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Developments toward the measurement of I-129 in lignite

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Abstract

The concentration of the long-lived radioisotope ^{129}I was determined in two Austrian lignite samples through ^{129}I/^{127}I isotopic ratio measurement by AMS, and through a measurement of the total iodine content with an ion-selective electrode. In addition, the uranium concentration of the samples was measured by α-spectrometry. From the mean values of the uranium concentrations the steady-state concentration of ^{129}I in lignite was calculated; the ^{129}I concentrations derived from the measured ^{129}I/^{127}I ratio and the total iodine content, however, were much higher than expected, clearly indicating that lignite does not represent a closed system for ^{129}I. The observed high ratio in the sample from the surface mine suggests the presence of anthropogenic ^{129}I, while the source for the high ^{129}I concentrations in the subsurface lignite is the addition of fissiogenic ^{129}I either from the lignite itself (from layers with much higher U content than in the samples investigated) or from nearby geological formations rich in uranium.

Keywords: ^{129}I; Accelerator mass spectrometry; Lignite

1. Introduction

In nature, ^{129}I with its half life of 15.7 Myr has two significant sources: it is produced in the atmosphere primarily by cosmic ray reactions on xenon [1], and in the lithosphere primarily by spontaneous fission of ^{238}U (induced fission of ^{235}U plays a minor role and can be neglected in most cases) [2]. Recent anthropogenic activities such as nuclear weapons tests, operation of reactors, and above all reprocessing plants (Sellafield (GB) and LaHague (F)) constitute a third source of ^{129}I, which has increased the levels of this isotope in certain domains on Earth by several orders of magnitude.

As iodine is fairly mobile in ground water and is commonly assumed to sorb negligibly on most rocks and minerals, the natural as well as the artificial ^{129}I can be used as geochemical tracer (see e.g. [3–6]). Pre-bomb natural ^{129}I/^{127}I ratios were found to be in the range of 10^{-12}–10^{-13} [3]. Natural ^{129}I can be used to date old geologic materials containing organically-bound iodine, as was done successfully for oil field brines [7,8]. Lignite was the material of our interest with regard to age-determination. In lignite, a large fraction of the carbon is still in organic form, and the structure of the precursor plant material (wood, bark, roots) is well visible. As the uranium content of lignite can be quite high (up to 2500 ppm) a considerable amount of fissiogenic ^{129}I may have accumulated since the formation of the deposit during the tertiary period, if it has remained a closed system. In this case, the concentrations of ^{129}I and ^{238}U could be used for dating the lignite layers – in a way similar to the well-known method of uranium-series dating. However, as iodine adsorbs very well to coal, the lignite may represent a sink for iodine carried by groundwater or anthropogenic ^{129}I may have contaminated old lignite layers.

The aim of our investigation was to establish a procedure for the determination of the ^{129}I/^{127}I isotopic ratio in lignite and, in a first step, to decide whether or not lignite

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is contaminated by anthropogenic ^{129}I. We used fresh material from surface mining, and archived material from sub-surface mining, sampled in 1967. Since laboratory intercomparison efforts on ^{129}I have led to unsatisfactory results in organic samples [9], we investigated various methods of iodine extraction. After combustion of the crushed lignite, inorganic iodine was collected in KOH, with Na_2SO_3 or hydrazine as reducing agent, and then precipitated as AgI; organic iodine was trapped on charcoal and eluted with chloroform. A few samples showed rather high contents of sulfur which had to be separated as NiS prior to the AgI precipitation. The iodine content of solutions from different stages of the procedure was determined with an ion-specific electrode. The uranium content of the samples was measured by alpha counting following uranium separation by anionic exchange and microprecipitation. Finally, the ^{129}I/^{127}I ratio was determined by AMS at the Vienna Environmental Research Accelerator (VERA).

2. Samples and methods

2.1. Description of samples

Table 1 displays some previous information on the coal pits where our samples originate. Both deposits are situated in basins south of the north-east spur of the Central Alps; their formation took place during the tertiary period. Sample M originates from the under-ground mine near Mariasdorf, Tauchen, Burgenland (Austria). The thickness of the lignite seam is 18–25 m, and depth of overburden is ca. 200 m. The sample was taken in 1967 by a retiring engineer, when the mine was shut down. It was packed in plastic foil and a closed plastic container and was stored in cool and dark conditions. We think that these conditions minimized the danger of intrusion of anthropogenic iodine. At the time the sample was collected (more exactly for the years 1960–65) a ^{129}I/^{127}I isotopic ratio of 10^{-8} for meteoric water was reported from ice of the Fiescherhorn glacier [10,11]; the ^{129}I in the atmosphere mainly originated from the fallout of the atmospheric nuclear weapons testing.

Sample K originates from the surface mine in Köflach, Styria (Austria), which is still in operation. The sample was collected after removing a 2 m thick surface layer of lignite. The thickness of the seam is 15 m. The sampling was done especially for this work in May 2003 and is well documented. The shallow origin of the sample makes an anthropogenic contamination more likely than for sample M. The main sources of the modern ^{129}I are the reprocessing plants Sellafield (GB) and LaHague (F). Recent ^{129}I/^{127}I values for meteoric water are 10^{-6}–10^{-5}, for surface waters and the biosphere ratios of 10^{-8} are reported [10,12].

Table 1
characteristic data of typical lignite from the pits where our samples originated [13]

Site	H_2O (%)	Ash (%)	Sulfur (%)
Mariasdorf (M)	35–38	4–14	0.9–2
Köflach (K)	31–38	9–27	0.35–0.51

2.2. Sample preparation

About 10 g of the lignite samples were crushed to a grain-size of about 1–3 mm, placed in a ceramic boat and then combusted in a stream of oxygen in a quartz tube connected to gas wash bottles filled with KOH and a reducing agent (see e.g. [14]); iodine in organic form was trapped with charcoal (Fig. 1). The sample was heated gradually with a gas burner and the evolving gases streamed through the 800 °C zone of a tube furnace where a plug of quartz wool was situated. The oxygen flow as well as the burner heat had to be controlled very carefully to attain complete combustion; both too high and too low gas flow can result in pollution of the trapping solution by soot particles, tar and other products of incomplete combustion as well as iodine loss either before or after the washing bottles. Insufficient oxygen flow resulted also in incomplete combustion of sulfur; it was then trapped as sulfide. At the beginning of the combustion the oxygen flow was about 150 ml/min; it was then adjusted so that a steadily glowing sample zone was achieved. Still, even with similar samples, significant variations in the combustion conditions may arise.

The trapping solution was 100 ml 0.2 M KOH, containing also 200 mg of Na_2SO_3 as reducing agent. This agent is necessary to reduce possibly present hypoiodides and to prevent the re-formation of volatile I_2 in an oxidizing trapping solution. The disadvantage of the sulfite is that it will also partly reduce the Ag^+ during the precipitation step. Two other reducing agents, $NaNO_2$ and hydraziniumhydroxide (N_2H_5OH), were investigated; however, these agents influenced the determination of the total iodine content (see below). Another substance disturbing the total iodine determination was the above mentioned sulfide; it was separated as NiS by adding 30 mg $NiSO_4$ to the trapping solution. The solution was filtered, and after total iodine determination on an aliquot it was acidified (pH = 2–3) with 2 M HNO_3. AgI was precipitated after addition of a few drops of 0.5 M $AgNO_3$ solution. Co-precipitated chloride was re-dissolved with 25% NH_3 solution

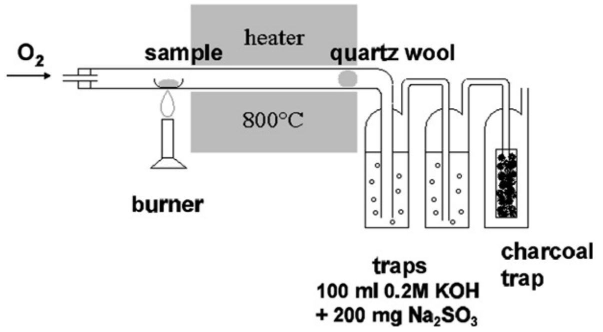

Fig. 1. Combustion apparatus for iodine separation from lignite.

as diammine complex. The precipitate was washed with 0.2 M HNO_3 until it was free of Ag^+ ions. After drying at 80 °C the AgI was mixed with Ag-powder and transferred to a target holder.

In some samples organically bound iodine was trapped on 2.6 g of charcoal grains contained in a small tube either before or after the gas washing bottles. The organic iodides adsorbed on the charcoal were eluted with chloroform and then transferred to an aqueous phase (saturated NaOH); in this step the organic iodides are transformed to inorganic iodides via the reaction $CH_3I + NaOH \rightarrow CH_3OH + NaI$. When the charcoal tube was arranged before the wash bottles, the charcoal was also rinsed with distilled water to collect inorganic iodide adsorbed on its surface, too. The aqueous phases were acidified, and further treated like the other sample solutions.

The total iodine content as well as the $^{129}I/^{127}I$ isotopic ratio of each trapping solution was measured separately. The solutions containing iodide from organically bound species were also measured despite a greater chance for laboratory contamination of these "small" samples.

2.3. Total iodine content

The iodine content of the respective solutions was determined with an ion selective electrode (ORION iodide electrode Model 9653 BN, Thermo Orion™, Beverly MA, USA). The iodide concentration range of the electrode is 1 M to 5×10^{-8} M. To achieve the required constant total ion concentration of about 0.1 M, 1 ml 5 M $NaNO_3$ solution was added to 50 ml of the investigated solution. At the beginning of each series of measurements a calibration line was generated with various standard solutions. Our sample solutions were in the range of 10^{-4}–10^{-7} M iodide.

As the electrode results are easily influenced by small amounts of sulfide, this ion was previously removed as NiS precipitate. Also the influence of the reducing agents Na_2SO_3, $NaNO_2$ and N_2H_5OH was investigated.

The accuracy of the electrode measurements depended mainly on the quality of the calibration line and was found to be in the range of 10%. The advantage of the electrode compared to more precise methods is the easy and fast measurement, which accelerates procedural developments significantly.

2.4. $^{129}I/^{127}I$ isotopic ratio

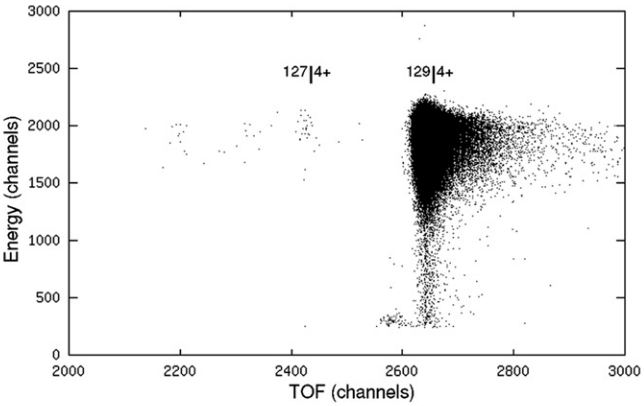

Fig. 2. Summed TOF-versus-Energy spectrum of 40 samples, standards, and blanks. New setup at VERA (since 2001).

The $^{129}I/^{127}I$ ratio was determined by AMS at the Vienna Environmental Research Accelerator (VERA). First investigations of the ^{129}I measurement potential of VERA were performed in 1998 [15]. These capabilities were improved significantly by the modifications of the analyser beam line in 2001 [16]. Compared to the previous setup with only a small Wien filter after the analysing magnet [17], the new large electrostatic separator suppresses background from neighbouring masses to negligible levels (Fig. 2). The separation of this background with a time-of-flight detector [18] is no longer required. Thus, the later part of the present measurement was performed without time-of-flight, which should result in ~100% efficiency using the ionisation chamber, instead of ~15% achieved with the time-of-flight system. However, in the present measurements significant ion-optical losses in the beam transport system to the detector were observed (65% and 22%, respectively). The reason for these losses is not yet understood. The scattering losses in the TOF system and the ion-optical losses were corrected by normalizing to standard materials of known isotopic ratio (standards "D" and "E" supplied by the Accelerator Laboratory at the PSI, Zürich, Switzerland). For blank materials, "Woodward" AgI (from the same source) and NaI from the Isotrace Laboratory (Toronto, Canada) were used. The measurements were performed at very low maximum source output (~1 μA $^{127}I^-$) to minimize cross contamination. Samples derived from trapping solutions with very low iodine content showed significantly lower beam currents. Most samples yielded a sufficient amount of stable iodine for AMS measurements. In a few cases, ^{129}I-free NaI was added to the samples as a carrier. However, since this method multiplies the influence of the uncertainty of the natural iodine content which could not be measured with sufficient precision, this method was abandoned.

Additionally, the improved background suppression allowed the use of the charge state 4+ instead of 5+, for which a stripping yield of 10% at 3-MV terminal voltage (instead of 7%) was achieved.

Besides the lignite samples, standards and blanks, all other iodine reagents in the laboratory (e.g. the calibration solution for the iodine electrode) were measured for its ^{129}I content. A potential source for ^{129}I contamination was the charcoal trap. Chemical blanks showed that the charcoal was very inhomogeneous with respect to iodine content; in one sample the $^{129}I/^{127}I$ blank ratio was found to be the same order of magnitude as the ratio of our lignite samples. The samples from the charcoal traps were excluded from our results also due to other reasons (insufficient AgI content, see below).

2.5. Uranium concentration

(13.85 ± 0.20) mBq of ^{232}U spike was added to lignite samples. After combustion the ashes were leached with carbonate or ethylenediamine-tetra-acetic acid (EDTA).

Between 0.4 and 0.6 g ash were added to 40 ml 0.5 M Na_2CO_3 solution and boiled for 5 h [19]; the volume was kept constant. 1 ml and 0.5 ml 30% H_2O_2 were added after 2 and 3.5 h, respectively. After centrifuging the residue was washed with 10 ml 0.5 M Na_2CO_3 solution. The solutions were combined and heated to dryness; after repeated evaporation to dryness with conc. HCl, the residue was taken up in 210 ml 8 M HCl (this large volume was necessary to dissolve all the NaCl precipitate).

The second leaching procedure investigated uses the fact that EDTA forms rather strong complexes with uranium. 0.4–0.5 g ash was added to 40 ml 0.25 M EDTA solution ($pH = 10$) and boiled for 4.5 h. After centrifuging and washing, the combined solutions were heated to dryness; to disintegrate the EDTA, the residue was taken up in 10 ml conc. HNO_3 plus a few drops of H_2O_2 and repeatedly evaporated to dryness. The residue was transformed into chlorides with conc. HCl; after evaporation the residue was again taken up in 180 ml 8 M HCl.

Uranium was separated by anionic exchange on Dowex 1 × 2 (100–200 mesh) from the 8 M HCl solution [20] and eluted with 100 ml 1 M HCl. This solution was repeatedly evaporated to dryness with conc. HNO_3 plus a few drops of 30% H_2O_2 to destroy any organic matter from the resin. After transformation into chlorides with conc. HCl, the residue was taken up in 1 M HCl and transferred to a plastic vial for uranium microprecipitation with neodymium fluoride [21]. 0.1 ml neodymium solution of a concentration of 0.5 mg/ml was added as well as acid $TiCl_3$ solution (15%) to reduce uranium was added. The fluorides were precipitated with 0.5 ml HF (40%), and after storage in an ice-bath for 30 min the solution was filtered through a Tuffryn™ membrane filter (pore size 0.2 μm). The filter was then counted for 14000 min using a Si surface barrier detector.

3. Results

3.1. Total iodine content

In order to get reproducible electrode measurement results of the trapping solution two points were important: (1) the removal of sulfides from the solution; and (2) the use of a suitable reducing agent. The removal of sulfides was studied with an artificial solution of 1×10^{-5} M $I^- + 1 \times 10^{-8}$ M H_2S with different amounts of $ZnSO_4$ and $NiSO_4$ as reagents. The solution without any reagent gave an iodide concentration more than a factor of 2 too high. Best results were achieved with about 30 mg of $NiSO_4$; this amount was added to all our solutions prior to the electrode measurements.

We also investigated the electrode adulteration of a solution containing iodide at a concentration of 5×10^{-5} M by the reducing agents Na_2SO_3, $NaNO_2$ and hydraziniumhydroxide N_2H_5OH (98% solution). The hydraziniumhydroxide solution generated values 66% too high; boiling off the reagent changed that elevated value only slightly. On the other hand, addition of $NaNO_2$ gave results 40% lower than the expected value. Addition of 200 mg Na_2SO_3 resulted in a slight increase of $\leqslant 10\%$; this was considered acceptable and so sulfite was added routinely to our trapping solutions.

The reproducibility of the total iodine content measured for our samples was improved considerably when we looked not only for inorganic iodide, but also for organically bound iodine. Organically bound iodine might be already present in the lignite (and is released at lower burner temperature, when the bonds cannot be cracked), and/or it is constituted during combustion (when the oxygen flow is rather low and pyrolysis results in e.g. methyl iodide). Three samples contained between 23% and 28% organically bound iodine; for two samples the results were the opposite: 80% and 64% organically bound iodine were detected. These results were independent of whether the charcoal trap was situated before or after the KOH washing bottles. These results indicate an inhomogeneity of our samples, but we cannot yet exclude that the variations were due to different behaviour during combustion.

Table 2 gives the results of the total iodine measurements for the Mariasdorf and Köflach samples. Column 2 gives the number of samples processed with the reducing agent given in column 3; for N_2H_5OH and $NaNO_2$ corrections of the measurement, decreasing the result by 66% and increasing it by 40%, respectively, were made due to the influence of the reducing agent on the iodide sensitive electrode. The last column gives the mean values of the measurement results and their 1σ-deviations.

It can be seen that the additional effort of trapping the organically bound iodine did not necessarily lead to higher total iodine contents. The scatter of the summarized results hints to iodine inhomogeneities within the lignite. For Mariasdorf, the results which included the organically bound iodine are the lowest with 31 and 33 ppm. The six

Table 2
Total iodine content measured

Site	Number of samples	Reducing agent	Organically bound iodine (%)	Mean value (ppm)
Mariasdorf (M)	6	Na_2SO_3	n.m.	51 ± 12
	1	Na_2SO_3	64	33
	1	–	38	62
	2	N_2H_5OH	n.m.	68 ± 15
	1	N_2H_5OH	33	31
	1	$NaNO_2$	n.m.	39
	All samples			*50 ± 16*
Köflach (K)	1	Na_2SO_3	34	11.4
	1	N_2H_5OH	80	9.7
	All samples			*10.6 ± 1.2*

The uncertainties are 1σ-deviations. (n.m.: not measured).

sulfite treated samples without organically bound iodine determination showed a large scatter between 12 and 82 ppm. Worth mentioning is the result of the sample processed without any reducing agent in the KOH trapping solution: obviously the iodine lost was caught in the charcoal trap which in this case was situated after the KOH solution.

3.2. $^{129}I/^{127}I$ ratio

Investigations of blank samples of different sizes showed an approximately inversely proportional increase of the measured isotopic ratio for very small sample sizes, up to $^{129}I/^{127}I \sim 10^{-10}$ for 10 μg iodine (see Fig. 3). This suggests a constant, small laboratory contamination with comparably higher (>>10^{-14}) $^{129}I/^{127}I$, containing a total of 6×10^8 ^{129}I atoms. For samples of 200 μg iodine, the measured $^{129}I/^{127}I$ value stays below 10^{-12}. If the true samples are significantly above this value (as in our case, see below), the influence of the contamination on the measured $^{129}I/^{127}I$ is negligible. Thus, samples below 200 μg iodine were excluded from the interpretation. Most of the lignite samples derived from additional iodine traps after the first wash flask were in the affected mass range and, if a sufficient set of comparable samples existed, showed an increased $^{129}I/^{127}I$ ratio for smaller sample sizes (see Fig. 3). Therefore, to avoid imponderabilities of varying procedures, only samples from the first wash flask, without reducing agent or treated with Na_2SO_3, were processed; so the charcoal trap samples, also prone to contamination, were not measured either.

Although the mixing with Ag powder was performed only by eye, a rough correlation between the iodine mass measured with the electrode and the $^{127}I^{4+}$-current from the ion source was observed. However, some samples with comparable high measured iodine content gave significantly low currents. Also, these samples showed increased $^{129}I/^{127}I$ ratios. Consequently, only samples with a measured iodine content of at least 200 μg and a current of at least 100 nA $^{127}I^{4+}$ were used for interpretation. For the first samples without Ni treatment, where no valid electrode measurements of the iodine concentrations existed, the ion current was used as the only criterion for sample rejection. From 18 AgI samples in question precipitated from lignite, 9 were rejected by the above mentioned criteria. However, these originated mainly from additional iodine traps. Only for one out of 10 lignite combustions no single fraction yielded sufficient AgI, and for another combustion two fractions gave enough AgI. Thus, 9 out of 10 lignite samples were measured successfully. Table 3 shows the results of the selected samples.

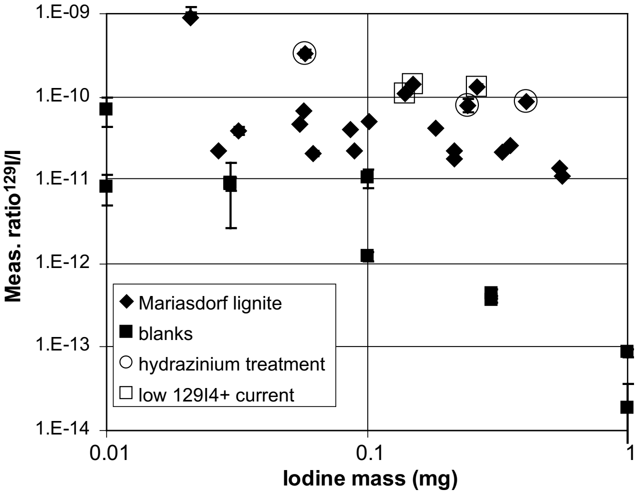

Fig. 3. Measured $^{129}I/^{127}I$ ratios for IsoTrace NaI blanks and Mariasdorf lignite.

Table 3
Iodine content, average $^{127}I^{4+}$ current (in nA) and $^{129}I/^{127}I$ ratio of selected samples; the error given is the 1 σ-deviation

Sample	I content (μg)	Average $^{127}I^{4+}$ current (nA)	$^{129}I/^{127}I$ ($\times 10^{-12}$)
M3	n.a.	904	6.0 ± 0.2
M7	n.a.	417	20.5 ± 0.5
M11	0.56	437	11.2 ± 0.2
M12	0.33	187	21.6 ± 0.3
M13	0.55	550	14.0 ± 0.2
M14	0.22	557	18.0 ± 0.2
Mariasdorf M (mean value)			*15.2 ± 6.0*
K1	n.a.	118	7.8 ± 0.6
K4	n.a.	193	12.7 ± 0.6
K7	0.39	697	8.9 ± 0.3
Köflach K(mean value)			*9.8 ± 2.6*

(n.a.: not analyzed).

The average $^{129}I/^{127}I$ value for Mariasdorf is $(15.2 \pm 2.4) \times 10^{-12}$, the value for Köflach is $(9.8 \pm 1.5) \times 10^{-12}$. A significant scatter is visible in the data, but the order of magnitude of the isotopic ratio is clearly 10^{-11}.

3.3. Uranium concentration

Generally, uranium concentrations in our samples are very low (Table 4). For the Mariasdorf samples good agreement was found between the two investigated methods, but results are clearly lower than a value from the literature for a mine just a few kilometers away (there the uranium was measured via the decay products ^{234}Th and ^{234}Pa [22]). For the Köflach samples the EDTA method gave a result 35% lower than the carbonate method; however, agreement with literature values is satisfactory. The $^{234}U/^{238}U$ activity ratio showed no significant indication for disequilibrium, despite one measurement (Köflach with CO_3^{2-} treatment) that showed a slightly increased value.

We have to consider that uranium typically is not part of the organic material forming the lignite, but was deposited together with organic rich material. As a consequence, the

Table 4
Uranium content in lignite and ash, chemical recovery and $^{234}U/^{238}U$ activity ratio derived by using two different leaching methods; the U content in ash is compared to a value from the literature [22]

Sample	Method	U in lignite (ppm)	U in ash (ppm)	Recovery (%)	$^{234}U/^{238}U$ activity ratio
Mariasdorf	CO_3^{2-}	0.103 ± 0.005	1.89 ± 0.09	26.1 ± 1.1	1.03 ± 0.07
	EDTA	0.084 ± 0.004	1.70 ± 0.07	61.6 ± 2.4	1.03 ± 0.06
	Lit.		9		
Köflach	CO_3^{2-}	0.583 ± 0.018	14.7 ± 0.5	42.2 ± 1.7	1.10 ± 0.05
	EDTA	0.403 ± 0.013	10.3 ± 0.3	73 ± 3	1.04 ± 0.05
	Lit.		9–11		

distribution of U in coal is very uneven, and our determination in just a few samples might not represent the mean U concentration of the whole lignite deposit (see below).

3.4. Calculated versus measured $^{129}I/^{127}I$ ratios

From the mean values of our uranium concentration results (Mariasdorf: 0.094 ± 0.006 ppm, Köflach: 0.493 ± 0.022 ppm uranium) we calculated the steady-state concentration of ^{129}I in lignite as 147 and 725 atoms/g for Mariasdorf and Köflach, respectively (calculations based on $\lambda_{sp} = 8.5 \times 10^{17}\ a^{-1}$ [23], $\lambda_{129} = 4.3 \times 10^{-8}\ a^{-1}$ [24], and spontaneous fission yield for mass 129: $Y_{129} = 0.03\%$ [25]). We only considered ^{129}I production by spontaneous fission of ^{238}U; the portion from induced fission of ^{235}U can be neglected (see [3]). Since the value for Y_{129} is only an estimate and various values can be found in the literature, we do not assign an uncertainty for this value. However, a factor of 3 seems possible.

Combined with the total iodine content, rather low $^{129}I/^{127}I$ isotope ratios of $(6 \pm 1) \times 10^{-16}$ and $(1.5 \pm 0.2) \times 10^{-14}$ for Mariasdorf and Köflach are calculated from these numbers for a closed system; these results are in contradiction to the measured isotope ratios of about 10^{-11}. From the systematic investigations on blanks, however, we consider ^{129}I contamination in the laboratory as unlikely.

For an explanation of our findings a closer look to our sampling sites is necessary. Köflach is a surface mine situated in a geological formation of limestone, and the sample was taken very near to the surface. Recent $^{129}I/^{127}I$ values for meteoric water are 10^{-6}–10^{-5}, while surface waters and biosphere ratios of 10^{-8} are reported [10,12]. The main sources of the ^{129}I are currently the reprocessing plants Sellafield (GB) and LaHague (F). Contamination of the Köflach lignite by this anthropogenic ^{129}I, transported to our sampling site by meteoric water, cannot be excluded.

In contrast to Köflach, Mariasdorf is an underground mine. The sample was taken at a depth of 200 m in the year 1967. A $^{129}I/^{127}I$ atomic ratio of 10^{-8} for meteoric water was reported for the years 1960–65 from the ice of the Fiescherhorn glacier [10,11]. At that time the ^{129}I originated mainly from the fallout of atmospheric nuclear weapons testing. As this ratio was 2 to 3 orders of magnitude lower than recent ratios for meteoric water (see above) it cannot explain a contamination of our "old" and deep Mariasdorf sample to nearly the same level than our "modern" near-surface sample from Köflach. However, the Mariasdorf lignite layers are situated very close to a shale formation with high uranium content; so we conclude that our sample might be enriched in natural ^{129}I migrating from that nearby geological formation into the lignite layers and being trapped there. We also cannot exclude the addition of fissiogenic ^{129}I from lignite layers with uranium concentrations higher than measured in our sub-samples.

4. Summary

The total iodine content, the isotopic ratio $^{129}I/^{127}I$ and the uranium content of lignite samples originating from two different mines were successfully determined after careful chemical analyses.

For determination of the total iodine content not only inorganic iodine, but also organically bound iodine was isolated from the lignite. The iodine content was measured with an ion selective electrode. Even small amounts of sulfide had to be removed from the solution prior to measurement in order to get correct results. Na_2SO_3 was the only reducing agent not influencing the electrode results.

When measuring the isotopic ratio samples with AgI masses smaller than 200 μg were excluded from interpretation as a small ^{129}I laboratory contamination enhanced the isotopic ratios for smaller sample masses. Only samples from the first iodine trap (first wash flask after the combustion apparatus), without reducing agent or treated with Na_2SO_3, were processed.

Uranium concentration was determined by anionic exchange from HCl solution after leaching procedures, followed by microprecipitation with neodymium fluoride and α-spectroscopy. However, as the distribution of uranium in lignite is very uneven, the determination in just a few samples might give a misleading result; we cannot exclude that uranium concentrations in nearby lignite layers are much higher, producing much more fissiogenic ^{129}I than calculated from our uranium results.

An age determination of the samples was impossible, as the lignite did not represent a closed system for ^{129}I: the $^{129}I/^{127}I$ isotopic ratios calculated from the total iodine contents and the uranium concentrations were 3 and 5 orders of magnitude lower than the measured ratios, indicating ^{129}I contamination. For the sample from the open-cast mine Köflach we suggest contamination by anthropogenic ^{129}I carried by meteoric water, while for the Mariasdorf lignite an intrusion of natural ^{129}I from a nearby uranium rich shale formation or from lignite with uranium concentrations higher than in the measured subsamples is presumed.

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