The behavior of chlorine and $\delta^{37}Cl$ during the oceanic crust alteration

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The oceanic crust (OC) is a vector of chemical exchanges between the surface and the Earth's interior. Hydrothermal circulation in the ocean's floor is the major control of chemical compositions of both seawater (SW) derived fluids and crust (before subduction). In order to bring new constraints on the OC alteration, chlorine stable isotope composition ($\delta^{37}Cl$) was determined in both high (HTF) and low (LTF) temperature fluids, at ridge axis and off-axis, respectively, and in fresh and altered basalts.

Worldwide HTF (T >230°C) have a large range of chlorinity (250 to 821 mM), but show very constant $\delta^{37}Cl$, indistinguishable from the SW $\delta^{37}Cl$ (0.0‰). This $\delta^{37}Cl$ homogeneity suggests that the phase separation process, responsible for chlorinity variation at HT, does not fractionate Cl isotopes [1]. In contrast, despite very small variations of chlorinity (550± 6mM), LTF (T≤ 60°C) show $\delta^{37}Cl$= -0.71± 0.67‰ (1σ). Moreover, $\delta^{37}Cl$ values show positive covariations with $\delta^{18}O$ (mainly modified by water-rock interactions) suggesting that a single process leads to a depletion in ^{37}Cl of the interacting fluids.

Basalts, both fresh and altered at LT, are also depleted in ^{37}Cl relative to SW (-2.0 <$\delta^{37}Cl$ <-0.2‰ and -2.8 <$\delta^{37}Cl$ <-0.5‰, respectively). Cl of the reacting fluids has precipitated in the pores of the altered basalts upon drying. It was recovered by leaching as described in [2]. These residual salts, representative of the reacting fluids (-5.1 <$\delta^{37}Cl$ < 0.0‰), have higher $\delta^{37}Cl$ than the associated whole rock, implying that $\Delta^{37}Cl_{R\text{-}F}$ <0. This contrasts with prior assumptions [3-4], and with classical fractionation laws predicting a ^{37}Cl enrichment of the solid phase.

Interaction of SW ($\delta^{37}Cl$ = 0‰) with fresh OC ($\delta^{37}Cl$ < 0‰) produces fluids and rocks with $\delta^{37}Cl \leq 0$‰. These data expose a mass balance problem.

References

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The metasomatic history of the lithospheric mantle beneath NE Spain

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The spinel peridotite suite at Olot, is remarkably bi-modal consisting of very fertile protogranular lherzolites, sometimes bearing texturally equilibrated pargasite amphibole (3 samples out of 60), and very refractory harzburgites showing secondary recrystallization textures. Bulk rock REE systematics are widely variable: lherzolites display flat or depleted LREE patterns (HREE concentration up to 2.7*Ch; La_N/Yb_N down to 0.42); harzburgites are extremely depleted in HREE (down to 0.21*Ch) displaying at the same time high LREE/HREE ratios (La_N/Yb_N=12.3-17.2); this LREE enrichment is coupled with relative enrichment in Th, U, Nb and Ta. In situ LA-ICP-MS analysis of clinopyroxene highlights LREE depleted compositions with a slight spike at Eu in anhydrous lherzolites (HREE up to 13*Ch, La_N/Yb_N down to 0.3, and Eu*=1.2-1.5); the presence of LREE depletion (La_N/Yb_N down to 0.2) coupled with a Eu positive anomaly (Eu* up to 1.7) also characterize the clinopyroxenes of two amph-bearing lherzolites. In these samples the clinopyroxene composition mimics, at slightly lower concentration, that of the coexisting amphiboles. The constituent clinopyroxenes of harzburgites display totally different REE distributions, characterised by remarkable HREE depletion (down to 0.4*Ch) and ubiquitous M/LREE enrichment. In these harzburgites, Nd_N/Yb_N (up to 20.7*Ch) is generally higher than La_N/Yb_N (up to 12*Ch) giving rise to upward convex patterns. Geochemical features of the harzburgites indicate that the mantle section sampled beneath this area suffered major episodes of melt extraction followed by metasomatic processes - triggered by highly alkaline melts - that induced cryptic enrichments. Lherzolites, on the other hand, possibly indicate modal re-fertilization by pervasive impregnation of subalkaline (LREE-depleted) melts.