Earth and Planetary Science Letters 459 (2017) 227–237

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

# Seawater storage and element transfer associated with mantle serpentinization in magma-poor rifted margins: A quantitative approach

Victor Hugo G. Pinto[a,b,*], Gianreto Manatschal[a], Anne Marie Karpoff[a], Marc Ulrich[a], Adriano R. Viana[c]

[a] Institut de Physique du Globe de Strasbourg, CNRS UMR7516, Université de Strasbourg, Strasbourg, France
[b] Petrobras S.A, E&P-EXP, Applied Geology to Exploration, Rio de Janeiro, Brazil
[c] Petrobras S.A, E&P-EXP, Applied Geophysics to Exploration, Rio de Janeiro, Brazil

ARTICLE INFO

*Article history:*
Received 16 March 2016
Received in revised form 12 November 2016
Accepted 14 November 2016
Available online 5 December 2016
Editor: M. Bickle

*Keywords:*
mantle exhumation
serpentinization
element transfer
water storage
magma-poor rifted margins
ocean continent transitions

ABSTRACT

Continental breakup in magma-poor rifted margins can develop, in some instances, after the formation of a wide exhumed domain that can be several hundreds of km wide. As exhumation of the continental mantle occurs serpentinization, due to seawater circulation, can extend as far down as 5–6 km, as observed in refraction seismic data. The impact caused by the process of serpentinization within the evolving ocean may have the potential to change: (i) seawater chemistry; (ii) sustain the evolution of primitive life; (iii) control depositional environments; and (iv) form weak zones preferentially used during the formation, reactivation and subduction of distal rifted margins. Based on geological observations, and geophysical and geochemical data from present-day and fossil zones of exhumed continental mantle, we present a first-order quantification showing that approximately 0.380 $km^3$ of water per $km^2$ can be stored in the mantle. Using simple methods, it can be shown that serpentinization may account for a significant loss of Si, Mg, Fe, Mn, Ca, Ni and Cr during serpentinization of mantle rocks. In particular during latest stages of rifting, when basins are often restricted and seaways are not yet connected, exhumation and the serpentinization of large areas of continental mantle may result in a major transfer of elements between the main Earth reservoirs, such as the mantle and seawater.



## 1. Introduction

It is well known that serpentinized mantle can store large volumes of water (Skelton et al., 2005; Skelton and Jakobsson, 2007). Moreover, serpentinites drilled or dredged at zones of exhumed continental mantle, slow spreading mid-ocean ridges as well as sampled in ophiolites have allowed the characterization of the reactions and mass transfer linked to the process of serpentinization (e.g. Skelton et al., 2005; Bach et al., 2006; Boschi et al., 2006). Fluids sampled in situ at present day active ultramafic-hosted hydrothermal vents associated with oceanic core complexes located at slow to ultraslow spreading mid-ocean ridges, have also showed that serpentinization is responsible for a significant mass transfer (Boschi et al., 2006; Schmidt et al., 2007; Seyfried Jr. et al., 2007; Edmonds, 2010 and references therein). Analysis of the compositions of these fluids reveals that they are often enriched in $H_2$ and $CH_4$ gases and have varying concentrations of dissolved Si, Mg, Ca, Fe, Mn, Ni and Co (Kelley et al., 2001; Fouquet et al., 2010). Although the remnants of fossil rifted margins in the Alps are not directly comparable with slow spreading ridges (e.g. Manatschal and Müntener, 2009), they also show large amounts of hydrothermal cherts ($SiO_2$) with botryoidal Mn-minerals and Fe–Ni alloys (Perseil and Latouche, 1989) that are directly linked to the serpentinization process (Pinto et al., 2015). Si-rich fluids are also expelled during the process of serpentinization as observed during controlled laboratory experiments (Daval et al., 2011; Ogasawara et al., 2013). In addition, it has been observed that the serpentinization results in the depletion of Ca, Mg and Si as described from drill hole data following the Ocean Drilling Program (ODP) along the Iberia margin (e.g. Gibson et al., 1996; Milliken and Morgan, 1996). Using complex geochemical assumptions, Skelton et al. (2005) calculated for exhumed and serpentinized domains the fluxes of $H_2O$, $H_2$ and $CH_4$. In this study, we use a different method to calculate not the flux but the total volume of water stored in the exhumed continental mantle. The

* Corresponding author at: Institut de Physique du Globe de Strasbourg, CNRS UMR7516, Université de Strasbourg, 1 rue Blessig, 67084, Strasbourg Cedex, France.
*E-mail address:* vhpinto@me.com (V.H.G. Pinto).

http://dx.doi.org/10.1016/j.epsl.2016.11.023
0012-821X/

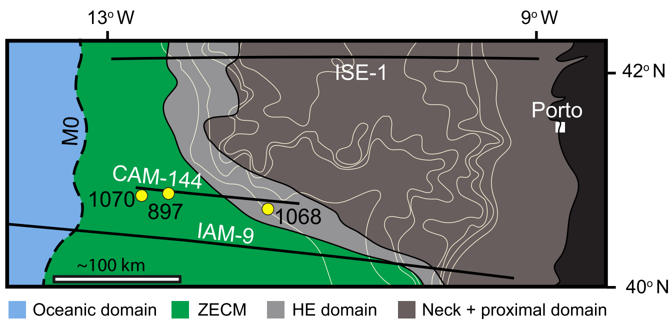


**Fig. 1.** Map of domains from the Central Western Iberian margin. The map was modified from Sutra and Manatschal (2012) and expanded to the south where is localized the IAM-9 section. Yellow circles are ODP Sites close to the IAM-9. Reflection seismic lines CAM-144 and ISE-1 were used to define the limits of the rift domains.

method is not only based on geochemical analyses, but also on geological and geophysical observations from the Iberia margin and, its analogue, the Alpine Tethys margins exposed in the Alps. Taking the direct relationship between seismic velocity, rock density and the degree of serpentinization, we can estimate the adsorption of water. Furthermore because serpentinization leads to element losses (Pinto et al., 2015), simple mass balance calculations can be proposed. We present estimates of mass balance calculations for the exhumed and serpentinized domains of the Western Iberia and fossil Alpine Tethys margins. At present, these are the only margins where drill hole and refraction seismic data, as well as full access to exhumed continental mantle rocks exist to allow us to constrain and quantify the element transfer during serpentinization. Based on these data sets, we present a mass balance calculation that has been performed to quantify element transfer due to serpentinization in the zone of exhumed continental mantle at these magma-poor rifted margins.

## 2. Exhumed mantle along the Western Iberia margin

The zone of exhumed continental mantle along the magma-poor Iberia rifted margin (Fig. 1) has been constrained by drill hole data (ODP; e.g. Tucholke and Sibuet, 2007) and by the interpretation of refraction and reflection seismic data (Sutra et al., 2013 and references therein). At its widest along the Iberian margin, exhumed continental mantle comprises a zone up to 180 km. The transition from the exhumed mantle to the unequivocal oceanic crust has been a matter of debate over the last two decades. Based on seismic velocity, drill hole data, gravity and magnetic anomalies, it is considered that the J-anomaly, which encompasses M3 to M0, marks the oceanward termination of exhumed subcontinental mantle (Bronner et al., 2011). Minshull et al. (2014) repositioned these anomalies in the refraction seismic sections of Dean and Minshull (2000), allowing a better constrain of the oceanward limit of exhumed continental mantle.

Fig. 2 synthesizes major geological observations, seismic velocity data and the reinterpreted reflection and refraction seismic section IAM-9. In Fig. 2B, the velocity intervals attributed to serpentinites are observed below the hyperextended continental crust, between km 240 and km 270, and along the zone of exhumed continental mantle (km 240–100). This zone is made of 5–6 km thick serpentinized mantle that progressively grades to an embryonic oceanic crust (km 100–30).

## 3. Relationship between $V_p$, density, water content and degree of serpentinization

Serpentine polymorphs are formed at different pressure–temperature (*P*–*T*) conditions and they have different water contents (i.e., hydroxyl [OH] groups in crystal lattice). Antigorite forms at higher *P*–*T* conditions (~20 kbar and ~500 °C) compared to lizardite and chrysotile (Deschamps et al., 2013). Antigorite is often related to subduction zones, and it has ~10 wt.% of water ($H_2O$). Lizardite and chrysotile are by far the most frequent minerals in exhumed continental mantle along continental margins. In this tectonic setting, lizardite and chrysotile form at temperatures and pressures lower than 350 °C and 10 kbar, respectively (Milliken and Morgan, 1996; Müntener et al., 2010), and contain 13wt.% of water. Although most of the water in serpentinized mantle rocks may be within serpentine minerals, other hydrated minerals such as talc, brucite, chlorite or clays may influence the water budget as well. However, their occurrence is minor compared to serpentines. This is corroborated by the analysis of serpentinite rocks, which show an average water content of 12.38 ± 2.99 wt.% (calculated on 109 samples, Deschamps et al., 2013). This suggests that the additional mineral phases that may occur in serpentinite rocks do not significantly affect the water budget.

A correlation between seismic velocity ($V_p$), density and degree of serpentinization (Fig. 3A–B) is given by Miller and Christensen (1997). We used a data set of serpentinized peridotites for which the degree of serpentinization is defined by petrological criteria, e.g., the presence of olivine/serpentine (Müntener et al., 2010; Pinto et al., 2015). Because these rocks are free of carbonates, the loss on ignition is related to water content only. Therefore, the correlation of the loss on ignition with variable degrees of serpentinization is related to the hydration of peridotites (Fig. 3C). By the relationship between $V_p$, density, serpentinization and hydration, it is possible to propose the model shown in Fig. 3D.

The correlation between $V_p$ and degree of serpentinization was used to transform the velocity contours to serpentinite contours in the IAM-9 seismic section (Dean and Minshull, 2000) (Fig. 2). The density values were used to calculate the loss of elements, and the correlation between serpentinites and hydration was used to calculate the volume of water absorbed in the mantle along the zone of exhumed mantle at the Iberia distal margin.

## 4. Method for calculation of the element transfer and water absorbed in the zone of exhumed continental mantle

A method is proposed to quantify the mass of element transfer and water absorption in the zone of exhumed continental mantle. The term element transfer is used because the flux of seawater in the mantle leads both to absorption of seawater in the mantle during serpentinization and to outflow of seawater that reacted with the mantle. The outflowing fluids carry dissolved mantle-derived elements. To quantify the element transfer in the mantle, a method referred to as *P*–*M* diagram (Potdevin and Marquer, 1987) was used. This method enables the estimation of the loss of elements due to serpentinization. The steps of the calculations are presented in Tables 1 to 3. Because the calculation of both element transfer and absorbed volume of water in the mantle share the same input data (e.g. seismic refraction data and mapped extent of exhumed serpentinized mantle; Fig. 2) they are described together.

### 4.1. Calculation of the loss of elements in mass fraction caused by serpentinization

The data used to perform all the calculations of mass transfer in the zone of exhumed continental mantle are shown in the median columns of Table 1. The median was used instead of the average values in-order to diminish the risk of calculating extremely high or low concentrations that may be related to either analytical error, or inappropriate sampling. The median was calculated from samples of serpentinized peridotites from the Malenco and the Platta nappes in the Alps (Müntener et al., 2010; Pinto et al., 2015), which are also the samples used in Fig. 3C. The