Divergent behaviors in global geochemical cycling of bromine and chlorine

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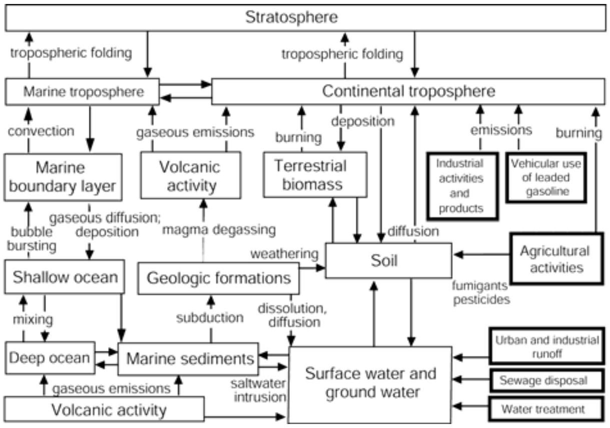
Global geochemical cycles of bromine (Br) and chlorine (Cl) largely parallel one another. Oceanic emissions dominate the atmospheric fluxes of both halogens, augmented by terrestrial biogenic sources and volcanic emissions. Wet and dry deposition and biological uptake transfer the halogens to soil and vegetation. Ultimately, the halogens return to their marine origins via surface runoff or are carried into the subsurface with groundwater.

Cl/Br ratios are widely used as natural tracers of groundwater history due to generally conservative behavior in this environment. In other parts of their geochemical cycles, however, multiple physical and chemical processes lead to differing rates of transformation and transport and subsequent fractionation of Cl/Br ratios. These include bursting bubbles at the ocean surface, partitioning between gas and particulate phases in the atmosphere, partitioning between organic and inorganic atmospheric compounds, photodissociation, aerosol acidification, precipitation scavenging, sorption onto organic and inorganic surfaces, plant uptake, and precipitation of salts from brines. A conceptual box model lays the groundwork for assessing past, present and future variations in Cl/Br ratios in global environmental compartments.

Figure 1: Chlorine and bromine geochemical cycles. (Only major compartments and transfer paths are shown. Bold boxes indicate anthropogenic activities.)



Formation waters are connate, meteoric, saline and their Cl / Br disclose tagging by brine-spray on land

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Shallow cycling groundwaters, are (a) of recent ages; (b) isotopicaly light (meteoric), and (c) tagged by airborne sea-spray (Cl/Br around 300 and no Ca-chloride).

In contrast, formation waters are (a) fossil (high He-4, Ar-40); (b) also meteoric, i.e. recharged by rain; and (c) tagged by airborne brine-spray, with Cl/Br of 80 to 220, and significant Ca-chloride concentrations.

Formation waters, encountered in adjacent drill holes, often reveal different compositions, indicating entrapment within hydraulically isolated rock- compartments, i.e. these are connate groundwaters.

The formation water hosting rocks are commonly of a marginal marine facies, whereas the isotopic composition of the water phase indicates on-land meteoric origin, and the composition discloses formation in intensive evaporitic environments. These boundary conditions lead to the working hypothesis that formation waters were formed on paleo-flatlands in the following stages: (a) sea transgression and sedimentation of marine rocks; (b) sea regression, exposing a low-land covered by sabkhas and lagoons, and subjected to rain, and the latter infiltrated to the exposed low rock landscape, flushed the originally contained interstitial water, and replaced it with meteoric brine-tagged groundwater; (c) upon the following sea invasion new rocks were sedimented, confining the former rocks with their contained on-land formed saline groundwaters. A multitude of such stages, as well as facies variations, formed the isolated rock-compartments that host the connate formation waters.

The presented geological-hydrological findings open a wide scope of studies of the halogens and their isotopes in marine and terrestrial aqueous systems, e.g.: (a) patterns of sea-spray tagged shallow groundwaters at different distances from the oceans; (b) patterns of a variety of evaporitic precipitates and residual brines; to be studied at different locations; (c) a variety of formation waters of different properties, from various locations and of different depths and ages.

The obtained isotopic data will serve to identify the origin of formation waters at different study areas and to check the above presented working hypothesis.

Iodide oxidation and iodate reduction by marine bacteria

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The mobility and the speciation of iodine are affected by bacteria through biological processes such as volatilization [1,2] and accumulation [3]. In aqueous environments such as seawater, the predominant chemical forms of iodine are iodide (I^-) and iodate (IO_3^-). Although IO_3^- is a thermodynamically more stable form of iodine in seawater, significant quantities of I^- can be observed in surface and near-bottom layers. Conversely, some oxidation of I^- must be mediated in seawater. However, autooxidation of I^- to IO_3^- does not occur in seawater, since the first step of I^- oxidation, i.e. oxidation of I^- to molecular iodine (I_2), is a thermodynamically unfavorable reaction. Thus, I^- oxidation and IO_3^- reduction are probably mediated by biological activities. The aim of this study is to isolate marine bacteria with capacities for oxidizing and reducing iodine.

I^--oxidizing bacteria (IOB), which oxidize I^- to I_2, were isolated from seawater and natural gas brine water [4]. Based on 16S rRNA gene sequences, they were divided into two distinct groups (*Roseovarius* sp. and unidentified bacteria), and I^- oxidation was mediated by an extracellular enzyme. Interestingly, IOB produced not only I_2 but also volatile organic iodine compounds, diiodomethane (CH_2I_2) and chloroiodomethane (CH_2ClI).

IO_3^- -reducing bacteria (IRB) were isolated from marine surface sediment. They were identified as *Pseudomonas stutzeri*, a bacterium known as a nitrate reducer. Although IRB could not use iodate as a sole electron acceptor for growth, cell suspension of IRB reduced iodate in the presence of electron donors (acetate, succinate, and glycerol) under anaerobic condition. Iodate-reducing activity was inducible by iodate but not by nitrate, and it was found to be a membrane-bound enzyme.

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Chlorine stable isotopes from passive and active continental margins as tracers of advective fluid flow

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Ocean drilling of the past two decades has lead to a growing awareness of the significance of advective fluid flow in modern continental margins and the recognition of fundamental differences in the flow patterns between passive and active margins. In this presentation, chloride and chlorine stable-isotope profiles from passive-margin ODP leg 164 (Blake Ridge; Hesse et al., 2000) and active-margin legs 131 and 190 (Nankai Trough; Spivack et al., 2002) are compared.

At passive-margin Site 997 (Blake Ridge gas-hydrate field) a pronounced steady downward depletion of ^{37}Cl in pore-water to nearly -4‰ $\delta^{37}Cl$ at ~750 m below sea floor (mbsf) is associated with a 10% Cl^- decrease relative to seawater. Chlorinity reductions in hydrate-bearing sediments commonly result from fresh-water release by hydrate melting. However, in-situ Cl^- measurements at Site 997 suggest that >50% of the chlorinity reduction occurred prior to hydrate dissociation. Modeling the chlorinity profile shows that *vertical* advection of a ^{37}Cl depleted, low-chlorinity (506 mM) water from below the drilled sequence (advection rate of 0.18 mm/y) can explain the reduction prior to sampling. Its source will be discussed.

In the Nankai Trough ODP site 808, $\delta^{37}Cl$ values decrease from near-seawater values (0‰) near the sediment/ water interface to a minimum of -7.8‰ below 600 mbsf in order to return to heavier values near the top of the oceanic basement indicating *rapid lateral* advection (estimated rates of up to 13.5 cm/y) of strongly ^{37}Cl-depleted fluids of different origin within the accretionary wedge parallel to the decollement zone. The depletion in ^{37}Cl is accompanied by Cl^- decreases below 400-600 mbsf between ~10% and 20%.

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Chlorine stable isotopes in two subduction zones: Nankai Trough and Mariana, and implication for fluid-sediment interactions and fluid flow

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Pore fluids at Nankai Trough and Mariana subduction zones were analyzed for chlorine stable isotope ratios ($^{37}Cl/^{35}Cl$). At Nankai subduction zone (ODP Sites 808, 1174, and 1173) pore fluids exhibit the largest range in $\delta^{37}Cl$, from seawater value of 0‰ to -7.8‰; the latter is the most negative value of all the ODP pore fluids analyzed so far; at the Mariana subduction zone (Site 1200) $\delta^{37}Cl$ ranges from 0‰ to +1.8‰.

Chlorine isotopes fractionate when they are incorporated into diagenetic or metamorphic hydrous minerals where Cl substitutes for OH group. At Nankai, because of the low Cl concentration in smectite (~30 ppm), even if a maximum $\delta^{37}Cl$ value in smectite of 8‰ is assumed (Magenheim et al., 1995), a 100% I/S transformation would not account for the very negative $\delta^{37}Cl$ values observed in the pore fluids (−7.8‰), at the chloride minimum (450-480 mM) depth interval at Site 808 and 1174 (Spivack et al., 2002). Arcward, at greater depths, the formation of high temperature (>250° C) hydrous minerals could preferentially consume ^{37}Cl (Schauble et al., 2003), thus enriching the residual fresher fluid in ^{35}Cl (negative $\delta^{37}Cl$). Accordingly, the negative $\delta^{37}Cl$ observed could be explained by mixing with a laterally advecting deep-sourced fluid carrying the negative $\delta^{37}Cl$ signal.

In contrast, the pore fluids at Mariana subduction zone (ODP Site 1200) are enriched in ^{37}Cl. $\delta^{37}Cl$ increases from seawater value at the seafloor to ~+1.8 ‰ at 71 meter below sea floor. Chloride concentration is also diluted as compared to bottom seawater by ~8-9%. The pore fluids at this site originate at greater depths, where serpentine dehydration occurs (Mottl et al., 2003). The serpentines in Mariana contain hundreds of ppm Cl. When they dehydrate, Cl with enriched ^{37}Cl, as well as H_2O, are released to the pore fluid. As a result, the upwelling fluid exhibits the positive $\delta^{37}Cl$ but lower Cl concentration.

Cl concentration and isotope systematics can thus supply critical information, not available from other measurements, about the source of fluids, flow paths, and reaction conditions. Here they are shown to distinguish different mechanisms of deep-sourced fluids at two subduction zones, i.e., between dehydration concurrent with the formation of high temperature hydrous minerals at Nankai Trough, and serpentine dehydration in Mariana.

Environmental change recorded in mid-latitude ice cores from southern North America and Central Asia: Comparison of chlorine-36 and iodine-129 profiles and the implications for stewardship of the environment

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The U.S. Geological Survey (USGS) is conducting a collaborative global research program in mid-latitude glacial environments to study the effects of increased loading of anthropogenic radionuclides and rapid climate change on alpine ecosystems. This global research program includes the collection of isotopic and geochemical data from the Upper Fremont Glacier, located in the Wind River Mountain Range, Wyoming, U.S.A., and the Inilchek Glacier, located in the Tien Shan Mountains, Republic of Kyrghyzstan, in central Asia. Mid-latitude glacial sites also are being studied in China, New Zealand, Nepal, and Russia. Geochemical records preserved in ice and snow collected from these mid-latitude sites include significant anthropogenic radioactive fallout such as plutonium, tritium, chlorine-36 (^{36}Cl), and iodine-129 (^{129}I), and signals from global and regional events such as volcanic eruptions, droughts, and forest fires. Organic matter preserved in the ice also provides a means to age-date sections of ice cores by using the carbon-14 inventory. Concentrations of the cosmogenic isotopes ^{36}Cl and ^{129}I in ice cores from the Upper Fremont Glacier and the Inilchek Glacier were significant. The ^{129}I concentrations in ice from the Upper Fremont Glacier were orders of magnitude greater than ^{129}I concentrations predicted by global fallout modeling and greater than the ^{129}I concentrations in ice from the Inilchek Glacier. The ^{36}Cl concentrations in ice cores from these two sites were similar. The largest ^{129}I concentration in the Upper Fremont Glacier could be a result of elevated atmospheric releases of ^{129}I from the U.S. Department of Energy's Hanford facility in the western United States in the late 1940s and early 1950s.

The isotopic and geochemical data gained from analyses of these glacial records has lead to a reevaluation of the timing of climate and environmental changes. For example, by better defining the glacial chronology at the Upper Fremont site using the ^{36}Cl and ^{129}I nuclear weapons-testing peaks in conjunction with other isotopic data, it was determined that, from the mid-1800s to the present, there have been relatively rapid changes in the regional climate of southern North America. These rapid changes in the mid-1800s are interpreted as an abrupt end of the Little Ice Age; these changes occurred within a period of less than 10 years and possibly within as few as 2 to 3 years. The environmental implications of these records will be discussed.

The development of $^{129}I/^{127}I$ ratios in Scottish sea water

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$^{129}I/^{127}I$ ratios of Scottish seawater taken at seven locations in 2003 were presented at the Goldschmidt 2004 conference (Schnabel *et al.*, 2004). These data constituted the first reported $^{129}I/^{127}I$ ratios in Scottish seawater since 1992. The estimate that iodine isotope ratios increased about by a factor of 7 between then and 2003 is in reasonable agreement with the increase in marine ^{129}I releases from Sellafield during that period. The new data presented at the current conference also include samples from the south-west of Scotland, closer to the emission source. Moreover, some locations were sampled in 2003, 2004 and early 2005 to follow the development of the isotope ratio.

The table below compares iodine isotope ratios obtained for the first samples in this work to the datapoint obtained in 1992 by Raisbeck *et al.* (1995).

Sample	$^{129}I/^{127}I$ (at/at)
Troon	$(4.91\pm0.29)*10^{-7}$
Sannox Bay	$(3.13\pm0.20)*10^{-7}$
Gruinard Bay	$(1.28\pm0.09)*10^{-7}$
Dornoch	$(1.15\pm0.15)*10^{-7}$
Vatersay East	$(8.58\pm1.07)*10^{-8}$
Pollachar	$(8.87\pm0.90)*10^{-8}$
Lossiemouth [Rai95]	$(1.6\pm0.2)*10^{-8}$

The agreement of the iodine isotope ratios of the two Hebridean sampling locations Vatersay East and Pollachar (their ^{129}I concentrations differ significantly) confirms that the isotope ratio is the tracer to follow pathways and not the radionuclide concentration.

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S Waldron (SUERC) took samples from the south-west of Scotland region. J Moran and G Snyder gave advice on ^{127}I ICP-MS measurements.

Incorporation of ^{129}I from nuclear sources into lacustrine sedimentary organic matter: a case study in the Great Lakes

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Large quantities of ^{129}I ($T_{1/2}$ = 15.7 Ma) have been released during the past six decades, primarily during nuclear fuel reprocessing and bomb testing. Due to the biological affinity of iodine, anthropogenic ^{129}I has become associated with organic material such as vegetation, soil and sediment. The current study was undertaken to investigate the presence of ^{129}I and its stable counterpart, ^{127}I in the sediments of Lake Erie and Lake Ontario. The watershed of these lakes is heavily industrialized on the American and Canadian sides, resulting in the contamination of lake sediments by toxic organic compounds, heavy metals, ^{137}Cs, ^{241}Am, and Pu isotopes. The predominant source of ^{129}I to the sediments in the study area (eastern Lake Erie and western Lake Ontario, which are connected by the Niagara River) is a defunct reprocessing facility at West Valley, NY which released approximately 10 kg of ^{129}I via site runoff and smoke stack emissions during 1966-72. ^{129}I and ^{127}I data from 3 sediment cores from Lake Ontario and 1 core from Lake Erie will be compared to published data on the bulk and molecular geochemical characteristics of these cores [1,2]. The data will be analyzed in the context of a conceptual model for the incorporation of ^{129}I and ^{127}I into the water and sediments of the Great Lakes.

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I-129 and I-127 in northern Germany

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The abundances of ^{129}I and ^{127}I were investigated in sea-water, air, precipitation, surface and ground waters, soils, plants, animals, foodstuffs, total diet, and human and animal thyroid glands from Lower Saxony, Germany. The iodine isotopes are in severe disequilibrium in the different environmental compartments. The pre-nuclear equilibrium ^{129}I/^{127}I ratio in the biosphere was determined to be 2.0×10^{-13}. Today, the environmental isotope ratios range from 10^{-6} to 10^{-10}. The highest ratios were found in North Sea water, the lowest in deep soil samples and ground water. A differentiation by about a factor of ten between the iodine isotopes was observed for different air-borne iodine species. Time series for iodine in precipitation show a decade-long increase of ^{129}I fallout until the 1980ties and an ongoing constant input of ^{129}I with deposition densities of ~ 15 mBq m^{-2} per year. In surface waters, a dilution of the fall-out iodine takes place by stable iodine which is just weakly adsorbed in the soils. The isotope ratios in soils and ground waters demonstrate a high mobility and an accumulation of ^{129}I in the water unsaturated soil zones and an efficient migration into water saturated soil layers and ground water. The transfer into the food chain is ruled by the complex situation in the water-soil system. Given the environmental ^{129}I abundances, the relatively low ^{129}I/^{127}I ratios in human thyroid glands (2×10^{-9} - 3×10^{-8}) can only be explained by additional iodine sources with low isotope ratios in the diet.

Duration of microbial gas generation in Upper Cretaceous Reservoirs, Montana and Canada – Interpretation from ^{129}I/I ratios

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More than nine trillion cubic feet of microbially generated methane has been produced from the Upper Cretaceous Belle Fourche Formation, Medicine Hat Sandstone and its lateral equivalents, Milk River Formation, and Eagle Sandstone in Alberta and Saskatchewan, Canada, and eastern Montana. The microbial methane was produced in an aqueous setting via CO_2 reduction. Twenty-five wells were sampled for gas and co-produced water in the producing formations. Chemical and stable isotopic compositions were determined for both gas and water fractions. Of the sampled wells, 14 samples showed equilibrium between the methane and water. ^{129}I/I ratios of the waters were also obtained.

Stable isotopes of water, patterns of methane-water equilibria, or regional trends in gas and water composition do not provide information on the time and duration of gas generation. However, they might be useful in indicating local and regional flow paths. ^{129}I/I of the produced water helps place constraints on the time and duration of gas generation by determining the residence time of the water in the reservoirs and the probable source of the iodine. For samples where the methane and water are in equilibrium, this also provides some time constraints on gas generation. Minimum ^{1291}/I ages for all samples range from 23.5 to 101.4 Ma. Preliminary corrected (for fissiogenic production) ^{129}I/I ages for all samples from range 24.4 to to 101.4 Ma, whereas samples in which the methane and water are in equilibrium have corrected ^{129}I/I ages ranging from 31.6 to 92.6 Ma. Ages are generally younger than any of the reservoir rocks and indicate some past mixing of connate and meteroic water. There is no regional pattern or depth relation to age distribution within the formations that would indicate the presence of a large continuous regional flow system. Rather, ^{129}I/I data when used in conjunction with other gas and water geochemical parameters indicate multiple flow paths affected by depositional patterns of local reservoirs and exsolution of free gas. Based on ^{129}I/I ages, methane was generated from the Middle Cretaceous through the Oligocene.

Sources of methane in continental margins: ^{129}I results from gas hydrate systems and fore arc fluids

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Fluids in continental margins are often enriched in methane to degrees which make derivation from local organic sources unlikely. Methane rich fluids also show very strong enrichments in iodine, demonstrating the link between this biophilic element and organic material. Iodine ages derived from the measurement of ^{129}I/I ratios in these fluids can then be used to determine potential source formations for iodine and methane in these settings. Recent applications of this system are investigations of gas hydrates and of fluids collected from the fore arc regions of active subduction zones, such as studies of the fore arc in the North Island, NZ and from gas hydrates of the Peru Margin (ODP 201; H 1230). Pore fluids from Site 1230 are strongly enriched in iodine and show a distinct decrease in ^{129}I/I ratios from 920×10^{-15} close to the surface to 140×10^{-15} at a depth of 200 mbsf. The fore arc fluids from New Zealand are also enriched in iodine and show a similar range in ^{129}I/I ratios. In both cases minimum ages are calculated to be between 40 and 60 Ma for these fluids. Because these ages are older than the host formations of the fluids as well as of the currently subducting sediments, the fluids must be derived from the overriding wedge in these cases. Investigations of gas hydrate systems at Nankai Trough and Hydrate Ridge and of fore arc fluids from Central America and Japan show similar results. Fluids in gas hydrate and fore arc systems are derived predominantly from old formations in the overriding wedge, in contrast to fluids in the main volcanic arc, which show the influence of subducting sediments.

Behavior of stable and radioactive iodine in the global environment

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We report here results of iodine determinations in various geological and environmental materials. ^{129}I/I ratios have also been measured in selected materials such as brines and hot springs collected in Japan to understand the age and origin of iodine. Additionally, ^{129}I levels in the soil environment near the reprocessing plant were studied.

The distribution of stable iodine in the earth's crust was estimated using analytical data in a suite of representative samples. The main reservoirs of the crust's iodine were found to be marine sediments and sedimentary rocks. High iodine concentrations were observed in underground brines. These brines have salinities close to that of seawater and are typically associated with the presence of hydrocarbons. Brine samples from the depth of 1000-2000m in the Kazusa Formation (Chiba Prefecture) showed the highest iodine concentrations of about 130ppm, which were typically more than 2000 times higher than that in seawater. The iodine ages, which were estimated from ^{129}I/I ratios, range between 37 and 53 Ma, and are much older than those of their host sediments. The results obtained for their ages and chemical characteristics indicate that iodine enrichment was caused by mobilization from subducting marine sediments in the fore-arc area and/or by recycling of fluids from older marine formations in the overriding wedge.

Behaviour of iodine in soil-plants-atmosphere system (e.g. sorption on soil, volatilization from soil-plants, effects of microorganisms) was also studied using radioiodine as a tracer.

The ^{129}I anthropogenic budget: Sources and sinks

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There has been considerable interest in utilizing anthropogenic ^{129}I as a geochemical tracer in a wide range of natural reservoirs. Consequently, large numbers of data are now generated with respect to the distribution of the isotope in the hydrosphere and atmosphere and to a lesser extent in the lithosphere and biosphere. In this report, a summary of ^{129}I data sets from our group and others are used to elucidate the expected concentration levels and inventory in the Earth's surface environments. These data are further evaluated in terms of ^{129}I releases from the different anthropogenic sources. The results show dependence of ^{129}I distribution on distance from the sources and from the sea. The European atmosphere contains much higher concentration of the isotope than in other continents. Apart from the Irish Sea and the English Channel, the North Sea, the Nordic Seas and the Eurasian basin of the Arctic Ocean show the highest concentration of ^{129}I compared to other marine waters. Distribution of anthropogenic ^{129}I in the lithosphere is not well constrained and the available data suggest strongly localized concentration patterns. The data on ^{129}I content in the biosphere is rather scarce, but a link to distance from sources can be inferred. A simple budget calculation indicates some discrepancy between the released amounts of ^{129}I and inventory in the natural reservoirs. This situation may relate to lack of complete environmental coverage or fate of releases from the sources, and to other unknown parameters.

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^{129}I/^{127}I ratios in surface waters of the English Lake District

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^{129}I concentrations in surface reservoirs have increased by anthropogenic release since the beginning of the nuclear age. At present, the main sources of ^{129}I are the two nuclear fuel reprocessing facilities (Sellafield and La Hague) in western Europe. ^{129}I/^{127}I ratios were measured in surface sea, lake and river water taken in 2004 in the area near the Sellafield nuclear fuel reprocessing plant in northern England, including the Lake District and southern Scotland. The ^{129}I/^{127}I ratio is a better tracer than ^{129}I concentration to determine the pathways of iodine emissions from the reprocessing plants and this is the first observation of the ^{129}I/^{127}I ratio in lake water in the Lake District. About 112 kg and 4 kg of ^{129}I were discharged from Sellafield into the Irish Sea and atmosphere, respectively, in 2002. Iodine is transferred from sea to land. The lakes in the Lake District receive ^{127}I from the sea and ^{129}I from both the sea and gaseous emission from Sellafield. Thus, ^{129}I/^{127}I in the water of these lakes depends on the distance from the sea and Sellafield, the geological character of the catchment area and the meteorological conditions.

The ^{127}I concentration was measured by ICP-MS. The ^{129}I concentration was measured using AMS at SUERC and/or ETH. The ^{129}I/^{127}I in samples was derived from ^{127}I and ^{129}I concentrations.

The ^{129}I/^{127}I ratio in sea water collected from the sea shore in Parton, 17km north of Sellafield, was 8.1×10^{-6}. This ratio is one order of magnitude higher than that in sea water collected from Maryport, 16 km north-east of Parton, in 1992 by Raisbeck *et al*. (1995). The ^{129}I/^{127}I ratios in lake water in the Lake District were lower but in the same order of magnitude as the ratio in sea water from Parton.

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Extraction and quantitative analysis of iodine in solid matrices

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^{129}I is gaining interest as a contaminant of concern at numerous federal and privately owned facilities. Several techniques have been identified to extract iodine from solid matrices; however, all of them rely on two fundamental approaches: liquid extraction or chemical/heat facilitated volatilization. While these methods are typically chosen for their ease of implementation, they lack the ability to result in total sample dissolution. Small partition coefficients have been measured for iodine on soil; therefore, extraction methods that do not result in total sample dissolution could underestimate the total iodine content of samples.

Approach

We conducted laboratory tests to define an extraction method contingent upon complete sample dissolution. Testing consisted of potassium nitrate/potassium hydroxide fusion of the sample, followed by sample dissolution in a mixture of sulfuric acid and sodium bisulfite. Direct analysis of the dissolved sample was performed via inductively coupled plasma mass spectometry (Perkin Elmer Elan DRC II) using a tertiary amine (Spectrasol CFA-C) carrier solution.

Discussion of results

Use of the fusion extraction method resulted in complete sample dissolution of all solid matrices tested: sediment, glass samples containing low-levels of iodine, as well as tank waste material collected from the Hanford Site. Quantitative analysis of iodine (^{127}I and ^{129}I) was better than ± 10% of certified reference standards, with the linear operating range extending more than three orders of magnitude (0.01 to 25 μg/L). Extraction and analysis of four replicates of standard reference material (San Joaquin Soil) from the National Institute of Standards and Technology, Gaithersburg, MD, resulted in an average recovery of 98% with a relative percent deviation of 6%.

Conclusions

These data highlight the success of the extraction and analytical techniques to quantitate total iodine (^{127}I and ^{129}I) in solid samples. Furthermore, these simple and cost-effective techniques can be applied to samples from multiple disciplines with little to no adaptation.

Depth profile of iodine and bromine in pore waters collected from the Nankai Trough

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Pore waters associated with methane have been found to show considerable enrichment of iodine (e.g. Fehn et al., 2003). In order to understand the detailed vertical distribution of iodine and bromine in marine sediments associated with methane hydrates, we have carried out ICP-MS analyses for a set of pore water samples collected from a borehole in the Nankai Trough area. Iodine concentrations in pore waters increased strongly with depth in the first 100 mbsf. The maximum iodine concentration of 60 ppm, corresponding to enrichment of 1000 times compared to seawater, was observed in layers below 100 mbsf, closely associated with the occurrence of methane hydrate. Concentrations of bromine also followed the iodine pattern with depth, but the highest enrichment compared to seawater (80 ppm) was only a factor of about 2. The iodine concentrations in the depth of 100 - 200 mbsf varied considerably. A similar depth profile was also observed for bromine and chlorine, indicating the presence of methane hydrate in this horizon. Iodine concentrations in solid phase of the sediment, after squeezing of pore fluid, were considerably lower than those in pore waters. The results indicate that most of iodine associated with gas hydrates resides in the pore waters under reducing conditions.

Reference

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The marine iodine system as a proxy for global deposition of organic carbon

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The biophilic nature of iodine has led to its net removal from the oceans and its enrichment in organic-rich marine sediments. We investigate the relationship between marine productivity and the accumulation of iodine in the open ocean and along continental margins. Both sediment and pore fluid fractions of sediment cores from several Ocean Drilling Program (ODP) Sites were measured using ICP-MS. This data was combined with previously published ODP data, in order to determine the distribution of iodine within different depositional environments. The majority of the iodine in the oceans is distributed along continental slopes (62%) while the next largest reservoir is in open ocean sediments (37%). In shallow sediments, iodine resides primarily in the solid phase. At sediment depths exceeding 20 meters below the sea floor (mbsf), iodine partitions primarily into the fluid phase (up to 83% of the total). Diagenetic modeling indicates that residence time of iodine in marine sediments on continental margins is on the order of several million years. Complex organic molecules are broken down at a similar rate, providing the precursor material for microbial methanogenesis. In general, the total iodine accumulation times are much longer than the calculated residence times. This would suggest that while only a few million years are required for iodine to be released from organic matter in these settings, the majority of the soluble iodide is reoxidized and reassimilated in shallow sediments, leading to a net accumulation over periods of tens of millions of years. Because iodine deposition is tied to marine productivity, it is reasonable to assume that marine margins have received a constant input of organic matter over the same time period. Iodine-129 data also support this concept of long-term iodine accumulation.

Based on the ODP core data, the total marine iodine reservoir is 4.4×10^{15} kg which is comparable with previous estimates. This is a minimum estimate, because it only considers the depth at which sediment cores were taken. Nonetheless, it is significantly larger than other major reservoirs such as the oceanic crust and continental sediments. The fact that this reservoir is concentrated on continental margins is indicative of the deposition of organic matter in the ocean over geological time.

Extraction of microgram quantities of iodine for ^{129}I/^{127}I AMS measurements in marine sediments

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Knie et al. have measured ^{60}Fe in a deep sea Mn crust, and interpreted an observed peak as evidence of matter from a supernova (SN) explosion deposited on the earth ~2.8 Myr ago. Then, there should be evidence of other SN products deposited at the same time. We are looking for evidence of ^{129}I in deep sea sediments, using the accelerator mass spectrometry technique (AMS) at the 2.5 MeV facility of Gif-sur-Yvette. In addition, if the ^{129}I background is low enough, the chemical procedure should be applicable for a new method of dating old sediments (>10 Myr).

The development of these applications requires that µg quantities of iodine available in reasonable amounts of sediment (a few grams) can be successfully extracted from these sediments and purified in a form appropriate for an AMS analysis, without introducing ^{129}I contamination above the level of $^{129}\mathrm{I}/^{127}\mathrm{I} = 1.5 \times 10^{-12}$ observed in pre-anthropogenic sediments (Moran et al., 1998).

We tested several procedures for the extraction of iodine from sediments and measured their stable iodine content by ICPMS. This allowed us to identify appropriate sediments in terms of iodine content and check that we can extract iodine from these sediments with a reasonable yield (> 60%).

After the extraction, the sample is purified using an anion-exchange column, and finally concentrated in a solid form by coprecipitation. When we performed AMS measurements, the technique gave good beam currents. However, the first blanks gave quite high ^{129}I/^{127}I ratios ($>10^{-11}$), which indicated an important source of anthropogenic contamination that we thought to be related to atmospheric contamination from reprocessing activities at La Hague. To test this hypothesis, we did measurements in rainwater from France which well illustrates the contamination as the measured ratio was $^{129}\mathrm{I}/^{127}\mathrm{I} \sim 10^{-7}$. To reduce the anthropogenic source of contamination during the manipulation, the procedure is now carried out in a glove box. Preliminary results that we are optimizing give blanks of $^{129}\mathrm{I}/^{127}\mathrm{I} \sim 2.10^{-12}$.

We applied the technique to sediments. We have acceptable currents but also an important contamination in the sediment ($^{129}\mathrm{I}/^{127}\mathrm{I} \sim 10^{-10}$), even treated in the glove box. We found this contamination in two sediments which were stored for years in France. This is a possible explanation for the contamination. We are currently trying to clean these sediments and to measure others.

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Halide systematics in pore waters of hydrothermal sediments: Some observations

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Measurements of Chloride, Iodide, Bromide, and Fluoride in pore fluids from several sedimentary hydrothermal systems are presented together with evidence from other isotopic systems (e.g., $^{87}Sr/^{86}Sr$) with the purpose of evaluating contributions of various processes to the halide systematics in the pore fluids. Whereas for chloride contents there is distinct evidence for both low Cl and high Cl fluids, especially in hydrothermally affected sediments of the Escanaba Trough, which can be traced back to hydrothermal processes, there is no evidence, as yet, for low chloride fluids in the Guaymas Basin of the Gulf of California. Data for both iodide and bromide show the influence of thermal decomposition of organic matter in the sediments, though complex patterns are evident in the pore fluids of the Escanaba Trough drill holes. For the distribution of fluoride no clear trends are observed. Further work on the chlorine isotope geochemistry in sedimentary hydrothermal fluids should be a worthwhile contribution to the overall understanding of the systematics of halides in these hydrothermal systems.

Pore water iodine concentrations and ^{129}I/I ratios of the Hydrate Ridge (ODP 204): Implication for the origin of gas hydrates

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We measured iodine and bromine concentrations in a total of 256 pore water samples collected from all nine sites drilled during ODP 204 at Hydrate Ridge, Oregon continental margin. In a subset of samples, focusing on Site 1245 and 1251, we have also determined ^{129}I/I ratios. Because of the strongly biophilic nature of iodine, concentrations and isotope ratios of iodine can be used to identify the origin of organic source material of gas hydrates.

A pronounced maximum of iodine concentration is observed at several sites, especially at the flank of the ridge. The highest value at the maximum reachs 2.2 mM in Site 1245. However, these maxima are less pronounced in the summit sites and absent in the sites located in a slope basin east of the Hydrate Ridge, although iodine is still strongly enriched (>0.5mM at depth) compared to seawater (0.0004 mM). All ^{129}I/I ratios are below the marine input ratio (R_i = $1500x10^{-15}$). The majority of the samples show iodine ages of Eocene time, which indicates the age of a major source of iodine and methane related to gas hydrates. This age range is beyond the ages of the currently subducting sediments and any local formations underlying Hydrate Ridge. It suggests that fluids must have traveled considerable distances and very likely come from the overriding wedge. Although the distribution of older formations in this wedge is still under investigation, profiles suggest Early Eocene marine sedimentary formations are present in contact with the crystalline backstop. Fluid flow models of active margins suggest that fluids may have moved along the decollement over long distances, transporting iodine and methane to the current locations.

The iodine maximum in site 1245 correlates well with an increase in ^{129}I/I ratios, suggesting the presence of a strong component of younger iodine in this location. These maxima reflect mixing between an old endmember (> 50 Ma) with a young endmember (< 10 Ma). The source for the latter material could be either the currently subducting sediments or formations in the immediate vicinity of Hydrate Ridge.

Dating water and solute additions to ice-covered Antarctic lakes

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The McMurdo Dry Valleys region of Antarctica is the largest expanse of ice-free area on the continent. Even at mean annual temperatures of ~-20ºC, ice-covered lakes containing liquid water exist in these valleys. Over the past decade we have extensively investigated the three major lakes in Taylor Valley (78ºS), as part of the McMurdo Dry Valleys Long-Term Ecological Research (MCM-LTER) program. Lakes Bonney, Fryxell and Hoare have very different geochemistries and evolutionary histories even though they are within 25 km of each other. We present recently published ^{36}Cl and ^{129}I data from these lakes along with a time series of ^{3}H, ^{3}He and CFC profiles in order to better ascertain the influence of climatic variation on the impact of water and solutes influx to the lakes. The ^{36}Cl and ^{129}I profiles from each lake document lower frequency, longer term variations in the hydrologic balance of each lake and demonstrate that the lakes have different ages and sources of solute input. The ^{3}H data suggest that over the past 50 years Lake Fryxell and Lake Hoare have had different sources of water or that the timing of water input into the lakes has been different. Changes over the past 10-15 years in the ^{3}H, ^{3}He and CFC concentrations document more subtle, higher frequency changes in water and solute flux. This data set supports the notion that these lakes can respond dramatically to small variations in temperature. This work also demonstrates that the MCM lakes serve as important indicators of climate change in this region of Antarctica.

Experimental results from iodine speciation and transport studies

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Application of fuel reprocessing ^{129}Iodine as a tracer in terrestrial systems is hampered by a lack of understanding of iodine cycling in soils and aqueous reservoirs. Through column and batch experiments, we examined sorption and transport of iodine species (iodide, iodate, and 4-iodoaniline) in several subsurface geological media collected at the Savannah River and Hanford Sites, where anthropogenic ^{129}I from fuel processing activities poses an environmental concern. The geological media examined exhibit a wide range in organic matter, clay mineralogy, soil pH, and texture. Transport of iodine in these sediments is complex with various processes occurring, including iodate conversion, irreversible retention/mass loss of iodide, rate-limited and nonlinear sorption. We observed appreciable iodate reduction to iodide, probably mediated by the structural Fe(II) in some clay minerals. In addition, iodine speciation in solid materials was examined using synchrotron X-ray techniques (XAS). This technique gives oxidation state and bond-length, which dictate biogeochemical interactions and reservoir residence times. Organoiodine compounds were identified alone and in combination with inorganic forms in soils, plants, and marine sediments.

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Near-conservative behavior of ^{129}Iodine in the Orange County Aquifer System, California

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Iodine is a biophilic element with one stable isotope, ^{127}I, and one long-lived radioisotope, ^{129}I. Radioiodine ^{129}I originates in the surface environment almost entirely from anthropogenic activities such as nuclear fuel reprocessing in Europe and thus provides a point source tracer. Very few studies have evaluated the geochemical behavior of iodine isotopes in the subsurface. The concentrations of ^{129}I and ^{127}I were measured in wells fed by a series of artificial recharge ponds in the Forebay Area of the Orange County groundwater basin (California, USA) to evaluate their potential use as hydrological tracers. To substantiate interpretation of ^{129}I and ^{127}I concentration data, the aquifer system was evaluated using literature values of aquifer water mass age based on ^{3}H/^{3}He, Xenon and δ^{18}O tracer data. The aquifer data demonstrate the nearly conservative behavior of ^{129}I, with ^{129}I/^{127}I ratios likely reflecting variations in source functions as well as climatic conditions, and with inferred particle-water partition coefficients (K_d) of 0.1 cm^3 g^{-1} or less.

Age-dating groundwater discharge in the Merced River basin, California using noble gasses and chlorine-36

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Using a combination of water quality and isotopic analyses, ages of groundwater inputs to the Upper Merced River were characterized. Between Nov. 2003 and July 2004, monthly water quality samples were taken from Happy Isles to the inlet of Lake McClure, a 75 km reach. These samples demonstrated the expected dilution due to snowmelt in the spring. In the fall, the spatial profile matched the geology with anion concentrations increasing as downstream of the transition from the Sierra Nevada batholith to the country rock, suggesting significant groundwater inputs. From July 2004 – January 2005, radon-222 and other noble gases (He, Ne, Ar, Kr and Xe abundances and ^{3}He/^{4}He ratio) were measured along a 40 km reach of the Merced River, extending from the top of Yosemite Valley to the confluence of the South Fork of the Merced River. Radon-222 activity varied from about 1 to 500 pCi/L indicating significant, spatially variable groundwater discharge into the Merced River. The highest ^{222}Rn were observed during baseflow. For a representative groundwater end-member, radon-222 activity measured in Fern Spring, Yosemite Valley was about 1200 pCi/L. Excess ^{4}He from U and Th decay is observed in samples with elevated ^{222}Rn. Preliminary ages range from 15 yr for Fern Spring to greater than 50 yr for some discharging groundwater. There is a trend of older water discharging further downstream. Chlorine-36 results corroborate the noble gas results.

Iodine distribution in pore fluids associated with methane plumes in the Sea of Japan

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Very large methane plumes were observed in echograms during UT04 Cruise (Aoyama et al., 2004; Matsumoto et al., 2004; Snyder et al., 2004) in the eastern margin of the Sea of Japan. A large set of pore water samples was recovered together with several chunks of gas hydrates using piston cores on a small ridge in this area. We measured I, Br and Cl concentrations in all the pore waters and are working on the determinations of $^{129}I/^{127}I$ ratios in a subset of the samples.

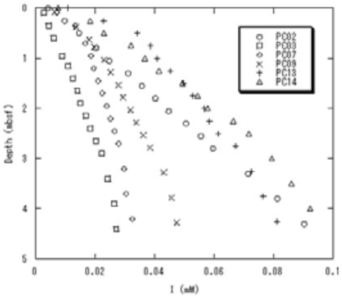

Figure 1: High-resolution depth profiles of dissolved iodine in pore fluid samples from the Sea of Japan.

Iodine concentrations in the pore fluids are at least ten times higher than in seawater even in the shallowest section of the cores, and progressively increase with depth (Fig. 1). Iodine concentrations are not correlated with those of bromine and chlorine, suggesting that the iodine distribution reflects the methane delivery at the ridge. $^{129}I/^{127}I$ determinations are in progress to determine the origin of iodine in these fluids and to assess their potential contribution to the development of gas hydrates.

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