Effects of mineralogical reactions on trace element redistributions in mantle rocks during percolation processes: A chromatographic approach

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Received 25 August 1994; revised 27 March 1995; accepted 16 May 1995

Abstract

Mantle rock studies provide evidence of interaction with upwelling magmas. In orogenic lherzolites, one of the most conspicuous effects of these interactions is the development of harzburgite and dunite bands. Recent studies have suggested that these bands were formed at the expense of the host lherzolites by melt–rock reactions associated with magma percolation. In order to better understand the geochemical effects associated with percolation–reaction processes, we propose a numerical model of melt infiltration that takes into account modal variations in time and space resulting from melt–rock reactions. Melt volume variations are considered by means of porosity variations, and a local equilibrium approach is used for trace element exchange between melt and minerals. The transport of trace elements by the interstitial melt is described by a mass balance equation while the modal variations are constrained by the mineralogical trends observed in refractory peridotites massifs. The model is applied to REE, Cr and Ni in percolated peridotites affected by an olivine-forming reaction, with the aim of reproducing the evolution of these elements in refractory peridotites from the Ronda massif. Our modelling can explain the negative correlation between the LREE/HREE ratio and the HREE content and between Cr and Ni in the Ronda refractory peridotites. Our results validate the hypothesis that, in the Ronda, the bands of refractory peridotites represent porous-flow channels formed by olivine-forming melt-rock reaction, at increasing melt volume. Because similar geochemical features are observed in ophiolitic peridotites and in mantle xenoliths, it is likely that melt–rock reactions associated with magmatic infiltration are widespread and represent important mantle processes.

1. Introduction

A major issue in the earth sciences with implications both for upper mantle properties and dynamics and for the geochemistry of mantle volcanics is to understand the mechanisms of melt migration from mantle sources to the surface. Diverse studies have pointed to the importance of melt and fluid migration as a major control on the geochemistry of the mantle lithosphere (e.g., mantle metasomatism ([1], and references therein)). Likewise, deep-seated melts can be affected by interactions with shallower mantle rocks during their ascent toward the surface [2,3].

The extent of the chemical and mineralogical effects associated with magma migration depends on the mechanisms of melt circulation. Large volumes...
of magma can be transported in fractures through the upper mantle [4,5], but melt–rock reactions are then limited to the wallrocks of magma conduits [1,6,7]. In contrast, porous flow is generally thought of as a very efficient mechanism for chemical and isotopic exchange between melts and mantle rocks. It was recently proposed that large-scale magma migrations are likely to occur in porous-flow channels [3,8,9]. Such channels have been identified in several alpine lherzolite bodies (e.g., Lanzo [8], Horoman [9], Ronda [10]), where they take the form of bands of refractory peridotites (olivine-rich lherzolites, harzburgites and dunites) of a few metres to tens of metres in thickness. These peridotites are characterized by relatively low Mg/(Mg + Fe) ratios and more enriched LREE and Sr–Nd isotopic compositions compared to the host lherzolites. It has been suggested that percolation channels could be formed as instabilities resulting from feedback relationships between the permeability of mantle rocks and the changes induced by melt–rock reactions (mineralogical changes, melt volume, the water content in the melt, etc. (e.g., [10,11] and references therein, [12]). For example, olivine-producing reactions may increase the permeability of the reacted peridotite [13] which, in turn, would favour further melt infiltration.

Several mathematical models have been proposed recently in order to describe the chemical effects of magma percolation. The standard chromatographic approach, where mineralogical reactions are ignored, helps to explain some of the geochemical characteristics of refractory mantle rocks [6,14,15]. In particular, it accounts for the selective enrichment of the LREE relative to the HREE in previously REE-depleted refractory peridotites. Yet, this approach fails to account for the REE evolution observed from fertile lherzolites to the more refractory rocks (i.e., a steady decrease of HREE concentrations while the LREEs tend to remain constant or slightly increase (see [8,9,16,17]) [18].

Kelemen [3] has proposed a different approach by comparing melt–rock reactions to the crystallization–assimilation processes that take place in the wallrocks of magma intrusions [19]. This model accounts for some geochemical effects associated with modal evolution of peridotites and melt volume variations. However, because melt circulation is not considered, this model fails to reproduce the effects associated with this process, such as chromatographic fractionation of trace elements.

The purpose of this paper is to present a numerical model taking into account the effects of both magma percolation and melt–rock reactions, with the aim of better understanding how the combination of these mechanisms affects the trace element composition of percolated mantle rocks. It is applied to trace element data (REE, Cr and Ni) in refractory peridotites from the Ronda lherzolite massif of southern Spain.

2. The percolation–reaction model

2.1. General assumptions

In this approach, upper mantle rocks are considered as a rigid saturated porous medium (matrix) through which a melt fraction can migrate. The transport of trace elements through these rocks is described by a set of mass balance equations established for a representative elementary volume [20], at the scale of which the chemical and physical properties of the medium can be averaged. The fluid phase and the solid matrix are then considered as two interacting continuous media. The melt (fluid phase 'f') has a density $\rho_f$ and forms an interconnected network occupying a fraction $\Phi$ (porosity) of the total volume of the rock. The matrix is composed of mineral phases characterized by their relative weight fractions $X_i$ ($i = 1, \ldots, n$). It is assumed that all the minerals have the same density ($\rho_s$), and that the density of the fluid and solid phases are constant. In one-dimensional space ($z$), the equations for conservation of mass in the melt and in the matrix (e.g. eq. A1 and A2 in [21]) are written as:

$$\frac{\partial (\Phi \upsilon_f)}{\partial z} = \left( \frac{\rho_s}{\rho_f} - 1 \right) \frac{\partial \Phi}{\partial t} \tag{1}$$

where $\upsilon_f$ is the average microscopic velocity of the fluid (magma).

It is assumed that trace element distribution between the melt and the minerals is controlled by chemical equilibrium relationships. Therefore, the quantity of a given trace element transferred between phases depends only on its partition coefficients.
2.2. Transport–reaction equations

The mass balance equation describing the conservation of mass of a trace element in the elementary volume is:

\[
\left( \rho (1 - \Phi) D_0^l + \Phi \right) \frac{\partial c_i^l}{\partial t} + \Phi v_t \frac{\partial c_i^l}{\partial z} - D_h \frac{\partial}{\partial z} \left( \Phi \frac{\partial c_i^l}{\partial z} \right) = \rho c_i \left( (\Phi - 1) \frac{\partial D_0^l}{\partial t} + (D_0^l - 1) \frac{\partial \Phi}{\partial t} \right)
\]

where \( \rho = \rho_f / \rho_t \), \( D_h \) is the diffusion coefficient within the fluid phase and \( D_0^l \) is the bulk partition coefficient between melt and matrix of element \( j \). \( D_0^l \) is a function of the modal composition of the matrix and of the partition coefficients of element \( j \) between the melt and the different mineral phases \( i \) (\( k_d^{i,j} \)):

\[
D_0^l = \sum_{i=1}^{n} k_d^{i,j} X_i
\]

The first term of Eq. (2) represents the variation of the mass of a trace element in the fluid and in the solid per time unit (i.e., the evolution of trace element concentrations within the minerals and the fluid) and the volume variation of each phase. The second term describes the transport of the trace element by the fluid (advection), and the third term describes the molecular diffusion within the fluid phase.

The right-hand side of Eq. (2) describes the evolution of trace element concentration in the matrix and in the fluid associated with the mineralogical reactions. It takes into account the effects of the modal variations (\( \partial D_0^l / \partial t \)) and of porosity changes (\( \partial \Phi / \partial t \)). To describe this evolution, the trace element transport equation must be coupled with a model of melt–rock reaction involving variations in the matrix mineralogy and melt volume.

In spite of recent progress in understanding melt–rock reactions at upper mantle conditions (e.g., [22],[23]), imposing constrained models for the phase proportions involved remains difficult. Phase diagrams constrained by experimental data are generally used to predict the modal evolution of peridotites reacting with melts in closed systems. However, this approach cannot be used to follow the evolution of natural peridotites because the melt–rock system is open and the major element composition of the reacting melt is generally unknown. On the other hand, studies of natural peridotites have identified typical end products of melt–rock reaction processes, as well as intermediate refractory peridotites affected by variable degrees of reactions [10,23] which display evolutionary modal trends that are significantly different from those predicted for the partial melting of mantle lherzolites (e.g., [24]).

In the present one-dimensional mineralogical model, a given melt–rock reaction is assumed to occur within a limited zone that progresses along a column of rock, the initial and final state of the rock being constrained by the modal composition of natural peridotites. The progression of the reaction zone along the percolated column implies that the more the rock has been infiltrated by a melt in chemical disequilibrium the more it reacts.

The solid–liquid reaction is modelled by two simultaneous processes: (1) a solid–solid mineral reaction, whereby some minerals are partly dissolved (e.g., pyroxene) while others precipitate (e.g., olivine), and (2) a solid–liquid reaction which results in a porosity variation. Assuming that these processes occur linearly within a given critical reaction time, the equations describing porosity and modal composition variations can be written as, respectively:

\[
\Phi = \Phi_0 + (\Phi_f - \Phi_0) f(v_R t - z)
\]

\[
X_i = X_{i,0} + (X_{i,t} - X_{i,0}) f(v_R t - z)
\]

with \( i = 1, \ldots, n \) mineral phases and where \( f \) is a ramp function defined by \( f(x) = 0 \) for \( x < 0 \), \( f(x) = x/(v_R t_c) \) for \( 0 \leq x \leq v_R t_c \), and \( f(x) = 1 \) for \( x > v_R t_c \). Accordingly, the modal composition of the peridotite matrix is assumed to vary linearly within a reaction zone of width \( v_R t_c \), from its initial composition downstream (e.g., a lherzolite) to its final reacted composition upstream (e.g., a harzburgite or a dunite). \( v_R \) characterizes the constant velocity of this reaction zone. \( v_R \) is imposed and, assuming that mineralogical reactions are triggered by incoming magma, it is less than the melt velocity \( v_t \). This mineralogical evolution scheme is coupled with the trace element transport equation to study the tran-
sient geochemical effects associated with the transformations of the percolated medium.

3. Effects of melt–rock reactions on trace element evolution

3.1. Instantaneous reaction: A simplified model

If one assumes that diffusion within the fluid phase is negligible and that the thickness of the reaction zone is zero, then, except along the reaction front defined by \( z = v_R t \), Eq. (2) can be simplified to:

\[
\frac{\partial c_t}{\partial t} + v_e \frac{\partial c_t}{\partial z} = 0
\]

(5)

with

\[
\theta = \frac{(1 - \Phi)}{\Phi} \frac{\rho_e}{\rho_t} \text{ and } v_e = \frac{v_t}{1 + \theta D_0}
\]

(6)

where the coefficients \( D_0, v_t \) and \( \Phi \) have constant values in the homogeneous regions of the \((z,t)\) plane (i.e., in the zones ahead of the reaction front \( z > v_R t \)) and behind the front \( z < v_R t \)). The solution of this hyperbolic equation is straightforward: In the \((z,t)\) plane, curves of constant concentration are straight lines of slope \( dz/dt = v_e \) (see Fig. 1), which are the characteristics of the problem [25]. When the matrix is infiltrated with a melt initially in disequilibrium for a given element, a chromatographic front corresponding to a particular characteristic appears and is propagated at the chemical velocity \( v_e \). Downstream from this front the interstitial melt is in equilibrium with the protolith, while upstream from the front it shows the composition of the infiltrated melt. When considering a set of trace elements \((j,j = 1, \ldots, n)\) with different partition coefficients \( k_{ij} \), the chromatographic fronts of these elements will move with different velocities \( v_e \). This explains the fractionation of trace elements in percolated mantle rocks [14,15]. From Eq. (6) it is clear that large chemical velocities \( v_e \) are associated with low porosity ratios (i.e., large porosity) and small bulk partition coefficients \( D_0 \).

When a mineralogical reaction occurs as a consequence of melt infiltration, it modifies the values of the bulk partition coefficient \( D_0 \), of the porosity \( \Phi \) and of the magma velocity \( v_t \). Ahead of the reaction...
front \( z > v_R t \), the original peridotite matrix is not modified; for a given element, it is characterized by a chemical velocity \( v_e = v_l / [1 + \theta D_G] \). Behind the front \( z < v_R t \), the peridotite is modified or ‘reacted’, and characterized by a chemical velocity \( v_e' = v_l' / [1 + \theta' D_G] \). In the two homogeneous regions \( z > v_R t \) and \( z < v_R t \), the characteristics are linear but with different slopes. The problem is to match their evolution in order to satisfy the boundary condition \( (c_t(0,t) = c_{t,0} \) and the initial one \( (c_t(x,0) = c_{t,0} \).

Depending on the relative magnitudes of \( v_e, v_e' \) and \( v_R \), six situations can be predicted. As illustrated in Fig. 1, different domains can be distinguished on the \( (z,t) \) plane according to trace element concentration in the interstitial melt \( c_t' \). Two domains are observed in all cases: one, for high \( z \) and/or low \( t \) values, is characterized by \( c_t' = c_{t,0} \) (initial condition), and the other, for high \( t \) and/or low \( z \) values, is characterized by \( c_t' = c_{t,1} \) (boundary condition). The third domain, where \( c_t' = c_t \), corresponds to intermediate \( z \) and/or \( t \) values. This intermediate domain is limited (1) by the reaction front (line of slope \( v_R \) and by the chromatographic front (line of slope \( v_e \) or \( v_e' \)) when \( v_R \) is higher or lower than the chemical velocities in both the reacted and non-reacted areas (Fig. 1a–b and e–f), (2) by both the chromatographic fronts when \( v_e > v_R > v_e' \) (Fig. 1d) or (3) to the reaction front when \( v_e < v_R < v_e' \) (Fig. 1c). The melt composition \( c_t' \) is calculated from mass balance: At any time the integrated flux of trace elements can be equated to the net variation of trace elements in the whole column.

When the chromatographic front is downstream from the reaction front (\( v_R < v_e < v_e' \) or \( v_R < v_e' < v_e \)), as illustrated in Fig. 1a–b, \( c_t' \) is given by:

\[
\frac{c_t'}{c_{t,1}} = \frac{v_l' - (1 + \theta' D_G) v_R}{v_l - (1 + \theta D_G) v_R} \cdot \frac{v_l - v_R}{v_l' - v_R} \tag{7}
\]

When \( v_e > v_e' \) the interstitial melt is enriched compared to the magma infiltrated at the base of the column \((c_{t,1} < c_t')\). Conversely, it is impoverished when \( v_e < v_e' \) \((c_{t,1} > c_t')\).

When the reaction front moves faster than the trace element signature of the infiltrated melt \( v_e < v_e' < v_e' < v_e \), the chromatographic front is upstream from the reaction front, as illustrated in Fig. 1e–f. In this case, \( c_t' \) is given by:

\[
\frac{c_t'}{c_{t,0}} = \frac{(1 + \theta D_G) v_R - v_l}{(1 + \theta' D_G) v_R - v_l'} \cdot \frac{v_l' - v_R}{v_l - v_R} \tag{8}
\]

When the chemical velocity increases during the reaction \( v_e < v_e' \), trace elements are accumulated between the reaction front and the chromatographic front \((c_{t,1} < c_t')\). Conversely, when it decreases \( v_e < v_e' \) trace elements are depleted \((c_{t,0} > c_t')\).

Finally, when the chemical front in the reacted peridotites is faster than the reaction front while the chemical front in the protolith is slower \((v_e < v_R < v_e')\), the chromatographic and the reaction fronts are merged into one front represented by the line of slope \( v_R \) in Fig. 1c. A singularity appears along this front, where trace elements accumulate. The instantaneous profiles are characterized by a Dirac distribution of amplitude:

\[
\frac{\Delta Q}{\Delta t} = c_{t,1}(v_e' - v_R)(\Phi' + (1 - \Phi') D_G) + c_{t,0}(v_e - v_R)(\Phi + (1 - \Phi) D_G) \tag{9}
\]

where \( \Delta Q / \Delta t \) is the quantity of trace element accumulated per time unit. Conversely, when the chemical front in the reacted peridotites is slower than the reaction front while the chemical front in the protolith is faster \((v_e < v_R < v_e')\), between the two chromatographic fronts, the interstitial melt concentration is zero (Fig. 1d).

3.2. Discussion

The instantaneous reaction model predicts that a local variation in trace element concentrations should be systematically observed in the vicinity of a reaction front progressing through percolated mantle rocks. The melt–rock reaction acts as a supplementary source, or sink, of trace elements—depending on the sign of the chemical velocity variation—in addition to the one represented by the infiltrated melt. In the interstitial melt, these variations are responsible for trace element anomalies compared to the infiltrated magma and to the liquid in equilibrium with the unreacted protolith. The amplitude of these anomalies depends on the difference between the
chemical velocities ($v_e, v_c^*$) and the reaction front velocity $v_R$. Eq. (7–9) show that the geochemical variations are more important the closer the chemical velocities and the reaction front velocity are.

The sign of the geochemical anomalies depends on the difference between the chemical velocities $v_e$ and $v_c^*$ and thus, on the changes in modal composition and in porosity resulting from the reaction. For example, when a rock becomes more refractory during a mineralogical reaction at constant porosity, the bulk partition coefficient of an incompatible element decreases, and consequently its chemical velocity in the reacted zone $v_c^*$ is greater than in the protolith $v_e$. The resulting source effect is controlled by the element partitioning between peridotite minerals and by the nature of the mineralogical change. This implies that elements partitioned in distinct minerals can behave in different ways during a given melt–rock reaction, even though they have comparable peridotite/melt bulk partition coefficients in the protolith (e.g., Cr and Ni). Conversely, the elements with distinct peridotite/melt bulk partition coefficients but similar intermineral partitioning (e.g., Cr and REE) can behave rather similarly. As such, the effects of melt–rock reactions at constant melt volume differ strikingly from those of partial melting and fractional crystallization.

Because porosity variations induce changes in the magma velocity (Eq. 1), the evolution of the chemical velocities is more complex when melt volume variations occur. When porosity increases, magma velocity as well as the porosity ratio $\theta$ decrease, and vice versa. For elements with large bulk partition coefficients, and for large porosity variations, these two effects of porosity changes may be counterbalanced. However, for all parameter values consistent with mantle processes, at a constant modal composition, a porosity increase results in a decrease in the chemical velocity and, thus, in the trace element content, whereas a porosity decrease gives trace element enrichments. Finally, when porosity variations are associated with mineralogical variations the geochemical effects resulting from the melt volume variations either enhance or smooth the geochemical effects associated with mineralogy variations, depending on the sign and amplitude of the chemical velocity changes.

A further implication of the instantaneous reaction model is that magmas enriched in incompatible elements can be locally generated in percolation–reaction systems forming refractory peridotites at constant or decreasing melt volume. Such enriched magmas can even evolve from depleted infiltrated melts. Although helpful for understanding trace element variations associated with mineralogical changes in percolation–reaction systems, the instantaneous reaction model discussed above is probably too simple for adequately representing natural systems. A more realistic model must involve a reaction zone rather than a reaction front. Indeed, field studies in peridotite massifs indicate that the bodies of refractory peridotites (harzburgites and/or dunites) are systematically separated from the host fertile lherzolites (e.g., [18]). Because of their transitional mineralogical and geochemical characteristics (e.g., REE in Fig. 2) these rocks are likely to represent incompletely reacted peridotites from reaction zones. Moreover, the effect of diffusion in the interstitial liquid must be taken into account. This is expected to smooth the transitions between different domains of trace element composition along the percolation column. In particular, such an unrealistic figure as the Dirac distribution predicted by the instantaneous model when $v_e < v_R < v_c^*$ would disappear if diffusion were considered. To take into account these comments in the application of the percolation–reaction model to the Ronda peridotites, we
have developed a numerical solution of Eq. (2) using a finite difference method.

4. Application to the trace element composition of refractory peridotites in the Ronda massif

4.1. Trace element data in Ronda refractory peridotites: REE, Cr and Ni

The Ronda lherzolite massif of southern Spain is characterized by a petrological and structural zoning [26,27] coupled with a systematic variation in LREE [28] and the Sr–Nd isotopes [29]. Recent isotopic and trace element studies suggest that the Ronda peridotite was affected by a major event of magma circulation, which evolved in time and space from crack propagation to pervasive percolation [10,30,31]. Percolation occurred in a late evolutionary stage of the massif, during its ascent to the surface [10,32].

Some areas containing abundant bodies of refractory peridotites are understood to represent the most active pathways for melt circulation. These areas are characterized by the occurrence of several lenses of harzburgites and dunites of a few metres to tens of metres in thickness hosted by spinel–plagioclase lherzolites [30]. The refractory rocks show textural evidence of secondary olivine precipitation and have cpx/opx ratios that are much higher than the values predicted for partial melting (e.g., [21]). These features are believed to result from a melt–rock reaction characterized by opx (±cpx) dissolution coupled with olivine crystallization. In addition, the refractory peridotites have low Mg/Mg + Fe ratios, that tend to decrease towards the most olivine-rich rocks (dunites) [10,11]. This feature is interpreted as the result of percolation–reaction processes [3,10].

As shown in Fig. 2, the Ronda peridotites have chondrite-normalized REE patterns marked by an uneven depletion of REE from fertile lherzolites to dunites (see also Yb vs. cpx% in Fig. 4). Such REE evolution has been previously observed in other lherzolite massifs as well as in some ophiolitic peridotites [8,16,17]. In several massifs, the progressive depletion of HREE is associated with nearly constant or slightly enriched LREE (e.g. [9,16]). In all cases, this evolution is responsible for a significant change in the shape of the chondrite-normalized REE pat-

![Fig. 3. Results of the percolation–reaction model showing the evolution of chondrite-normalized REE (c) patterns of peridotites along a percolation column affected by (a) a mineralogical reaction without porosity change, (b) a porosity increase (from 1 to 5%) without modal changes and (c) a mineralogical variation coupled with a porosity increase (from 1% in the protolith to 5% in the reacted peridotite). The magmatic and reaction velocities were set at 1.0 and 0.55 cm yr⁻¹ respectively and the diffusion–dispersion coefficient was set at 10⁻⁶ cm² s⁻¹. The magmatic front is at \( L = 200 \) m. The reaction zone is 20 m long. The modal composition of the protolith (cpx = 0.15, Opx = 0.245, olivine = 0.58, spinel = 0.025) and that of the reacted peridotite (cpx = 0.008, Opx = 0.095, olivine = 0.895, spinel = 0.002) was established from the mineralogical trends of the Ronda refractory peridotites [10,32]. REE content of the protolith ([10], chondrite-normalized): La = 0.5, Ce = 0.84, Nd = 1.2, Sm = 1.7, Eu = 1.9, Dy = 2.2, Er = 2.1, Yb = 2. Mineral/melt partition coefficients [31]: Cpx: La = 0.068, Ce = 0.08, Nd = 0.156, Sm = 0.243, Eu = 0.267, Dy = 0.39, Er = 0.4, Yb = 0.39. Opx: La = 0.0014, Ce = 0.0014, Nd = 0.0027, Sm = 0.0064, Eu = 0.009, Dy = 0.024, Er = 0.043, Yb = 0.074. Olivine: La = 0.0007, Ce = 0.0003, Nd = 0.0006, Sm = 0.00046, Eu = 0.0008, Dy = 0.0016, Er = 0.0019, Yb = 0.0037. Spinel: La = 0.0009, Ce = 0.0008, Nd = 0.0003, Sm = 0.0004, Eu = 0.0008, Dy = 0.0004, Er = 0.0004, Yb = 0.0004. The REE content of the infiltrated magma was fixed on the basis of the average composition of OIB proposed by [41].
terns, from the classical N-MORB-type in fertile lherzolites to flat, or U-shaped, REE patterns in refractory peridotites. As already stressed by several authors, this REE evolution cannot be explained by classical partial melting models. On the other hand, the chromatographic effects associated with magma percolation can reproduce the U-shaped REE patterns of refractory peridotites [6,14,15]. However, because they do not consider melt–rock reactions, the published chromatographic models cannot account for the HREE depletion coupled with olivine enrichment.

Whereas they display similar variations in the host lherzolites, Cr and Ni show very contrasting evolution in the Ronda refractory peridotites (Fig. 4). In the lherzolites (cpx > 6%), both elements moderately increase from the most fertile rock types (cpx = 15%) to the most refractory ones (cpx = 6%). Such correlated increases in Cr and Ni concentrations are consistent with partial melting. In the refractory peridotites (cpx < 6%), Cr decreases drastically, down to very low concentrations in certain dunites (Cr < 1000 ppm). In contrast, Ni shows a very marked increase in the harzburgites (Ni > 3000 ppm in some samples) and then slightly decreases in the dunites. Remaidi [11] noted that the Cr–Ni evolution in refractory peridotites is not consistent with partial melting and possibly results from a percolation–reaction process.

4.2. Modelling: Input parameters

In order to test and refine the hypothesis that REE and Cr–Ni evolution in the Ronda refractory peridotites results from a percolation–reaction process, the numerical model was applied to the data reported by Remaidi [10,11] and Van der Wal and Bodinier [32]. For the calculation, the mineralogical and trace element composition of the protolith was fixed at the average composition of the fertile spinel–plagioclase lherzolites, while the modal composition of the reacted peridotite was established from the average composition of the dunites (caption to Fig. 3). The area studied by Remaidi [10] contains websterite layers, which are considered as representing liquidus mineralogical assemblages segregated from magmas circulating into vein conduits, during a crack-propagation event precursory to melt percolation [30,31]. With regard to the REE, these magmas show geochemical characteristics that are typical of alkaline basalts (e.g., La = 150 × chondrite and Yb = 13 × chondrite). The trace element composition of the infiltrated melt is consequently assumed to be that of primary ocean island basalt (OIB), which is taken as an analogue composition. For REE, cpx/melt partition coefficients were fixed from published experimental data whereas opx/melt and olivine/melt partition coefficients were obtained from data on minerals separated from the Ronda peridotites [31]. For Cr and Ni, the partition coefficients were established by using experimental data constrained by intermineral partition coefficients for the stability field of spinel peridotites [33].

Intergranular magma velocity through mantle rocks is currently considered to be of the order of a few centimetres per year (e.g., [34,35]). In our modelling, this parameter was set at 1 cm yr⁻¹. A wide range of values has been proposed for the porosity of mantle rocks, from very low values (down to 0.001%) in lithospheric peridotites percolated by volatile- or carbonate-rich melt fractions [36] to extremely high values (up to 40%) in melt-saturated dunites beneath mid-ocean ridges [37]. Intermediate values of the order of a few percent are generally proposed for melt extraction domains [38]. We fixed the porosity of the infiltrated protolith at 1%, but this value was allowed to increase in the reacted peridotites to take into account melt production associated with melt–rock reaction. With the chosen melt velocity and porosity values, the geochemical data are best fitted with reaction zones of a few tens of metres in thickness and reaction front velocities in the range (0.35–0.55) × v₉. For these parameters, the chromatographic fronts of LREE are downstream from the reaction zone, whereas these values of v₉ lie between the chemical velocities (vᵣ) of less incompatible REE.

4.3. Results REE

The results describing the evolution of REE from fertile to refractory peridotites are illustrated in Fig. 3 for three situations, a modal variation without porosity change (Fig. 3a), a porosity increase from 1 to 5% without mineralogical variations (Fig. 3b), and a mineralogical variation coupled with a porosity
increase from 1 to 5% (Fig. 3c). Models assuming increasing porosity rather than decreasing porosity were chosen to illustrate the effect of melt volume variation because they provide a better fit of the Ronda data. This example is for a 200 m long percolation column at time $t = 20000$ yr where the reaction zone is 20 m wide and progresses at a velocity $v_R = 0.55$ cm yr$^{-1}$.

When the mineralogical reaction is not associated with porosity variations (Fig. 3a), a striking feature of the reaction zone is the existence of positive anomalies of REE which occur at variable distances from the reaction front, depending on their partition coefficients. For the LREE, the anomaly is located very close to the reaction front, while for the less incompatible REE it is located at some distance behind the front. These transient REE enrichments are predicted by the instantaneous reaction model when the reacted peridotite is more refractory than the protolith ($v'_c > v_c$).

A porosity increase without mineralogical changes induces a decrease in the chemical velocity of the incompatible elements ($v'_c < v_c$) and consequently a transient decrease in the REE content (Fig. 3b). In

![Diagram](image-url)

**Fig. 4.** Results of the percolation-reaction model compared to the composition of Ronda peridotites, for Yb, Cr and Ni vs. clinopyroxene proportion. Three numerical experiments were performed, using different porosity variations: (1) constant porosity $\Phi = 1\%$, (2) porosity increasing from 1 to 5%, and (3) porosity increasing from 1 to 15%. The results are also shown for three different durations of the percolation process: 2500 yr (dotted lines), 3000 yr (dashed lines) and 3500 yr (solid lines). The duration of 3500 yr corresponds approximately to the critical reaction time $t_c$. Cr and Ni concentrations in the protolith were fixed at 2740 and 2160 ppm respectively [11]. Mineral/melt partition coefficients for these elements were established from published experimental data for the stability field of spinel peridotites, and were also constrained by intermineral data [33]: Cpx: Cr = 7, Ni = 1.5. Opx: Cr = 5, Ni = 3.5. Olivine: Cr = 0.5, Ni = 14. Spinel [42]: Cr = 200, Ni = 10. For the composition of the infiltrated magma, we used typical compositions of primary basalts (i.e., 700 ppm for Cr and 250 ppm for Ni). Except for the porosity variation, all the other parameters are the same as for the model presented in Fig. 3. For the Ronda peridotites, the symbols for the different peridotite rock types are the same as in Fig. 2.
this case, the amplitude of the variation in the LREE content is more important than for HREE. Yet, the most incompatible elements reach equilibrium with the incoming magma before the most compatible ones. These features are similar to the source effect induced by mineralogical changes where trace element behaviour depends on the degree of compatibility of the latter. During porosity changes, variations in trace element content are controlled by the magma velocity and by porosity ratio variations (Eq. 6–9), whereas the chemical variations due to modal changes are determined by the intermineral partition coefficients only.

When the mineralogical reaction is associated with a porosity variation (Fig. 3c), the evolution of the REE patterns is marked by an uneven evolution from MORB-type REE patterns in fertile lherzolites (downstream of the reaction zone) to relatively flat REE patterns in dunites (upstream of the reaction zone). The first stage of this evolution is a decrease in LREE content ahead of the reaction zone, followed by a rapid decrease in REE content during the reaction. Upstream of the reaction zone an increase in LREE content is observed while the concentrations of the most compatible elements still decrease. These features are consistent with the REE evolution observed in the Ronda peridotites (Fig. 2), such as the LREE depletions observed in fertile lherzolites and the flat REE patterns in refractory peridotites.

In the reaction model involving an increase in porosity, melt volume variations are important because they counterbalance the source effect of the reaction. This is illustrated in Fig. 4, by the evolution of Yb in peridotites vs. cpx proportion when porosity is constant ($\Phi = 1\%$) and for two different porosity variations ($\Phi = 1–5\%$ and $\Phi = 1–15\%$). When the porosity increases from 1 to 5%, the lesser Yb over-enrichment in minerals results in a significant smoothing of the transient positive anomaly observed for this element in the constant porosity model (Fig. 4). For a large increase in melt volume ($\Phi = 1–15\%$) the anomaly vanishes and the reacted peridotites show an almost regular trend of decreasing concentration. This evolution can be compared to that expected from partial melting. In the model, the existence of whole-rock transient anomalies for incompatible elements strongly depends on the chosen parameters. The distance and the duration of the percolation process, as well as the melt velocity, play a major role because these parameters control the position of the chromatographic front relative to the reaction front.

4.4. Results: Cr and Ni

Transient concentration anomalies in melt and minerals are predicted for compatible elements such as Cr and Ni by the instantaneous reaction model. In the case of olivine-producing reactions, positive anomalies are expected for pyroxene-hosted elements such as chromium ($u_c > u_e$), while negative anomalies are predicted for olivine-hosted elements such as Ni ($u_c < u_e$). However, these anomalies are never observed in whole-rocks. To illustrate the effect of mineralogical reactions with or without melt volume variations, calculations were performed with constant porosity ($\Phi = 1\%$) and two different porosity variations accounting for increasing melt volume ($\Phi = 1–5\%$ and $\Phi = 1–15\%$).

In the constant porosity model of Fig. 4, Ni and Cr are almost constant throughout the reaction zone; the transient concentration anomalies of Cr and Ni in the minerals is then totally counterbalanced by mineralogical variation. Upstream from the reaction zone (cpx < 3%) these elements show an abrupt change toward concentrations controlled by the composition of the infiltrated melt and the mineralogy of the most reacted peridotites. For Cr, this change corresponds to a drastic decrease from 2700 to about 550 ppm, whereas Ni increases from 2200 to 3200 ppm.

It is worth noting that strong enrichment is observed for Cr in the percolating melt. Hence Cr appears to be strongly leached from peridotites affected by olivine-forming melt–rock reactions (or, the modelling illustrated in Fig. 4, the Cr content increases from about 1000 to 2100 ppm in the interstitial melt of the reaction zone). The excess of Cr released by this process is transported downstream through the percolation column by strongly over-enriched melt. This mechanism would nicely account for the frequent occurrence of chromite ores associated with refractory peridotites in several ophiolites (e.g., [43]) and in the Ronda peridotite [10,39].

When an increase in melt volume is assumed, the strong discontinuity of Ni occurring at the chromatographic front of that element is smoothed. The re-
acted peridotites are characterized by an overall Ni enrichment towards the most reacted rock types. Nevertheless, this evolution is distinguished from partial melting trends by the persistence of a discontinuity in the slope of Ni enrichment, even for high degrees of melt formation. A smoothing effect associated with melt formation is also observed for Cr. However, the evolution of this element remains distinctly different from that expected from partial melting.

4.5. Best fit of the Ronda data

Variation of melt volume during melt–rock reaction appears to be a critical parameter in the evolution of trace elements with either incompatible or compatible characteristics in the reacted peridotites. Increasing melt volume in the reaction zone results in a transient ‘batch-melting’ effect superimposed on trace element evolution resulting from the percolation–reaction process. Due to this effect, the transient over-enrichment of incompatible elements in melt and minerals (e.g., REE in olivine-forming percolation–reaction systems) is reduced. The opposite evolution is predicted for compatible elements (e.g., Ni), and also for reactions occurring at decreasing porosity.

For the most compatible elements, the analytical data for the Ronda peridotites samples are better fitted by the models assuming a large increase in porosity. This result is consistent with previous studies suggesting that olivine-forming melt–rock reactions generally occur at increasing melt volume [8–10]. In the modelling shown in Fig. 4 the maximum porosity increase is from 1% in the protolith (lherzolite) to 15% in the reacted rocks (dunites). Actually, melt formed in the reaction zone was possibly extracted during the reaction, with porosity remaining relatively low at every stage. To take account of this process it would be necessary to consider compaction of the matrix, but this is beyond the scope of this study. However, the effect of melt extraction may be qualitatively predicted from previous studies on the compaction of molten peridotites [34]. Matrix compaction would be apparent by virtue of smoother incompatible (Yb) and compatible (Ni) element profiles for a given melt volume formed during the reaction. Elements with bulk partition coefficients close to 1 in reacted peridotites (Cr) would not be significantly affected. In other words, a model taking into account matrix compaction should also generate trace element profiles similar to the Ronda peridotites but for lower degrees of melt formation than the constant volume model. Solid diffusion would also smooth discontinuities [15] like those observed in the Cr and Ni evolution, and therefore could improve the fit of the Ronda data.

5. Conclusion

The mathematical model proposed in this study allows the prediction of different types of trace element evolution resulting from melt percolation processes associated with melt–rock reactions. These different types of evolution differ markedly from those produced either by melting and crystallization processes (e.g., [33]) or by interstitial percolation in peridotites of constant mineralogical composition (e.g., [14]). Whereas trace element variations induced by the latter processes are mainly controlled by peridotite/melt partition coefficients, those resulting from the percolation–reaction processes are controlled by both peridotite/melt and intermineral partition coefficients. In schematic terms, peridotite/melt partitioning governs the chromatographic fractionation of trace elements associated with magma transport, while intermineral partitioning controls the source/sink effect associated with melt–rock reactions.

Good correspondence between trace element patterns obtained with the percolation–reaction model and the Ronda data validates the assumption that the bands of refractory peridotites observed in the Ronda massif represent porous-flow channels formed at the expense of the host lherzolites by melt–rock reactions involving pyroxene dissolution and olivine precipitation, at increasing melt volume [10]. The excess of melt formed by the reaction was possibly expelled by compaction throughout the percolation process. It is especially worth noting that several trace element characteristics of the Ronda refractory peridotites (e.g., flat and U-shaped REE patterns, discontinuities in Cr and Ni variations, and Cr depletion in the most refractory rocks) could not be explained without invoking the chromatographic effects of kilometre-
scale percolation coupled with the migration of reaction fronts. This precludes the formation of the refractory peridotite bodies by coalescence of reacted wallrocks after closure of magma conduits. Seeing as they display similar geochemical characteristics, the bands of refractory peridotites observed in other lherzolite massifs were probably formed by the same process.

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