

Chlorine cycling during subduction of altered oceanic crust

P. Philippot

CNRS-ESA 7058, Lab. de Pétrologie, UPMC, 4 place Jussieu,
75005 Paris, France

P. Agrinier

Lab. de Géochimie des Isotopes Stables, IGP, UDD, 2 place
Jussieu, 75005 Paris, France

M. Scambelluri

Dipartimento di Scienza della Terra, Corso Europa 26, 16000
Genova, Italia

Understanding the exchange of volatiles between the mantle and the exosphere, including their accumulation in surface reservoirs via outgassing of the Earth's interior, the degree of mantle depletion and the extent of recycling back into the mantle, represents a central issue of terrestrial geodynamics. A process of great significance to the global volatiles inventory is the devolatilisation of the subducted oceanic slab. Estimates of fluxes out of the subducted slab are very uncertain and there are a range of conflicting models.

Little is known about the Cl content of subducted materials. As a consequence, attempts to model the cycle of chlorine have generally considered that the budget of chlorine in the exosphere was due to mantle degassing alone or, in other words, that all the chlorine incorporated in the altered oceanic crust was lost during early subduction [1]. Recently however, on the basis of chlorine isotope analysis of oceanic material, [2] showed that the current evolution of the Earth's Cl distribution likely involved a combination of degassing of the mantle and the recycling of altered crust through subduction. The quantity of exospheric Cl that can be transferred back to the mantle remains largely unknown, however.

The aim of this study is to show that eclogitic rocks, that have experienced devolatilisation, with little or no interaction with external fluid sources, can be viewed as relevant analogues for crustal material that may be transferred back into the mantle. Thus they can be used to evaluate the magnitude of Cl recycling into the mantle during subduction. The approach we use combines oxygen isotope analysis of high-pressure minerals with fluid inclusion analysis. This correlation between $^{18}\text{O}/^{16}\text{O}$ ratios, which are good monitors of fluid movement in metamorphic rocks, and chlorine concentration of the fluid phase, which is likely to be buffered by the fluid (not the host rock), is invaluable in assessing the dynamics of chlorine during devolatilisation processes.

We report oxygen isotope ratios of omphacite and fluid inclusion data determined in eclogitic metagabbros of the Rocciavré massif, Italian Alps. The data are compared with those obtained for the Monviso [3], Cyclades [4] and the Franciscan Complex [5] high-pressure rocks. In all localities, relics of early dehydration fluids are preserved as primary fluid inclusions in the cores of omphacite megacrysts (Rocciavré, Monviso and Franciscan Complex) or garnet (Cyclades). Salinity estimates of the inclusion fluids range from 32 to 45 wt.% NaCl in Rocciavré, 17 to 21 wt.% NaCl in Monviso, and are similar to seawater in other areas. Omphacite and bulk-rock $\delta^{18}\text{O}$ values of Rocciavré (5.1–6.8‰) and Monviso (3.0–5.3‰) metagabbros are markedly lower than those of Cyclades (6.8–14.3‰) and the Franciscan (6.7–13.1‰) metabasites.

The eclogitic metagabbros from Monviso and Rocciavré are part of a coherent metaophiolitic sequence. The presence of a cumulate structure and of local diabase dikes clearly demonstrates that the rocks were part of the transition zone (gabbroic layer or high-temperature alteration zone). In contrast, the metabasic rocks of Sifnos and Franciscan Complex consist of metavolcanic rocks (blueschists, eclogites) either interbedded with thin layers of metasediments as is the case in Sifnos, or occurring as exotic blocks within matrices of metasedimentary and meta-ultramafic rocks (Franciscan Complex). Although the history of these latter rocks may have been complex, it is likely that they originally formed as extrusive material where the interaction with seawater was maximum (low-temperature alteration zone).

We present a compilation of the fluid inclusion salinities expressed in wt.% equivalent NaCl as a function of the $\delta^{18}\text{O}$ compositions of their host rocks from a variety of oceanic dredged samples, unmetamorphosed ophiolites and the high pressure rocks documented above. A striking feature emerging from this compilation is the similarity in

the salinity - $\delta^{18}\text{O}$ systematics recorded between oceanic rocks and their high-pressure equivalent. This suggests that high pressure metamorphism, and associated processes, did not modify significantly the variability in chlorine concentrations and oxygen isotope ratios documented along a typical section of the altered oceanic crust.

It is important, when evaluating the Cl inventory of the deep mantle, to realize that the chlorine content of the rocks under consideration must be considered a net amount, without assumptions on what is expelled in forearc regions and arc magmas. Indeed, Monviso and Rocciavré eclogites contain omphacite and garnet with no hydrous phases and thus have achieved complete devolatilisation. The only fluid phase preserved in Alpine rocks occurs in fluid inclusion, which are thought to be derived from the breakdown of hydrous minerals such as amphibole and chlorite. The H_2O contents of low-strain rocks from Monviso, due to the presence of fluid inclusions, is of the order of 2000 to 3000 ppm [3]. Such a small amount of H_2O (c. 10% of pre-subduction water), is equivalent to that stored in nominally anhydrous mantle minerals and hence could easily remain in the rocks down into the deep mantle. With regards to the Cyclades and Franciscan-type of high-pressure rocks, uncertainties arise from the presence of hydrous minerals which are likely to breakdown with ongoing metamorphism to produce H_2O , which in turn can dilute the Cl content of the inclusion fluids. However, primary fluid inclusions occurring in nominally anhydrous minerals like omphacite and garnet, some of which being texturally similar to the primary inclusions of Alpine eclogites (see [6] for details) are likely to escape further interaction with external fluids during

progressive metamorphism. Accordingly, it is suggested that Alpine eclogites and possibly Cyclades and some of the well-preserved Franciscan rocks can be viewed as relevant analogues of the type of material to be transferred back into mantle.

Extrapolating the estimated H_2O and Cl contents of eclogitic rocks to a representative section of the subducted oceanic crust indicates that a minimum of 100 to 200 ppm Cl could be recycled into the mantle during subduction. This yields a Cl/ H_2O ratio of 3.6 to 7.5×10^{-2} for the subducted oceanic crust, which is similar to E-MORB. On the basis of available Cl isotopic data [2], we infer that a large proportion (70%) of the Cl stored in the altered crust should be recycled to the mantle to generate an isotopic composition of the subducted crust equivalent to the source of unaltered mid-ocean ridge basalt ($\delta^{37}\text{Cl} = 4.7\text{‰}$, [2]).

References

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