

Chlorine/fluid cycling in subduction zones: Evidence from chloride concentrations and chlorine stable isotopes

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Pore waters with chloride concentrations less than seawater are a characteristic feature of accretionary complexes in convergent margins. One well-documented case where such freshened fluids have been documented is in the Nankai Trough, Japan, Ocean Drilling Project (ODP) Site 808. The enigmatic profile of pore water chloride concentration versus depth in these sediments is characterized by an extensive section of lower than seawater chloride concentrations between 560 and ~1200 mbsf, with a broad minimum of about 450 mM (~20 % seawater dilution) at ~1,100 mbsf (Fig. 1).

Newly obtained chlorine stable isotopic ratios ($^{37}\text{Cl}/^{35}\text{Cl}$) in the pore fluids at the Nankai drill site are highly fractionated (-7.4‰) compared to seawater (0‰), with the most extreme fractionation (Fig. 2) coinciding with the lowest pore water chloride concentration (Fig. 1). Chlorine stable isotopes in subduction zone settings can be fractionated by water-rock exchange when ^{37}Cl is preferentially incorporated over ^{35}Cl into the structural (OH) site of diagenetic or metamorphic hydrous minerals (e.g. smectite, illite, chlorite, serpentine, talc, and amphibole) and by diffusion. In the case of mineral uptake, lower temperature minerals fractionate Cl isotopes more highly than those formed at higher temperatures; but their maximum Cl contents are generally an order of magnitude lower (e.g. < 100 ppm in smectite versus several parts per thousand in amphibole).

The source of the freshened fluids at Nankai is presently being debated. On the basis of pore water chloride data alone, previous studies have suggested that clay mineral reactions, in particular those involving smectite, are primarily responsible for the freshening observed. These studies attribute the increase in pore water chloride to ~560 mbsf (Fig. 1) to the *in situ* hydration of volcanic glass and formation of clays and zeolites. The decrease in chloride between 560 and 1100 mbsf is proposed to

result from clay mineral (and zeolite) dehydration reactions. Below 1100 mbsf, the formation of hydrous minerals in the underlying volcanoclastic section is invoked. Data from Cl stable isotopes now permit us to evaluate these hypotheses. In the case of simple loss of H_2O from smectite interlayers or zeolites, the Cl stable isotope ratios of associated pore waters are unaffected. However, reactions that involve smectite or other Cl-bearing hydrous silicate minerals will affect the Cl stable isotopic signature of the pore fluids. Below ~560 mbsf, the two profiles are decoupled. The decrease in pore water chloride to ~1100 mbsf is accompanied by a strong decrease in pore water $\delta^{37}\text{Cl}$; the opposite of what would be expected if this isotopic signature was the result of clay mineral dehydration that involved the destruction of smectite and/or other low temperature hydrous layer silicates. Such a reaction would tend to release ^{37}Cl into the pore waters, not remove it. Likewise, decoupling is evident between the two profiles below 1100 mbsf where hydration reactions are thought to be occurring. The decoupling of pore water chloride and the chlorine stable isotope data between 560 and 1100 mbsf provides important evidence that H_2O in freshened fluids at Nankai are coming from mineral reactions occurring in the seismogenic zone.

Calculations demonstrate that contributions to the observed freshening in Nankai, due to the release of H_2O from smectite interlayers and zeolites in the section drilled can account for only 4 % freshening of seawater, at best, instead of the 20% observed. Neither is there any physical evidence for recent fluid flow along the décollement (~960 mbsf). Porosity in sediments below the décollement is higher (40% vs 30% in the overlying sediments) than in sediments above; and Sr, He, and O isotope data, as well as pore water chloride and sulphate, suggest that freshened pore waters at Nankai originate from repeated transient episodes of fluid incursion from the high

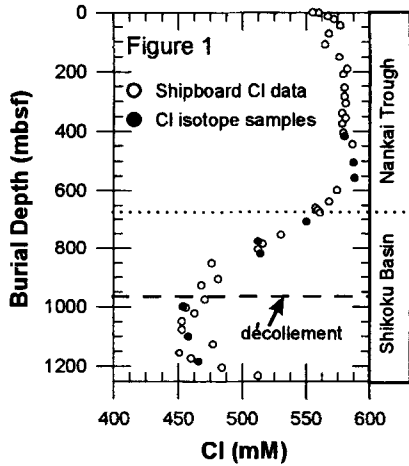


FIG. 1.

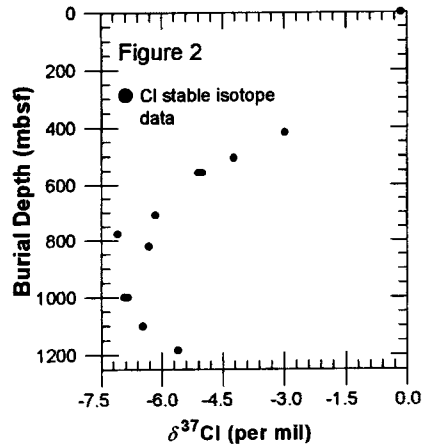


FIG. 2.

porosity zone below the décollement (Kastner *et al.*, 1993).

Between 560 to 820 mbsf, the pore water chloride trend has a diffusive geometry. Ficks Law was used to estimate the time required to establish a similar gradient. The Nankai Trough is a high heat flow area (~10°C per 100 m) and results of our calculations suggest that low-Cl fluids have been present at the 820 mbsf level for at least the last 100,000 to 150,000 years, based on the assumptions: (1) that the profile reflects the mixing of a high chloride fluid in the sediment above 560 mbsf with a low chloride fluid in the sediment below 820 mbsf; (2) that the bulk diffusion coefficient of pore water Cl⁻ is (10⁻⁵ cm² s⁻¹ at 100°C); (3) that Cl is geochemically conservative; and (4) that the source of the freshened fluids is arcward.

The decoupling of the profiles in Figs 1 and 2, between 820 and 1100 mbsf, reflects the interplay between mineral dehydration reactions from: (1) the net loss of structural (OH) from hydrous minerals undergoing metamorphic dehydration reactions in the seismogenic zone; (2) the net uptake of Cl, and in particular ³⁷Cl, by hydrous minerals forming during these reaction; and (3) the loss of H₂O from smectite interlayers and zeolites during the accretion/subduction process. These reactions are occurring in parts of the section with considerably lower porosity than in the parts to which the released fluid is channeled by faulting, microfracturing, or hydrodynamic flow. Thus, each mole of H₂O released in a deep source region has a more significant 'dilution' effect on its pore water than that released in a higher porosity setting, such as ODP Site 808. The isotopic

fractionation shown in Fig. 2 results, in large part, from reaction along the subducting slab involving low temperature, diagenetically formed, hydrous minerals with low absolute Cl concentrations (e.g. smectite) that contain highly fractionated Cl (i.e. enriched in ³⁷Cl). These minerals react to form higher temperature metamorphic hydrous minerals (e.g. amphibole) with significantly higher Cl concentrations (1000 ppm or more). Even though these latter minerals fractionate Cl to a lesser extent than their diagenetic counterparts, their overall uptake of ³⁷Cl is greater owing to the continuous increase of ³⁷Cl in the system as this isotope is stored in the solid phases and ³⁵Cl-rich fluids are expelled to areas of lower pressure and higher porosity. This mechanism may preferentially move heavy Cl into the mantle during subduction and provides a mechanism for increasing lower crustal Cl contents.

Elevated Cl concentrations in hydrous metamorphic minerals, when destabilized at higher temperatures and pressures to form anhydrous mineral assemblages (e.g. eclogites), will release their Cl to the intergranular fluid. This Cl may play an important role in the origin of high Cl brines that have been found in eclogites (P. Philippot, per. comm.) which represent subducted crustal residues. It should also be noted that the fractionation we have observed indicates that, contrary to what is generally assumed, Cl cannot be considered a conservative pore water species in subduction zones. In addition, models of pore water chloride freshening need to include provision for mineral reactions other than those just related to the release of H₂O from smectite interlayers and zeolites and the reaction of smectite to form illite.