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Chlorine Recycling in Subduction Zones: New Constraints from Chlorine Stable Isotopes

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The study of fluids expelled in subduction zones tells us about the geodynamic and geochemical evolution of active convergent margins. The complex fault system occurring in these zones allows the ascension of fluids along "decollement" zones and the mixing of internal and superficial fluids. Their expulsion probably results from the reduction of porosity during sediment consolidation processes, diagenetic or metamorphic dehydration and/or from the breakdown of hydrous minerals and gas hydrates and from seawater diffusion or convection through sediments. These fluids originate from the oceanic crust layer as well as from local fluids trapped in sediments. "Residual fluids" left after these processes are likely to participate to the melting of the mantle wedge and to the arc volcanism. Studying all these fluids may help us to understand magma formation dynamics in a subduction context.

Chlorine is often the main anion in geological fluids. The stable isotope composition of chlorine ($^{37}Cl/^{35}Cl$) is a powerful tool to trace the evolution of subduction zone fluids. We have measured chlorine stable isotope ratios of various geological materials by IRMS on CH_3Cl^+. Results are given in δ units, in ‰ versus SMOC (Standard Mean Ocean Chloride) with a mean accuracy of 0.03‰.

Chlorine isotope distribution is not uniform and its total range of variations is of more than 18‰. The few subduction zone chlorine isotope data published to date cover the whole range of variation of $\delta^{37}Cl$ (from -8‰ to +10‰). They are scattered over several subduction zones and concern several different types of samples. However, these data do not bring enough information on the behaviour of chlorine to be able to constrain its global geochemical cycle. We focused our isotopic study on the Atlantic oceanic plate subduction under the Caribbean micro-plate, using a collection of fluids (54 interstitial fluids and 20 expelled fluids) from two sites on the Barbados accretionary prism and from the Lesser Antilles island arc (96 hot spring samples, 13 gas condensates and an andesite).

At the outer edge of the Barbados sedimentary complex, hot fluids (20ºC) expelled by sub-marine (5000mbsl) mud volcanoes (Manon site, Dia et al., 1995) show a large range of $\delta^{37}Cl$ between -5.3‰ and +0.1‰, in agreement with four data of Ransom et al. (1995). We interpret our data as a three-component system: mixing between two chemically different deep fluids, both with low $^{87}Sr/^{86}Sr$ and negative $\delta^{37}Cl$ signatures, and then mixing with seawater at 0‰. At the inner edge of this prism, hot fluids expelled by terrestrial mud volcanoes (Trinidad, Dia et al., 1999) show, for a similar range of chloride contents, a less negative range of $\delta^{37}Cl$ from -3.2‰ to -0.3‰. Few samples having lower chloride concentrations are interpreted as diluted with rainwaters, but without significant effect on the $\delta^{37}Cl$ values. Expulsion of negative $\delta^{37}Cl$ fluids through the prism may produce positive $\delta^{37}Cl$ residual fluids subducted deeper towards the mantle and eventually partly expelled later.

$\delta^{37}Cl$ and chloride contents from samples of hot springs and gaseous emanations of the Lesser Antilles island arc (Montserrat, Guadeloupe, Dominica and Martinique) are presented here for comparison (Bigot et al., 1987 and Bigot et al., 1994). They were obtained as part of the French Volcanological Observatory survey program. The $\delta^{37}Cl$ of these fluids show a even less negative range of isotopic compositions from -0.8‰ to +0.1‰ for hot waters up to strictly positive values for condensates (+0.8‰ to +2.0‰). In summary, there is an increase in $\delta^{37}Cl$ values of the expelled fluids when going from the prism to the island arc. This range of variation may correspond to the evolution of the $\delta^{37}Cl$ of the residual fluids expelled from the descending oceanic crust.

The study of volcanic rocks from the Lesser Antilles island arc (Saba, S^t Kitts, Montserrat, Guadeloupe, Dominica, Martinique, S^t Lucia and S^t Vincent) has just begun and our first result, from an andesite of Mount Pelée (Martinique) has a $\delta^{37}Cl$ value of 0‰ (±0.2‰). This is within the range of $\delta^{37}Cl$ of fluids or gas from the Lesser Antilles island arc. Altered MORB should complete this data set and allow us to model the chlorine budget at a regional scale and constrain recycling of chlorine towards the mantle and its isotopic composition.

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