

## A preliminary geochemical model of the fluid-rock interaction processes forming the eastern Liguria ophiolite (northern Apennines, Italy)

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**ABSTRACT.** — The Northern Apennine ophiolites are likely the Jurassic equivalent of the present-day Lost City and Rainbow submarine hydrothermal systems, where complex tectonic, sedimentary and hydrogeochemical processes occur. The aim of this research work is to simulate the interaction of a peridotite of the Northern Apennines ophiolites with a reconstructed Jurassic seawater, and to verify whether the ophiolite formation is enhanced or hampered. The Jurassic seawater has been reconstructed on the basis of literature data. The seawater during the Lower Jurassic was characterised by higher Ca/Mg ratios, lower SO<sub>4</sub> and higher HCO<sub>3</sub> contents, when compared with the present-day composition. The simulations have been conducted using the program REACT of the Geochemist Work Bench package, in a temperature range of 25-200 °C, and TOUGHREACT, at 25° and 100 °C for reactive flow modelling. The thermodynamic modelling results indicate that the alteration products are antigorite, brucite, chlorite, carbonates and andradite, whereas anhydrite does not reach conditions of oversaturation, and, therefore, precipitation. The indication is that the Jurassic seawater enhances the formation of calcite and does not allow a significant precipitation of anhydrite, which is formed when the present

seawater composition is used. The occurrence of andradite, even at low temperature, is in agreement with the petrographic data of the Ligurian ophiolite. This opens the possibility of an ocean-floor metamorphism origin also for the garnet phase. Reactive flow modelling indicates that significant amount of calcite (up to approximately 15 vol%) can precipitate in a fractured serpentinitized peridotite at low temperatures, compatible with the conditions of the uppermost part of the Levanto Breccia, close to a deep sea sedimentary environment and therefore permeated by cold waters.

**RIASSUNTO.** — Le ophioliti dell'Appennino settentrionale sembrano essere gli equivalenti giurassici di sistemi idrotermali-sedimentari sottomarini attuali, come ad esempio *Lost City and Rainbow* (Dorsale medio-atlantica). La formazione di breccie serpentinite associate a cementi e sedimenti costituiti prevalentemente da calcite è un processo complesso, dove sono attivi simultaneamente processi geochimici, sedimentari e geomeccanici. Si è cercato di riprodurre, mediante simulazione numerica, i processi geochimici che hanno contribuito, nel Giurassico superiore, alla formazione della Breccia di Levanto. Sulla base di dati di letteratura è stata ricostruita la composizione del mare giurassico, e si è poi simulata la sua reazione con una peridotite.

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La modellistica di equilibrio termodinamico (25-200 °C) indica che l'acqua marina giurassica, più povera di solfati, ritardava o diminuiva la precipitazione di anidride, che è in effetti un minerale assente nelle oficalciti appenniniche. La modellistica termodinamica di equilibrio è incapace di generare delle corrette proporzioni dei componenti mineralogici delle oficalciti. Inoltre, il fatto che le oficalci si formassero in presenza di alti rapporti fluido/roccia, in un sistema aperto e in presenza di continui ricambi di acqua marina nella matrice rocciosa, consigliano l'utilizzo delle modellistica accoppiata geochimica-fluidodinamica. Un modello di flussaggio di acqua marina in un metro cubo di peridotite indica che, a 25 °C, è possibile sia la serpentinizzazione, sia la deposizione di significative, quantità di calcite (fino a circa il 15 % in volume) Temperature maggiori (100 °C) modificano di poco questo scenario.

KEY WORDS: *Ophiolite, Northern Apennines, ophicalcite, peridotite carbonation, reactive flow modelling.*

## INTRODUCTION

The Northern Apennine ophicalcites are well known rocks of the ophiolite suite, consisting of submarine lavas and pyroclastics, gabbros, ultramafics and clastic sediments, which underwent ocean floor metamorphism during Late Jurassic (Cortésogno *et al.*, 1975). Ophicalcites mostly consist of calcite-supported breccias of serpentinized harzburgite or lherzolite. A complex pattern of calcite veins of different generations crosscut the serpentinite fragments. The breccia clasts are unsorted and have variable size. Part of the breccia clearly shows a "jigsaw-puzzle" texture typical of hydrothermal breccias, but also sedimentary structures are present, indicating that the environment of formation of the ophicalcite was at or close the Jurassic sea floor. Complex tectonic, sedimentary and hydrogeochemical processes have been responsible for the formation of these rocks. Sub-sea floor exposure of peridotite along faults is the main tectonic process; submarine slides, reworking and sedimentation affected the uppermost part of the exposed ultramafic rocks. Seawater permeated and hydrated the peridotite, allowing the replacement of olivine and pyroxenes mostly by serpentine minerals. The water-rock

interaction process then continues with the partial replacement of the serpentine minerals by calcite, and the deposition of this mineral as hydrothermal veins. The massive serpentinization by seawater of the Northern Apennine ophiolites is also proved by the microstructures of the serpentine minerals (Viti and Mellini, 1998) and the occurrence of up to 0.6 wt% chlorine in the bulk rock (Anselmi *et al.*, 2000). The strong analogy of the Northern Apennines ophicalcite with the present-day active submarine hydrothermal systems hosted in ultramafic rocks (e.g. Lost City, 30°N, MAR, Kelley *et al.*, 2001; Rainbow, 36°14'N, MAR, Douville *et al.*, 2002) strongly suggests that the Northern Apennine ophicalcites are the fossil Jurassic equivalent of these systems.

The present paper deals with the ophicalcite hydrogeochemical aspects and its aim is to present a preliminary geochemical model able to reproduce the water-rock interaction processes leading to the transformation of peridotite into ophicalcite as a consequence of the penetration of seawater into a fractured body of ultramafics. Geochemical modelling is performed by computer codes which take into account the thermodynamic properties of minerals, aqueous species and gases present in the geochemical system of interest, the kinetic properties of minerals, and also the flow properties and the petrophysical characteristics of the fractured rock permeated by seawater. The fundamentals of geochemical modelling have been established by Garrels and Christ (1965) and the equations and algorithms to be used in computer modelling have been presented in a number of paper and textbook (e.g., Helgeson, 1968, 1969; Helgeson *et al.*, 1969, 1978, 1981; Wolery, 1979; Bethke, 1996). Geochemical modelling has already been applied to the study of peridotite-seawater interaction to form ophicalcite. Palandri and Reed (2004) performed thermodynamic equilibrium calculations between harzburgite and seawater and fresh water in a temperature range of 25-300 °C and pressures of 1 to 10 MPa. Their results show that a mix of cold (4 °C) marine water with the hydrothermal fluid derived from serpentinization (at 300 °C) produces significant calcite and magnesite deposition at temperatures from approximately 150 to 4 °C. Allen and Seyfried (2004) present a geochemical thermodynamic model of seawater interaction with peridotite, and conclude that a 200 °C seawater-

peridotite interaction, followed by conductive cooling to 75 °C and mixing with cold seawater, can explain carbonate deposition at the Lost City and Rainbow submarine hydrothermal vents. The thermodynamic equilibrium simulations, as that of Palandri and Reed (2004), or Allen and Seyfried (2004), do not consider the mineral kinetics, so the evolution of the process can be simulated as a “titration” of the fluid equilibrated with a given amount of rock. In our study we applied kinetic and reactive flow models in order to predict the evolution of the serpentinization and carbonation process of a peridotite as a function of time and the hydrodynamic properties of the medium. We also considered the fact that the Upper Jurassic seawater had a chemical composition different from the modern seawater. In performing our model we had in mind the classic outcrops of ophicalcite of the Eastern Riviera, i.e. the famous “Rosso di Levante” ornamental stone (Cimmino *et al.* 2004, and references therein). The stratigraphic position of this unit (Levanto Breccia) is well described by Treves and Harper (1994); it lies at the top of the serpentinized peridotites and below the sedimentary Framura Breccia with clasts derived from the Levante Breccia in a calcite matrix. Its thickness is a few tens of meters.

#### COMPUTER CODES and METHODS

The calculations were performed with two computer codes: 1) for the thermodynamic equilibrium and kinetic batch modelling the REACT code (Bethke, 1996) and a thermodynamic data bank based on the SUPCRT92 code (Johnson *et al.*, 1992); 2) for the reactive transport modelling the code TOUGHREACT (Xu *et al.*, 2004), with a thermodynamic data bank largely derived from the same source.

REACT calculates the aqueous species distribution and the saturation indices of minerals at the P-T modelling conditions. Then the water is forced to react with the peridotite mineral phases, and calculates the amounts of minerals theoretically dissolved or precipitated, on the basis of their chemical affinity A:

$$A = R * T * \ln(K/Q)$$

where, R = gas constant (1.987 cal mol<sup>-1</sup> K<sup>-1</sup>), T = temperature in K, K = equilibrium constant, Q = activity product of the species involved in an hydrolysis reaction of a given mineral.

In the kinetic modelling, when we assume an initial state of non equilibrium and different reaction rates for the mineral phases in the heterogeneous fluid-rock reactions, the code uses the kinetic law of Lasaga (1981).

$$r_k = S * k_r (1 - Q/K) \quad k_r = A * e^{-(E_a/RT)}$$

where, k<sub>r</sub> = kinetic constant (mol cm<sup>-2</sup> s<sup>-1</sup>); S = active surface area (cm<sup>2</sup>); A = pre-exponential factor; E<sub>a</sub> = activation energy (joule); R = gas constant; T = temperature.

TOUGHREACT performs calculations able to predict the geochemical evolution of a water-rock system when a fluid flows through a porous or fractured system. The calculations are based on mass and heat transport equations and define the chemical system and kinetic parameters. The fundamentals on the procedures applied by the reactive transport modelling can be found in a number of textbook (e.g. Appelo and Postma, 1993).

The mineral kinetic law of the code is based on the Lasaga's (1981) model.

#### CONSTRAINTS OF THE MODELS

##### *Conceptual model*

The serpentinization and calcite vein formation responsible for the Levante Breccia ophicalcite have been described by Treves and Harper (1994). Five stages of brittle fracturing and vein formation followed an high-T (amphibolite facies conditions) ductile deformation (Cortesogno *et al.*, 1981), after which the peridotites are assumed to be almost completely serpentinized. The different brittle deformation stages are characterised by: 1) growth of serpentine minerals in shear and extension veins; 2) first deposition of calcite in shear and extension veins; 3) replacement of serpentine minerals by calcite and widespread hematitisation of the rock matrix; 4) hydrothermal fracturing and filling of the fractures by both sparry calcite and

a pink micritic calcite, a calcareous mud lacking of biogenic particles that likely originated by reworking of hydrothermal calcite (Treves *et al.*, 1995); 5) filling of fractures and cavities by drusy calcite and talc (Treves and Harper, 1994). There is no evidence of an high temperature environment of formation for the Levanto Breccia. Its mineralogy is similar to that of serpentinized and hydrothermally carbonated peridotites found in different sectors of present-day ocean floor. Serpentine minerals (lizardite, chrysotile) are accompanied by talc, tremolite, andradite, but the P-T conditions of formations are not defined. It is worth noting that the opicalcites lie on top of rocks exposed to an algid environment, with external seawater temperatures of the order of few degrees. Even assuming a hot layer at the base of the Levanto Breccia, the continuous flow of seawater should have act as a powerful coolant. The best temperature constraints for the serpentinization process of the Eastern Liguria ultramafics are the geothermometric estimates derived from whole-rock, oxygen and hydrogen stable isotopes data. The estimated temperatures for the serpentinization of opicalcites is 79-135 °C (Barret and Friedrichsen, 1989; the same authors suggest that calcite deposition occurred closer to the sea floor, i.e. in a cooler environment).

The evolution model proposed by Treves and Harper (1994) is different from the models proposed from the serpentinization of modern peridotite exposed at the sea floor, in the assumption that the Levanto Breccia clasts were already serpentinized before the formation of calcite vein and matrix. It however to note that, according to Viti and Mellini (1998), the alteration of the Northern Apennines peridotites develops in two stages, with an early alteration near thermodynamic equilibrium, followed by lizardite crystallization in presence of massive seawater circulation. This is probably related to the transition from a low-permeability, quasi-plastic medium to a brittle, fractured rock, through which the seawater was able to percolate in large amount. The present day sea floor peridotite serpentinization is explained assuming a massive seawater flow through a continuously fracturing brittle ultramafic rock. This is also necessary to balance the fracture sealing processes, due to both mineral deposition and the large (40%) volume expansion as a consequence of the peridotite

serpentinization (e.g. Schroeder *et al.*, 2002). Peridotite serpentinization occurs during multistage, polythermal process at the ODP Leg 209 site, MAR 15°N because of hydrothermal circulation of marine water in a fractured medium. Pyroxenes are replaced at relatively high temperatures (350-400 °C), but olivine at  $T < 250$  °C (Bach *et al.*, 2004). Früh-Green *et al.* (2004) report evidence of high-T followed by low-T serpentinization for ten ODP sites. Früh-Green *et al.* (2003) support a model of low temperature (40-75 °C) serpentinization and carbonate precipitation for the Lost City vent field. The serpentinization rate is estimated extremely fast,  $1.2e^{-4}$  km<sup>3</sup>/yr, about five order of magnitude higher than the estimated laboratory values, and enhanced by a large flow of seawater in fractured ultramafics.

#### Solid phase

Considering the discussion above, we assume only an incomplete serpentinization of the Eastern Liguria peridotite before its exposure at the seafloor. The idealized composition (vol%) of the rock reacting with seawater is olivine (70-75), enstatite (13-15), diopside (6-11), anorthite (0-5), hercynite (0-5) in variable proportion (range between brackets), for the thermodynamic models. For the kinetic models see table 1. For the reactive flow models we used forsterite (70), fayalite (5) enstatite (15), diopside (10) as primary minerals, and antigorite, calcite, brucite, talc, dolomite, magnetite, magnesite, quartz, andradite, pyrite and hematite as secondary minerals. These compositions are representative of the average ultramafics of the Ligurian Ophiolite. It is to be noted that slight variation in the proportion of the

TABLE I  
Moles of kinetic minerals used in the simulations

Antigorite	5.717e-005
Calcite	0.002708
Diopside	0.1513
Enstatite	0.4796
Fayalite	0.002156
Forsterite	1.599

main mineral components do not affect very much the result of the simulation, as does the occurrence of accessory phases. In all case the main driving reaction is the destabilization of olivine producing serpentine. Antigorite is a proxy for lizardite, which is the serpentine mineral commonly found in the Northern Apennines and sea floor ultramafics (Aumento and Loubat, 1971). The lack of accurate thermodynamic data for lizardite obliged us to this choice.

### Fluid phase

Previous peridotite-seawater interaction modelling used the modern composition of the sea (e.g. Palandri and Reed, 2004; Allen and Seyfried, 2004). However, when applying a geochemical modelling to the Northern Apennines ophiolite we should consider that the Jurassic sea was different from the present one. There is increasing and well documented evidence for this, based on fluid inclusions, isotopic and chemical analysis of fossil Echinoderms (Lowenstein *et al.*, 2001; Steuber and Veizer, 2002; Dickson, 2002). Global mass

balance modelling based on these data allows estimates of the seawater and atmosphere composition during the Phanerozoic time (Berner and Kothavala, 2001; Berner, 2004; Bergman *et al.*, 2004; Arvidson *et al.*, 2006). During the Upper Jurassic the seawater had less sulphate (approximately 40% lower of the present-day content), a lower Ca/Mg molal ratio (approximately 33% less) and was in equilibrium with an atmosphere characterized by a  $\text{CO}_2$  partial pressure at least 7-10 time higher than the current one. In our simulations we used a reconstructed seawater obtained modifying the sulphate, calcium and magnesium content, and equilibrating the fluid at a fixed  $\text{P}(\text{CO}_2)$ . Charge balance was obtained modifying the  $\text{H}^+$  activity. Fig. 1 shows the fluid compositions and their comparison with the modern average seawater.

Treves *et al.* (1995) report the chemical compositions of calcites forming the Levanto Breccia veins and found lower Mg and Sr contents with respect to those of present-day calcite cements. This can be due to seawater modification by interaction with the rock,

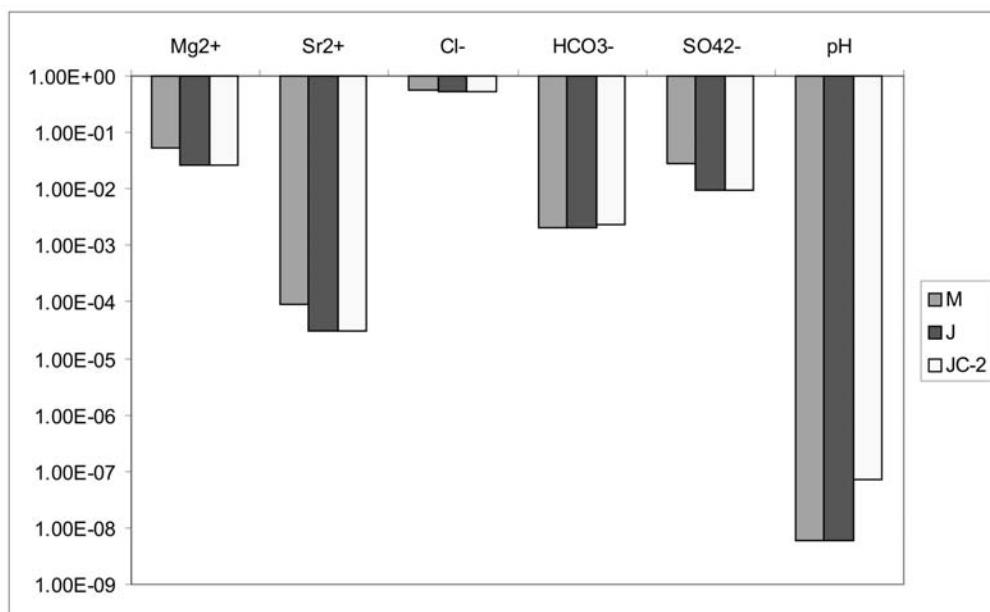


Fig. 1 – Main composition differenced between the modern seawater (M) and the reconstructed Jurassic seawater assuming the modern atmospheric  $\text{CO}_2$  (J) and at  $\text{P}(\text{CO}_2)$  increased to 0.005 atm (JC-2). Values in moles, logarithmic scale.

as proposed by Treves *et al.* (1995), but can also reflect an original lower content of these elements in the Jurassic sea.

### *Limitations of the model*

For the thermodynamic equilibrium simulation the limitation is obvious: in natural hydrothermal processes the local equilibrium assumption between fluid and rock occurs only if fluid flow rates are low. Nevertheless, these simulations are useful because they give an overview of water-rock interaction processes when they approach and reach equilibrium, though it is to remind that the type and proportions of the theoretical alteration minerals produced usually might not reflect the real mineralogy.

For the kinetic simulation the main flaws are linked to the kinetic constants of the minerals. We largely used the kinetic data selected by Palandri and Kharaka (2004), but it is worth noting that these data are continuously subject to revision and improvement. Besides, the laboratory kinetic parameters cannot reflect the mineral reaction rates as estimated on the basis of natural observations (e.g. Brantley *et al.*, 2001; Freyssinet and Farah, 2000). The kinetic parameters of common minerals, such as calcite, are continuously revised and updated (e.g. Gutjahr *et al.*, 1996; Pokrovski *et al.*, 2005). Moreover, the dissolution is different from the precipitation kinetics, and only in some cases both data are available.

In the thermodynamic and kinetic simulations we did not use mineral phases suppression options. This procedure is sometimes used to ignore in the calculations unwanted secondary minerals that do not occur in the natural system under consideration. For example, Allen and Seyfried (2004) suppress dolomite in simulating peridotite-seawater interaction, in order to allow the formation of calcite. Any suppression option represents a model limitation, because the simulation results are clearly biased, and should be well justified and be adherent to the natural system.

The reacting flow modelling has the same limitations of the kinetic models, plus the limitations deriving from the simplified medium geometry, and the reduced number of minerals considered, in order to avoid unreasonable duration of the simulations.

## SIMULATIONS

### *Equilibrium thermodynamic models*

Firstly we have checked the thermodynamic data used by performing a simple polythermal reaction with a seawater of present-day composition, and compared the results with those of Palandri and Reed (2002). In a temperature range of 25-200 °C the seawater reacts with the peridotite and equilibrates with different minerals, among which antigorite and calcite, the main components of ophicalcite, are present (Fig. 2). A second set of computed minerals (andradite, brucite, hematite, magnetite, anhydrite, chlorite) is found in minor amounts, or locally, in the real ophicalcites. A third set (monticellite) does not include components of the real ophicalcite (both on land or at the sea floor). Moreover, the proportions of the secondary minerals formed clearly do not accurately reproduce the ophicalcite composition. These results are conform to those of Palandri and Reed (2004) with the same discrepancies between the real and the modelled mineralogy. This simulation shows that: a) the calculations performed with thermodynamic data base used produces results comparable with that used by Palandri and Reed (2004), and b) the equilibrium thermodynamic approach is not able to accurately reproduce the ophicalcite forming processes. Note that, despite these limitations, Palandri and Reed (2004) considered their simulation successful, and able to reproduce the processes leading to the formation of serpentinized and carbonated ophiolites cropping out both at the sea floor and in the orogenic belts. We still used this approach in order to perform a sensibility test on the effects of the Jurassic seawater composition.

When this composition is used, instead of the modern seawater, anhydrite precipitation is hampered (Fig. 3a,b). At 80 °C this sulphate does not precipitate. At 150 °C anhydrite has a limited range of stability, when plotted as a function of the rock/water (R/W hereafter) ratio. It forms when hematite disappears and magnetite and calcite appear. Then, by increasing the amount of rock dissolved, the sulphate dissolves, while andradite starts to form.

The simulation indicates that less sulphate in the seawater produces less or no anhydrite,



a mineral not found in the Northern Apennine ophicalcite. Other results are: a) as the amount of reacted peridotite increases, the fluid becomes more reducing, magnetite stabilizes instead of hematite,  $\text{Fe}^{3+}$  is incorporated also in andradite; b) proportions of the different ophicalcite components are not realistic.

Some useful hints come from this simulation: a) it is realistic that the seawater equilibrated with serpentinite can be highly reducing (methane-rich gas have been sampled at hydrothermal vents: e.g. Charlou *et al.*, 2002; Allen and Seyfried, 2004 and references therein; Früh-Green *et al.*, 2004); b) it is evident that, being hematite a significant component of the Levanto Breccia, this rock was formed in an oxidizing environment under very high W/R ratios. This consideration may not be valid for other ophicalcites of the Northern Apennines, where hematite is not present; c) if hematite and andradite are coexisting phases, their simultaneous presence constraints the R/W ratio to a limited range, in the order of 45 to 95 g of reacted peridotite per kg of seawater, at temperatures of

150° and 80 °C, respectively. Summing up, the W/R ratio was high during the formation of the Levanto Breccia, and this suggests a model where a continuous, important seawater flow occurred through the ultramafics. This is the opposite of an equilibrium model, because in such a process we have to take into consideration the mineral kinetics and the flow properties of the medium.

#### Kinetic models

Kinetic simulations have been applied to the water-rock interaction process forming the Levanto Breccia at 25, 50 and 150 °C. To avoid too long times of simulations and calculation failures we limited the numbers of kinetic minerals (Table 1). All the other minerals present in the data bank are considered as thermodynamic phases, and they are dissolved or precipitated on the basis of their saturation state with the equilibrium solution at a given step of the reaction progress, controlled by the rates of the kinetic minerals. The kinetic parameters of the minerals are reported in table 2. Note that

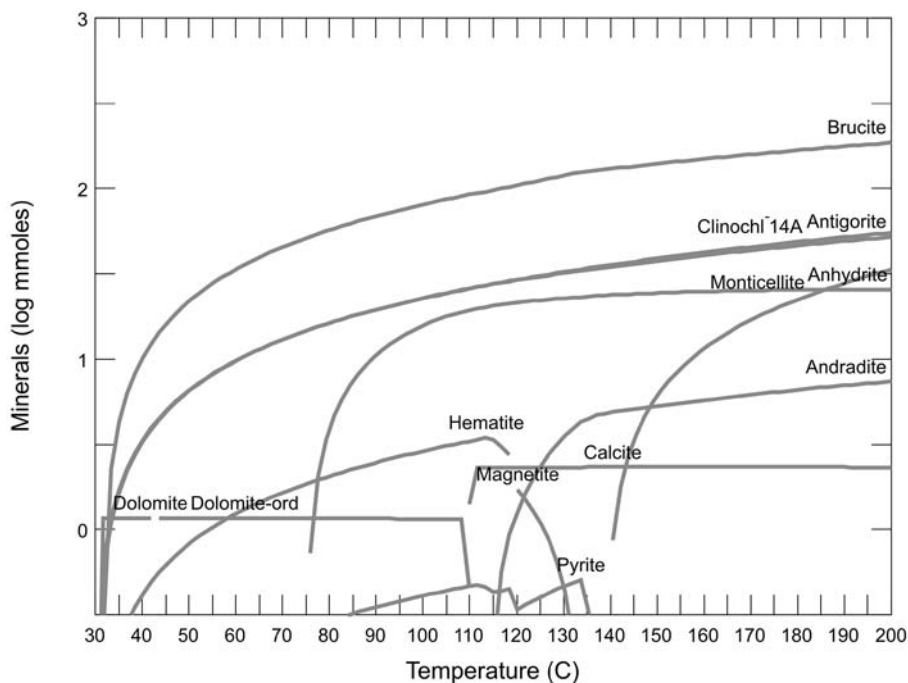


Fig. 2 – Polythermal reaction of peridotite with modern seawater.

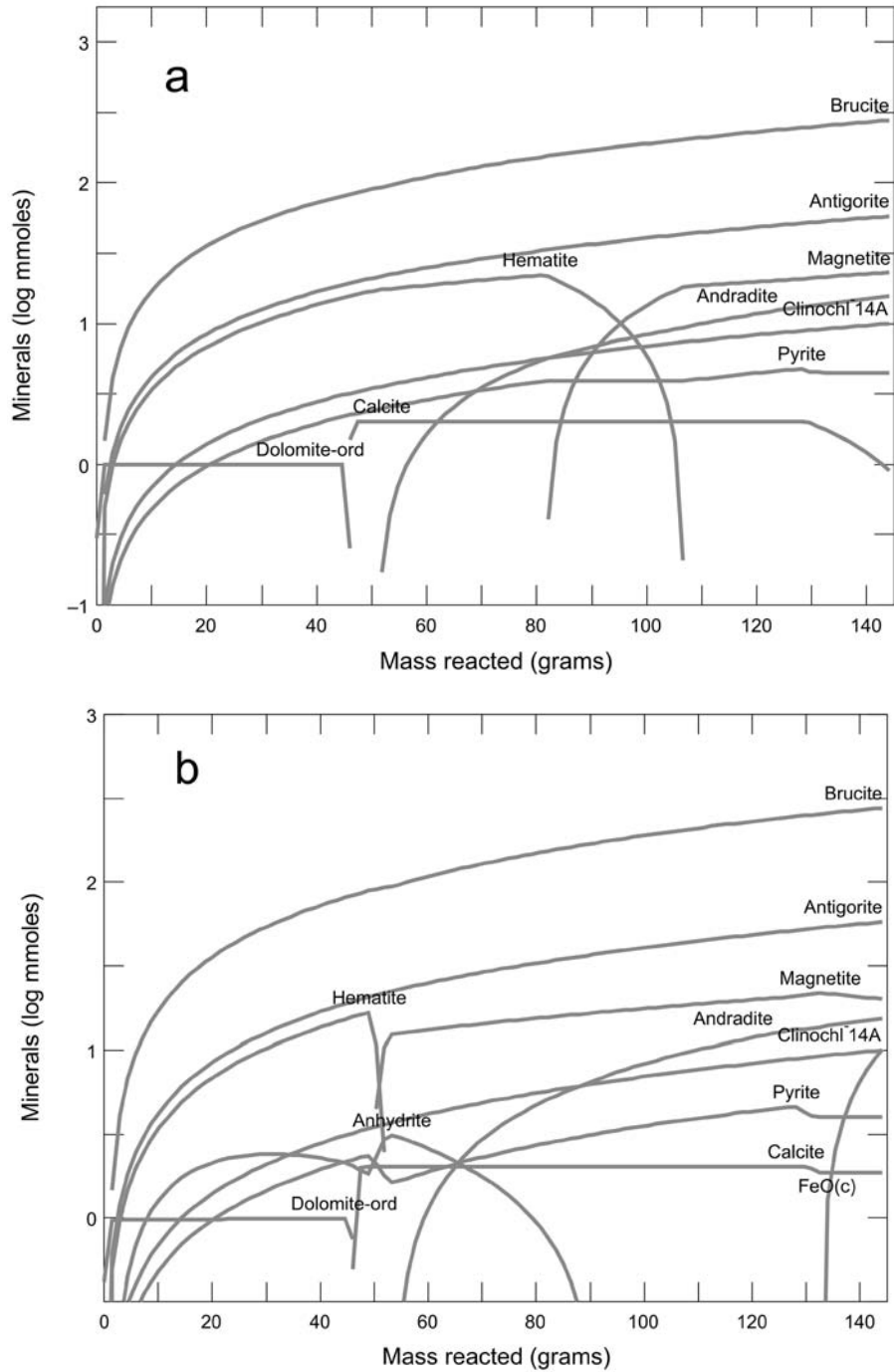


Fig. 3 – Reaction of a peridotite with the modelled Jurassic seawater at 80 °C (a) and at 150 °C (b).



antigorite instead of lizardite is used because of the scarce accuracy of lizardite thermodynamic data.

From Figs. 4a, b, c it is possible to see that the simulation of the processes forming ophicalcite have been reproduced with some success only assuming 150 °C. At low temperatures calcite remains undersaturated, whereas at 150 °C calcite precipitates (approximately 0.5 g per kg of solution) for 500 years. From this time the solution changes its redox state, as shown by the disappearance of fayalite and the precipitation of magnetite (part of Fe<sup>2+</sup> passes to Fe<sup>3+</sup>), and the amount of calcite formed is progressively dissolved. The redox state of the fluid will be further discussed in the reactive flow modelling section. When compared with the thermodynamic equilibrium simulation at the same temperature (Fig. 2b), the main difference is the lack of pyrite and hematite and the appearance of a very minor amount of colemanite. For the rest the two simulations are comparable: olivine rapidly reacts to form antigorite and brucite instead of talc (which immediately disappear after its very early appearance in the simulation) forms. A discussion on the brucite-talc behaviour in the simulation will be discussed later.

#### Reactive transport simulation

Since the literature data and the above simulations indicate that the peridotite serpentinization and carbonation is a process dependent on the amount of water flowing through a fractured rock, we have to consider the hydrodynamic parameters and the petrophysic parameters of the medium. A simple 0-D flush model has been made. A cubic metre of peridotite is first equilibrated with seawater, and than flushed with more seawater at mass rates of 1.0e<sup>-8</sup> and 1.0e<sup>-7</sup> kg<sub>fluid</sub> s<sup>-1</sup>; the water contained in the ultramafic element is totally replaced after 400 and 40 years, respectively, when the porosity reaches the value of 15 vol%. The choice of these mass rate is based on the estimated values of the molar flux rate of seawater into peridotite at the Iberia Abyssal Plain and Galicia Bank (Skelton *et al.*, 2005). Considering that temperatures not higher than 135 °C and likely lower, have been suggested on the basis of stable isotope data (Barret and Friedrichsen, 1989), that (see conceptual model) the formation of the breccia body occurred close to the sea floor, and that, in a pelagic environment, the

temperature of the seawater is of the order of a few degrees, we have taken into consideration a water-rock interaction process in a “cold” environment, and we have tested two temperatures, 25 and 100 °C. The initial porosity of the rock was 0.4 volume fraction. The kinetic parameters of the minerals are listed in Table 2.

The fluid used is a seawater (JC-2), reconstructed assuming a Jurassic atmospheric P(CO<sub>2</sub>) of 0.005 atm. This assumption was done after sensibility tests showed that only in this case calcite formed in a significant amount. Two different types of simulations have been performed. In one case we simply simulated a continuous flow of seawater in the peridotite for a period of about 250,000 years. The second case assumes a flow of JC-2 seawater mixed with a “serpentinization fluid” (SF hereafter, see composition in Table 3), obtained from the previous simulation at the time of 10,000 years, when an almost complete serpentinization of peridotite occurs. We tested two different ratios SF/JC-2 of 1:1 and 1:10, for a period of 250,000

TABLE 2  
Kinetic parameters of the minerals used in the simulations

name	rate const. 25°C mol*m <sup>-2</sup> *s <sup>-1</sup>	act. energy kJ*mol <sup>-1</sup>	sp. surface cm <sup>2</sup> *g <sup>-1</sup>
Pyrite	3.0200e-08	56.90	12.87
Calcite	1.5800e-06	35.40	9.80
Dolomite	2.9512e-12	52.20	9.80
Magnesite	4.5709e-10	23.50	9.80
Hematite	2.5119e-15	66.20	12.87
Magnetite	1.6596e-11	18.60	9.80
Forsterite	2.2909e-11	79.00	200.00
Fayalite	1.5849e-12	94.40	200.00
Andradite	1.9953e-11	103.80	200.00
Antigorite	1.0031e-12	65.50	200.00
Enstatite	1.9055e-13	80.30	200.00
Talc	1.0000e-12	42.00	200.00
Diopside	7.7625e-12	40.60	200.00
Brucite	5.7544e-09	42.00	9.80
quartz	1.0233e-14	87.70	9.80

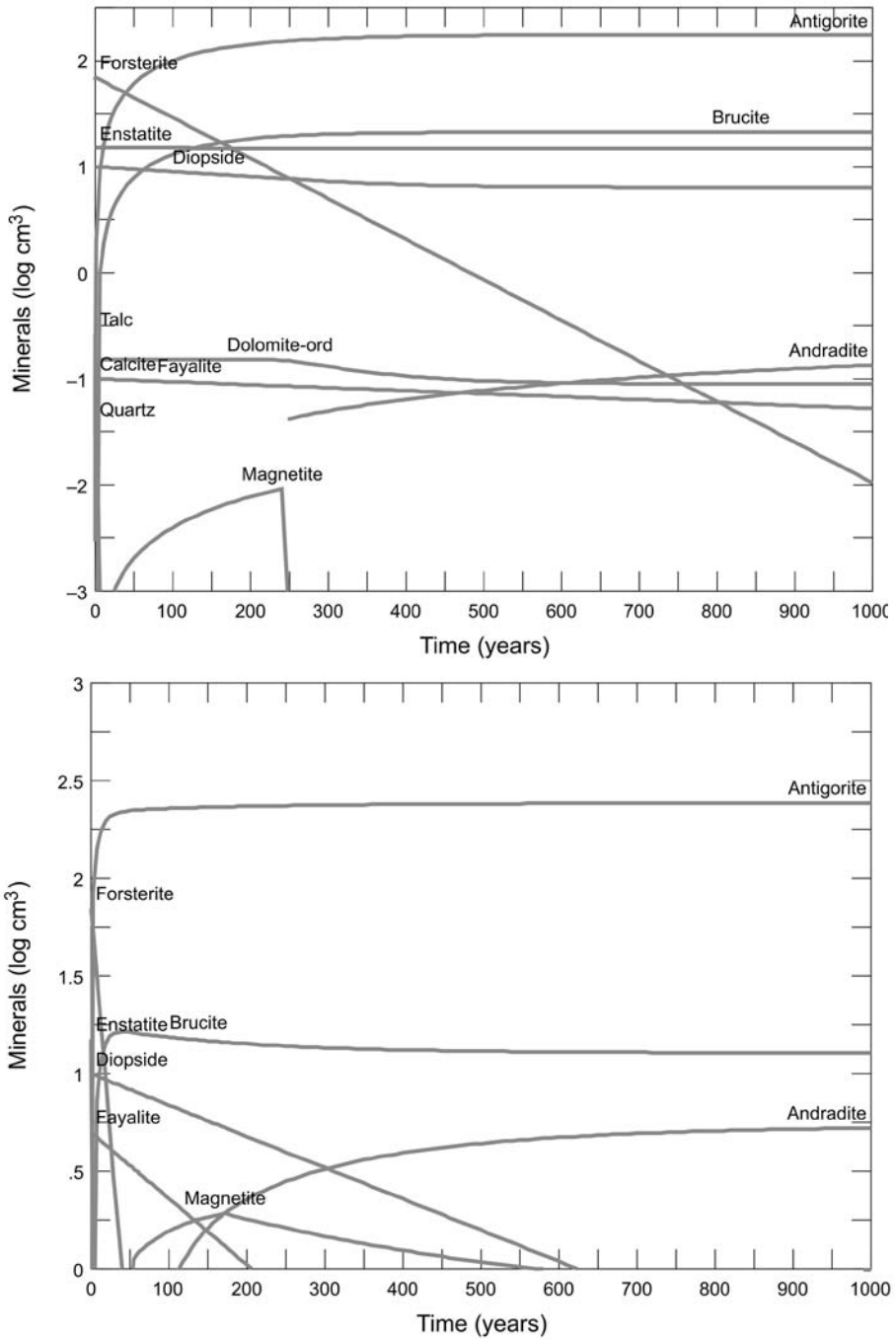


Fig. 4a (upper) and b (lower). Kinetic reaction of peridotite with the modelled Jurassic seawater at 25 (a) and 50 °C (b), respectively.

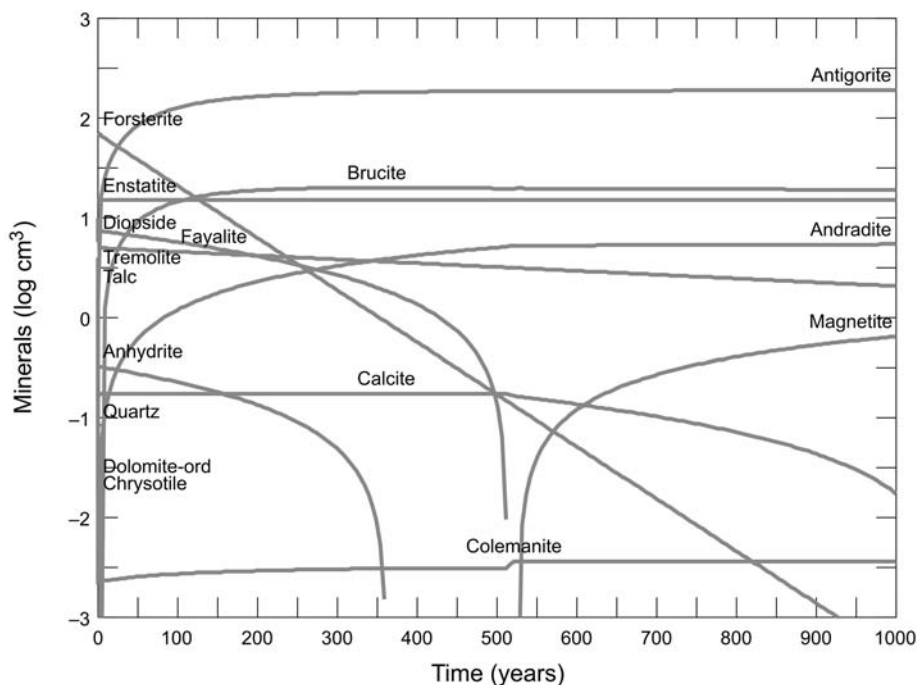


Fig. 4c – Kinetic reaction of peridotite with the modelled Jurassic seawater at 150 °C.

years. The main characteristics of SF, when compared with JC-2, are: a) a significantly higher pH; b) much lower Mg and higher Ca contents, in agreement with the findings of the fluids sampled at the MAR in presence of serpentinized ultramafics (Charlou *et al.*, 2002); c) a reducing redox state.

#### 25 °C simulation, JC-2 and mixing with SF

High pH values and reducing conditions characterize the initial reaction of JC-2 with the peridotite and the serpentinization process. At a mass rate of  $1e^{-7}$  kg  $s^{-1}$ , the chemistry of the fluid is controlled by the alteration of forsterite into antigorite (Fig. 5a-d). After the serpentinization process, the chemical evolution of the fluid is mainly controlled by the water mass rate. Approximately 0.055 calcite and 0.015 magnesite volume fractions are formed in 250,000 years. After this time the simulation failed. However, as the formation rates of carbonates are constant, calcite and magnesite will likely continue to deposit after this time. The initial high pH and low redox state of the fluid allows the formation of andradite (the

$Fe^{3+}$  being incorporated in garnet rather than in hematite). Then the fluid returns to more oxidizing conditions, favouring hematite deposition. The high mass rate progressively drives the system to conditions dominated by unmodified seawater (e.g. the Ca/Mg ratio and sulphate return to the JC-2 value). After 250,000 years the simulation was stopped and a new run with a “flushing fluid” derived from the mixing of SF with JC-2 in the proportion 1/10 was started for a period of 350,000 years. The smooth flexes in the calcium and magnesium curves are due to the disappearance of magnesite (time = 380,000 yr) and brucite (time = 480,000 yr). After brucite is totally dissolved, pH values (and consequently  $HCO_3^-$  concentration) come close to that of unreacted JC-2 seawater.

When using this “flushing fluid” (flow rate  $1e^{-7}$  kg  $s^{-1}$ ) the main result is that the calcite deposition is accelerated and part of the antigorite dissolves. Magnesite and brucite dissolve with different rates and, when brucite is totally disappeared, talc forms in small but significant amounts (1 vol%). This result is consistent with a process of partial replacement of serpentinite by calcite and

TABLE 3  
Serpentinization fluid composition (totals as mole/kgH<sub>2</sub>O) after reaction with the rock

T(°C)	25		100
	mass rate=1.e <sup>-7</sup> kg*s <sup>-1</sup> time=10,000yr	mass rate=1.e <sup>-8</sup> kg*s <sup>-1</sup> time=20,000yr	mass rate=1.e <sup>-7</sup> kg*s <sup>-1</sup> time=10,000yr
pH	11.01	11.05	8.92
Ca <sup>+2</sup>	0.3510E-01	0.3446E-01	0.3602E-01
Cl <sup>-</sup>	0.5177E+00	0.5180E+00	0.5377E+00
HCO <sub>3</sub> <sup>-</sup>	0.1005E-04	0.1008E-04	0.1002E-04
K <sup>+</sup>	0.1001E-01	0.1002E-01	0.1040E-01
Mg <sup>+2</sup>	0.1025E-04	0.8561E-05	0.4197E-04
Na <sup>+</sup>	0.4592E+00	0.4595E+00	0.4769E+00
SiO <sub>2</sub> (aq)	0.1899E-06	0.2029E-06	0.3455E-06
SO <sub>4</sub> <sup>-2</sup>	0.9425E-02	0.8681E-02	0.9858E-02
Fe <sup>+2</sup>	0.1125E-09	0.1047E-09	0.1698E-09
AlO <sub>2</sub> <sup>-</sup>	0.7266E-07	0.7271E-07	0.7547E-07
Log a <sub>O<sub>2</sub></sub>	-73.5	-73.5	-49.1

a late-stage formation of talc+calcite, as reported in the Levanto Breccia ophicalcite (Treves and Harper, 1994). Note that this simulation is a kind of “pick up” of the previous one at 250,000 years, and the reacting rock is now a serpentinite with some calcite and magnesite. The latter mineral is completely consumed during the mixing process. The porosity after 600,000 is below the value of 0.05 volume fraction due to self-sealing.

A sensibility test on the SF/JC-2 ratio indicates that, at a ratio of 1/1, the main evolutionary features are a conspicuous deposition of calcite so that the porosity goes to zero at approximately 600,000 years, and that disappearance of all the Mg-bearing minerals is accelerated.

#### 25 °C simulation, mass rate 1.e<sup>-8</sup> kg s<sup>-1</sup>

When decreasing the mass rate at 1.e<sup>-8</sup> kg s<sup>-1</sup>, the result is a reduced reactivity of the system (Fig. 6 a-d). When only the JC-2 seawater is present, the fluid initially (10,000 years) is reducing, with a CH<sub>4</sub> content of 0.003 molal in the fluid phase. The lower system reactivity allows a better display of the redox evolution: a) during the serpentinization process, the fayalite dissolution releases Fe<sup>2+</sup>, which in turn

is oxidized to Fe<sup>3+</sup> and incorporated in magnetite; b) with the disappearance of andradite, the system is characterized by the progressive formation of hematite coupled with the dissolution of magnetite. In general, both the formed and dissolved minerals follow the same trend of the higher mass rate simulation. We can note (Fig. 6c) the enhanced precipitation of andradite at approximately 20,000 years, due to the persistence of high pH values. However, under these conditions, the amount of calcite formed at 500,000 years is only 1 vol%. Continuing the simulation with a mixing JC-2 and SF (Fig. 6d), we observe calcite deposition, partial dissolution of antigorite, and talc formation after complete dissolution of brucite. Other features in the evolution of the fluid phase are present and discussed in the previous case. Note that the process can be active for as long as 1M year, due to the slower rate of the self-sealing process.

#### 100 °C simulation. Mass rate 1.e<sup>-7</sup> kg s<sup>-1</sup>.

In this simulation, performed with the same thermodynamic data of the previous runs, calcite does not develop, and Mg-bearing carbonates (dolomite and magnesite) form instead. This

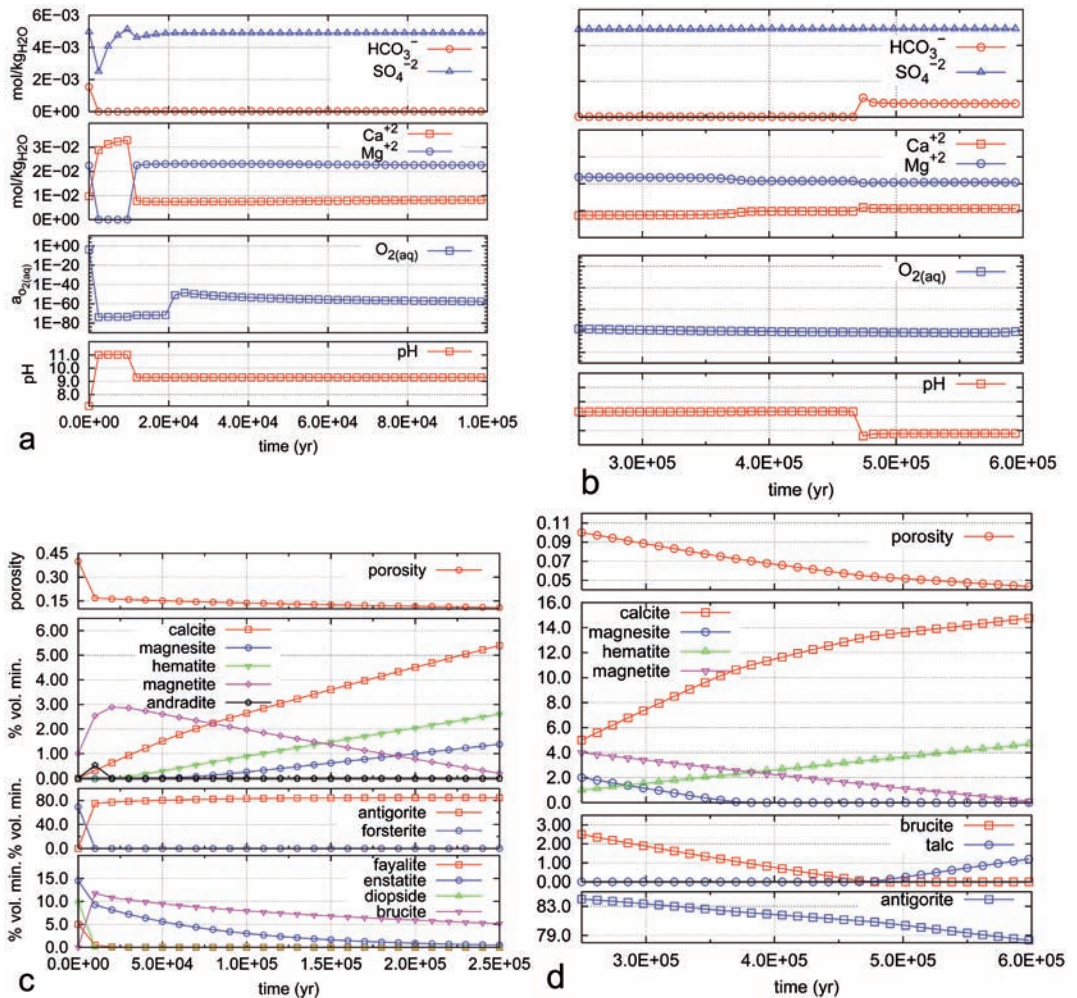


Fig. 5 – a) Evolution in time of the fluid composition for a flush of JC-2 at a mass rate of  $1 \cdot 10^{-7} \text{ kg s}^{-1}$ . b) Evolution in time of the fluid composition after mixing JC-2 with SF in a ratio of 10/1. The vertical axis values are the same in both a) and b). c) Mineral evolution for the flush of JC-2 at a mass rate of  $1 \cdot 10^{-7} \text{ kg s}^{-1}$ . d) Mineral evolution for the flush with a mix fluid of JC-2 and SF in the mass ratio of 10/1. The composition of serpentinization fluid is taken from the simulation c) at the time of 10,000 years. The mineralogical composition of the simulation shown in d) is taken from that obtained at the end of simulation shown in c). Only minor variations for brucite and magnetite are needed to avoid numerical instabilities at the end of the simulation.

result is the consequence of the thermodynamic stability of the carbonate minerals used. (Fig. 7). At low temperature (25 °C) calcite is the more stable carbonate, followed by magnesite and then dolomite. The values of the Gibbs free energy as a function of temperature show that, at temperatures around 100 °C, there is an inversion of stability between calcite and magnesite, whereas also

dolomite approaches the stability conditions. By further increasing the temperature dolomite is the more stable carbonate. However, there is a recognized and well documented uncertainty in the thermodynamic data of the Ca and Mg carbonates (e.g., Machel, 2004, with references therein), which allows a selection of thermodynamic and kinetic data suitable to reproduce the modelled process.



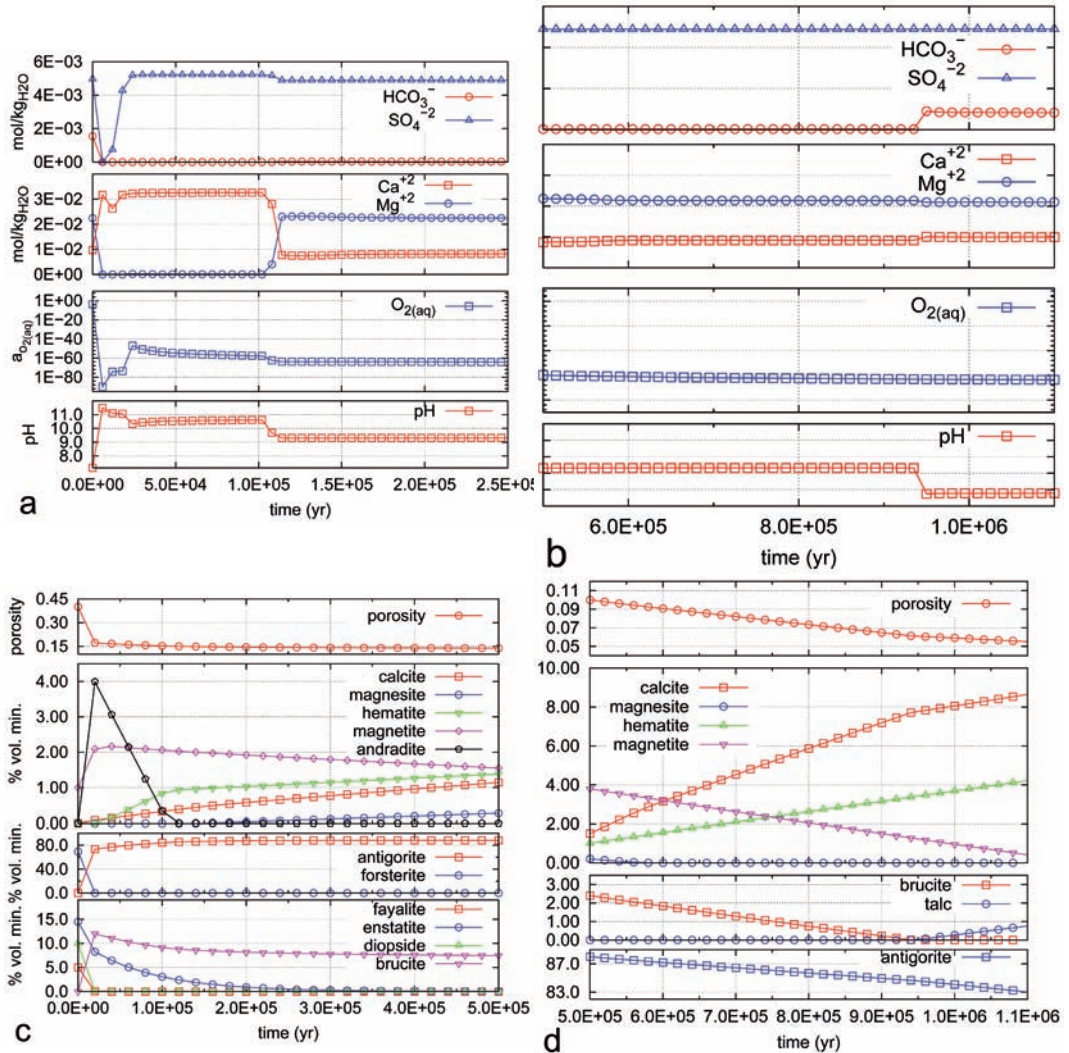


Fig. 6 – a) Evolution in time of the fluid composition for a flush of JC-2 at a mass rate of  $1e^{-8}$  kg  $s^{-1}$  and at  $T = 25$  °C; b) Evolution in time of the fluid composition after mixing JC-2 with SF in a ratio of 10/1. The vertical axis values are the same in both a) and b). c) Mineral evolution for the flush at a mass rate of  $1e^{-8}$  kg  $s^{-1}$ . d) Mineral evolution for the flush at a mass rate of  $1e^{-8}$  kg  $s^{-1}$  after mixing with SF from case c) at a time of 20,000 years.

Therefore we used different thermodynamic data for magnesite and dolomite (Rock *et al.* 2001, Mandell and Rock, 1998.) in order to make the simulation consistent with the geological data. From Fig. 7 we can evaluate the increased instability of both magnesite and dolomite, and the fact that calcite is the

more stable phase at high temperatures. The results of the simulations performed using the new thermodynamic data set (Fig. 8a-d) are substantially equivalent to the simulation runs at 25 °C. The main difference is that, in the mixing case, there is no talc formation after the disappearance of brucite



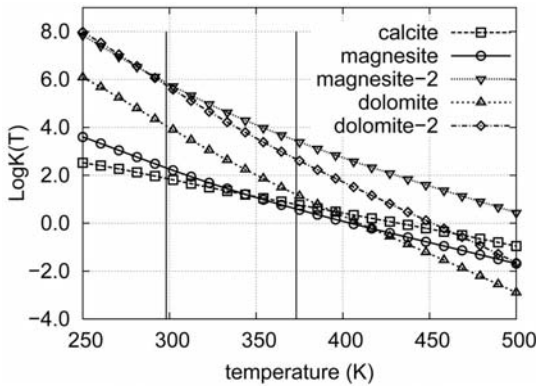


Fig. 7 – logK vs. T stability of magnesite and dolomite respect to calcite using different thermodynamic data. Gibbs free energy values of dolomite-2 and magnesite-2 are from Rock *et al.* (2001), other data from the EQ3/6 thermodynamic database (Wolery, 1992). The two vertical lines represent the temperatures (25 and 100 °C) used in the simulations discussed in the text.

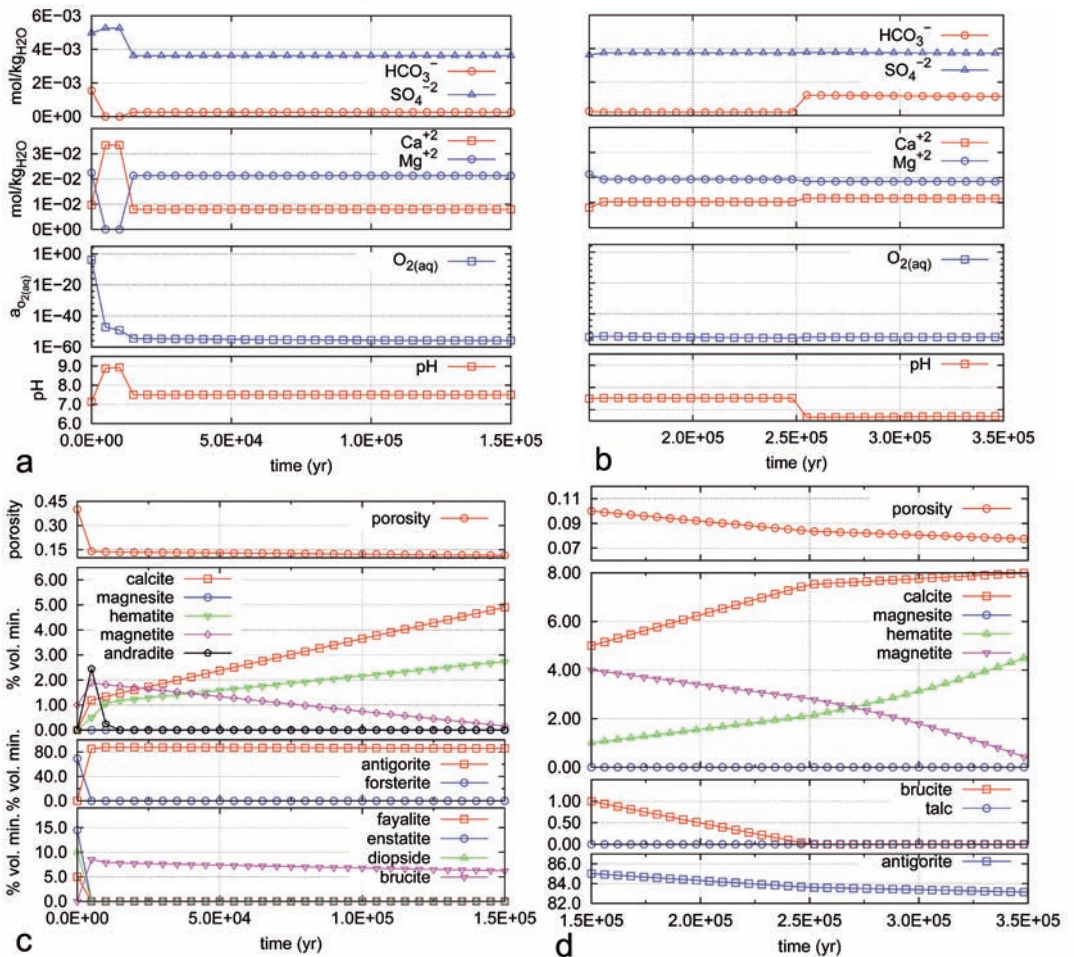


Fig. 8 – a) Evolution in time of the fluid composition for a flush of JC-2 at a mass rate of  $10^{-8} \text{ kg s}^{-1}$  and at  $T = 100 \text{ }^{\circ}\text{C}$ . b) Evolution in time of the fluid composition after mixing JC-2 with SF in the ratio of 10/1. The vertical axis values are the same in both a) and b). c) Mineral evolution for the flush at a mass rate of  $10^{-8} \text{ kg s}^{-1}$ . d) Mineral evolution for the flush at a mass rate of  $10^{-7} \text{ kg s}^{-1}$  after mixing with SF from case c) at a time of 10,000 years. The choice of the time cut depends on the faster evolution of the process.

## CONCLUSIONS

The serpentinization and carbonation of exposed peridotite at the sea floor is a complex process involving not only water-rock chemical interaction, but also tectonic activity to open fluid paths, and deposition and lithification of calcareous ooze (Schroeder *et al.*, 2002). In our work, only some geochemical aspects of the process have been reproduced. The main positive results are:

1) The use of a Jurassic seawater hampers the formation of anhydrite (favouring an oxidizing condition of the solution and, therefore, the occurrence of hematite) and (in the case of a carbonic seawater), the formation of calcite. Other features of the Levanto Breccia, such as the low Mg and Sr contents of the calcite cement, may reflect the low concentration of these elements in the Jurassic seawater.

2) High water/rock ratio are needed. The main factor controlling the process is not the thermodynamic equilibrium, but the mineral kinetics and the hydraulic parameters of the fractured medium. This confirms that reactive flow instead of thermodynamic modelling should be used.

3) The “cool water” model tested indicates that both serpentinization and significant calcite deposition can occur in an environment where the breccia body was a few meters below a deep seawater, which penetrate the ocean floor and acted as a powerful coolant, as likely occurred during the Jurassic, at least for the uppermost part of the Levanto Breccia.

4) Talc and brucite are minor components, and their behaviour is interesting. Talc formation is enhanced by high flow rates and it appears after the complete dissolution of brucite, in agreement with the late appearance of talc+calcite druses, well documented in the Levanto Breccia (Treves and Harper, 1994). Talc requires water-rock interaction of more than 500,000 to 950,000 years at mass rates of  $1.e^{-7}$  and  $1.e^{-8}$  kgs<sup>-1</sup>, respectively. Brucite is a common component of the modern sea floor hydrothermal vents, but is rare in the Northern Apennines ophicalcites. This discrepancy can be explained with a long duration of the ophicalcite-forming process, assuming that brucite forms in an early stage, and then disappears being replaced by late-stage talc.

5) Andradite is a very minor mineral found in the Northern Apennines ophicalcites. Equilibrium thermodynamic simulation indicates that this mineral can be formed at low temperatures. The reactive flow modelling shows that andradite appears at the very beginning of the process, being favoured by the low mass rates, and then disappears when the magnetite starts to decrease, and hematite to increase. The redox state of the fluid controls the stability of these Fe-bearing phases.

The model can of course be improved. Our ongoing research work will take into consideration the simulation of a section of the Jurassic sea floor in 1-D and possibly 2-D models.

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