Natural Hydrogen Exploration Guide

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ABSTRACT

Based on previous detection of natural hydrogen seepages in ophiolitic massifs (Oman, Dinarides, New Caledonia), the bases of a natural hydrogen emissions exploration guide within the Western Alpine orogenic system is presented: (I) the geodynamic evolution of ophiolites in this area, (II) the seismic background associated with fluid circulation and (III) the mineralogy, have been analyzed to identify the optimum environment for natural hydrogen formation and migration. The production of hydrogen results from, among other aspects, the mineralogical composition of the rock in which the fluid circulated, the degree of alteration of the rock and the geological history of the ophiolite. The hydration of the peridotite is supposed to happen during a pre-obduction stage (hydrothermalism of the seabed), by ascension (metasomatism) and a secondary cycle of syn- and post-obductions by percolation (meteoric). Presences of antigorite and/or chrysolite are evidence to this significant fluid circulation. Nethertheless only small proportions of H_2 have been recorded in the investigated zones with almost negligible flow rates. The remaining key factor to be identified seems to be related to a favorable underground zone, like aquifers, where accumulation of H_2 can occur.

INTRODUCTION

Natural hydrogen production can be induced by abiotic reactions such as serpentinization (oxidation of Fe^{2+}), hydration of peridotite, bacterial activity, radiolysis of water, degassing of the mantle, cracking of organic matter at high maturity (Vacquand, 2011). As many ophiolitic massifs in orogenic context exhibits significant hydrogen seepages (e.g. Oman, New-Caledonia), the potential existence of similar hydrogen fluxes in the Western Alps is still an open question. Here, we propose a geological, geodynamic, seismic and mineralogical analysis of the ophiolitic environment of the Western Alps in order to localize possible hydrogen concentration at ground surface. In this study, we focus on H_2 supposed to be generated as a result of water interaction with ultrabasic oceanic rocks of the Western Alps from the Tethys ocean basin (Manatschal and Muntener, 2009).

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The serpentine system (Fig. 1) is generally attributed to the hydration of a paleo seafloor as well as the hydration of the peridotite from the mantle during the subduction process. The latter results from the interaction of water with minerals rich in Fe-Mg, such as olivine or pyroxene (Marcaillou, 2012). Ophiolitic complexes that have been subducted and exhumed may also undergo several additional episodes of serpentinization during the metamorphic prograde and retrograde paths (Cedric et al., 2013). Subsequently, they can be altered by alkaline meteoric fluids ($pH > 9$) at the surface which also induced hydrogen (Ulrich, 2013).

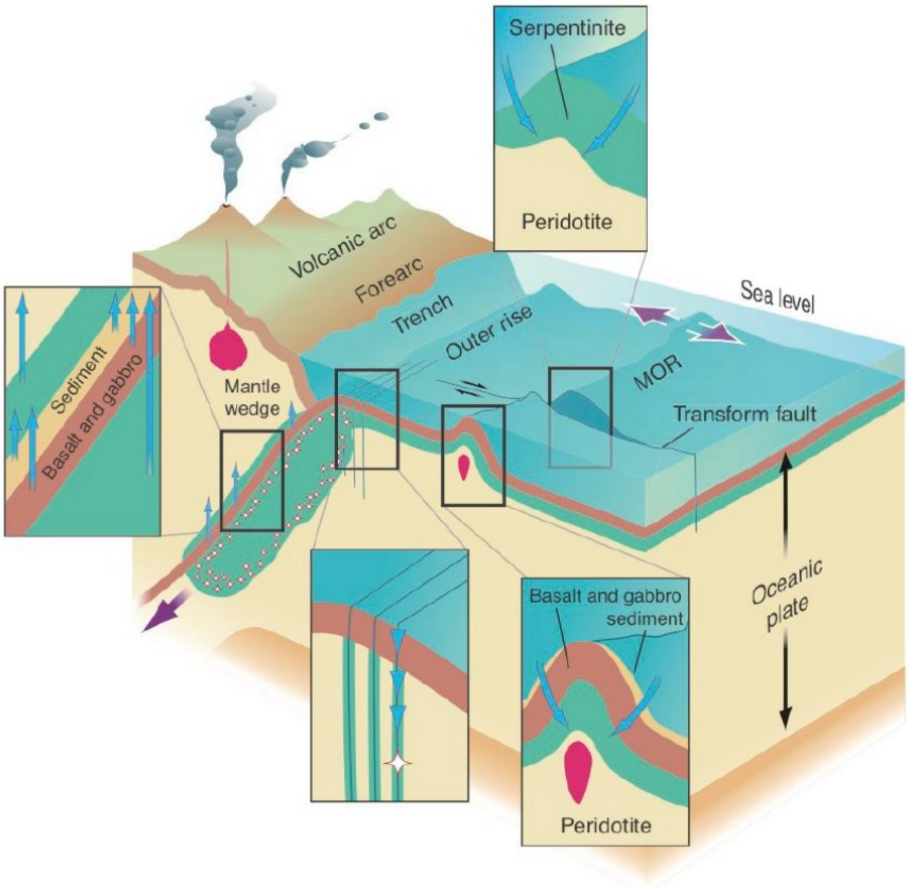

Figure 1: Schematic representation of the main serpentine formation areas (from Kerrick, 2002; Ulrich, 2010). The pink arrows represent the movement of the plates, the magmatic areas are represented in red, the blue arrows show the infiltration and extraction areas of fluid. (1) Circulation of hydrothermal fluids in the ridge axis. (2) Serpentinization of the abyssal peridotite triggered by transforming faults. (3) Serpentinization induced by the play of normal faults formed by the subduction plunging of the plate forming a local extensive regime. (4) Serpentinization of the mantel corner by fluids resulting from the dehydration of the plunging plate.

Hydrogen forms during the oxidation of ferrous iron (Fe^{2+}) in olivine and orthopyroxene to ferric iron (Fe^{3+}) in secondary minerals through reaction with water by means of these serpentine processes. During this process, serpentine and magnetite are generated (Hosgormez. et al., 2008) as described in the following reaction:

$$6(Mg, Fe)_2SiO_4 + 7H_2O = 3(Mg, Fe)_3Si_2O_5(OH)_4 + Fe_3O_4 + H_2$$

Olivine + Enstatite + Water = Serpentinite + Magnetite + Hydrogen

Significant sources of hydrogen are found in the ophiolites massifs of Oman, Turkey, New Caledonia and the Western and Eastern Alps (Dinarides and Lanzo Massif).

Ophiolite from New Caledonia

Ophiolites (mainly peridotite: Fe-Mg silicate) in New Caledonia are outcropped of the southwestern edge of the lithospheric mantle that forms the base of the Outaouais Valley (Deville and Prinzhofer, 2016).

Within the hyperalkaline springs in the peridotite massif south of New Caledonia (Prony area), a seepage presence of natural gas rich in N_2-H_2-CH_4 was analyzed containing proportions of N_2 between 50 - 62%, H_2 between 26 - 36% and CH_4 between 11-16% in hyperalkaline thermal springs (pH = 10.5-10.9, T°C = 30 - 40 °). These sources are associated with low-temperature serpentinization processes reducing water during the oxidation of Fe2+ in a shallow aquifer (Deville & Prinzhofer, A., 2016).

The presence of anastomosed penetrating serpentine veins is related to the initial phase of serpentinization processes that affect peridotite. This network consists of lizardite whose crystallization corresponds to the classical destabilization reaction of olivine in the presence of fluid. The fluid source is believed to be of deep origin (ante-obduction: seawater and metasomatic fluids from dehydration of the plunging plate) and meteoric (supergenic nature: post-obduction). A few micro-veinlets of chrysotile fibrous crystallization intersecting lizardite were observed at the edge of the serpentine basement. This is an evidence of fluid circulation (Ulrich, 2013).

Balkan ophiolite (Dinarides)

Peridotite massifs (mainly lherzolite) of the Balkans belong to the fractured, mylonitized and serpentinized ophiolitic belt of the Dinarides. They are part of the Alpine-Himalayan suture zone originated from the Neo-Tethys Ocean. Within these peridotites, olivine, orthopyroxene and clinopyroxene are the primary minerals that composed the rock associated with high proportion of MgO, spinel and amphibole. Secondary minerals of the serpentine group (lizardite, clinochrysotile and antigorite), enstatite and magnetite are also widely distributed.

This ultrabasic belt is separated by two faults systems: the Spreca-kozara fault in the NE and the Novi Grad-Banjaluka-Olovo-Vegrad fault in the SW. Gas sources are located along the contact zone between ultramafic rocks and sedimentary rocks, i.e. graywacks, cherts, amphibolites and limestone.

The geothermal gradient within this Dinarides belt is 30°C/km. High temperatures (120°C) can occur due to fluid convection. The pH of these fluids is about 12.3. According to the isotopic ratio ($\delta^2H_{H20} - \delta^{18}H_{H20}$), the nature of this hyperalkaline water is a likely consequence of meteoric water.

A hydrogeological scenario of these waters predicts a deep circulation of these fluids in ultramafic rocks, thereby inducing serpentinization. These fluids can also react with a formerly serpentinized rock. A reaction between the meteoric fluids and the environment can induce the formation of H_2 which can migrate as a gas phase or be transported by groundwater and stored in a permeable and porous rock reservoirs (like aquifers). The karst aquifer is hosted in a tectonized peridotite, intersected by faults that act as drainage pathways (Etiope et al., 2017).

Ophiolite of the Lanzo Massif (Western Italian Alps)

The Lanzo Massif is a large body of ultramafic rocks (peridotite) located in the internal part of the Western Italian Alps. This body is a remnant of the Mesozoic Tethysian lithosphere that underwent peak eclogite – facies metamorphism during the Cenozoic Alpine subduction at 550-600°C and 2-2.5 GPa. These ultramafic rocks experienced various interactions with fluids during seafloor hydrothermalism but also inside the subduction zone. The latter generated a large domain dominated by serpentinization (20-100% serpentine) in the mantle peridotite associated with a significant H_2 production at high temperature subduction zone (400°C).

In the northern part of the Lanzo Massif, a body of ophicarbonate is localized within the serpentinized peridotites which locally preserve their primary mantle structure. The ophicarbonate is characterized by various deformed clasts of serpentinite within a carbonate-dominated matrix. This outcrop is generally affected by intense deformation along the ductile shear zone that results in fragmentation, stretching, boudinage of serpentine clasts and intense veining. These veins are evidence of significant fluid circulation. Ophicarbonates that underwent little deformation are composed of serpentinite clast such as antigorite as well as chlorite and magnetite (Brovarone et al., 2016).

WEST OF THE WESTERN ALPS

The present Alpine chain has been generated by a multi-phase geodynamic history (compressive and extensive episodes) of the remnant Alpine/Tethysian oceanic lithosphere (see Fig. 2).

During the Africa-Europe convergence (80 Ma ago), the structure of the internal Alpine zone is inherited from the overlapping between the European plate and the microplate of the Southern Alpine (Le Golf et al., 2009, Sue and Tricart, 2003).

From the Triassic to the Cretaceous, an opening of the Tethysian Ocean followed by its closure induces significant fracturation in the basement associated with accretion prism and obduction process. Evidences of this ocean are found in the ophiolitic massifs (serpentinized peridotite) along the Alpine arc (Le Golf et al., 2009).

During the Eocene, the European passive margin (external part of the Alpine chain) is subducted by the Apulian plate (internal zone), which induces the formation Piemont and Briançon zones. Between the external (European) and internal (Penninic) units in the Western Alps, the so-called Penninic thrustfront is localized (Le Golf et al., 2009).

The opening of the Bay of Biscay (Oligocene - Miocene) leads to the rotation of the Apulian plate, which induces an extensive regime in the Piemont and Briançon zones of the chain alpine. The Briançon overlap plays then into a detachment fault (a normal fault of regional importance with a shallow dip) and the late alpine normal faults of the Haute-Durance and Serenne are generated.

The current internal part of the Alps are subjected to a transtensive regime, perpendicular to the alpine structures axis, of about 1 to 1.5 mm/year allowing the installation of dextral normal faults NS to NO-SE. (Sue and Tricart, 2003; Le Golf et al., 2009).

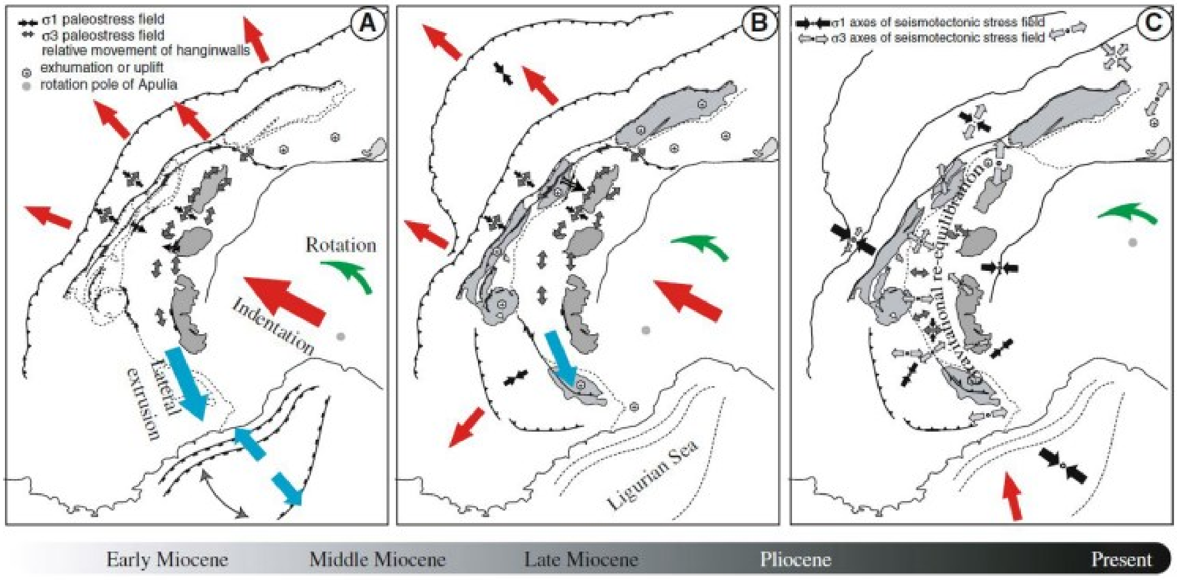

Figure 2: Tectonic diagram representing the evolution of the geodynamic context of the Western and Central Alps from the Miocene to the present day: compressive movements in red, extensive movements in blue and descending in green); black and white arrows represent respectively: compressive and extensive constraints. (from Sue et al., 2007).

Geological context of the western alpine range

The Alps result from the closure of the Ligurian Ocean and the collision of the European and Apulian margins. This massif is composed of oceanic (meta-phiolites and oceanic metasediments) and continental (European and Apulian margins) units. Ophiolites outcrop mainly in the west in the Western Alps. The Eastern Alps, generally described as Austro-Alpine domain, contain portions of Apulian oceanic lithosphere deformed and metamorphosed under ecologic facies conditions (see Fig. 3), (Lardeaux et al., 2006).

The first area of interest (zone A) is located within:

- The Briançon unit, which is mainly, composed of Paleozoic and Mesozoic sediments and Precambrian basement rocks (magmatic and metamorphic).
- The Piemont unit, which consists of Queyras shale facies derived from Mesozoic oceanic sediments and the eclogitized ophiolitic complexes of Mount Viso and Rocciavré.
- The external unit of the crystalline Massif (Argentière-Mercantour, Pelvoux)
- Heminthoid's flysch unit (Lardeaux et al., 2006).

Regarding this first area, a field data collection has been done during October 2018 (black dots, Fig. 3)

A second area of interest (Zone B) (yellow dots, Fig. 3) was investigated in August 2018. It is located southeast of the Dent Blanche nappe or klippe, northeast of the Sésia-Lanzo zone of the periadriatic zone, between the Austroalpine units (Dent Blanche nappe and Sesia zone) within the Piemont blue schist facies and northeast of the Belledome.

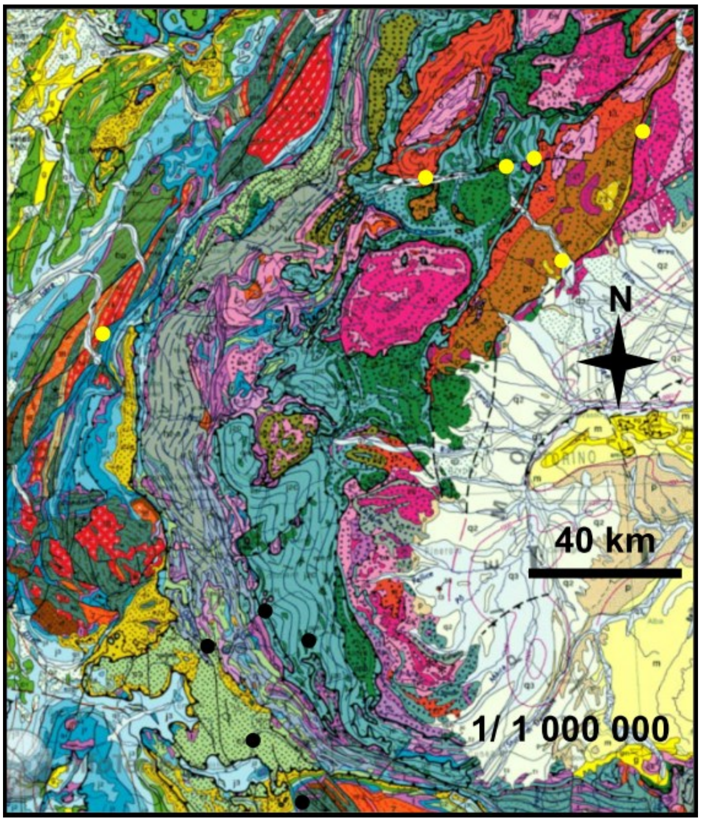

Figure 3: field data collection (black dots for zone A and yellow dots for zone B) from the two 2018 field trips (Geological map: BRGM, 1996).

Seismic context and fluid circulation in the area A

The geological environment of area A is characterized by numerous ophiolitic complexes. Two determining parameters could justify this area to be investigated for potential accumulation of hydrogen in the Western Alps: the seismic context (Fig. 4-5) associated with fluid circulation.

The area of interest is sandwiched between the outer zone (Helvetic-Dauphine) and the inner zone (Valaisane, Brianconnaise, Piemontaise, Astro and Sub-Alpine) near the Pennique Front and within and near the Sérenne, Haute-Durance, Argentera-Bersezio and NE-SW transverse fault systems (Fig, 4), (Le Golf et al., 2009):

- The fault system of the Haute Durance with an orientation of N165° extends over a width of 6 to 7 km and is composed of normal, conjugate or restricting faults of collapsed and tilted blocks,
- The Serenne fault system (N130°E) is located in the meridional extension of the Durance fault. It is described by a pull-apart structure with major dextral NW-SE and secondary N-S faults,
- The dextral Argentera-Bersezio fault system mainly affects the basement of the external part of the Alps (Argentera-Mercantour Massif).

- The NE-SW transversal faults system of kilometric length is mainly visible in the inner Alps. These faults, which are sinistral and transversal to the faults of the Haute Durance and Serenne, would still play an active role in this part of the Alps.

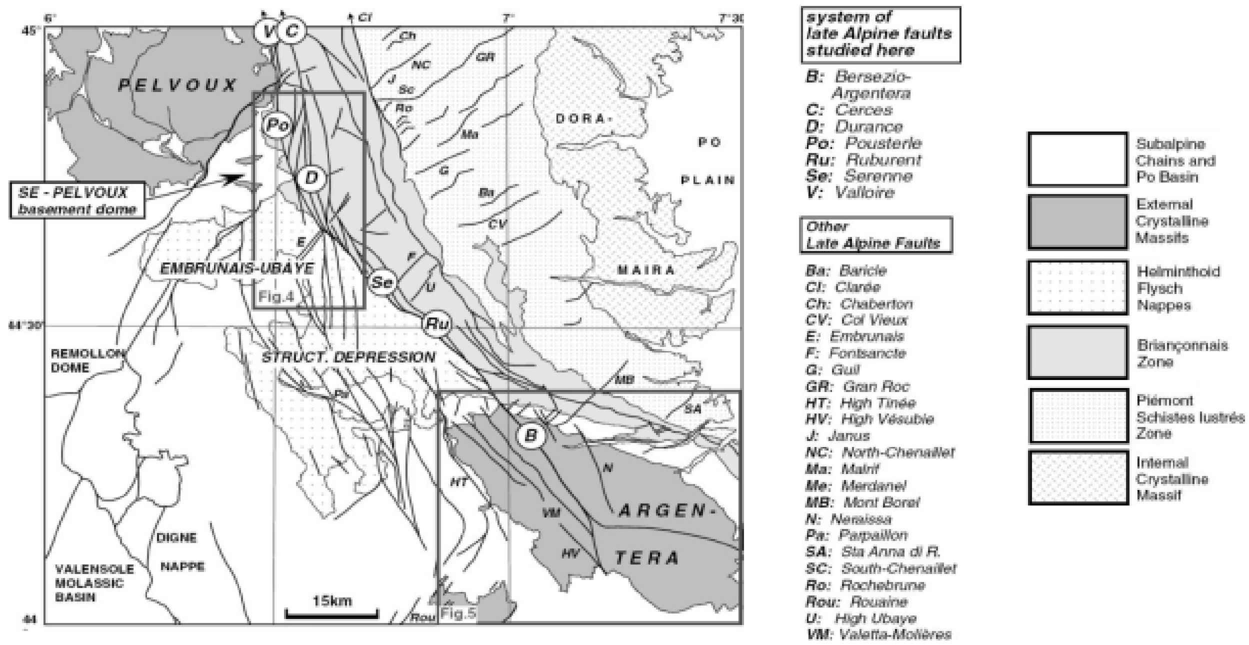

Figure 4: Schematic map of the longitudinal and transverse faults between Pelvoux and Argentera (from Tricart, 2004)

This study area is thus described as a highly earthquake prone region where seismic activity is continuous (Fig. 5; Thouvenot, 2002):

- From 1959 to 2015, many earthquakes of magnitudes 4.5 to 5.5 (Medvedev-Sponheuer-Karnik scale) as well as more than 20,000 seismic swarms occurred north of Barcelonnette at the border of Saint-Paul sur Ubaye, La Condamine-Chatelard and Crévoux,
- To the north, the Queyras massif is located in a Serenne fault system intersected by a NE-SW transverse fault system,
- To the south, the Argentière massif is also marked by the Argentera-Bersezio fault system.

Several mechanical processes are likely to cause earthquake swarm. The spatial and temporal variation in fracture activity can be modelled by a migration of high pressure fluid into a porous fault zone (Yamashita, 2014).
Analyzing the behavior of the spatio-temporal seismicity in 2012 and 2015 in the upper Ubaye valley and in 2003-2004, Thouvenot et al. (2016) suggested a fluid migration in this environment corresponding to a hydraulic diffusivity of 0.05 $m^2.s^{-1}$. This migration would result from a stress transfer due to the main shocks on the surrounding faults, thus modifying fluid flow and allowing fluid migration and seismicity.

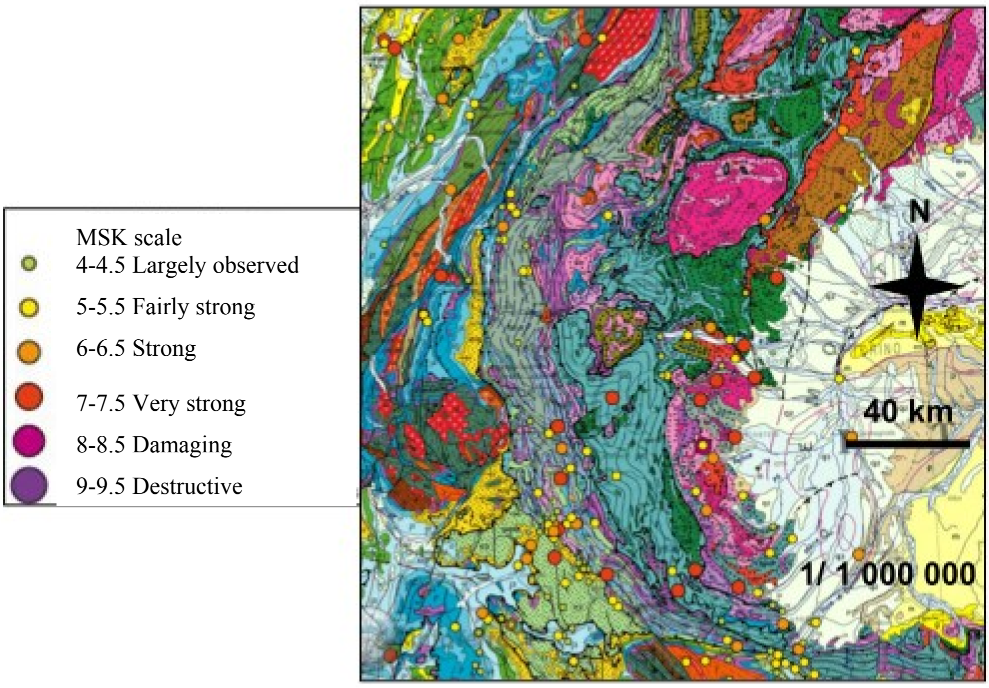

Figure 5: Geological map describing the areas impacted by seismic and their associated seismic intensities (BRGM, 2018).

APPARATUS – NATURAL HYDROGEN DETECTION USING GA 5000

In order to study the level of hydrogen in the areas of interest in the Western Alps, a Ga 5000 detector was used (SGX sensortech 2017). The SGX electrochemical sensors detect gases by producing a chemical reaction between the gas and oxygen contained in the sensor. The sensor is a type of fuel cell (Fig 6A).

The reaction occurs on two electrodes: a sensing electrode and a counter electrode (Fig. 6A – B) thought the oxidation of a reducing agent (anode), and the reduction of an oxidant on the counter electrode (cathode) (Pettinger, 2017).

The electrodes are kept apart and wetted with an acid electrolyte to allow an ionic current to pass between them. This is done by using discs of absorbent materials or separators (Fig. 6B). The oxygen required for the reaction is found dissolved in the electrolyte. Oxygen diffusion comes from the housing located behind the sensor (not shown in Fig. 6) (SGX sensortech 2017, H_2Sys 2017). Because the electrodes have limited catalytic activity (which can vary with temperature and time), it is necessary to reduce the diffusion rate of the target gas in the sensor using a barrier. This barrier takes the form of a small hole in the sensor housing.

The chemical reaction within the fuel cell is (fig. 6):

$$2H_2 + O_2 => 2H_2O$$

At the anode, the hydrogen molecule in contact with the catalyst decomposes and releases electrons that will create the electric current:

$$2H_2 => 4H^+ + 4e^-$$

At the cathode, the oxygen reacts with the electrons released by the previous reaction:

$$O_2 + e^- = 2\ O^{-2}$$

Finally, when the hydrogen protons reach the cathode, they react with the oxygen ions and induce water:

$$H^+ + 2O^{-2} => 2H_2O$$

The water thus formed is trapped in a filter and is measured at the same time as the dry hydrogen.

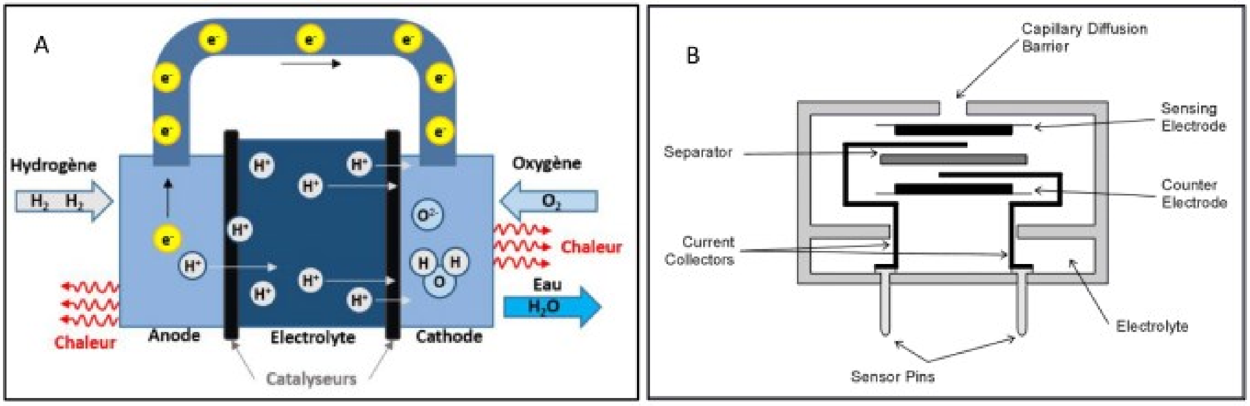

Figure 6: (A) Schematic representation of a fuel cell (H_2Sys Hydrogen to system, 2019) and (B) the hydrogen detector installed in the Ga 5000 (SGX, Sensortech, 2017).

FIELD DATA COLLECTION

To get monitoring points in soils or rocks, holes between 25 mm and 30 mm in diameter were drilled in which the collecting tube of the GA5000 was plugged (see Fig. 7).
Despite the ophiolitic complexes and the seismic context associated with fluid flow in zone A (see Fig. 3, black dots), hydrogen contents remained very low.
The average proportion of H_2 on 54 measured sites varies mainly between 1 and 69 ppm with a peak at 99 ppm. The latter is located in the serpentine quarry veined with calcite called Green Marble in Saint-Véran. This higher proportion of hydrogen was found in a finely fibro-laminar crystallization plane of pale green color, centimetric to decametric thick, affecting the green marble massif (Fig. 8). The nature of this fribo-lamellar crystallization may refer to antigorite (fribo-lamellar variety with high serpentine temperature) and/or chrysolite (fibrous variety with medium serpentine temperature).

Figure 7: Top left: first stage: drilling in the rock. Top right: plugging the hose connected to the GA5000 to collect and analyze the gas. Bottom left: drilling in a soil before collecting gas to be analyzed. Bottom right: collecting gas directly for a hydrothermal spring.

The fibro-lamellar crystallization layer is not perpendicular to the walls (angle < 45°) and presents clear boundaries with the Green Marble of Saint-Véran (Fig. 8a). Subparallel to the walls, this structure seems to be similar to shear zones in which the surrounding peridotite has been serpentinized and crushed (Lahondère et al., 2012). These shear zones are evidence of fluid flow in deep and/or surface rock. The circulation of these fluids and their interaction with the peridotite of the surrounding rock would have allowed the acceleration of the serpentinization process and the formation of serpentine. This crystallized fibro-lamellar structure is believed to have been generated under the effect of significant compressive deformations throughout the serpentine formation (Lahondère et al., 2012) (see Fig. 8). Other structures may correspond to a very dense network of highly connected veins, providing a significant fluid circulation environment. These veins suggest an extensive regime associated with an increase in fluid pressure induced by serpentine reactions (dilating deformation) (Zhang et al., 2018). The nature of these fluids may be related to the ascension of the magmatic fluids which may interact with a fluid phase trapped in the serpentines or a fluid phase percolating to the depths (Lahondère et al., 2012). The presence of these veins inside the serpentines is consistent with the geodynamic position occupied by these ophiolites at that time above the subduction zone. The potential presence of a significant displacement plane shows that several deformation stages have impacted these structures. A detailed study of the mineralogy of both, fibro-lamellar crystallization and the orientation of their potential motion, may be of great interest to understand this hydrogen-enriched environment.

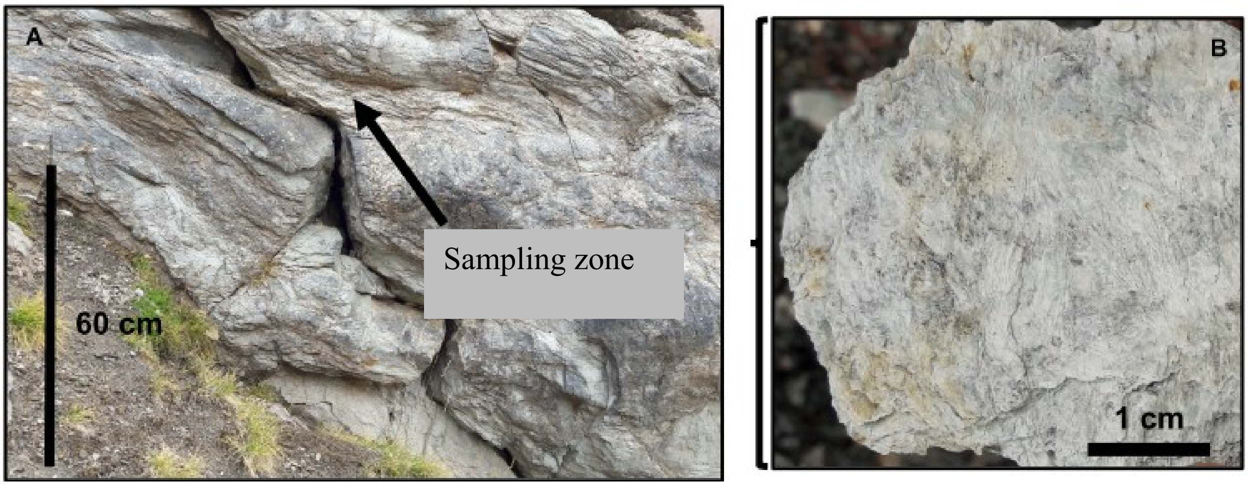

Figure 8: Outcrop photo (a) and sample (b) taken from the Saint-Veran Green Marble Mine.

The investigation carried out northwest of the Western Alps (zone B, see Fig. 3, yellow dots) identified several areas of interest containing a proportion of hydrogen mainly from 1 to 88 ppm, including 7 peaks ranging from 98 to 142 ppm. The latter are located north of the peri-Adriatic line within a peridotite shear zone and northeast of the Belledonne range to the West of the Penninic thrustfront, in ferruginous soil.
It is considered that a proportion of hydrogen below 30 ppm is not significant and can be generated by a mechanochemical reaction between the fresh surfaces of silicate minerals and water molecules. Indeed, during the crushing in drilling processes, Si molecules are created by breaking with Si-O bonds and will then react with water molecules to form hydrogen (Itsuro and Matsuo, 1982; Kamedo et al., 2003) as described in the following reaction:

$$2(\equiv Si\cdot) + H_2O \Rightarrow 2(\equiv SiOH) + H_2$$

DISCUSSION

Despite the presence of ophiolitic complexes and a seismic context associated with fluid flow, small proportion of hydrogen was observed except for a few slight peaks between 98 and 142 ppm. By analyzing other sources of hydrogen found in particular in the ophiolites of Oman, Turkey, New Caledonia and the Western and Eastern Alps (Dinarides and Lanzo Massif), it is interesting to note some similarities: the nature of the fribo-lamellar crystallization carrying H_2 and describing compressive veins and shears zones underlined by antigorites and/or chrysotiles refers to the ophicarbonates of the Lanzo Massif (Brovarone et al., 2017; Groppo & Compagnoni, 2007) as well as to the peridotite beds of New Caledonia (Lahondère et al., 2012) and to the ophiolites of the Balkan Massif in the Dinarides (Etiope et al., 2017).

At least two processes lead to the formation of antigorite veins from pre-existing serpentine (lizardite, lherzolite, harzburgite). They can thus be derived from the transformation of chrysotile in response to shear (Ulrich, 2010) or would crystallize from lizardite by circulation of hot fluids at the base of the ophiolite (heat advection by rapid ascent of metamorphic rocks under the ophiolite) as in the antigorite veins of the Lanzo massif (Ulrich, 2010). It is therefore a late crystallization set up in a syn-post subduction context.

The recrystallization of chrysotile from lizardite will take place at 250°C with a pressure below 1 kbar. This formation is due to the circulation of meteoric fluids as demonstrated by $\delta^{18}O$ isotopic analysis. Percolation of these hyperalkalin fluids is also found in isotopic analyses of ophiolites from the Dinarids, Oman and northeast Kansas (Guélard et al., 2017).
This fibrogenesis process, intimately related to the hydration of peridotite and fluid circulation, has been induced by an endogenous ante-obduction cycle (hydrothermalism of the seabed), by ascension (metasomatism) and by a secondary supergenic syn- and post-obduction cycle by percolation (meteoric) (Lahondère et al., 2012).

Note that another mechanism favorable to the formation of hydrogen is found in the Lanzo Mountains, MonViso, Erro Tobbio, Cime di Gagnone, Cima Lunga, for examples. With a high-grade metamorphism, an early deserpentinization process can occur in a ferrous environment, leading to dehydration of the antigorite to a secondary olivine under eclogite facies conditions. Fe^{3+}-rich antigorite combined with deserpentinization olivine could induce hydrogen production during dehydration of the subducting plate (Debret, 2013).

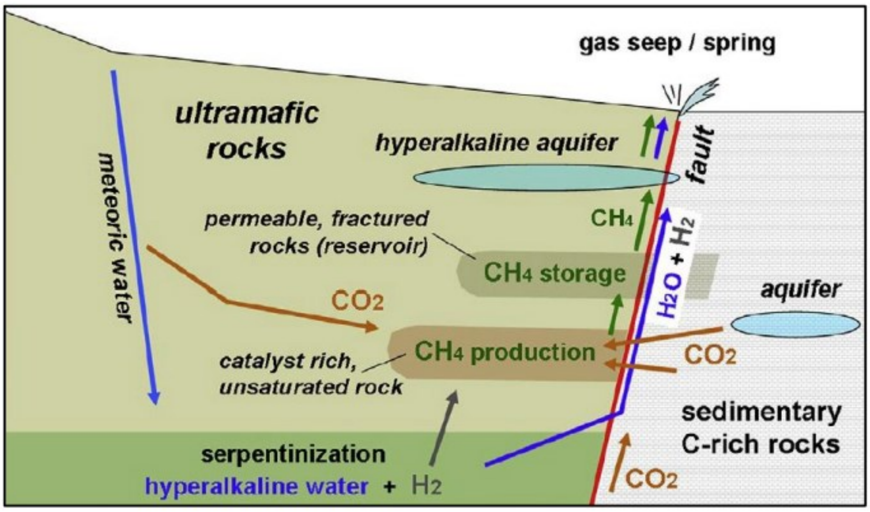

Figure 9: Schematic representation of abiotic hydrogen and methane production during serpentinization (from Etiope et al., 2017)

Queyras serpentinizations have been incorporated into the accretionary wedge where there is petrological evidence of serpentinization/sediment interaction (Cs, Li, B) associated with a maximum burial of 60 km. The serpentinites of the Lanzo massif correspond to detachment of subducting oceanic lithosphere buried between 10 and 100 km depths and having not interacted with the accretionary prism during subduction (Debret, 2013). Thus, it is estimated that the proportion of hydrogen in the Queyras massif was produced under the same fluid circulation conditions but probably in a lower temperature environment.
Many hydrogen sources are found near fault systems and stored in a relatively shallow aquifer such as ophiolites in Northeast Kansas, the Balkans, the Dinarids, Oman, Turkey and the Philippines (Vacquand, 2011):

- In northeastern Kansas, hydrogen generated by the oxidation of Fe^{2+} coupled with reduced water within the fractured Precambrian continental crust is trapped into an aquifer just above this Precambrian basement. This sedimentary aquifer is a karst reservoir underlying the lignite-enriched Permian layer (Guélard et al., 2017).
- Six hydrothermal springs of the Semail ophiolithic groundwater and the Hajar limestone formation in Oman describe a composition rich in H_2 (69 to 81%), methane and nitrogen. These sources emerge from major structural discontinuities within the transition: earth crust and mantle rock (paleo-Moho) (Vacquand, 2011). Inside the catalyzed, mylonitized and serpentinized ophiolites of the Balkans, hydrogen is found in a Triassic carbonate aquifer. The latter are surrounded by Miocene marl sediments and volcano-sedimentary rocks (sandstone, shale, chert, ultra-basic rocks and amphibolite) (Etiope et al., 2017) (see Fig. 9).

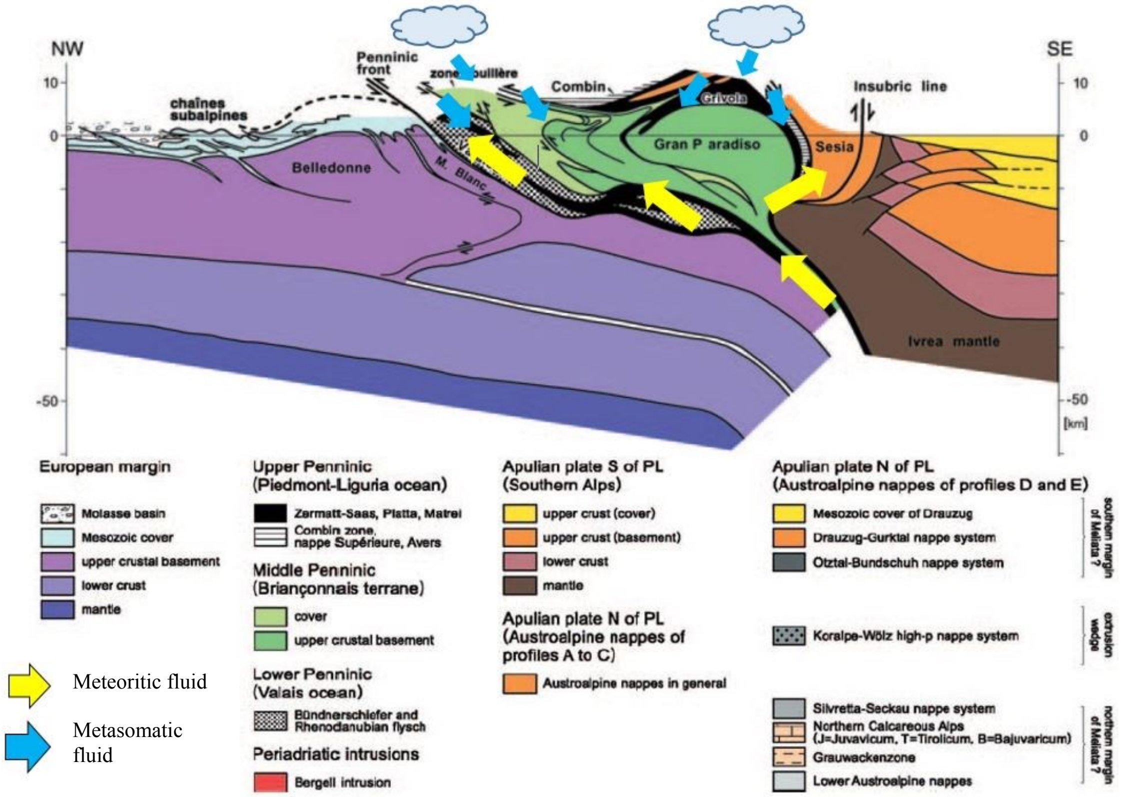

Figure 10: Geophysical geological schematic section of the western Alps (from Schmid & Kissling, 2000 and Escher et al., 1997)

During the Alps orogeny, according to Ferrando et al. (2010) and Boulart et al. (2013), the significant production of H_2 mainly formed before the final exhumation of ophiolitic complexes. The hydration of peridotite and fluid circulation would have been induced by: an endogenous anterior-obduction cycle (hydrothermalism of the seabed), by ascension (metasomatism) and a secondary cycle supergenic syn and post - obduction by percolation (meteoric) (Lahondère et al., 2012). At present, where serpentinization process may be still active, H_2 signature seems to remain at a low level at the ground surface. This is probably due to a lack of potential storage reservoir.

CONCLUSION

The production of natural hydrogen results from, among other processes, the mineralogical composition of the rock in which the fluids circulate, the degree of alteration of the rock and the geological history of the ophiolite. The analysis of the geodynamic evolution of ophiolites in the Western Alps, their seismic context related to fluid circulation and their mineralogy have made it possible to propose a favorable environment for the formation and migration of hydrogen in the eastern part the of Western Alps.
The hydration of peridotite is supposed to have been induced by an endogenous ante-obduction cycle (hydrothermalism of the seabed), by ascension (metasomatism) and a secondary cycle of syn and post supergens - percolation obduction (meteoric) (Lahondère et al., 2012). The presence of antigorite and/or chrysolite supports the scenario of an important fluid circulation. A key point to get significant values of H2 concentration at ground surface seems to be related to the presence of an aquifer near the fault zones. This would facilitate the storage of hydrogen, which seems rarely preserved othewise.

In order to specify the potential locations of these hydrogen sources, geophysical and hydrogeological methods can be used:

- Gravimetric anomaly: Some mineral deposits may be associated with minerals of higher density that cause local disturbances of gravity potential by excess mass. The lack of high resolution of the gravity data in the Alps does not allow detailed analyses of these anomalies.
- Magnetic anomaly: The hydrothermal alteration of ultramafic rocks leads to a deep mineralogical transformation corresponding to the serpentinization process. During this process, Fe^{2+} initially contained in olivines and/or pyroxenes, can oxidize to Fe^{3+} by incorporating newly formed phases such as serpentine and magnetite. A combination of these metals in large quantities will create a magnetic anomaly. The magnetic data currently available on the Western Alps are part of a global grid of magnetic anomalies compiled from satellite, naval and airborne magnetic measurements. The altitude resolution would be 5 km above the geoid, which is still not accurate enough compared to the metric resolution required to analyze metal concentrations (GeoMapApp data, 2018).
- Location of aquifers to identify potential hydrogen storage areas.

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REFERENCES

BRGM, Geological map of France at 1:1 000 000, 1996

BRGM, InfoTerre, http://infoterre.brgm.fr/, 2018

Boulart, C., Chavagnac, V., Monnin, C., Delacour, A., Ceuleneer, G., and Hoareau, G., Differences in gas venting from ultramafic-hosted warm springs: the example of Oman and Voltri Ophiolites, Ohioliti, vol. 28, no. 2, pp 143-156, 2013

Brovarone, A.,V., Martinez, I., Elmaleh, A., Compagnon, R., Chaduteau, C., Ferraris, C., and Estève, I., Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps, Nature et Communication, 2017

Debret, B., Serpentinites, vecteurs des circulations fluids et des transferts chimiques de l'océanisation à la subduction : exemple dans les Alpes Occidentales, Thèse, Université Blaise Pascal, 2013

Deville, E. and Prinzhofer, A.: The origin of N2-H2-CH4-rich natural gas seepages in ophiolitic context: A major and noble gases study of fluid seepages in New Caledonia, Chemical Geology, 2016

Etiope, G., Samardzic, N., Grassa, F., Hrvatovic, H., Miosic, N., and Skopljak, F., Méthane and hydrogen in alkaline groundwater of the serpentinized Dinarides ophiolite belt, Bosnia and Herzegovina, Applied geochemistry, vol. 84, 286-296, 2017

Escher, A., Hunziker, J., Masson, H., Sartori, M., and Steck, A., Geologic framework and structural evolution of the Western Swiss Alps, in Pfiffner, O.A., Lehner, P., Heitzmann, P., Müller, S., and Steck, A., eds.. Basel, Birkhäuser. pp 205-221, 1997

GeoMapApp data, http://www.geomapapp.org/, 2018

Guelard, J., Beaumont, V., Rouchon, V., Guyot, F., Pillot, D., Jezequel, D., Ader, M., Newell, D. and Deville, E., Natural H2 in Kansas : deep or shallow origin? 2017.

H2Sys Hydrogen to system, https://www.h2sys.fr/en/, 2019

Kerrick, D., Serpentinite seduction. Science, vol. 298, no. 5597, pp 1344-1345, 2002.

Kita, I., and Matsuo, S., H2 Generation by reaction between H2O and crushed rock: an experimental study on H2 degassing from the active fault zone, Journal of geophysical research, vol. 87, pp 10789-10795, 1982

Lafay, R., Baumgartner, L.P., Schwartz, S., Suzanne, P., German, M-H. and Torsten, V. Petrologic and stable isotopic studies of a fossil hydrothermal system in ultramafic environment (Chenaillet ophicalcites, Western Alps, France) : Processes of carbonate cementation, Lithos, vol. 294, pp 319-338, 2017

Lahondère, D., Serpentinisation et fibrogenèse dans les massifs de péridotites de Nouvelle-Calédonie : Atlas des occurrences et des types de fibres d'amiante sur mine, BRGM/RP-61426-FR, 2012

Lardeaux, L.M., Schwartz, S., Tricart, P., Paul, A., Guillot, S., Béthoux, N., and Masson, F., A crustal-scale cross section of the south-western Alps combining geophysical and geological imagery, TerraNova, vol. 18, pp 412-422, 2006

Le Golf, B., Bertil, D., Lemoine, A. and Terrier, M. : Systèmes de failles de Serenne et de la Haute-Durance (Hautes-Alpes) : évaluation de l'aléa sismique, BRGM/RP-57659-FR, P. 242, 2009

Manatschal, G., & Müntener, O., A type sequence across an ancient magma-poor ocean–continent transition: the example of the western Alpine Tethys ophiolites. Tectonophysics, vol. 473, no. 1-2, pp 4-19, 2009.

Marcaillou, C., Serpentinisation et production d'hydrogène en contexte de dorsale lente : approche expérimentale et numérique, thèse, Université de Grenoble, P. 303, 2012

Masson, F., Verdun, J., Bayer,R., and Debeglia, N. Une nouvelle carte gravimétrique des Alpes occidentales et ses consequences structurales et tectoniques, géophysique interne, Earth & Planetory Sciences, vol. 329, pp 865-871, 1999.

Mayhew, L.E., Ellison, E.T., McCollom, T.M., Trainor, T.P., and Templeton, A, S., Hydrogen generation from low-temperature water-rock reactions, nature geoscience, vol. 6, 2013

Omori, F.: On the after-shocks of earthquakes, the University, vol. 7, 1894

Pettinger, N.W., The non-classical crystallization of CeO 2 nanoparticles. Diss. Montana State University-Bozeman, College of Letters & Science, 2017

Scholz, C.H., The Mechanics of Earthquakes and Faulting, Cambridge Univ. Press. Cambridge, U.K, 2002 Sensortech SGX, Introduction to electrochemical EC Gas Sensors, 2017

Shapiro, S.A.: Fluid-Induced Seismicity, Cambridge Univ. Press. Cambridge, U. K., 2015

Schmid, S. M., and Kissling E. The arc of the western Alps in the light of geophysical data on deep crustal structure." Tectonics 19.1: pp 62-85, 2000.

SGX, Sensortech, Ga5000 Operating manual 6, https://www.sgxsensortech.com/, 2017

Sue, C., Delacou, B., Champagnac, J.-D., Allanic, C., Tricart, P., and Burkhard, M., Extensional neotectonics around the bend of the Werstern/Central Alps : an overview, International Journal of Earth Sciences, vol. 96, no. 6, p1101-1129, 2007

Sue, C. and Tricart, P., , Neogene to ongoing normal faulting in the inner western Alps: A major evolution to the late alpine tectonics, Tectonics, vol. 22, no. 5, 1050, 2003

Thouvenot, F. and Fréchet, J., Seismicity along the northwestern edge of the Adria microplate, in The Adria Microplate : GPS Geodesy, Tectonic, and Hazards, edited by N.Pinter et al., pp 100-120, Springer, Dordrecht, Netherlands, 2006

Thouvenot, F., Jenatton, L., Scafidi, D., Turino, C., Potin, B. and Ferretti, G., Encore Ubaye : Earthquake Swarms, Foreshocks, and Aftershocks in the Southern French Alps, Bulletin of the Seismological Society of America, vol. 106, no. 5, 2016

Tricart, P., From Extension to Transpression during the Final Exhumation of the Pelvoux and Argentera Massifs, Western Alps. Eclogae Geologica Helveticae, 97, pp 429-439, 2004

Ulrich, M., Péridotites et serpentinites du complexe ophiolitique de la Nouvelle Calédonie, Etudes pétrologiques, geochimique, et minéralogiques sur lévolution d'une ophiolite de sa formation à son altération, Thèse, Université de la Nouvelle Calédonie et Université de Grenoble Alpes, 2010

Vacquand, C. : Genèse et mobilité de l'hydrogène naturel : source d'énergie, ou vecteur énergétique stockable, thèse, IFP Energie Nouvelles et IPGP, 2011.

Yamashita, T., Pore Creation due to Fault Slip in a Fluid-permeated Fault Zone and its Effect on Seismicity: Generation Mechanism of Earthquake Swarm, Pure Appl. Geophys., vol. 155, pp 625-647, 1999

Zhang, L., Nasika C., Donzé F.V., Zheng X., Renard R., and Scholtès L., Modeling porosity evolution throughout reaction-induced fracturing in rocks with implications for serpentinization, Journal of Geophysical Research, submitted 2018.