## Balance of fluid exchange between sediments and seawater. The perspective of the chlorine isotopes of chlorides.

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Chlorine isotope ratios of chlorides ( $\delta^{37}$ Cl) in pore fluids from 24 globally distributed oceanic sedimentary sites show a depletion of <sup>37</sup>Cl in chlorides with depth. The mean value for  $\delta^{37}$ Cl is -2.4 ‰, whereas that of seawater is 0 ‰. Assuming that the pore fluids were originally seawater, the balance of chlorine isotopes in the porefluids implies the disappearance of <sup>37</sup>Cl-enriched chlorides. Since chlorides are the dominant ions in these fluids, this loss of <sup>37</sup>Cl-enriched Cl reveals an important process operating in the sediments. The widespread distribution of our samples suggests that this process is independent of the tectonic environment in which the sediments were deposited and is accentuated by the presence of clays in the sediments.

Examination of the Cl budget in oceanic sediments shows that the pore fluid chlorides are the dominant Cl reservoir. Other potential Cl contents (minerals, organochlorides,...) are very modest and cannot store the <sup>37</sup>Cl-enriched loss in the fluids. A review of all the processes that are known to decrease the  $\delta^{37}$ Cl of chlorides either by fractionation of chlorine isotopes in chlorides (diffusion, gravity, filtration) or by mixing (advection of <sup>37</sup>Cl-depleted chlorides) suggests that this process could be the ion filtration of pore fluid chlorides through clay membranes. During ion filtration, <sup>37</sup>Cl-enriched chloride would be expelled from the porefluids into the seawater.

The expelled chloride fluxes required to explain the observed <sup>37</sup>Cl depletions in worldwide porefluid sediments range from 1 to 40 mole of Cl.m<sup>-2</sup>.kyr<sup>-1</sup>. This suggests that sediment pore fluids and seawater exchange chlorides on the time scale of 6 to 250 Myr (mean  $\approx 12.5$  Myr). On this time scale, the  $\delta^{37}$ Cl of seawater is controlled by the nature of the continental detrital clays that are deposited on the seafloor and the range of  $\delta^{37}$ Cl variations in seawater must be within -0.3 to +0.3 ‰. Minerals with high surface charge density, such as smectites, which are associated with strongly <sup>37</sup>Cl-depleted pore-fluids, strongly increase the  $\delta^{37}$ Cl of seawater, whereas minerals with low surface charge density, such as illites-chlorites, kaolinites, carbonates, which are associated with weakly <sup>37</sup>Cl-depleted pore fluids, slightly increase the  $\delta^{37}$ Cl of seawater.