblages were also observed: i) serpentine (mainly chrysotile), ii) serpentine + magnetite (Figure 2a; occasionally magnetite is altered to Fe-oxides and hydroxides), and iii) serpentine + talc $\pm$ Al-spinel (Figure 2e). Frequently a younger generation of serpentine richer in Fe is observed in the inner parts of veins rimmed by older serpentine richer in Mg (Figure 2f). Rarely, veins containing subsequent layers (from the outer to the inner parts) of chlorite, serpentine and magnetite were detected.

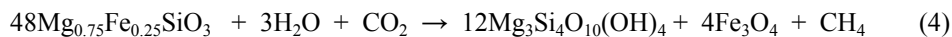
3.2. Dolerites

The collected dolerite samples show subophitic, porphyry and locally intergranular textures. They are composed mainly of plagioclase whereas relics of primary diopside occur, too. Accessory phases include titanite, magnetite, pyrite and chalcopyrite. Secondary products include actinolite, chlorite, Fe-Ti oxides, albite and quartz dispersed within the dolerite. Further petrographic details can be found in Tsikouras *et al.* (2009).

4. Discussion

Distinguishing present-day (meteoric water driven) from ancient (seawater driven) serpentinisation is not an easy task, as both events yield similar mineralogical products. The highly alkaline waters (pH = 10.7 – 11.3) of Ca-OH type from the Archani and Ekkara springs (Etiope *et al.* 2013) are very similar to brines that pass through present-day serpentinising peridotites (Barnes and O'Neil, 1969; Neal and Stanger, 1985). Indisputably, serpentinisation has also occurred as an ocean-floor metamorphic event in the ophiolite. Serpentinisation is a process that favours the production of fluids with low silica activity, normally of the order of $10^{-2.5}$ to 10^{-5} , depending on temperature.

On the other hand, talc formation after orthopyroxene is promoted by rather high silica activity ($>10^{-2}$; Frost and Beard, 2007; Evans, 2008) and may appear by a reaction similar to 4, which produces directly methane, too:



orthopyroxene

talc

magnetite

The lack of hydrogen in the Othrys springs can be explained either by: (i) its normal production (with the incorporation of low silica activity fluids alone, reactions 1 and 2) and subsequent consumption by CO_2 hydrogenation (Sabatier reaction) and/or expulsion to the surface by water degassing (H_2 solubility is one order of magnitude lower than that of CH_4); (ii) direct methanation (reactions 3 and 4) with the implication of low and high silica activity fluids. Although the first hypothesis cannot be excluded, there is enough petrological evidence that supports direct methanation in the case of the Othrys peridotite. The coexistence of magnetite and serpentine in mesh cores and bastitic textures, as well as in veins (Figure 2a) is compatible with the reaction 3 and the implication of low silica activity. Formation of garnet in the Othrys serpentinites provides further evidence for the establishment of low silica activity, which may have consequently partitioned ferrous iron in the andradite molecule (Beard and Hopkinson, 2000; Frost and Beard, 2007; Evans, 2008). Carbonate minerals (Figure 2d) are more stable phases relative to serpentine + brucite and their formation is favoured in CH_4 -rich fluids and low pressures (Früh-Green *et al.*, 2004), explaining the inferred brucite deficiency. However, often brucite forms cryptically in interlayers or is even misinterpreted as talc, serpentine, micas or clay minerals; hence its presence at higher percentages cannot be definitely precluded. Reaction 4 explains well the association of talc with orthopyroxene and magnetite (Figure 2c), as well its occurrence in veins with serpentine, denoting conditions of high silica activity. The CO_2 , which is required for the above reactions 3 and 4 can be provided by meteoric water and/or deep fluids related to the Jurassic carbonate basement of the Pelagonian Zone underlying the ophiolitic block (e.g. Karipi *et al.*, 2006).

The distribution of serpentine + magnetite veins indicates the flow directions of a fluid with low silica activity whereas the talc-bearing veins show the directions of a high silica activity fluid. Talc formation around orthopyroxene suggests large variations of silica activity even on the scale of a thin section. Notably, some talc-bearing veins crosscut some serpentine + magnetite veins (Figure 2e) and along with the formation of tremolite (a typical high-silica product) after garnet (Figure 2b) indicate a late stage entrance of the high silica activity fluids in the serpentinising system. Further evidence for a late high silica event is indicated by the presence of listwaenite after serpentinised peridotites, at the Iti Mountain, to the south part of the Othrys ophiolite (Tsikouras *et al.*, 2006). Such an increase in the potential of SiO_2 can lead to reaction of magnetite towards growth of Fe-rich serpentine (Evans, 2008), similar to that observed in some vein centers in the Othrys serpentinised peridotites (Figure 2f). Formation of Fe-rich serpentine is favoured at low temperatures and high silica activity, being stable even at ambient conditions (Streit *et al.*, 2012). Hence this younger Fe-rich serpentine most likely traces the present-day serpentinising episode. It is likely that the high silica activity fluid was sourced in the mafic sequence (e.g., dolerite or gabbro), lying tectonically below the ultramafic rocks in the Othrys ophiolite, being in equilibrium with their secondary assemblage (chlorite, actinolite, quartz). This rather hot fluid moves upwards and upon cooling, at near surface conditions, it is involved, concurrently with the existing low silica fluid, to reactions of serpentinisation, contributing to methane formation.

Methane and hydrogen emanations associated with high temperature (>100 – 200 °C) hydrothermal fluids in the mid-Atlantic Ridge have been widely studied (Charlou *et al.*, 2002; Proskurowski *et al.*, 2008; Lang *et al.*, 2010). The occurrence of abiogenic methane in low temperature (generally <100 °C) continental serpentinisation sites (Etiope *et al.*, 2011; Etiope *et al.*, 2013) implies that high enthalpy hydrothermal conditions are not necessary for the hydrocarbon synthesis, which can then occur in a broad range of environments, either on Earth or other planets. Lizardite and chrysotile that occur in the assemblage of the Othrys peridotites are stable up to 300 – 350 °C, unlike an-

tigorite that is the high-temperature polytype of serpentine. Talc and tremolite are usually considered as high-temperature products, since they are predicted to form above 370 °C (Bucher and Frey, 2002; McCollom and Bach, 2009). However, talc is known to be stable at much lower temperatures, even at around 25 °C (Klein and Garrido, 2011), which is in line with the circulation of a low-temperature-high-silica fluid that also imposed the late Fe-rich serpentine in veins.

5. Conclusions

Petrographic observations on mafic and ultramafic rocks collected in the Othrys ophiolite, around methane-bearing hyperalkaline springs (Etiope *et al.*, 2013) show some mineralogical features that may explain the paucity of H₂ in the brines. The serpentinised peridotites contain the secondary assemblage: serpentine (lizardite + chrysotile), magnetite, garnet, and minor brucite, indicating alteration under low silica activity conditions. Formation of talc after orthopyroxene and tremolite after garnet, as well as the occurrence of Fe-rich serpentine in vein centers are compatible with a late-stage involvement of a fluid of high silica activity. Two reactions of direct methanation of olivine and orthopyroxene are proposed as a possible explanation for the paucity of hydrogen in the Archani and Ekkara spring-waters, during present-day serpentinisation. Another explanation is that the implication of the high silica activity fluid that probably ascends upwards from the tectonically underlying mafic rocks may have prohibited further production of H₂, which then was consumed by hydrogenation and degassing. The occurrence of late-stage Fe-rich serpentine advocates to a low-temperature present-day serpentinising event while the occurrence of talc does not contradict low temperature serpentinisation, as documented in other similar sites. Future work must include petrographic observations in other present-day serpentinisation sites for comparison, as well as additional analyses, including Raman spectroscopy and geothermometric calculations, to better understand the production of methane and hydrogen in relation to the formation of certain mineral phases. Microbiological analyses are then planned to evaluate possible microbial contribution to gas production and consumption, providing further elements to understand the role of serpentinisation in the origin of life on Earth.

6. Acknowledgements

The authors gratefully acknowledge funding from the project “Low temperature methanation in geologic environments” by Petrobras. Critical reviews from Dr. I. Baziotis and two anonymous reviewers are gratefully acknowledged.

7. References

- Bach W., Paulick H., Garrido C.J., Ildefonse B., Meurer W.P. and Humphris S.E. 2006. Unraveling the sequence of serpentinization reactions: Petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274), *Geoph. Res. Lett.*, 33, 13.
- Barnes I. and O’Neil J.R. 1969. The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States, *Geol. Soc. Am. Bull.*, 80, 1947-1960.
- Barnes I., O’Neil J.R. and Trescases J.J. 1978. Present day serpentinization in New Caledonia, Oman, and Yugoslavia, *Geochim. Cosmochim. Acta*, 42, 144–145.
- Barth M.G. and Gluhak T.M. 2009. Geochemistry and tectonic setting of mafic rocks from the Othris Ophiolite, Greece, *Contrib. Mineral. Petrol.*, 157, 23–40.
- Barth M.G., Mason P.R.D., Davies G.R., Dijkstra A.H. and Drury M.R. 2003. Geochemistry of the Othris Ophiolite, Greece: Evidence for Refertilization?, *J. Petrol.*, 44, 1759-1785.
- Beard J.S., and Hopkinson L. 2000. A fossil, serpentinization-related hydrothermal vent, Ocean Drilling Program Leg 173, Site 1068 (Iberia Abyssal Plain): Some aspects of mineral and fluid chemistry, *J. Geoph. Res.*, 105, 16.527-16.539.

- Boschetti T., Etiope G., Guerrot C., Pennini M., Romani M. and Toscani L. 2013. Boron, lithium and methane isotope composition of hyperalkaline waters (Northern Apennines, Italy): terrestrial serpentinization or mixing with brine?, *Appl. Geochem.*, 32, 17-25.
- Bucher K., Frey M. 2002. *Petrogenesis of metamorphic rocks*, 7th ed. Springer-Verlag, Berlin, Heidelberg, New York, 341 pp.
- Charlou J.L., Donval J.P., Fouquet Y., Jean-Baptiste P. and 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.
- Dijkstra A.H., Drury M.R. and Vissers R.L.M. 2001. Structural petrology of plagioclase peridotites in the West Othris mountains (Greece): melt impregnation in mantle lithosphere, *J. Petrol.*, 42, 5-24.
- Etiope G. 2012. Methane uncovered, *Nature Geosci.*, 5, 373-374.
- Etiope G., Schoell M. and Hosgormez 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. and 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>.
- Etiope G. and Sherwood Lollar B. 2013. Abiotic methane on Earth, *Rev. Geoph.*, 51, doi:10.1002/rog.20011.
- Etiope G., Tsikouras B., Kordella S., Idandi E., Christodoulou D. and Papatheodorou G. 2013. Methane flux and origin in the Othrys ophiolite hyperalkaline springs, Greece, *Chem. Geol.*, 347, 161-174.
- Evans B.W. 2008. Control of the products of serpentinization by the Fe²⁺Mg⁻¹ exchange potential of olivine and orthopyroxene, *J. Petrol.*, 49, 1873-1887.
- Frost B.R. and Beard J.S. 2007. On silica activity and serpentinization, *J. Petrol.*, 48, 1351-1368.
- Früh-Green G.L., Connolly J.A.D., Plas A., Kelley D.S. and 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., Craig Cary, S. eds., *The seafloor biosphere at Mid-Ocean-Ridges: American Geophysical Union*, Washington, D.C., doi: 10.1029/144GM08.
- Garuti G., Zaccarini F. and Economou-Eliopoulos M. 1999. Paragenesis and composition of laurite from chromitites of Othrys (Greece): Implications for Os-Ru fractionation in ophiolitic upper mantle of the Balkan peninsula, *Miner. Deposita*, 34, 312-319.
- Holm N.G., Dumont M., Ivarsson M. and Konn C. 2006. Alkaline fluid circulation in ultramafic rocks and formation of nucleotide constituents: a hypothesis, *Geochem. Trans.*, 7, 7 doi:10.1186/1467-4866-7-7.
- IGME 1962. Geological Map of Greece, Leontarion Sheet, Institute of Geology and Mineral Exploration, Athens, Greece.
- IGME 1970. Geological Map of Greece, *Sperkhis Sheet*, Institute of Geology and Mineral Exploration, Athens, Greece.
- Karipi S., Tsikouras B. and Hatzipanagiotou K. 2006. The petrogenesis and tectonic setting of ultramafic rocks from Iti and Kallidromon Mountains, continental Central Greece: vestiges of the Pindos ocean, *Can. Mineral.*, 44, 267–287.
- Katayama I., Kurosaki I. and Hirauchi K-I. 2010. Low silica activity for hydrogen generation during serpentinization: An example of natural serpentinites in the Mineoka ophiolite complex, central Japan, *Earth Plan. Sci. Lett.*, 298, 199-204.
- Klein F. and Garrido C.J. 2011. Thermodynamic constraints on mineral carbonation of serpentinized peridotite, *Lithos*, 126, 147-160.
- Lang S.Q., Butterfield D.A., Schulte M., Kelley D.S. and Lilley M.D. 2010. Elevated concentrations of formate, acetate and dissolved organic carbon found at the Lost City hydrothermal field, *Geochim. Cosm. Acta*, 74, 941–952.

- Marques J.M., Carreira P.M., Carvalho M.R., Matias M.J., Goff F.E., Basto M.J., Graça R.C., Aires-Barros L. and Rocha L. 2008. Origins of high pH mineral waters from ultramafic rocks, Central Portugal, *Appl. Geochem.*, 23, 3278–3289
- McCollom T.M. and Bach W. 2009. Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks, *Geochim. Cosmochim. Acta*, 73, 856–879.
- Miura M., Arai S. and Mizukami T. 2011. Raman spectroscopy of hydrous inclusions in olivine and orthopyroxene in ophiolitic harzburgite: implications for elementary processes of serpentinization, *J. Miner. Petrol. Sci.*, 106, 91–96.
- Neal C. and Stanger G. 1985. Past and present serpentinisation of ultramafic rocks from the Semail nappe of northern Oman. In Drever, J.I., ed., *The Chemistry of Weathering, Reidel. NATO ASI Series C*, 149, 249–275.
- Oze C. and Sharma M. 2005. Have olivine, will gas: serpentinization and the abiogenic production of methane on Mars, *Geoph. Res. Lett.*, 32, L10203.
- Papanikolaou D. 2009. Timing of tectonic emplacement of the ophiolites and terrane paleogeography in the Hellenides, *Lithos*, 108, 262–280
- Papathanassiou G., Valkaniotis S. and Pavlides S. 2007. Applying the INQUA scale to the Sofades 1954, Central Greece, earthquake, *Bull. Geol. Soc. Greece*, 40, 1226–1233.
- Proskurowski G., Lilley M.D., Seewald J.S., Früh-Green G.L., Olson E.J., Lupton J.E., Sylva S.P. and Kelley D.S. 2008. Abiogenic hydrocarbon production at Lost City hydrothermal field, *Science*, 319, 604–607.
- Robertson A.H.F. 2002. Overview of the genesis and emplacement of Mesozoic ophiolites in the Eastern Mediterranean Tethyan region, *Lithos*, 65, 1–67
- Robertson A., Karamata S. and Šarić K. 2009. Overview of ophiolites and related units in the Late Palaeozoic–Early Cenozoic magmatic and tectonic development of Tethys in the northern part of the Balkan region, *Lithos*, 108, 1–36.
- Russell M.J., Hall A.J. and Martin W. 2010. Serpentinization as a source of energy at the origin of life, *Geobiology*, 8, 355–371.
- Sachan H.K., Mukherjee B.K. and Bodnar R.J. 2007. Preservation of methane generated during serpentinization of upper mantle rocks: Evidence from fluid inclusions in the Nidar ophiolite, Indus Suture Zone, Ladakh (India), *Earth Planet. Sci. Lett.*, 257, 47–59.
- Smith A.G. 1993. Tectonic significance of the Hellenic-Dinaric ophiolites, In Prichard, H.M., Alabaster, T., Harris, N.B.W., Neary, C.R., eds., *Magmatic Processes and Plate Tectonics, Geol. Soc. Sp. Publ.*, 76, 213–243.
- Smith A.G., Hynes A.J., Menzies M., Nisbet E.G., Price I., Welland M.J. and Ferriere J. 1975. The stratigraphy of the Othris Mountains, eastern central Greece: a deformed Mesozoic continental margin sequence, *Eclog. Geol. Helv.*, 68, 463–481.
- Streit E., Kelemen P. and Eiler J. 2012. Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite, Oman, *Contrib. Mineral. Petrol.*, 164, 821–837.
- Tsikouras B., Karipi S., Grammatikopoulos T.A. and Hatzipanagiotou K. 2006. Listwaenite evolution in the ophiolite melange of Iti Mountain (continental Central Greece), *Eur. J. Mineral.*, 18, 243–255.
- Tsikouras B., Karipi S., Rigopoulos I., Perraki M., Pomonis P. and Hatzipanagiotou K. 2009. Geochemical processes and petrogenetic evolution of rodingite dykes in the ophiolite complex of Othrys (Central Greece), *Lithos*, 113, 540–554.