

Residence times and source ages of deep crustal fluids: interpretation of ^{129}I and ^{36}Cl results from the KTB-VB drill site, Germany

U. FEHN¹ AND G. T. SNYDER²

¹*Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY, USA;* ²*Department of Earth Science, Rice University, Houston, TX, USA*

ABSTRACT

We present here $^{129}\text{I}/\text{I}$ and $^{36}\text{Cl}/\text{Cl}$ ratios, together with halogen concentrations in crustal fluids from the continental deep drill site (KTB-VB) in Germany, where fluids were collected from 4000 m depth during a pump test carried out in 2002 and 2003. Compared with seawater, the fluids are enriched by factors of 2, 8 and 40 for Cl^- , Br and I, respectively, and show little variation over the test period. The $^{129}\text{I}/\text{I}$ ratios are between 1700 and 4100×10^{-15} ; the $^{36}\text{Cl}/\text{Cl}$ ratios are below 10×10^{-15} . Co-variation between ^{129}I and ^{36}Cl concentrations in the fluids indicates that anthropogenic components are absent and that the ratios reflect an addition from crustal sources. The results suggest residence times of 10 Ma or more for the fluids in formations with uranium concentrations of 1 ppm. A minimum age of 30 Ma for the iodine source was derived from the correlation between ^{129}I and ^{36}Cl concentrations in the fluids. The results demonstrate that the halogen characteristics of the KTB fluids are very similar to those of other deep crustal fluids and that the combination of ^{129}I and ^{36}Cl systematics allows determination of residence times and source ages of such fluids.

Key words: Crustal fluids, ^{129}I , KTB site, source ages, residence times

Received 29 June 2004; accepted 27 October 2004

Corresponding author: U. Fehn, Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY, 14627, USA.

Email: fehn@earth.rochester.edu. Tel: 585-275-7884, Fax: 585-244-5689.

Geofluids (2005) 5, 42–51

INTRODUCTION

Aqueous fluids play a very important role in processes of the crust, such as in the exchange of elements, cooling of intrusions, formation of ore deposits or mineral formation. From recent investigations it has become evident that fluids are present at larger quantities, move with greater mobility and penetrate to greater depth than previously assumed (Hanor 1994; Bottomley *et al.* 2002; Starinsky & Katz 2003; Frape *et al.* 2004). While the presence of deep-seated fluids is thus no longer in question, the origin and history of these fluids has been an issue of an ongoing debate. In order to improve our understanding of processes in the deeper crust, several deep holes have been drilled over the last two decades, among them the German Continental Deep Drill Hole (KTB) in Windischeschen-

bach, Northern Bavaria. The project was started with a pilot hole (KTB-VB) to 4000 m depth, and completed with the main hole (KTB-HB) which in 1999 reached its final depth of 9101 m. During drilling, several horizons produced significant amounts of fluids, but the testing of these fluids was impacted by potential contamination problems associated with the drilling process. A large amount of crustal brine was collected, however, in a later pump test in KTB-VB, with fluids collected mainly from a depth of 4000 m. The pump test was repeated from July 2002 to June 2003 with a bi-weekly collection of fluids. We report here results of ^{129}I and ^{36}Cl determinations in a set of samples from this test together with a few results from the earlier pump test in 1991. The purpose of our study is to apply these results toward understanding the history and origin of the fluids collected in KTB-VB, to develop

methods for the distinction between cosmogenic and fissionogenic components of these radioisotopes and to compare the results for the KTB site to those for other crustal fluids.

GEOLOGIC SETTING

The drill hole of the KTB site is located in northern Bavaria, at the western margin of the Bohemian Massif, where a large section of basement rocks is exposed. Only a brief outline of the geology is given here, more detailed descriptions can be found in the special issue of the *Journal of Geophysical Research* devoted to this drilling enterprise (Emmermann & Lauterjung 1997). The drill site is located in a unit called the Zone of Erbdorf-Vohenstrauss (ZEV), which consists of an association of paragneisses, orthogneisses and metabasic rocks (Fig. 1). The unit is rather small and sits close to the boundary between the Moldanubian and Saxothuringian units. All the basement units in this area are of Variscan origin (approximately 400–330 Ma) and underwent polymetamorphism. To the west of this complex, the Franconian Line indicates the contact with the Permo-Mesozoic sedimentary cover sequence of central Germany.

Important for hydrologic considerations is the presence of numerous major faults in this area, especially associated with the Franconian Lineament to the west of the drill site.

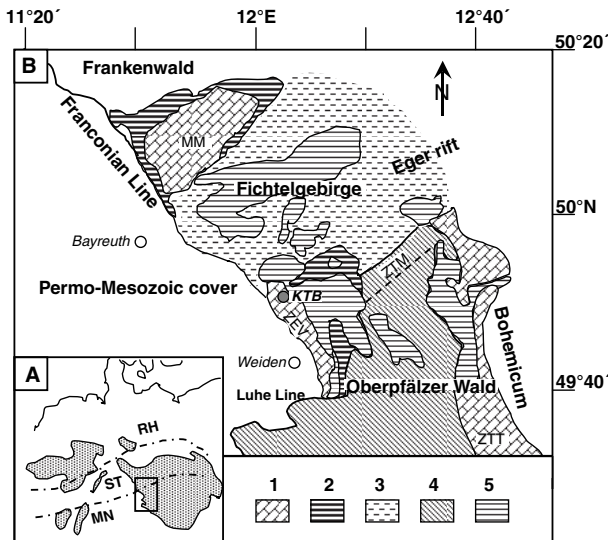


Fig. 1. Geologic map of the KTB site (after Weber 1990 and Pechnig *et al.* 1997). (A) Surface exposure of the Variscan orogenic belt in central Europe with its main units Rhenohertzynikum (RH), Saxothuringikum (ST) and Moldanubikum (MN). The box outlines the area covered in B. (B) Area around the KTB site: (1) Metamorphic units consisting of Zone of Erbdorf-Vohenstrauss (ZEV), Münchberger Gneissmasse (MM), and Zone of Tepla-Taus (ZTT); (2) greenschist facies units; (3) Saxothuringikum, separated by the shear zone of Tirschenreuth Mähning (ZTM) from (4) Moldanubikum; (5) post-Variscan granites.

Several of these faults apparently intersect the surface, although it is not clear whether active flow occurred recently in them. Several horizons were identified during the drilling as conduits for fluid flow. A most striking event was the encounter of large quantities of fluids at the bottom of the pilot hole (4000 m). After the completion of the drilling, pump tests were carried out in order to provide samples of pristine fluids from this horizon. Although in many respects contamination introduced from, for example, the mud used during the drilling activities were sorted out, results from these samples indicate that the fluids still carried considerable contamination (Möller *et al.* 1997). The recent pump test is an attempt to provide another opportunity for the collection of uncontaminated crustal fluids from the pilot hole at the KTB site. An overview of the range of measurements carried out for this experiment can be found in this issue (Erzinger 2005). Companion studies of the fluids and gases demonstrate strong enrichment in halogen contents, with enrichment factors of 2, 8 and 40 for Cl^- , Br and I, respectively, and a high dissolved methane content (Lippmann *et al.* 2005; Möller *et al.* 2005).

SYSTEMATICS OF ^{129}I AND ^{36}Cl

The two isotopic systems employed here, ^{129}I and ^{36}Cl , are commonly listed in the group of cosmogenic isotopes, which also includes ^{14}C and ^{10}Be . The name refers to the production of these isotopes by the interaction of cosmic rays with atoms at the surface of the earth. In the case of the two isotopes in question, this categorization is somewhat misleading because both of them also have significant contributions from sources in the crust and, more recently, from nuclear activities. All three sources need to be considered separately for these two isotopes in order to make an appropriate interpretation of the results.

Halogen systematics

Iodine as an element is strongly associated with organic material and is rarely incorporated in mineral phases because of its large ionic radius. It is typically enriched in fluid phases associated with organic material such as pore fluids in organic-rich marine sediments and oil field brines. Typical concentrations of iodine range from $0.01 \mu\text{M}$ in meteoric water to $0.4 \mu\text{M}$ in seawater, but can reach much higher values in oil field brines (0.15 mM ; Moran *et al.* 1995) or porewaters associated with marine gas hydrates (2 mM ; Fehn *et al.* 2000). Although as a halogen iodine shares some similarities with chlorine, it has a much stronger association with organic material than chlorine and is typically not enriched in halide deposits. In terms of its geochemical behavior, bromine falls somewhat in between the other two elements, specifically with respect to

association with organic material and enrichment in pore fluids and oil field brines. Because of the differences in geochemical behavior, concentration ratios of the halogens are specific for fluids such as seawater, oil field brines or meteoric water and are commonly used for the source determination of fluids.

The ^{129}I system

Iodine has one stable isotope, ^{127}I , and one long-lived radioisotope, ^{129}I ; results in the ^{129}I system are reported as $^{129}\text{I}/\text{I}$. The only method used for the determination of natural $^{129}\text{I}/\text{I}$ ratios is accelerator mass spectrometry (AMS), because of the very small isotope ratios (e.g., Sharma *et al.* 2000). With a half-life of 15.7 Ma, ^{129}I is the longest-lived radioisotope among the cosmogenic isotopes. It is produced in the atmosphere by the interaction of cosmic rays with xenon isotopes and in the crust as a product of the spontaneous fission of ^{238}U . These two production mechanisms contribute similar amounts to the ^{129}I budget in the oceans (Fabryka-Martin *et al.* 1985). Because of the long residence time of iodine in the oceans (approximately 0.3 Ma; Broecker & Peng 1982), seawater acts as a well-mixed isotopic reservoir for iodine. The pre-anthropogenic $^{129}\text{I}/\text{I}$ ratio in the oceans is $(1500 \pm 150) \times 10^{-15}$ (Moran *et al.* 1998), which is used as the initial ratio for age determinations, signifying the time of separation of iodine from the open ocean reservoir. Because atmospheric iodine exchanges readily with marine iodine, the pre-bomb isotopic signal is identical in all surface reservoirs in exchange with the atmosphere or oceans. We will use the term ‘cosmogenic’ for this component, to differentiate it from the ‘fissiogenic’ component, the *in situ* addition of ^{129}I from the spontaneous fission of ^{238}U within the crust. A third source of ^{129}I is the recent addition of an anthropogenic component, produced as a fission product of neutron-induced fission of ^{235}U and ^{239}Pu . The increase in ^{129}I concentrations in surface reservoirs was initially related to fall-out from atmospheric weapon tests, the so-called bomb-peak. In contrast to other anthropogenic radioisotopes, the level of ^{129}I in the environment has remained high because of ongoing releases from reprocessing plants (e.g., Rao & Fehn 1999; Moran *et al.* 2002). Although most of the sources for anthropogenic ^{129}I are located in the northern hemisphere, the mobility of iodine in the atmosphere is sufficient to have elevated ^{129}I concentrations on a global basis (Snyder & Fehn 2004).

The three components of the ^{129}I system have different uses for the characterization of sources and history of fluids. The cosmogenic signal is dominant in fluids associated with organic material, where the measured $^{129}\text{I}/\text{I}$ ratio is used to determine the time of separation from surface reservoirs, specifically from the marine system.

This age is calculated following a standard decay equation:

$$T = \frac{\ln(R_m/R_i)}{(-\lambda_{129})} \quad (1)$$

R_m is the measured ratio, R_i the initial ratio (1500×10^{-15}) and λ_{129} the decay constant of ^{129}I ($4.41 \times 10^{-8} \text{ yr}^{-1}$). This approach has been very successful in fluids derived from organic-rich sources, such as oil field brines (Moran *et al.* 1995), marine gas hydrates (Fehn *et al.* 2000) or coal-bed methane deposits (Snyder *et al.* 2003). Because the presence of fissiogenic and/or anthropogenic sources increases the measured ratio, the measured ratio overestimates the cosmogenic component and the calculated age is a minimum value for the age of the source material. Iodine in fluids derived from organic-rich sources usually is dominated by the cosmogenic component, so that corrections for the other two components in these cases are minor.

Contributions of fissiogenic ^{129}I to fluids depend on the uranium concentration in the host formation, release rate of fissiogenic ^{129}I into the fluids and the time fluids have remained in a given reservoir formation. The calculation of a residence time in a host formation follows an equation, initially developed and applied by Fabryka-Martin *et al.* (1989) for the Stripa Granite of Sweden:

$$N_{129} = N_{238} \lambda_{\text{SF}} \gamma_{\text{SF}} \rho E / P \frac{(1 - \exp - \lambda_{129} T_R)}{\lambda_{129}} \quad (2)$$

N_{129} is the number of ^{129}I atoms in the fluid, N_{238} the number of ^{238}U atoms in the host formation, λ_{SF} the decay constant for spontaneous fission of ^{238}U ($8.5 \times 10^{-17} \text{ yr}^{-1}$), γ_{SF} the yield for mass 129 (0.0003), and ρ the formation density. The ratio of the escape probability E to the fracture porosity P in the formation is the least well known of these parameters, but varies between 1 and 100 in most situations (Fabryka-Martin *et al.* 1989; Fehn *et al.* 1992; Bottomley *et al.* 2002; Katz & Starinsky 2003). Because of the uncertainty in E/P values, this approach has only sparingly been used, but was applied for the determination of residence times in the Stripa Granite (Fabryka-Martin *et al.* 1989) and more recently, for deep fluids from the Canadian Shield (Bottomley *et al.* 2002).

The recent addition of anthropogenic ^{129}I has elevated the concentration of this isotope by several orders of magnitude in all surface reservoirs. While applications of this component have been developed for the tracing of ocean currents (Santschi *et al.* 1996) and the global cycling of iodine in the environment (Snyder & Fehn 2004), it rarely plays a role in deep fluids other than as a tracer for potential contamination during sampling. Because the measured $^{129}\text{I}/\text{I}$ ratio in a given sample reflects the potential presence of the three components, other indicators such as ^{36}Cl are used in order to derive

acceptable interpretations of age and residence times of fluids.

The ^{36}Cl system

Chlorine is a much more abundant element than iodine, with concentrations of 0.03 mM in meteoric water and of 550 mM in seawater. It is also a common component of minerals and is the main anionic species in halide deposits. In deep crustal fluids it is often found enriched to about twice the concentration of seawater, although the specific reasons for this observation are not well agreed upon. Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , the ratio of which has found recent applications in the distinction of potential sources for fluids (Hesse 2003) and one radioisotope, ^{36}Cl with a half-life of 0.3 Ma.

Like ^{129}I , ^{36}Cl also has three sources. The cosmogenic component is formed in the atmosphere and in the surface rocks by cosmic rays, and is used for the determination of groundwater ages (Purdy *et al.* 1996) and for the exposure ages of surface rocks (Phillips *et al.* 2003). The high concentration of chlorine in marine systems and the relatively low production rate of cosmogenic ^{36}Cl prevent its use for dating of waters derived from marine sources.

The fissiogenic component is a result of the capture by ^{35}Cl of neutrons produced by the decay of uranium and thorium isotopes. The production of ^{36}Cl in a fluid is given by Andrews *et al.* (1989):

$$N_{36} = \frac{\sigma\Phi N_{35}(1 - \exp(-\lambda_{36} T_R))}{\lambda_{36}} \quad (3)$$

N_{35} , N_{36} are the numbers of ^{35}Cl and ^{36}Cl (in atoms per vol.), respectively, in the fluid. The cross section for neutron capture by ^{35}Cl , σ , and the decay constant for ^{36}Cl , λ_{36} , are well-known parameters. The neutron flux, Φ , is a function of the concentration of U and Th in a given formation. $^{36}\text{Cl}/\text{Cl}$ ratios in crustal fluids can then be used either for the determination of residence times of fluids, if the neutron flux is known, or, in case that the system is close to or has reached secular equilibrium (approximately 1.5 Ma), the neutron flux and the associated uranium concentration in the host formation of the fluids can be estimated.

The anthropogenic component of ^{36}Cl is also produced by the neutron capture reaction responsible for the fissiogenic component, occurring on ^{35}Cl in surface reservoirs by neutrons related to nuclear weapon tests. Because this reaction was active only during the period of atmospheric weapon testing, atmospheric ^{36}Cl shows a pronounced bomb-peak and has largely returned to pre-bomb ratios since about 1980 (Suter *et al.* 1987). Thus this isotope has a very different behavior from that of anthropogenic ^{129}I and the difference can be used for the determination of anthropogenic contamination in fluids.

SAMPLES AND METHODS

We received samples (2 l each) bi-weekly during the year-long pump test starting from July 2002 and report here results for the period between July 2002 and March 2003. Iodine and bromine concentrations were measured using an ICP-MS system (Thermal X7), and chloride concentrations by ion chromatography (Dionex BioLC). Analytical accuracies for these measurements are better than 3% and are not recorded individually.

Seven samples were selected for $^{129}\text{I}/\text{I}$ determinations, in four of those samples $^{36}\text{Cl}/\text{Cl}$ ratios were also measured. For these determinations, I was extracted and precipitated as AgI, Cl as AgCl, in both cases following established methods (Fehn *et al.* 1992). The actual AMS determinations were carried out at PrimeLab, Purdue Univ., again following established routines (Sharma *et al.* 2000) and individual accuracies are included in the data table. In addition to the samples measured during this pump test, we also include results from the pump test of 1991 (Fehn & Moran 1993), the measurements of which followed essentially the same protocol.

RESULTS

Results for halogen concentrations and isotope ratios are listed in Table 1, together with the results from the earlier pump test and, for comparison, values for pre-anthropogenic seawater and meteoric water, as well as for anthropogenic meteoric water in southern Germany. Halogen concentrations (Fig. 2) in the waters varied little over the test period. Chloride concentrations range between 827 and 1494 mM, with most of them being close to the average of 1097 mM. With one exception, bromine values are close to 7 mM, the high value of 9.42 mM (KTB 2-10-02) coincides with one of the higher Cl^- values. Iodine concentrations follow a similar pattern, with an average of 17.3 μM , and a high value of 23.6 μM . All of these concentrations are higher than those of seawater, with enrichment greatest for iodine, and least for chloride. The pattern over the pump test is quite comparable for the three halogens. The concentration values fall in the same range as those determined by other researchers (Möller *et al.* 2005); values for the pump test of 1991 are also quite close (Fehn & Moran 1993; Lodemann *et al.* 1998).

We measured $^{129}\text{I}/\text{I}$ ratios in seven samples from this test, roughly one sample per month (Fig. 3). All ratios are greater than 1500×10^{-15} , the pre-anthropogenic marine input ratio. The ratios also show considerable variation with no obvious relation to changes in the iodine concentrations. The result from the earlier pump test compares well with the new data set. In four of the samples with ^{129}I results, we also determined $^{36}\text{Cl}/\text{Cl}$ ratios and found

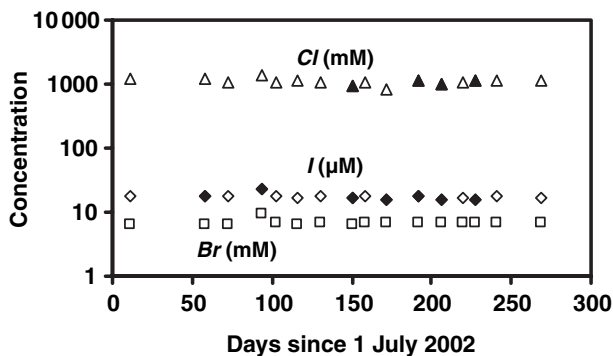
Table 1 Halogen concentrations and cosmogenic isotopes in fluids from KTB pump tests.

Sample	Days*	I (μM)	Br (mM)	Cl (mM)	$^{129}\text{I}/\text{I}$ (10^{-15})	\pm (10^{-15})	^{129}I (atoms μl^{-1})	$^{36}\text{Cl}/\text{Cl}$ (10^{-15})	\pm (10^{-15})	^{36}Cl (atoms μl^{-1})
KTB-PT	11	17.5	6.52	1198						
KTB-VB-FPT-3	58	17.6	6.60	1186	4100	1000	43.4			
KTB-VB-FPT-2	73	17.3	6.50	1099						
KTB 2-10-02	94	23.6	9.42	1416	2280	300	32.5			
KTB 11-10-02	103	17.3	6.81	1083						
KTB 24-10-02	116	17.1	6.50	1106						
KTB 8-11-02	131	17.3	6.93	1092						
KTB 28-11-02	151	17.1	6.52	926	1700	380	17.5	5.4	1.6	3013
KTB 5-12-02	158	17.3	6.95	1067						
KTB19-12-02	172	15.9	7.02	827	1700	1400	16.3			
KTB-8-01-03	192	17.3	7.00	1109	2650	220	27.7	9.4	1.5	6282
KTB-22-1-03	206	15.8	6.88	989	4060	170	38.7	9.7	1.4	5783
KTB 5-2-03	220	16.5	6.78	1092						
KTB 12-2-03	227	15.8	6.81	1109	2780	250	26.4	7.2	1.7	4814
KTB 26-2-03	241	17.3	6.83	1140						
KTB 26-3-03	269	16.5	6.75	1110						
Average		17.3	6.93	1097						
KTB 1991†		24.8	na	1494	3461	212	51.5	10.8	3.0	9670
Seawater		0.4‡	0.84‡	560‡	1500§		0.4	<0.5		<160
Meteoric water¶		0.01		0.03	1500		0.02	200		4
Anthrop. water¶		0.01		0.03	1×10^7		60	<1000		<20

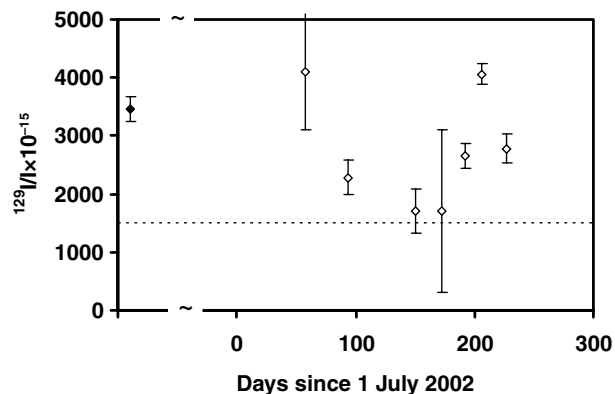
*Days from July 1, 2002, the beginning of the pump test.

†Fehn & Moran (1993).

‡GERM (2004).

§Moran *et al.* (1998).¶Estimates based on figures from Snyder & Fehn (2004), Suter *et al.* (1987) and Moran *et al.* (2002).**Fig. 2.** Halogen concentrations in waters from the pump test in 2002–03. Days counted from the start of the pump test, July 1, 2002. Concentrations for iodine (diamonds) in μM , for chloride (triangles) and bromine (squares) in mM. Solid symbols indicate samples, where $^{129}\text{I}/\text{I}$ or $^{36}\text{Cl}/\text{Cl}$ ratios were determined.

ratios around 10×10^{-15} in these samples. In spite of being close to the AMS detection limit, the ratios clearly are above background. The result from the earlier pump test is also in the same range. Although there was considerable evidence for contamination by drilling fluids during the earlier pump test (Möller *et al.* 1997), ratios for $^{129}\text{I}/\text{I}$ or $^{36}\text{Cl}/\text{Cl}$ apparently were not influenced due to the low concentrations of iodine and chlorine in the drilling materials. There are a few measurements of $^{36}\text{Cl}/\text{Cl}$ ratios from

**Fig. 3.** $^{129}\text{I}/\text{I}$ ratios in waters from pump test in 1991 (solid diamond) and from 2002–03 (open diamonds) as function of time. The broken line indicates the pre-anthropogenic ratio of 1500×10^{-15} (Moran *et al.* 1998).

the earlier pump test reported in Lodemann *et al.* (1998). While two results are close to 10×10^{-15} , that is in the range of our results, they found also one considerably higher ratio of $(163 \pm 72) \times 10^{-15}$.

INTERPRETATION OF ISOTOPE RESULTS

The concentrations of the two radioisotopes used here, ^{36}Cl and ^{129}I , reflect the potential presence of the three

different components which have different signatures and have to be sorted out before the results can properly be interpreted. For that purpose, we will use the isotopic ratios and the concentrations of the radioisotopes in the fluids (listed in Table 1) as well as the relation between the production processes for the two isotopes.

Anthropogenic component

All the $^{129}\text{I}/\text{I}$ ratios are higher than the pre-anthropogenic input ratio of 1500×10^{-15} and could therefore reflect an anthropogenic component in them. The current $^{129}\text{I}/\text{I}$ ratio in surface waters in Central Europe is very high (approximately 10^{-8} ; Snyder & Fehn 2004), leading to concentrations of ^{129}I atoms in surface waters comparable to those found in the KTB fluids (see Table 1). In order to lower the ratio in meteoric waters to the levels found in the KTB fluids, the meteoric water content would have to be about 50%, which would mean that the original fluids were diluted by a factor of 2 or more, a proposition not supported by other geochemical tracers such as Cl concentrations. The absence of an anthropogenic signal in the $^{36}\text{Cl}/\text{Cl}$ ratios also speaks against a significant anthropogenic component in the fluids.

Fissiogenic component

In the absence of a significant anthropogenic component in the waters, the $^{129}\text{I}/\text{I}$ ratios must reflect the presence of fissiogenic ^{129}I . Before the concentration of fissiogenic ^{129}I can be calculated from equation 2, uranium concentrations in the host formations have to be known. During the drilling, the concentration of radioactive elements was estimated using gamma ray logs. The resulting uranium concentrations are between 1.3 and 2.7 ppm (Pribnow *et al.* 1992). Direct measurements of U concentrations in a set of samples taken from the drill cores gave, however, considerably lower values, around 0.5 ppm (Teichmann & Basu 1996). Because it is unlikely that the formations immediately adjoining to the drill site served as host for the fluids, these two sets of the uranium values might not reflect the concentration responsible for production of fissiogenic ^{129}I . As the production of both radioisotopes, ^{129}I and ^{36}Cl , is the consequence of the presence of uranium, although through different reactions, we can use the build-up of fissiogenic ^{36}Cl to estimate the uranium concentration of potential host formations. Given the relatively short half-life of ^{36}Cl , the formation of this isotope reaches secular equilibrium within 1.5 Ma, and equation 3 can be simplified to

$$N_{36} = \frac{\sigma \Phi N_{35}}{\lambda_{36}} \quad (4)$$

With $\sigma = 44 \times 10^{-24} \text{ cm}^2$ and $\lambda_{36} = 2.3 \times 10^{-6} \text{ yr}^{-1}$, we calculate neutron fluxes between 371 and 774 n

($\text{cm}^{-2} \text{ year}^{-1}$) responsible for the generation of fissiogenic ^{36}Cl in the fluids. Neutron fluxes in this range typically reflect U concentrations between 0.7 and 1.5 ppm, together with Th concentrations between 4 and 10 ppm (Fehn *et al.* 1992). These concentrations are at the lower end of the concentration range for uranium indicated by other investigators (Pribnow *et al.* 1992; Teichmann & Basu 1996).

Applying these U concentrations, we can calculate residence times of the fluids in the formations following equation 2. The average number of ^{129}I atoms μl^{-1} is 31.7 ± 12.3 for the eight samples. The escape probability for rock formations is not well known, but probably ranges between 1 and 20% (Fabryka-Martin *et al.* 1989), while porosities in deep crustal rocks probably are between 0.1 and 1% (Möller *et al.* 2005). Given the co-variation between these two parameters, the likely E/P ratio is close to 15. If we use this value, together with a uranium concentration of 1 ppm and rock density $\rho = 2700 \text{ kg m}^{-3}$, the residence time is 17.5 Ma. Given the uncertainties of the approach, this result is, however, only an order-of-magnitude estimate. As the observed variation in $^{129}\text{I}/\text{I}$ ratios does not correspond to changes in iodine concentrations, this variation reflects differences in ^{129}I concentrations in the fluids. These differences are likely caused by variations in uranium concentrations and/or escape probabilities in the host formations of the fluids.

Cosmogenic component

In a first assessment, the cosmogenic components of these two radioisotopes are not readily discernible in the KTB fluids. The residence times prevalent for the fluids indicate that the cosmogenic component of ^{36}Cl has decayed away and that the ^{36}Cl concentrations in the fluids are made up of the fissiogenic contribution to this system. As the build-up of both radioisotopes depends on the presence of uranium, we can use this observation in order to estimate the cosmogenic component of ^{129}I in the fluids. The concentrations of both isotopes in the fluids show a good correlation (Fig. 4). This comparison also provides further evidence for the absence of a significant anthropogenic component in the fluids, as the concentrations for anthropogenic waters are clearly off the regression line. The good correlation ($R = 0.93$) suggests that the build-up of both radioisotopes is related and that the intersection of the regression line with the y -axis gives the concentration of ^{129}I in the fluids before they entered the host formations. The data point for the earlier pump test falls also on the regression line, a further indication that the fluids have not changed substantially between the pump tests, in good agreement with observations using other geochemical tracers (Möller *et al.* 2005). Using all five data points for this calculation, the intersect is at 2.9 atoms μl^{-1} ($R = 0.93$);

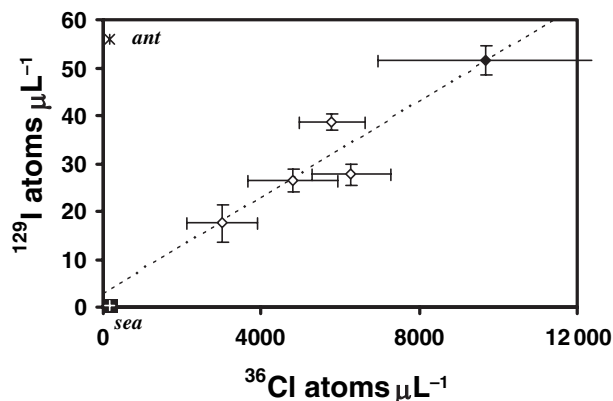


Fig. 4. ^{129}I versus ^{36}Cl concentrations in the fluids from pump tests of 1991 (solid diamond) and of 2002–03 (open diamonds) with linear regression line. Values for anthropogenic meteoric water (ant) and pre-anthropogenic seawater (sea) are also indicated.

changing to $4.4 \text{ atoms } \mu\text{L}^{-1}$ ($R = 0.77$) for the data set from the recent pump test alone. These values represent an estimate of the ^{129}I concentrations in the fluids before the addition of the fissiogenic component in the formations in which the fluids resided for the build-up of the fissiogenic component.

The cosmogenic component can be used to calculate the age of the source providing iodine to the fluids. With iodine concentrations between 16 and $25 \mu\text{M}$, the initial $^{129}\text{I}/\text{I}$ ratios of the fluids were between 200 and 460×10^{-15} before the addition of fissiogenic ^{129}I . These ratios allow the calculation of source ages following equation 1 and using the input ratio $R_i = 1500 \times 10^{-15}$ (Moran *et al.* 1998), resulting in source ages for these fluids between 26 and 45 Ma. Because the ratios do not take into account fissiogenic contributions in the source formation of iodine, they are maximum values and the likely source ages are older than the values given here.

DISCUSSION

Origin and history of the KTB fluids

The main purpose of an investigation using cosmogenic systems is the evaluation of origin and history of the fluids. Although the presence of a strong fissiogenic component in the KTB fluids precludes direct dating of the source of iodine (and, by analogy, that of organic material), the results presented here suggest that the fluids have resided in formations with relatively low uranium contents (approximately 1 ppm) for periods of more than 10 Ma and contain iodine with ages older than 30 Ma. The good correlation between the build-up of ^{36}Cl and ^{129}I indicates that the addition of these two isotopes occurred simultaneously and that the fluids entered the formation

with similar concentrations of Cl and I as found in the current fluids. The results are in reasonably good agreement with the understanding that the high chloride concentrations are the result of processes such as albitization (Möller *et al.* 2005), which, because of the low temperatures involved, are slow-acting processes and require substantial residence times. Residence times suggested by noble gas methods are between 4.2 and 5.9 Ma, which constitute, however, minimum ages because relatively high crustal He fluxes were assumed for this estimate (Lippmann *et al.* 2005). If we used the same uranium concentrations (2 ppm) as was used for the noble gas model ages, our residence times would be around 9 Ma, and reasonably good agreement between these two methods would exist. We prefer the uranium concentration based on the build-up of ^{36}Cl , because it reflects the likely process leading to the addition of fissiogenic isotopes in the reservoir formation, which is not necessarily represented by the gamma-ray investigations in the drill hole. As the noble gas methods as well the ^{129}I approach are based on parameters with considerable uncertainties attached, the results agree reasonably well and suggest residence times for the fluids of probably more than 10 Ma, but at least of 5 Ma.

Iodine enrichment and iodine ages found here point to the addition of iodine and bromine from relatively old, organic-rich sedimentary layers. The presence of high methane concentrations in the gas component of the fluids (Lippmann *et al.* 2005) also supports derivation from organic-rich formations. An alternative explanation for iodine enrichment is related to serpentinization processes occurring during the release of fluids from mud volcanoes and similar features (Snyder *et al.* 2004), although this process is less likely in the given geologic situation. As the results provide minimum ages, derivation from the sedimentary formations to the west of the drill site is possible, although all of these formations are of Cretaceous age or older. The iodine ages argue, however, against derivation from Recent sources, as suggested by a model based on the cryogenic enrichment of seawater during glaciation cycles (Starinsky & Katz 2003).

Comparison with other crustal fluids

The concentrations of Cl and Br found in the KTB fluids fall well within the range observed for crustal fluids (Frape *et al.* 2004). The halogen pattern observed in the KTB site is typical for crustal fluids, where Br shows stronger enrichment than Cl when compared with seawater, resulting in a molar Br/Cl ratio of 0.006. As the Br/Cl ratio in organic matter is substantially higher than in seawater, the relative enrichment of Br in crustal fluids can be explained by the decomposition of organic matter and subsequent release of Br. Only relatively few data are available for the concentration of iodine in crustal fluids (Bottomley *et al.* 2002;

Starinsky & Katz 2003), but the high I/Cl ratios (compared with seawater) observed in these fluids are also indicative of derivation from organic matter.

The methods and results derived for the ^{129}I and ^{36}Cl systems can be compared with other cases where data for both radioisotopes are available, such as the Stripa Granite (Fabryka-Martin *et al.* 1989), Milk River (Fabryka-Martin *et al.* 1991) and Clear Lake (Fehn *et al.* 1992). A good correlation between ^{36}Cl and ^{129}I concentrations is visible in the data from Stripa Granite (Fig. 5). Because the chloride concentrations there are only around 500 ppm, the production of ^{36}Cl is relatively lower than in the KTB fluids, resulting in a steep slope of the correlation between ^{129}I and ^{36}Cl concentrations. The elevated concentrations of ^{129}I are a consequence of the very high uranium concentrations, which reach values of 50 ppm in the Stripa Granite. Although a general correlation between the two radioisotopes exists also in the other two cases (Fig. 5, inset), concentrations of both radioisotopes in the Milk River and Clear Lake systems are much lower than at KTB and Stripa. As uranium concentrations there are similar to those derived for the KTB fluids, the low concentrations reflect relatively short residence times in Milk River and Clear Lake. Because the residence times are less than 0.5 Ma in the cases other than KTB, the cosmogenic component of ^{36}Cl is still present and the regression trends toward the estimates for pre-anthropogenic meteoric water or seawater, resulting in negative intercepts for ^{129}I in Stripa and Milk River. In these two cases, the presence of the cosmogenic components of these two isotopes results in an essentially horizontal shift toward the right in Fig. 5. At the long residence times estimated for the KTB fluids, all the cosmogenic ^{36}Cl has decayed, allowing the derivation of the cosmogenic ^{129}I component in this case. The data

from Clear Lake also allow the calculation of an initial ratio ($^{129}\text{I}/\text{I} = 170 \times 10^{-15}$) which translates into a minimum age of 50 Ma, in reasonable agreement with the earlier estimate of 70 Ma derived for this system (Fehn *et al.* 1992).

The other three cases differ in one important way from the KTB study, as they all reflect samples from different locations taken within a narrow time frame, rather than one sample location over a period of 10 years, if the two pump tests are considered for KTB. Other processes such as dilution, evaporation or ion filtration could potentially change the concentrations of the two radioisotopes simultaneously, but these processes would also affect the concentrations of the halogen concentrations. As the changes in radioisotopes are not accompanied by similar changes in the concentrations of halogen concentrations, the model developed here, that is addition of radioisotopes reflecting varying degrees of uranium concentration in host rocks, is the most likely explanation for the observed correlation between ^{129}I and ^{36}Cl concentrations.

Crustal fluids commonly display geochemical characteristics quite similar to those of the KTB fluids, including elevated halogen concentrations and increased I/Cl or Br/Cl ratios relative to seawater. Mechanisms suggested for the formation of these brines call either for extended residence times to allow the interaction with host formations and addition of iodine and bromine from organic-rich sediments (Bottomley *et al.* 2002) or for processes related to recent glaciation cycles (Katz & Starinsky 2003; Starinsky & Katz 2003). The formation of natural cryogenic brines, as suggested in the latter two papers, is a mechanism active also in surface fluids in Antarctic settings (Lyons *et al.* 2004). Cryogenic formation of crustal fluids is an attractive process in situations such as the Canadian Shield with the

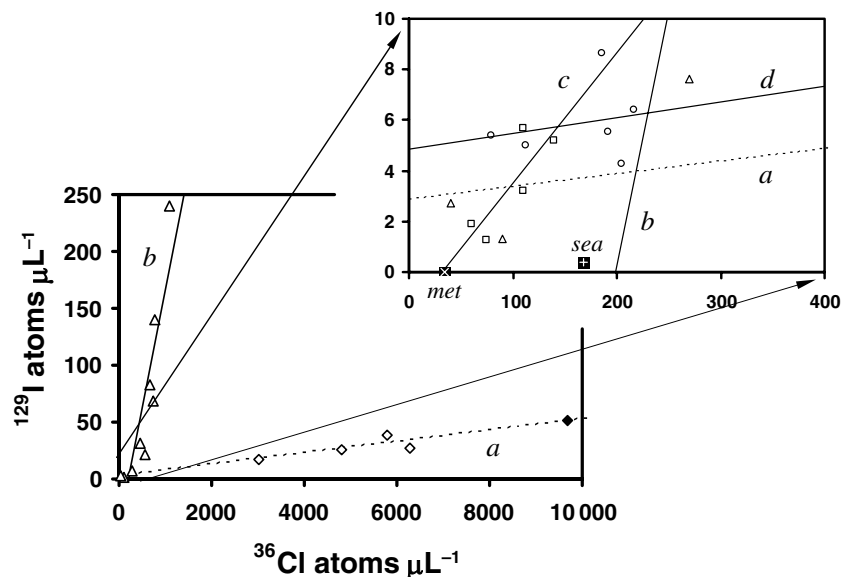


Fig. 5. Comparison of ^{129}I versus ^{36}Cl concentrations in fluids from the KTB site (diamonds; line a) to those from the Stripa Granite (triangles and line b; Fabryka-Martin *et al.* 1989), Milk River (squares and line c; Fabryka-Martin *et al.* 1991) and Clear Lake (circles and line d; Fehn *et al.* 1992). The inset is an enlargement of the area close to the origin and also indicates the values for pre-anthropogenic meteoric water (met) and seawater (sea).

presence of glacial conditions and close proximity to the oceans, but such conditions were not present in the study area during the time period proposed here for the derivation of iodine in the KTB fluids. Because climatic conditions during that period were relatively warm, iodine probably was formed from the diagenesis of marine organic matter of that age.

CONCLUSIONS

We measured ^{129}I and ^{36}Cl concentrations in fluids collected from a depth of 4000 m during the pump test carried out in 2002–03 at the KTB-VB, Germany. The fluids are characterized by elevated concentrations of halogens compared with seawater, showed little variation over the test period and also compared well with samples taken from a pump test in 1991 from the same location. Ratios of $^{129}\text{I}/\text{I}$ in these fluids were consistently above pre-anthropogenic values. The co-variation between ^{129}I and ^{36}Cl concentrations in the fluids indicates that both radioisotopes are dominated by the addition of ^{129}I and ^{36}Cl atoms from crustal sources. The build-up of ^{129}I reflects the residence of the fluids for periods of 10 Ma or longer in formations with uranium concentrations of approximately 1 ppm. Our results suggest that KTB fluids are derived from old seawater sources, which increased their chloride content due to long-term interaction with host rocks. The elevated iodine and bromine concentrations reflect interaction of fluids with organic-rich marine sediments (with minimum ages of 30 Ma), which probably also served as the source of the high methane content observed in the fluids.

Crustal fluids such as those collected from the KTB site provide a window into processes occurring over long periods of time at depths of several kilometers. As in other crustal fluids, the KTB samples reflect increased concentrations of bromine and iodine, probably related to derivation from organic-rich sediments. Slow movement and long residence times provide for extensive interaction with host rocks resulting in increased concentrations of chlorine in the fluids. Although the cosmogenic isotopes used here reflect a mixture of several sources, the combined use of ^{129}I and ^{36}Cl systematics allowed the determination of source ages and residence times in the KTB fluids, suggesting the future application of these isotopes in other crustal fluids.

ACKNOWLEDGEMENTS

We thank J. Erzinger and his group for providing the samples from the KTB pump test, and P. Möller and J. Lippmann for preprints of papers on the KTB fluids. We appreciate help from Zunli Lu on the determination of halogen concentrations and are grateful for the isotope

determinations carried out at PrimeLab, Purdue University, by D. Elmore and his group. The paper benefited from thoughtful reviews by J. Hanor and an anonymous reviewer.

REFERENCES

- Andrews JN, Davis SN, Fabryka-Martin J, Fontes J-Ch, Lehmann BE, Loosli H, Michelot J-L, Moser H, Smith B, Wolf M (1989) The *in situ* production of radioisotopes in rock matrices with particular reference to the Stripa granite. *Geochimica et Cosmochimica Acta*, **53**, 1803–15.
- Bottomley DJ, Renaud R, Kotzer T, Clark ID (2002) Iodine-129 constraints on residence times of deep marine brines in the Canadian Shield. *Geology*, **30**, 587–90.
- Broecker WS, Peng TH (1982) *Tracers of the Sea*. Eldigio Press, Palisades, NY.
- Emmermann R, Lauterjung J (1997) The German Continental Deep Drilling Program KTB: overview and major results. *Journal of Geophysical Research*, **102**, 18179–202.
- Erzinger J (2005) Introduction to Special Issue: Long-term fluid production in the KTB Pilot Hole, Germany. *Geofluids*, **5**, 1–7.
- Fabryka-Martin JT, Bentley H, Elmore D, Airey PL (1985) Natural iodine-129 as an environmental tracer. *Geochimica et Cosmochimica Acta*, **49**, 337–437.
- Fabryka-Martin JT, Davis SN, Elmore D, Kubik PW (1989) In situ production and migration of ^{129}I in the Stripa granite, Sweden. *Geochimica et Cosmochimica Acta*, **53**, 1817–23.
- Fabryka-Martin JT, Whitemore DO, Davis SN, Kubik PW, Sharma P (1991) Geochemistry of halogens in the Milk River aquifer, Alberta, Canada. *Applied Geochemistry*, **6**, 447–64.
- Fehn U, Moran JE (1993) *Determination of ^{36}Cl and ^{129}I in Fluids from the KTB Project*. KTB Report 93–2, 439–42. Niedersächsisches Landesamt für Bodenforschung, Hannover, Germany.
- Fehn U, Peters KE, Tullai-Fitzpatrick S, Kubik PW, Sharma P, Teng RTD, Gove HE, Elmore D (1992) ^{129}I and ^{36}Cl concentrations in waters of the eastern Clear Lake Area, California: residence times and source ages of hydrothermal fluids. *Geochimica et Cosmochimica Acta*, **56**, 2069–79.
- Fehn U, Snyder G, Egeberg PK (2000) Dating of pore waters with ^{129}I : relevance for the origin of marine gas hydrates. *Science*, **289**, 2332–5.
- Frape SK, Blyth A, Blomqvist R, McNutt RH, Gascoyne M (2004) Deep fluids in the continents: II. Crystalline rocks. *Treatise on Geochemistry*, **5**, 541–80.
- GERM (2004) *Geochemical Reference Model*. <http://earthref.org/GERM/>.
- Hanor JS (1994) Origin of saline fluids in sedimentary basins. In: *Geofluids: Origin, Migration and Evolution of Fluids in Sedimentary Basins* (ed. Parnell J), pp. 151–74. Geological Society, Special Publication, 78. Geological Society of London, London.
- Hesse R (2003) Pore water anomalies of submarine gas-hydrate zones as tool to assess hydrate abundance and distribution in the subsurface – what have we learned in the past decade? *Earth-Science Reviews*, **61**, 149–79.
- Katz A, Starinsky A (2003) Iodine-129 constraints on residence times of deep marine brines in the Canadian Shield: Comment and Reply. *Geology*, **31**, 93–4.
- Lippmann J, Erzinger J, Zimmer M, Schloemer S, Eichinger JL, Faber E (2005) On the geochemistry of gases and noble gas isotopes in deep crustal fluids. The 4000 m KTB-pilot hole fluid production test 2002/03. *Geofluids*, **5**, 52–66.

- Lodemann M, Fritz P, Wolf M, Ivanovich M, Hansen BT, Nolte E (1998) On the origin of saline fluids in the KTB (Continental Deep Drilling Project of Germany). *Applied Geochemistry*, **13**, 653–71.
- Lyons WB, Welch KA, Snyder G, Olesik J, Graham EY, Marion GM, Poreda RJ (2004) Halogen geochemistry of the McMurdo Dry Valleys Lakes, Antarctica: clues to the origin of solutes and lake evolution. *Geochimica et Cosmochimica Acta*, in press.
- Möller P, Weise SM, Althaus E, Bach W, Behr HJ, Borchardt R, Bräuer K, Drescher J, Erzinger J, Faber E, Hansen BT, Horn EE, Huenges E, Kämpf H, Kessels W, Kirsten T, Landwehr D, Lodemann M, Machon L, Pekdeger A, Pielow H-U, Reutel C, Simon K, Walther J, Weinlich FH, Zimmer M (1997) Paleofluids and Recent fluids in the upper continental crust: results from the German Continental Deep Drilling Program (KTB). *Journal of Geophysical Research*, **102**, 18233–54.
- Möller P, Woith H, Dulski P, Lüders V, Erzinger J, Kämpf H, Pekdeger A, Hansen B, Lodemann M, Banks D (2005) Main and trace elements in KTB-VB fluid: composition and hints to its origin. *Geofluids*, **5**, 28–41.
- Moran JE, Fehn U, Hanor JS (1995) Determination of source ages and migration patterns of brines from the U.S. Gulf Coast Basin using ^{129}I . *Geochimica et Cosmochimica Acta*, **59**, 5055–69.
- Moran JE, Fehn U, Teng RTD (1998) Variations in $^{129}\text{I}/\text{I}$ ratios in recent marine sediments: evidence for a fossil organic component. *Chemical Geology*, **152**, 193–203.
- Moran JE, Oktay SD, Santschi PH (2002) Sources of iodine and iodine 129 in rivers. *Water Resources Research*, **38**, 24–31.
- Pechnig R, Haverkamp S, Wohlenberg J (1997) Integrated log interpretation in the German Continental Deep Drilling Program: lithology, porosity, and fracture zones. *Journal of Geophysical Research*, **102**, 18363–90.
- Phillips FM, Ayarbe JP, Harrison JBJ, Elmore D (2003) Dating rupture events on alluvial fault scarps using cosmogenic nuclides and scarp morphology. *Earth and Planetary Science Letters*, **215**, 203–18.
- Pribnow D, Buecker C, Rauen A, Spangenberg E, Wienand J, Soffel H (1992) KTB-Hauptbohrung. Geoscientific investigations in the KTB-field-laboratory, depth interval 0–6000m: Geophysics. *KTB-Report 92 (2)*, D1–42. Niedersächsisches Landesamt für Bodenforschung, Hannover, Germany.
- Purdy CB, Helz GR, Mignerey AC, Kubik PW, Elmore D, Sharma P, Hemmick T (1996) Aquia aquifer dissolved Cl- and Cl-36/Cl: implications for flow velocities. *Water Resources Research*, **32**, 1163–71.
- Rao U, Fehn U (1999) Sources and reservoirs of anthropogenic iodine-129 in Western New York. *Journal of Geophysical Research*, **63**, 1927–38.
- Santschi PH, Schink DR, Corapcioglu O, Oktay-Marschal S, Fehn U, Sharma P (1996) Evidence for elevated levels of ^{129}I in the deep western boundary current in the Middle Atlantic Bight. *Deep Sea Research*, **43**, 259–65.
- Sharma P, Bourgeois M, Elmore D, Granger D, Lipschutz ME, Ma X, Miller T, Mueller K, Rickey G, Simms P, Vogt S (2000) PRIME Lab AMS performance, upgrades and research applications. *Nuclear Instruments and Methods*, **B172**, 112–23.
- Snyder G, Fehn U (2004) Global distribution of ^{129}I in rivers and lakes: implications for iodine cycling in surface reservoirs. *Nuclear Instruments and Methods*, **B223/224**, 579–86.
- Snyder GT, Riese WC, Franks S, Fehn U, Pelzmann WL, Gorody AW, Moran JE (2003) Origin and history of waters associated with coal-bed methane: ^{129}I , ^{36}Cl , and stable isotope results from the Fruitland Formation, CO and NM. *Geochimica et Cosmochimica Acta*, **67**, 4529–44.
- Snyder GT, Savov IP, Muramatsu Y (2004) Iodine and boron in Marianas serpentinite mud volcanoes (ODP 125 and 195). Implications for forearc processes and subduction recycling. (eds Shinohara M, Salisbury MH, Richter C), *Proceedings ODP Scientific Results*.
- Starinsky A, Katz A (2003) The formation of natural cryogenic brines. *Geochimica et Cosmochimica Acta*, **67**, 1475–84.
- Suter M, Beer J, Bonani G, Hofmann HJ, Michel D, Oeschger H, Synal HA, Wölfli W (1987) ^{36}Cl studies at the ETH/SIN-AMS Facility. *Nuclear Instruments and Methods*, **B29**, 211–5.
- Teichmann F, Basu AR (1996) Nd-Sr isotopic and trace element study of rocks and fluids from the Continental Deep Drilling Project (KTB), Germany. *Geologische Rundschau*, **85**, 162–71.
- Weber K (1990) Observations on the ductile deformation path of the paragneisses of the KTB pilot hole. *KTB Report 90–8, J1–J-19*. Niedersächsisches Landesamt für Bodenforschung, Hannover, Germany.