Available online at www.sciencedirect.com
ScienceDirect
Earth and Planetary Science Letters 265 (2008) 396–409
EPSL
www.elsevier.com/locate/epsl

Noble gas anomalies related to high-intensity methane gas seeps in the Black Sea

C.P. Holzner [a,b,*], D.F. McGinnis [c], C.J. Schubert [c], R. Kipfer [a,d], D.M. Imboden [b]

[a] *Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology (Eawag), Dübendorf, CH-8600, Switzerland*
[b] *Institute of Biogeochemistry and Pollutant Dynamics, Swiss Federal Institute of Technology (ETH), Zürich, CH-8092, Switzerland*
[c] *Department of Surface Waters-Research and Management, Swiss Federal Institute of Aquatic Science and Technology (Eawag), Kastanienbaum, CH-6047, Switzerland*
[d] *Institute of Isotope Geochemistry and Mineral Resources, Swiss Federal Institute of Technology (ETH), Zürich, CH-8092, Switzerland*

Received 12 April 2007; received in revised form 12 October 2007; accepted 15 October 2007
Available online 23 October 2007
Editor: M.L. Delaney

Abstract

Dissolved noble gases and tritium were analyzed at a series of high-intensity methane gas seeps in the Black Sea to study the transport and gas exchange induced by bubble-streams in the water column. These processes affect marine methane emissions to the atmosphere and are therefore relevant to climate warming. The seep areas investigated are located in the Dnepr paleo-delta, west of Crimea, and in the Sorokin Trough mud volcano area, south-east of Crimea. Noble gas concentration profiles at active seep sites revealed prominent anomalies compared to reference profiles that are unaffected by outgassing. Supersaturations of the light noble gases helium and neon observed relatively close to the sea floor are interpreted as effects of gas exchange between the water and the rising bubbles. Depletions of the heavy noble gases argon, krypton and xenon that were detected above an active, bubble-releasing mud volcano appear to be related to the injection of fluids depleted in noble gases that undergo vertical transport in the water column due to small density differences. In both cases, the noble gas anomalies clearly document seep-specific processes which are difficult to detect by other methods. Helium is generally enriched in the deep water of the Black Sea due to terrigenic input. Although exceptionally high helium concentrations observed in one seep area indicate a locally elevated helium flux, most of the seeps studied seem to be negligible sources of terrigenic helium. Noble gas analyses of sediment pore waters from the vicinity of a mud volcano showed large vertical gradients in helium concentrations. The helium isotope signature of the pore waters points to a crustal origin for helium, whereas the deep water of the Black Sea also contains a small mantle-type component.

Keywords: noble gases; tritium; terrigenic helium; methane gas seeps; mud volcanoes; plumes; bubble-streams; depletion; gas-exchange; Black Sea

1. Introduction

Methane (CH_4) gas seeps in marine and lacustrine environments are currently of scientific interest due to their potential influence on global carbon cycles and climate warming (e.g. Judd, 2004; Walter et al., 2006).

* Corresponding author. Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology (Eawag), Dübendorf, CH-8600, Switzerland. Tel.: +41 44 823 55 27; fax: +41 44 823 52 10.
E-mail address: christian.holzner@eawag.ch (C.P. Holzner).

0012-821X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2007.10.029

Gas release from seeps and rising bubbles in the water column can be detected by hydroacoustic systems (e.g. Hornafius et al., 1999; Artemov, 2006; Naudts et al., 2006; Greinert et al., 2006). Using this technology, marine CH_4 gas seeps have been documented worldwide, but detailed studies of gas exchange between rising CH_4 bubbles and the water column are rare (e.g. Leifer et al., 2000; Leifer and Patro, 2002; Clark et al., 2003; McGinnis et al., 2006a) and are commonly restricted to shallow seeps. Hence, more information on the processes controlling gas/water partitioning during the rising of CH_4 bubbles in the open water column is essential to better quantify the contribution of marine seeps to CH_4 in the atmosphere. We present noble gas analyses from different active seep sites that give new insights into CH_4 transport in the Black Sea.

In the Black Sea, intense gas seepage has been observed on the northern shelf and slope, as well as from mud volcanoes on the abyssal plain (Fig. 1). Within the EC-funded project CRIMEA ("Contribution of high-intensity gas seeps to the methane emission to the atmosphere", http://www.crimea-info.org/), numerous seeps releasing gas bubbles into the Black Sea were characterized using various oceanographic and geochemical techniques to evaluate the potential effects of these 'high-intensity gas seeps' on the atmosphere (Schmale et al., 2005; Kourtidis et al., 2006). The Black Sea is a unique environment in which to study marine CH_4 emissions because the water column is permanently stratified, with anoxic conditions and strong CH_4 accumulation below the chemocline at 100–150 m depth (e.g. Reeburgh et al., 1991). CH_4 concentrations in the isolated deep water body of the Black Sea reach values of up to ~12 μM. The majority of the CH_4 seeps observed during the CRIMEA cruises are situated at water depths shallower than 725 m. This depth limit corresponds to the upper boundary of the stability zone for pure methane hydrates at the ambient temperature and salinity conditions prevailing in the Black Sea (Naudts et al., 2006). Hence it appears that the seepage of CH_4 bubbles from the sediments is inhibited by the formation of gas hydrate layers in the sediment. Additionally, several gas-emitting mud volcanoes were studied south-east of the Crimea peninsula at about 2000 m water depth. These deep seeps occur within the gas hydrate stability zone. The mud volcano structures seem to provide migration pathways where gaseous or dissolved CH_4 may be released from the sediments without being trapped in the gas-hydrates. Indications of CH_4 release and the presence of gas-hydrates have

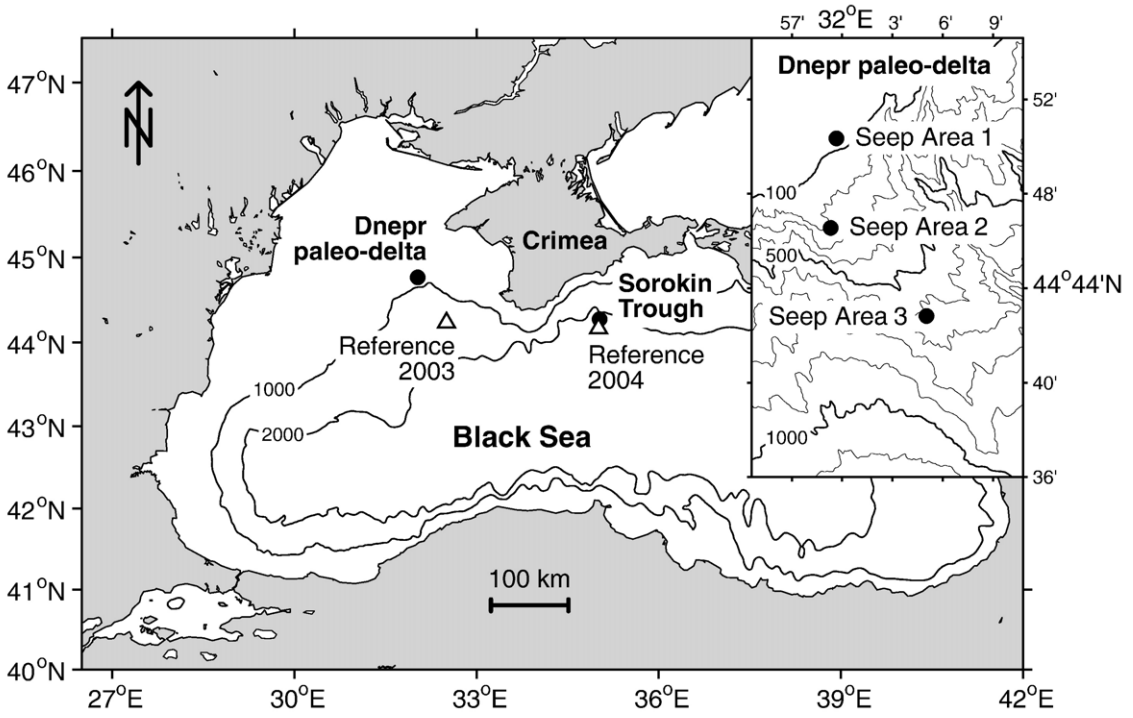


Fig. 1. Map of the Black Sea showing the study sites. Our work focused on two areas of intense gas seepage (●): the Dnepr paleo-delta region and the Sorokin Trough. The inset shows a detailed map of the Dnepr paleo-delta with the locations of Seep Areas 1–3. The deep seep site in the Sorokin Trough (Vodyanitskiy mud volcano) and two reference sites (△, no influence of gas seepage) are indicated in the main panel.

already been documented for neighboring mud volcanoes (Bohrmann et al., 2003). Hydroacoustically detectable bubble streams develop in the water column above the CH_4 seeps. Echo-sounder surveys of the deep mud volcanoes revealed bubble streams that rise up to 1300 m above the sea floor before they completely dissolve (Greinert et al., 2006). Rising bubbles do not only release gases to the water column during dissolution, but also force simultaneous stripping of dissolved gases which were initially absent in the gas phase (Clark et al., 2003). This process leads to characteristic anomalies of dissolved noble gases in the water column (Holzner et al., 2005, 2006). Studies of aeration systems and very intensive marine seeps describe upwelling flows induced by the bubble streams that reduce the bubble dissolution rate because dissolved gas concentrations in the rising water that surrounds the bubbles increase and may reach saturation (Wüest et al., 1992; Clark et al., 2003; Leifer et al., 2006). However, in these studies the bubbling gas flow was much higher than observed in the Black Sea. Note that on the Black Sea shelf at depths $\leqslant 100$ m, bubbles can reach the water surface, and might emit CH_4 directly to the atmosphere. CH_4 bubbles released from seeps located in the hydrate stability zone are expected to form a hydrate rim which may reduce gas exchange between bubbles and surrounding water (Rehder et al., 2002; McGinnis et al., 2006a). Nevertheless, the influence of such a hydrate rim on the noble gas abundance remains open and has to our knowledge not been investigated experimentally.

Dissolved noble gases in lakes and oceans are mainly of atmospheric origin. Therefore the concentrations in the water column generally correspond to atmospheric equilibrium concentrations, which are determined by the temperature and salinity prevailing during gas exchange at the water surface. As noble gases are chemically inert, only physical processes like radioactive decay and/or exchange with geochemical reservoirs other than the atmosphere can change the dissolved noble-gas abundance; hence such physical processes are responsible for any deviations from the initial partition equilibrium with the atmosphere. Due to these properties, noble gases are very useful for tracing water dynamics in marine and lacustrine systems (Kipfer et al., 2002).

2. Methods

2.1. Study area

Various high-intensity methane seeps situated in two areas south-east and west of the Crimea peninsula were investigated during the cruises of the CRIMEA project in 2003 and 2004 (Fig. 1 and Table 1). Part of the samples were collected at three sites in the Dnepr paleo-delta on the north-western Black Sea shelf and slope (Seep Area 1–3). Additionally, we studied the deep seep at the Vodyanitskiy mud volcano (VMV), located in the Sorokin Trough mud volcano area.

For comparison, samples were collected from sites in the open water away from active seeps, where no hydroacoustic signals of CH_4 gas seepage were detected. In the following, these sites will be referred to as "reference sites" and used as a baseline to interpret the results from the active seep sites. The 2003 reference site is situated between the two main study areas at a distance of ~70 km from the Dnepr paleo-delta and ~200 km from the Sorokin Trough. The 2004 reference

Table 1
Overview of the water column profiles and sediment cores sampled for noble gases

Water column profiles		
	Sampling date	Sample type[a]
Reference 2003 (1700 m depth)		
CTD064	08 June 2003	Reference
Reference 2004 (2130 m depth)		
CTD138	16 June 2004	Reference
Dnepr paleo-delta		
Seep area 1 (90 m depth)		
CTD038	04 June 2003	Off-seep
CTD046	05 June 2003	On-seep
Seep area 2 (200 m depth)		
CTD107	29 May 2004	On-seep
Seep area 3 (630 m depth)		
CTD108	29 May 2004	Off-seep
CTD109	30 May 2004	On-seep
CTD110	30 May 2004	On-seep
Sorokin trough (Vodyanitskiy Mud Volcano, 2070 m depth)		
CTD072	10 June 2003	On-seep
CTD115	03 June 2004	On-seep
CTD135	15 June 2004	On-seep

Sediment cores		
	Sampling date	Distance from VMV
Reference 2003 (1700 m depth)		
GC14	08 June 2003	~200 km
Sorokin Trough (Vodyanitskiy Mud Volcano, 2070 m depth)		
GC17	10 June 2003	~2700 m
GC41	15 June 2004	~400 m

[a] Reference: sampled at sites which are not affected by active seeps. On-seep: sampled above a seep. Off-seep: sampled in the vicinity of a seep but outside the current bubble stream.

site was chosen closer to one of the seep sites studied, i.e. ~9 km south of VMV.

2.2. Noble gases and tritium

Water samples for noble gas and tritium analysis as well as the corresponding CTD (Conductivity, Temperature, Depth) measurements were obtained using an SBE 911-plus CTD with a water-sampling rosette (12 Niskin bottles, 10 l volume each). Contact of the water samples with air during sampling was avoided. The water samples (~23 g) were transferred to copper tubes on the ship immediately after recovery of the CTD probe, and the tubes were sealed gas-tight using pinch-off clamps. Noble gas concentrations and helium isotope ratios were measured using noble gas mass spectrometry in the Noble Gas Laboratory at ETH Zürich (Beyerle et al., 2000). Tritium concentrations were determined by the ^{3}He-ingrowth method using a high-sensitivity compressor source noble gas mass spectrometer (Baur, 1999; Kipfer et al., 2002). Typical overall 1σ errors for the water analyses are ~1% for noble gas concentrations and ^{3}He/^{4}He ratios, and ~3% for ^{3}H. In total, 93 water samples were analyzed for this work. We partly or completely omitted 19 samples: 4 of those because gas extraction failed, 13 because our measurements indicate gas loss, contamination or analytical problems and 2 surface water samples were excluded from the interpretation because the results indicated solubility disequilibrium due to exceptionally high water temperatures.

Sediment cores for the analysis of noble gases in the pore water were taken using a gravity corer and sampled according to the procedures developed by Brennwald et al. (2003). Sub-samples for noble gas analysis were taken immediately after recovery of the sediment cores to minimize exsolution of supersaturated gases. The bulk sediment (~10 g, containing ~6 g of pore water) was transferred from the sediment cores into copper tubes without exposure to the atmosphere and sealed gas-tight. Dissolved noble gases in the sediment pore water were determined according the experimental protocols described by Brennwald et al. (2003) and Beyerle et al. (2000). This method consists of noble gas extraction from the pore water by degassing the sediment in an evacuated extraction vessel followed by noble gas analysis by mass spectrometry. Typical overall 1σ errors of the sediment pore water analyses are ~4% for noble gas concentrations and ~9% for ^{3}He/^{4}He ratios. We present noble gas data for 9 sediment samples from three Black Sea cores. Three other samples from these cores were omitted due to problems during sampling (degassing or air contamination).

Atmospheric equilibrium concentrations in the water column were calculated using the parameterizations recommended by Kipfer et al. (2002) for the measured salinity and potential temperature. A total atmospheric pressure of 1 atm was assumed for all partition equilibrium calculations, in accordance with measurements during the 2003 cruise (O. Schmale, pers. comm.). As pressure differences have a linear effect in the partition equilibrium concentrations, the given uncertainty in the average atmospheric pressure is negligible compared to the overall errors of the noble gas analyses.

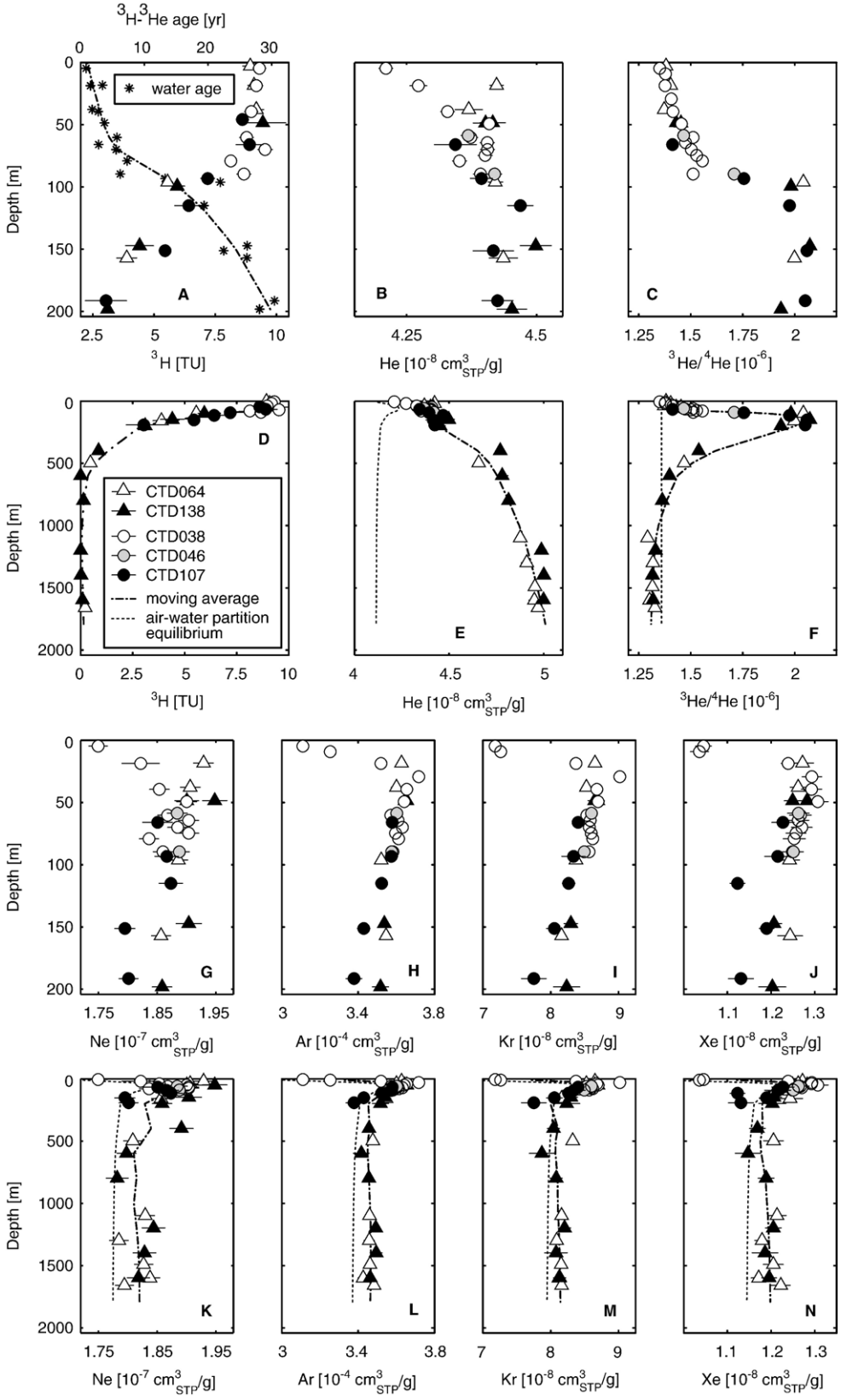
3. Results and discussion

3.1. Reference profiles of tritium and noble gases

The dissolved noble gas concentrations and tritium (^{3}H), as well as the apparent ^{3}H–^{3}He ages determined for the two reference profiles (CTD064 and CTD138) agree within experimental error (Fig. 2). This is remarkable as the profiles were sampled in two consecutive years and at very different positions relative to the seep sites.

The tritium concentration profiles are indistinguishable for all sites studied (Fig. 2A, D). In the mixed surface layer, ^{3}H concentrations were as high as ~9 TU (1 TU = 1 tritium unit = 1 ^{3}H atom per 10^{18} ^{1}H atoms), dropping below the detection limit (<0.1 TU) at ~600 m depth. Large amounts of ^{3}H were released to the atmosphere by thermonuclear bomb tests in the 1960s. Atmospheric ^{3}H was oxidized to tritiated water and subsequently transported to the oceans by the hydrological cycle. The observed ^{3}H distribution in the water column is a result of ^{3}H transport by vertical mixing (turbulent or advective), deep intrusions of Bosphorus water or river inflows and ^{3}H decay (Özsoy et al., 2002). Therefore, the upper water layers with non-zero ^{3}H concentrations must have been exchanged within approximately the last 40 years; i.e. since bomb-tritium has been released to the atmosphere. The ^{3}H data suggests that within this time interval, vertical water transport was confined to the uppermost 600 m and did not significantly affect the deep water of the Black Sea.

The determination of concentrations of ^{3}H and Helium-3 (^{3}He; see below) for the same water sample allow the so-called ^{3}H–^{3}He water age to be calculated (Torgersen et al., 1977). For this calculation, tiritiogenic ^{3}He was separated from the atmospheric and terrigenic components (Kipfer et al., 2002). We observed apparent ^{3}H–^{3}He ages close to


^{3}H-^{3}He age [yr]
water age
Depth [m]
A
^{3}H [TU]
B
He [10^{-8} cm$^3_{STP}$/g]
C
^{3}He/^{4}He [10^{-6}]
D
CTD064
CTD138
CTD038
CTD046
CTD107
moving average
air-water partition equilibrium
E
F
G
Ne [10^{-7} cm$^3_{STP}$/g]
H
Ar [10^{-4} cm$^3_{STP}$/g]
I
Kr [10^{-8} cm$^3_{STP}$/g]
J
Xe [10^{-8} cm$^3_{STP}$/g]
K
L
M
N

zero at the surface, and an increase to about 40 years at 500 m depth (Fig. 2A). Below ~600 m depth, ^{3}H–^{3}He age calculations become meaningless because the ^{3}H concentrations are virtually zero. The observed depth limit of measurable ^{3}H at ~600 m depth corresponds to distinct changes in other geochemical parameters (e.g. CH_4 concentration; see Schubert et al., 2006b). Yet, the shape of the ^{3}H distribution is hardly affected by the permanent chemocline, a hydro-chemical and density boundary in the Black Sea at about 100 m depth.

Dissolved helium (He) concentrations are in partition equilibrium with the atmosphere in the mixed surface layer, and increase continuously with depth (Fig. 2B, E). As a result, He is supersaturated by ~20% in the deep water of the Black Sea. This supersaturation is caused mostly by the input of terrigenic He that emanates from the Black Sea sediments and accumulates in the deep water, since vertical transport is slow. In the deep water, the contribution of tritiogenic ^{3}He to the He excess is negligible, as ^{3}H was only detected down to about 600 m depth.

The isotopic composition of dissolved He, i.e. the ^{3}He/^{4}He ratio, is in equilibrium with the atmosphere at the surface and increases down to ~150 m, where a strong positive anomaly (i.e. ^{3}He enrichment) is present. Below ~1000 m depth a slight negative anomaly (i.e. ^{4}He enrichment) is found (Fig. 2C, F). The ^{3}He/^{4}He peak around 150 m depth is caused by the decay of ^{3}H and the accumulation of tritiogenic ^{3}He. Low ^{3}He/^{4}He ratios near the sea floor indicate the input of isotopically heavy terrigenic He produced in the Earth's crust (^{3}He/^{4}He $<10^{-7}$; see Mamyrin and Tolstikhin, 1984; Ballentine and Burnard, 2002).

To further investigate the terrigenic He input, we applied a 1-dimensional vertical transport model that was initially developed for lakes (Aeschbach-Hertig et al., 2002; Kipfer et al., 2002; Holzner, 2001). The model was numerically integrated using the simulation software for aquatic systems AQUASIM (Reichert, 1994). Our model describes the temporal evolution of ^{3}H and He concentrations in the Black Sea as a result of gas exchange at the sea surface (Wanninkhof, 1992), gain or loss of ^{3}H and He due to water in-and outflow, ^{3}He production by the radioactive decay of ^{3}H, vertical water transport and terrigenic He input. The inverse fitting tools of AQUASIM were applied to tune the vertical mixing rates and to estimate the terrigenic He input. Only the ^{3}H and He data collected in this study were used as fitting targets. The resulting vertical mixing rates range from 3×10^{-7} m^2 s^{-1} (below mixed surface layer) to 4×10^{-4} m^2 s^{-1} (deep water). Assuming that He emanates homogeneously over the entire area of the Black Sea, we determine a terrigenic He flux of 7×10^9 atoms m^{-2} s^{-1} from the sediments into the water column. Our estimate of the terrigenic He input is in the range of the values given by Top and Clarke (1983) for the Black Sea (1.3×10^{10} atoms m^{-2} s^{-1}) and for the mean world–ocean flux (3×10^9 atoms m^{-2} s^{-1} ; Craig et al., 1975).

Top and Clarke (1983) and Top et al. (1991) report He and ^{3}H concentrations for different stations in the central and southern Black Sea for the years 1975 and 1988, respectively, which agree remarkably well with our data. The earlier ^{3}H concentrations were much higher in the uppermost ~300 m, but no measurable ^{3}H was found below ~500 m depth with the exception of a few samples from 1975. According to Top et al. (1991), the observed non-zero ^{3}H concentrations cannot be representative of the entire deep water. The ^{3}He/^{4}He maximum due to ^{3}H decay also appears in the data from 1975 and 1988, but at shallower depths, because at that time the majority of the bomb-^{3}H input was still concentrated in the surface waters. The sum of ^{3}H and tritiogenic ^{3}He can be considered as a measure of the "total ^{3}H" input into the water body. The "total ^{3}H" content of a water body is unaffected by radioactive decay and only depends on input and output processes. We computed the budget of ^{3}H and tritiogenic ^{3}He in the Black Sea by integrating the observed concentration profiles over depth. Using this method, the "total ^{3}H" mass stored in the water column was calculated from the literature data (Top and Clarke, 1983; Top et al., 1991) and our new measurements. A comparison of the two results shows that "total ^{3}H" has decreased by ~35% in the uppermost 600 m since 1975/88. Our measurements indicate that part of the tritiogenic ^{3}He produced has been lost to the atmosphere due to vertical mixing and gas exchange.

Concentrations of the heavier noble gases neon (Ne), argon (Ar) krypton (Kr) and xenon (Xe) at the reference

Fig. 2. Tritium (^{3}H) and dissolved noble gas data for the reference profiles (▲) sampled in 2003 (CTD064) and 2004 (CTD138) and for the shallow profiles (●) of Seep Area 1 (CTD038, CTD046) and Seep Area 2 (CTD107). He and Ne data for selected samples of the 2003 reference profile (CTD064) have already been presented by Schubert et al. (2006a). (A–C) Tritium, helium (He) and apparent ^{3}H–^{3}He ages in the uppermost 200 m of the water column. (D–F) ^{3}H and He profiles in the entire water column. The dotted lines indicate the calculated partition equilibrium concentrations with the atmosphere, the dash-dotted lines show moving-average concentrations and isotope ratios for the reference samples. ^{3}H concentrations are above the detection limit (>0.1 TU) in the upper 600 m of the water column. He concentrations are strongly supersaturated in the deep water and the ^{3}He/^{4}He isotope ratio shows a large positive anomaly around 150 m depth due to ^{3}H decay ("bomb peak"). (G–J) Neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) concentrations in the uppermost 200 m of the water column. (K–N) Full profiles of Ne, Ar, Kr and Xe. The reference profiles for these atmospheric noble gases show uniform, slightly supersaturated concentrations (2.5–4.5%) in the deep water.

sites are close to partition equilibrium with the atmosphere (Fig. 2G–N). Generally, Ne, Ar, Kr and Xe in lakes and oceans can only be of atmospheric origin because there are no other significant sources of these gases in natural waters (Kipfer et al., 2002). The profiles of dissolved Ne, Ar, Kr and Xe show similar shapes, and all these gases are slightly supersaturated in the deep water at the prevailing temperature and salinity conditions (Ne ~2.5%, Ar ~2.8%, Kr ~2.3%, Xe ~4.5%). Atmospheric noble gas supersaturations have been described for other marine waters (e.g. Craig and Weiss, 1971; Peeters et al., 2000) and are commonly explained by air injection; i.e. air bubbles that are introduced by breaking waves and that dissolve partially or completely (Keeling, 1993). Air injection mainly affects lighter noble gases due to their low solubilities. Hence, the observed supersaturation of Ne is presumably caused by air injection. The enrichment of the heavier noble gases seems to be caused by the nonlinear effect of mixing saturated water masses at different temperatures and salinities. This process will cause supersaturations when Bosporus inflow mixes with less saline and colder surface and intermediate waters. It is likely that the nonlinear effect of mixing also affects the noble gas concentrations in the deep water of the Black Sea because of the long water residence time (~2000 years; see Sorokin, 2002). The concentration profiles of Ne, Ar, Kr and Xe show shallow maxima at ~40 m depth that coincide with a minimum of ~7°C in the measured water temperature (data not shown), which corresponds to the mean winter surface temperature of the Black Sea (Sorokin, 2002). Therefore, winter circulation reaching down to ~40 m seems to generate the cold, noble-gas-rich layer. Stanev et al. (2004) modeled convection in the Black Sea and found a mixed layer of the same thickness during winter.

Noble gas concentrations for three profiles from the shallow Seep Areas 1 (90 m water depth) and 2 (200 m water depth) are also included in Fig. 2 (CTD038, CTD046, CTD107). Although these profiles were sampled in active seep areas, the observed noble gas concentrations differ little from the reference concentrations. There are numerous shallow seeps (Naudts et al., 2006), but their gas flows are small, and so they do not significantly affect the noble gas concentrations in the water column on the Black Sea shelf.

3.2. Depletion of heavy noble gases above high-intensity CH_4 gas seeps

Three noble gas concentration profiles (Fig. 3) were sampled above Vodyanitskiy mud volcano (VMV, located in the Sorokin Trough at 2070 m water depth; see Fig. 1), which was active at the time of sampling. A stream of emitted gas bubbles rose up to 1300 m above the sea floor (Greinert et al., 2006). Despite this strong activity, no significant differences in CH_4 concentrations were observed between the Sorokin Trough and the reference sites (Fig. 3H; see also Schubert et al., 2006b). Although the distribution and amount of bubbles released at VMV was continuously monitored with an echo-sounder during water sampling, samples were likely not always collected right at the intended positions within the bubble stream due to ship drift (up to several 100 m during a CTD cast) and/or displacement of the water sampling device by currents.

Noble gas data for 2003 (CTD072) and 2004 (CTD115) that cover the entire water column above VMV will be discussed first. Compared to the reference samples, the He and Ne concentrations are slightly depleted (maximum depletions: He <2%, Ne <3%; see Fig. 3A, B). Remarkably, the concentrations of the heavy noble gases Ar, Kr and Xe are depleted to a much higher extent (maximum depletions: Ar ~5%, Kr ~10%, Xe ~15%; see Fig. 3E–G). All heavy noble gases show a distinct concentration minimum at ~1200 m depth. The maximum noble gas depletion above VMV increases with atomic mass, i.e. with increasing solubility and with decreasing diffusion coefficient respectively. Note that bubble-mediated gas transfer is controlled by the diffusivity and solubility of the gases (e.g. Keeling, 1993). The observed depletion anomaly disappears at ~1100 m above the sea floor, close to the depth where the bubble stream disappears, as observed hydro-acoustically (1300 m; see Greinert et al., 2006). The overall depletion pattern above VMV seems to persist over longer time scales, since the noble gas concentrations for the two profiles sampled about one year apart agree within analytical errors. Horizontal currents might reduce noble gas depletions due to mixing with ambient water, but currents in the deep Black Sea waters were found to be weak (Greinert et al., 2006; Korotaev et al., 2006) and seem to have a negligible effect on the observed depletion patterns.

CTD135 (Fig. 3) was sampled during very calm weather conditions with negligible ship drift. Hydroacoustic observations during sampling indicated that the water-sampling probe hit the bubble stream above VMV. Thus, we are quite confident that the deep-water samples for this profile were collected within the active bubble stream. The two other profiles from VMV were likely taken in the near-field of the bubble stream. As the CTD135 cast was focused on the root zone of the bubble stream, no samples were taken above 1500 m water depth.

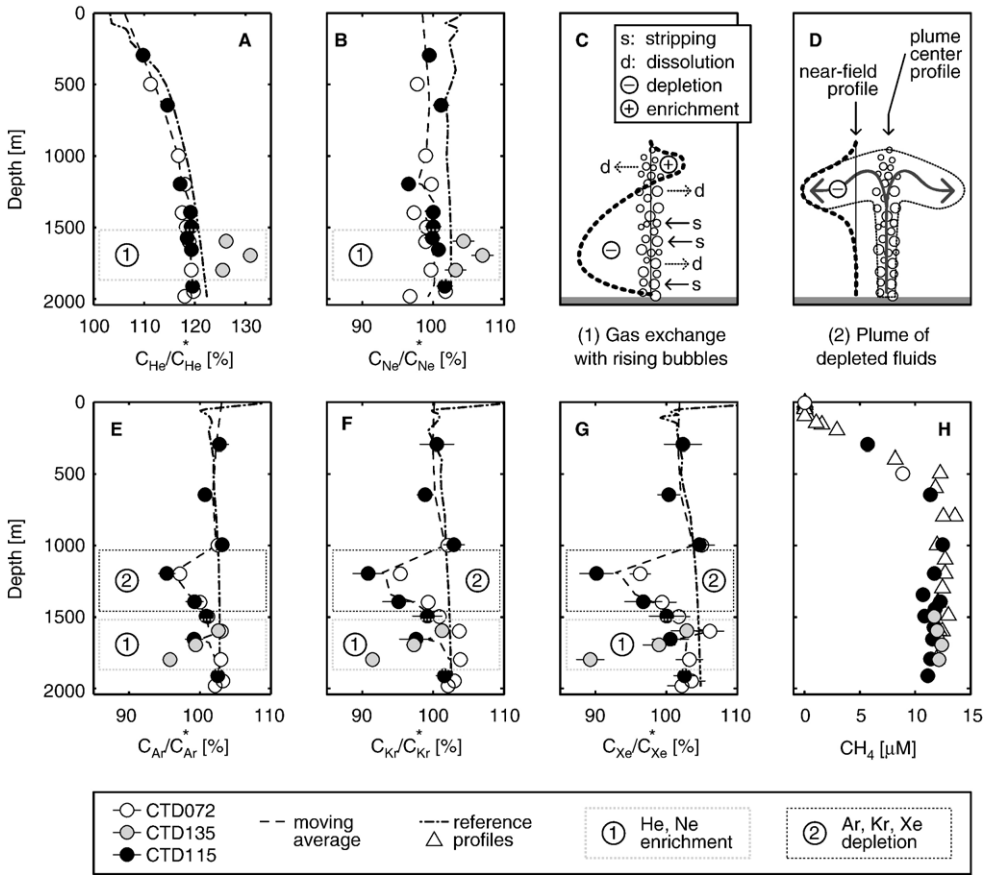


Fig. 3. (A, B, E–G) Concentrations of dissolved noble gases at the deep seep site (normalized to atmospheric equilibrium concentrations C*). Helium (He) and neon (Ne) data for selected samples of the 2003 profile (CTD072) have already been presented by Schubert et al. (2006a). The dashed lines show moving-average concentrations of the deep seep profiles (CTD135 excluded). Mean reference profiles are shown as dash-dotted lines for comparison. (C–D) Illustrations of the two mechanisms that might cause the observed noble gas anomalies at the deep seep site. The expected shape of the noble gas concentration profiles with areas of depletion (−) and enrichment (+) is indicated by the dashed line. (H) Concentration profiles of CH_4 at the deep seep site and at the reference sites (S.E. Beaubien, pers. comm.). In profiles CTD072 and CTD115, the water between ~1000 m and ~1400 m depth (zone 2) is strongly depleted in the heavy noble gases argon (Ar), krypton (Kr) and xenon (Xe). In contrast, samples from profile CTD135 are enriched in He and Ne below ~1500 m (zone 1) and depleted in heavy noble gases near the sea floor. Note that no significant differences in CH_4 concentrations were observed between the deep seep and the reference sites.

The noble gas concentration profile CTD135 differs strikingly from the other profiles sampled at the deep seep site. He and Ne concentrations are above saturation levels and exceed their reference concentrations by 5–10% (Fig. 3A, B). In contrast, Ar, Kr and Xe near the sea floor are depleted to a similar extent as in the previously discussed deep seep profiles at ~1200 m depth (Fig. 3E–G). Farther from the sea floor, the concentrations of heavy noble gases increase towards the open-water reference concentrations.

3.3. Proposed mechanism of noble gas depletion

The prominent depletion in heavy noble gases found above VMV indicate that processes related to the activity of the mud volcano affect the concentrations of dissolved noble gases. There are only two plausible mechanisms that might deplete dissolved noble gases in the water column above a mud volcano:

(1) *Gas exchange with bubbles depleted with respect to noble gases* (Fig. 3C). Rising bubbles from marine gas seeps force a secondary gas exchange with the surrounding water (Clark et al., 2003). During this process, dissolved gases in the water are stripped by the bubbles while the host gas (e.g. CH_4) continuously dissolves from the bubbles until an equilibrium is reached between the bubbles and the surrounding water or the bubbles disappear. Therefore, gas exchange with bubbles depleted with respect to noble gases or free of noble gases would lead to

noble gas depletions in the surrounding water in the depth range where stripping occurs. The effect of stripping on the concentrations of dissolved noble gases is expected to vary with diffusivity, with the highest impact on the elements with the highest diffusion coefficients (i.e. He and Ne).

(2) *Depleted fluid input* (Fig. 3D). As an alternative explanation for the observed noble gas profiles, an expulsion of fluids depleted in noble gases relative to the reference concentrations would locally decrease the noble gas concentrations in the water column. Such depleted fluids might rise as a plume in the weakly stratified Black Sea deep water due to buoyancy caused by elevated temperature, injected bubbles, or a combination of both. The depleted fluids are transported vertically until the plume can no longer overcome the density gradient. As a consequence, the mud volcano fluids are injected into the water column and spread horizontally within a layer of equal density (McDougall, 1978; Wüest et al., 1992; McGinnis et al., 2004). At this depth, the depleted water replaces or mixes with water which initially had the reference noble gas concentrations, thus causing the observed noble gas depletions.

In the following paragraphs, both mechanisms will be discussed. Considering only mechanism 1, it should be noted that the bubbles released from VMV dissolve completely within the water column (Greinert et al., 2006; McGinnis et al., 2006a). Therefore, all stripped gases redissolve. In this case, we would expect considerable noble gas enrichment to occur in the area of complete bubble dissolution. However, the profiles CTD072 and CTD115 (Fig. 3A, B, E–G) show no noble gas enrichment relative to the reference profiles close to the top of the bubble stream (i.e. above ~1000 m water depth). The existence of a thin enrichment layer, as found for CH_4 in the north sea (Leifer and Judd, 2002), cannot be ruled out completely, given the coarse sampling resolution. Nevertheless, the observed increase in noble gas depletion with increasing atomic mass contradicts the fractionation expected by stripping. Stripping should be faster and more efficient for the light noble gases than for the heavier noble gases. It therefore appears unlikely that the depletion of heavy noble gases at ~1200 m depth is predominantly caused by mechanism 1, i.e. gas exchange between rising bubbles and the surrounding water column.

Profile CTD135, however, can be interpreted in terms of mechanism 1. The near-bottom noble gas anomalies observed for this profile (Fig. 3A, B, E–G) seem to be directly related to bubble-driven gas exchange. During the sampling of CTD135, bubbles were tracked hydroacoustically up to ~1500 m water depth, which corresponds to the upper boundary of the He and Ne enrichment. The reduced bubble rise height follows a general decrease in mud volcano activity that was recorded between 2003 and 2004 (Greinert et al., 2006). The supersaturations of He and Ne as well as the concentration increase of Ar, Kr and Xe towards the reference values occur just below the depth where the bubble stream disappeared at the time of sampling. These structures can reasonably be interpreted as a signal of noble gas redissolution from collapsing bubbles containing noble gases stripped from the water column close to the sea floor.

The strong depletions in Ar, Kr and Xe at ~1200 m depth are conceptually consistent with mechanism 2, a rising plume of water depleted in noble gases. As the casts CTD072 and CTD115 most likely did not sample the center of the observed bubble stream, the profiles probably represent the conditions prevailing in the near-field of the plume, which is not directly affected by bubble gas exchange (Fig. 3D). The depleted mud-volcano fluid would be deposited at the equilibrium depth, where upwelling ceases and the plume water disperses horizontally over a larger area. At that depth range, the anticipated noble gas anomaly could hardly be missed even if ship positioning were inaccurate. Water-column profiles sampled relatively close to VMV should therefore always show a depletion signature if depleted fluids were expelled from VMV at that time.

Noble gas depletion of water within the mud volcano can either occur as a result of stripping during bubble emanation or because of gas hydrate formation. Stripping mainly affects the light noble gases, and could therefore account for the slight depletion of He and Ne detected in profiles CTD072 and CTD115. Gas hydrates were found in sediment cores sampled at VMV during the CRIMEA project and have also been discovered at various other mud volcanoes in the Sorokin Trough (Bohrmann et al., 2003). Winckler et al. (2002) showed that CH_4 hydrates from Hydrate Ridge (Pacific Ocean) contain significant amounts of Ar, Kr and Xe, but virtually no He and Ne. This specific fractionation occurs because the relatively large atoms of the heavier noble gases are preferentially incorporated as guest molecules into the gas hydrate structure. Gas hydrate formation in the sediments of the Sorokin Trough could therefore lead to depletion of the heavy noble gases in the remaining sediment pore water, which is then injected into the water column of the Black Sea by the mud volcanoes. Thus, the depletion of the heavy noble gases that were observed in the water column at the deep seep site might be linked to gas hydrate formation in the mud-volcano sediments.

To summarize, we propose that the expulsion of fluids depleted in noble gases from VMV, followed by the formation of an upwelling plume that disperses at an equilibrium depth of ~1200 m, leads to the observed depletion of heavy noble gases. Bubble-induced stripping also seems to fractionate the noble gases in the water column above VMV, but this effect is only relevant for samples from the center of the active bubble stream. The proposed mechanism of an upwelling plume is further supported by the detection of enhanced turbulence in water temperature profiles from the Sorokin Trough and by the results of plume modeling (McGinnis et al., 2006b). Strong upwelling flows caused by rising bubbles were previously documented for shallow, highly active marine seeps (e.g. Clark et al., 2003; Leifer et al., 2006).

For the profiles sampled at Seep Area 3 (630 m water depth), we observed a similar depletion in the heavy noble gases (shown for Xe in Fig. 4C). These profiles show the same characteristic features that were found at VMV: a depletion in the heavy noble gases near the sea floor and a prominent concentration minimum of the heavy noble gases at the depth where the rising bubbles dissolve completely. These similarities indicate that at the shallower site, seep-related processes also induce noble gas depletion in the water column.

3.4. Helium concentrations and isotopic composition in the water column

The highest concentrations of dissolved He were observed in three profiles (CTD108, CTD109 and CTD110) sampled at Seep Area 3 in 2004 (Fig. 4A, B). These He maxima exceed the concentrations in the Black Sea deep water by more than 5%. Seep Area 3 also showed the highest dissolved CH_4 concentrations (up to 14 μM in 2004 and up to 16 μM in 2003). Total He in all three profiles is elevated within the lowermost ~300 m of the water column, where active bubble streams were detected. Above the bubble streams, He concentrations at Seep Area 3 match the concentrations found at the reference sites. CTD108 was sampled "off-seep", i.e. at a location where no gas bubbles were observed, but still within the far-field of various seeps. CTD109 and CTD110 were taken right above active gas seeps ("on-seep"). The shapes of the off seep and on-seep He profiles (Fig. 4A) differ considerably. The off-seep He concentration is maximal near the sea floor and decreases gradually towards the water surface. In contrast, the profiles sampled on-seep within a bubble stream show a distinctive He concentration maximum at ~500 m depth. In general, the positive He anomalies at Seep Area 3 occur at a greater depth than that of the maximum depletion of the heavy noble gases (Fig. 4C).

The differences in He concentration between off-seep and on-seep profiles indicate that He emission is linked to the CH_4 gas seepage. We speculate that He emanates from the seeps together with CH_4 as free gas. The on-seep He enrichment seems to be caused by He dissolution from the rising bubbles. As He diffuses much faster out of the rising bubbles than CH_4, it is expected to be transferred to the water column at an early stage of bubble dissolution, substantially below the top of the bubble stream. The observed He concentration maximum is similar to the

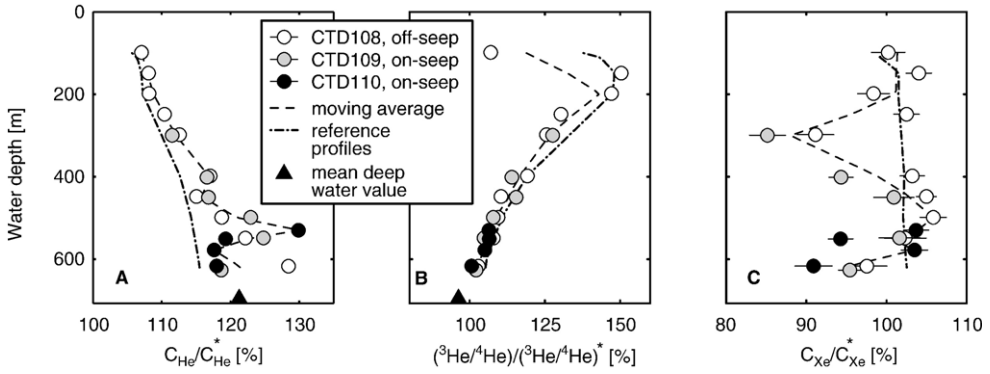


Fig. 4. Helium (He) and xenon (Xe) data (normalized to atmospheric equilibrium concentrations) for profiles sampled at Seep Area 3 in the Dnepr paleo-delta region. The dashed lines show moving-average concentrations and isotope ratios for the data presented. Mean reference profiles are shown as dash-dotted lines for comparison. The symbol ▲ indicates mean deep water He concentrations and isotope ratios. (A) He concentrations at ~500 m depth exceed corresponding reference values and even exceed the concentrations found in the deep water of the Black Sea. (B) The $^3He/^4He$ isotope ratios do not differ considerably from those at the reference sites. (C) Depletion in the heavy noble gases (e.g. Xe) is similar to that at the deep seep site in the Sorokin Trough (Fig. 3C–E). The concentration profiles of Ne, Ar and Kr (not shown) are qualitatively similar to the concentration profile of Xe.

positive He anomaly found near the sea floor at VMV (Fig. 3A). The enrichment of dissolved He, which was observed for the off-seep profile CTD108, is most likely related to the emissions from the adjacent seeps. Horizontal mixing presumably transports He-enriched water from the active gas seep sites towards CTD108.

In contrast to the He concentrations, the He isotope ratios at Seep Area 3 are indistinguishable from those at the reference site (Fig. 4B). Accordingly, the observed excess He shows a similar $^3He/^4He$ ratio to that generally found in the Black Sea, and seems to have the same terrigenic source (Fig. 2E, F).

3.5. Helium emanation from the sediment

To gain further insight into the sources of terrigenic He in the Black Sea, we analyzed the sediment pore water for noble gases. Fig. 5A, B shows He concentrations and $^3He/^4He$ ratios determined in pore-water samples from two cores collected close to VMV in the Sorokin Trough, and from one core from the 2003 reference site (locations are shown in Fig. 1). Sediment cores taken at the center of VMV were not suitable for noble gas analysis as they contained CH_4 hydrates which dissociated and induced degassing during core recovery. Core GC41 and GC17 were taken ~400 m and ~2700 m, respectively, from the center of VMV. The reference core GC14 was taken ~200 km from VMV.

All He concentrations and $^3He/^4He$ ratios measured in the pore water of the reference core GC14 are the same within experimental errors (Fig. 5A, B). The $^3He/^4He$ ratios correspond to the values found in the Black Sea deep water, indicating that non-atmospheric He in the pore water of this core and in the deep water have the same source. The pore waters are slightly enriched in He (by ~15%) compared to the deep water, and therefore seem to emit He to the Black Sea.

In contrast, the pore waters of the cores from the Sorokin Trough show strong He concentration gradients and a characteristic decrease in the $^3He/^4He$ ratio with sediment depth (Fig. 5A, B). The gradients in the He concentration and in the $^3He/^4He$ ratio are steeper for GC41, which was taken closer to VMV, than for GC17. Pore-water He concentrations in the lower part of the cores from the Sorokin Trough are enriched by up to ~400% relative to the Black Sea deep-water concentrations. Towards the water/sediment interface, the pore-water He concentrations and $^3He/^4He$ ratios approach the water column values, indicating that noble gases diffuse from the sediment into the water column. He transport within the sediment pore water can be estimated from the observed concentration gradients using the equations given by Strassmann et al. (2005). We assume a sediment porosity of 70% (e.g. Ross et al., 1978) and consider only diffusive fluxes. The estimate for GC17 of 9×10^9 atoms m^{-2} s^{-1} is slightly higher then the terrigenic He flux that was derived from the water column data (7×10^9 atoms m^{-2} s^{-1}; see above). The data for GC41 indicate a highly increased flux of 33×10^9 atoms m^{-2} s^{-1}.

As He transport within the Earth's crust occurs primarily by advection of fluids (Ballentine and Burnard, 2002), He release at the sea floor depends on the presence of geological structures which allow fluid

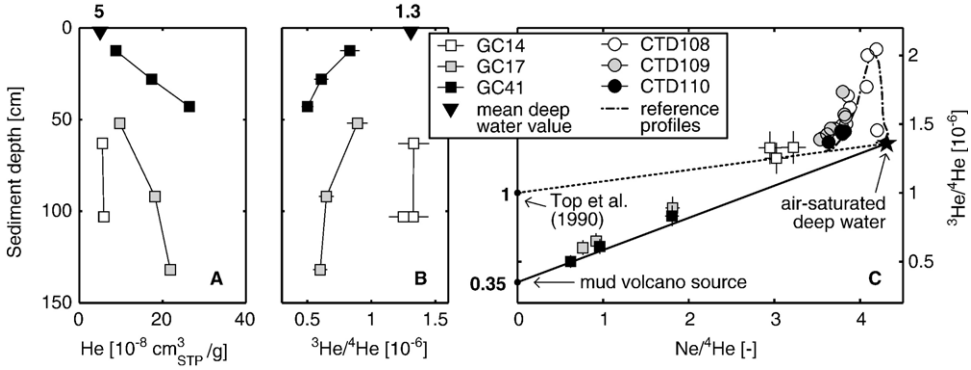


Fig. 5. (A) Helium (He) concentrations and (B) $^3He/^4He$ isotope ratios in the pore water of three sediment cores from the Sorokin Trough (GC17, GC41) and the 2003 reference site (GC14). (C) $^3He/^4He$ ratio as a function of $Ne/^4He$ for the sediment pore water samples (■), the open water samples from Seep Area 3 (●; see also Fig. 4) and for the mean open water reference profile (dash-dotted line). Straight lines indicate mixing between air-equilibrated Black Sea deep water and a seafloor source with a $^3He/^4He$ ratio of 1×10^{-6} (dotted line) as determined by Top et al. (1990) for the southern Black Sea, or with an estimated mud volcano source with a $^3He/^4He$ ratio of 3.5×10^{-7} (solid line). The data for the deep water samples and sediment pore water are in agreement with the higher $^3He/^4He$ ratio determined by Top et al. (1990), while the pore water results from the Sorokin Trough indicate a local source of helium with lower $^3He/^4He$.

migration. In the Sorokin Trough, mud volcanoes occur at the southern border of a diapiric zone/fold, formed by compressive deformation (Krastel et al., 2003), and provide possible migration pathways. The sediment core with the highest He gradient (GC41) was taken right on the southern border of this active structure. Core GC17 was taken ~1 km NW of that border and shows a considerably smaller He gradient. At Seep Area 3, there are no clear indications of conduits for upward fluid migration. Seismic data showed no evidence of shallow faults in the uppermost 250 m of the sediment column (Naudts et al., 2006); however, the shallow seismic results do not rule out that deeper structures, such as the mud diapirs and deep faults documented in the region by Lüdmann et al. (2004) and Kutas et al. (2004), may enhance He transport.

A plot of $^3He/^4He$ against $Ne/^4He$ (Fig. 5C) allows us to differentiate between atmospheric input (denoted by a ★) and non-atmospheric sources of He in the Black Sea. Water samples from depths around 150 m are shifted towards higher $^3He/^4He$ ratios due to the production and accumulation of tritiogenic ^3He ("bomb peak"). Deep-water samples and pore-water samples from the reference core have a $^3He/^4He$ ratio that is slightly lower than that of air-saturated deep water, and show lower $Ne/^4He$ ratios due to terrigenic He input. The much stronger accumulation of terrigenic He in the sediments from the Sorokin Trough leads to substantially lower $^3He/^4He$ ratios and $Ne/^4He$ ratios.

All samples shown in Fig. 5C, except for the open-water samples containing tritiogenic ^3He, can be interpreted as binary mixtures of air-saturated deep water and virtually Ne-free terrestrial inputs. At least two types of terrigenic He determine the $^3He/^4He$ ratios of the non-atmospheric He excess in the Black Sea. Samples from the deep water of the Black Sea and from the reference core GC14 show a terrigenic He component with a $^3He/^4He$ ratio of $\sim 10^{-6}$. The existence of such a ^3He-rich terrigenic He source was postulated by Top et al. (1990) based on measurements of He isotopes in the water column. Using our water column model (see above), we estimated a similar $^3He/^4He$ ratio of 7×10^{-7} for the terrigenic He input. The sediment pore water samples from the Sorokin Trough (GC17 and GC41) indicate a different He source with a significantly lower $^3He/^4He$ ratio of $\sim 3.5\times10^{-7}$. Therefore, He in the sediment cores from the Sorokin Trough area must be of crustal origin ($^3He/^4He < 10^{-7}$; Mamyrin and Tolstikhin, 1984; Ballentine and Burnard, 2002), with the addition of small amounts of mantle-type He ($^3He/^4He > 10^{-5}$; Mamyrin and Tolstikhin, 1984). The deep water of the Black Sea as well as the reference core, however, are dominated by a terrigenic He component that is more enriched in ^3He.

Overall, He emission into the Black Sea is heterogeneous and originates from different terrigenic He sources. There are indications of enhanced He release in Seep Area 3 and at VMV. However, sediment pore-water analyses for the Sorokin Trough exclude VMV as a major source of terrigenic ^3He in the Black Sea.

4. Conclusions

We compiled a broad set of noble gas and ^3H data for the water column at active seep sites located on the shelf, on the slope and in the abyssal region of the Black Sea. The data gathered allowed us to assess the influence of gas seepage on the abundance of noble gases in the Black Sea. Reference profiles sampled at sites unaffected by seepage show Ne, Ar, Kr and Xe concentrations that are close to atmospheric equilibrium concentrations. In contrast, He is supersaturated due to the injection of terrigenic He. The concentrations of ^3H and tritiogenic ^3He imply that bomb-^3H has penetrated the Black Sea to a depth of ~600 m. Compared to earlier measurements, "total ^3H" (i.e. the sum of ^3H and tritiogenic ^3He) in this depth range has decreased by about one third due to the escape of ^3He to the atmosphere.

Profiles sampled at active gas seep sites demonstrate the clear effects of the bubble release on the noble gas concentrations in the water column. Two types of noble gas anomaly were identified. Relatively close to the sea floor, within active bubble streams, the water was found to be supersaturated with respect to the light noble gases and simultaneously to be depleted with respect to the heavy noble gases. These anomalies seem to be the result of gas exchange between the rising bubbles and the surrounding water column. Additional profiles from the deep seep in the abyssal zone of the Black Sea revealed no enrichment of light noble gases, but prominent depletions in Ar, Kr and Xe. We suggest that the depletion in the heavy noble gases is the result of the expulsion of fluids depleted in noble gases from a mud volcano. Because of their lower density, these fluids rise as a plume in the water column and disperse at their equilibrium depth by mixing with the surrounding water.

Sediment cores from the mud volcano area at the Sorokin Trough show strong He concentration gradients and characteristically low $^3He/^4He$ ratios, which seem to be related to the local geological structure. The $^3He/^4He$ signatures in the sediment pore waters of the Sorokin Trough, however, differ substantially from those found

in the Black Sea deep-water body and in the pore-water of sediments sampled far from the mud volcano area. Both the latter are enriched in ^{3}He. Terrigenic sources that are not related to mud volcanoes must therefore account for the ^{3}He-enriched helium excess that prevails in the Black Sea. The analysis of sediment pore-water for noble gases has proven useful to characterize the heterogeneity in subsurface He release at a gas and/or fluid emitting mud volcano. Water column He concentrations, in contrast, do not reflect the spatial variations of the terrigenic He flux, and hence can be used to determine the mean He input over the entire area of the Black Sea.

Acknowledgments

We greatly appreciate the support by the officers and crew of the R/V Professor Vodyanitsky during the cruises. We are also grateful to the whole CRIMEA team for their excellent collaboration during the project and particularly to S.E. Beaubien and S. Lombardi (Universita di Roma "La Sapienza") for providing the CH_4 data. We thank H. Amaral, M.S. Brennwald, M. Hofer, S. Klump and Y. Tomonaga from the Environmental Isotopes Group at Eawag, as well as H. Baur and U. Menet from ETH for their support in the laboratory. We further thank D.M. Livingstone, M.L. Delaney (Editor EPSL) and two anonymous reviewers for their detailed comments that improved our manuscript. The CRIMEA project was funded by the European Union (Contract no. EVK2-CT-2002-00162) and by the Swiss Federal Office of Education and Science (Contract no. 02.0247). Further financial support came from TUMSS (the ETH methane cluster) to C.P. Holzner and R. Kipfer and from the Swiss National Science Foundation to D.F. McGinnis (Grant 200020-111763), C.J. Schubert (Grants 2100-068130 and 2160-067493) and R. Kipfer (Grants 200020-101725 and 200020-105263).

References

Aeschbach-Hertig, W., Hofer, M., Schmid, M., Kipfer, R., Imboden, D.M., 2002. The physical structure and dynamics of a deep, meromictic crater lake (Lac Pavin, France). Hydrobiol. 487 (1), 111–136.

Artemov, Y.G., 2006. Software support for investigation of natural methane seeps by hydroacoustic method. Mar. Ecol. J. 1, 57–71.

Ballentine, C.J., Burnard, P.G., 2002. Production, release and transport of noble gases in the continental crust. In: Porcelli, D., Ballentine, C.J., Wieler, R. (Eds.), Noble gases in geochemistry and cosmochemistry. Vol. 47 of Rev. Mineral. Geochem. Mineralogical Society of America, Geochemical Society, pp. 481–538.

Baur, H., 1999. A noble-gas mass spectrometer compressor source with two orders of magnitude improvement in sensitivity. American Geophysical Union, Fall Meeting. EOS, Trans. Am. Geophys. Union, vol. 80. American Geophysical Union, San Francisco, p. F1118.

Beyerle, U., Aeschbach-Hertig, W., Imboden, D.M., Baur, H., Graf, T., Kipfer, R., 2000. A mass spectrometric system for the analysis of noble gases and tritium from water samples. Environ. Sci. Technol. 34 (10), 2042–2050.

Bohrmann, G., Ivanov, M., Foucher, J.P., Spiess, V., Bialas, J., Greinert, J., Weinrebe, W., Abegg, F., Aloisi, G., Artemov, Y., Blinova, V., Drews, M., Heidersdorf, F., Krabbenhöft, A., Klaucke, I., Krastel, S., Leder, T., Polikarpov, I., Saburova, M., Schmale, O., Seifert, R., Volkonskaya, A., Zillmer, M., 2003. Mud volcanoes and gas hydrates in the Black Sea: new data from Dvurechenskii and Odessa mud volcanoes. Geo-Mar. Lett. 23 (3), 239–249.

Brennwald, M.S., Hofer, M., Peeters, F., Aeschbach-Hertig, W., Strassmann, K., Kipfer, R., Imboden, D.M., 2003. Analysis of dissolved noble gases in the pore water of lacustrine sediments. Limnol. Oceanogr. Methods 1, 51–62.

Clark, J.F., Leifer, I., Washburn, L., Luyendyk, B.P., 2003. Compositional changes in natural gas bubble plumes: observations from the Coal Oil Point marine hydrocarbon seep field. Geo-Mar. Lett. 23 (3), 187–193.

Craig, H., Weiss, R.F., 1971. Dissolved gas saturation anomalies and excess helium in the ocean. Earth Planet. Sci. Lett. 10 (3), 289–296.

Craig, H., Clarke, W.B., Beg, M.A., 1975. Excess ^{3}He in deep water on the East Pacific Rise. Earth Planet. Sci. Lett. 26 (2), 125–132.

Greinert, J., Artemov, Y., Egorov, V., De Batist, M., McGinnis, D., 2006. 1300-m-high rising bubbles from mud volcanoes at 2080 m in the Black Sea: hydroacoustic characteristics and temporal variability. Earth Planet. Sci. Lett. 244 (1–2), 1–15.

Holzner, C., 2001. Untersuchung der Tiefenwassererneuerung in meromiktischen Seen mittels transienter Tracer und numerischer. Modellierung. Diploma thesis, Eawag Dübendorf/ETH Zürich.

Holzner, C.P., Amaral, H., Brennwald, M.S., Hofer, M., Klump, S., Kipfer, R., 2005. Methane bubble streams in the Black Sea traced by dissolved noble gases. EGU General Assembly. Geophys. Res Abstr., vol. 7. European Geosciences Union, Vienna, Austria, p. 03846.

Holzner, C.P., Graser, N., Brennwald, M.S., Kipfer, R., 2006. Noble gases as tracers for gas-exchange processes at bubble-streams in lakes and oceans. 16th Annual V.M. Goldschmidt Conference. Geochim. Cosmochim. Acta, vol. 70 (18, Suppl. 1), p. A262. Melbourne, Australia.

Hornafius, J.S., Quigley, D., Luyendyk, B.P., 1999. The world's most spectacular marine hydrocarbon seeps (Coal Oil Point, Santa Barbara Channel, California): quantification of emissions. J. Geophys. Res. 104 (C9), 20703–20712.

Judd, A.G., 2004. Natural seabed gas seeps as sources of atmospheric methane. Environ. Geol. 46 (8), 988–996.

Keeling, R.F., 1993. On the role of large bubbles in air-sea gas exchange and supersaturation in the ocean. J. Marine Res. 51, 237–271.

Kipfer, R., Aeschbach-Hertig, W., Peeters, F., Stute, M., 2002. Noble gases in lakes and ground waters. In: Porcelli, D., Ballentine, C.J., Wieler, R. (Eds.), Noble gases in geochemistry and cosmochemistry. vol. 47 of Rev. Mineral. Geochem. Mineralogical Society of America, Geochemical Society, pp. 615–700.

Korotaev, G., Oguz, T., Riser, S., 2006. Intermediate and deep currents of the Black Sea obtained from autonomous profiling floats. Deep-Sea Res. II 53, 1901–1910.

Kourtidis, K., Kioutsioukis, I., McGinnis, D.F., Rapsomanikis, S., 2006. Effects of methane outgassing on the Black Sea atmosphere. Atmos. Chem. Phys. 6, 5173–5182.

Krastel, S., Spiess, V., Ivanov, M., Weinrebe, W., Bohrmann, G., Shashkin, P., Heidersdorf, F., 2003. Acoustic investigations of mud volcanoes in the Sorokin Trough, Black Sea. Geo-Mar. Lett. 23 (3), 230–238.

Kutas, R.I., Paliy, S.I., Rusakov, O.M., 2004. Deep faults, heat flow and gas leakage in the northern Black Sea. Geo-Mar. Lett. 24 (3), 163–168.

Leifer, I., Judd, A.G., 2002. Oceanic methane layers: the hydrocarbon seep bubble deposition hypothesis. Terra Nova 14 (6), 417–424.

Leifer, I., Patro, R.K., 2002. The bubble mechanism for methane transport from the shallow sea bed to the surface: a review and sensitivity study. Cont. Shelf Res. 22 (16), 2409–2428.

Leifer, I., Clark, J.F., Chen, R.F., 2000. Modifications of the local environment by natural marine hydrocarbon seeps. Geophys. Res. Lett. 27 (22), 3711–3714.

Leifer, I., Luyendyk, B.P., Boles, J., Clark, J.F., 2006. Natural marine seepage blowout: contribution to atmospheric methane. Glob. Biogeochem. Cycles 20, GB3008.

Lüdmann, T., Wong, H.K., Konerding, P., Zillmer, M., Petersen, J., Flüh, E., 2004. Heat flow and quantity of methane deduced from a gas hydrate field in the vicinity of the Dnieper Canyon, northwestern Black Sea. Geo-Mar. Lett. 24 (3), 182–193.

Mamyrin, B.A., Tolstikhin, I.N., 1984. Helium isotopes in nature, 1st Edition. Developments in Geochemistry, vol. 3. Elsevier, Amsterdam.

McDougall, T.J., 1978. Bubble plumes in stratified environments. J. Fluid Mech. 85 (4), 655–672.

McGinnis, D.F., Lorke, A., Wüest, A., Stöckli, A., Little, J.C., 2004. Interaction between a bubble plume and the near field in a stratified lake. Water Resour. Res. 40, W10206.

McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E., Wüest, A., 2006a. Fate of rising methane bubbles in stratified waters: how much methane reaches the atmosphere? J. Geophys. Res. 111, C09007.

McGinnis, D.F., Holzner, C.P., Kipfer, R., Wüest, A., 2006b. Vertical methane fluxes in the black sea deep-water: are there plumes? Proceedings of the 6th International Conference on Stratified Flows. Perth, Australia, pp. 787–792.

Naudts, L., Greinert, J., Artemov, Y., Staelens, P., Poort, J., Van, Rensbergen, P., De Batist, M., 2006. Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea. Mar. Geol. 227 (3–4), 177–199.

Özsoy, E., Rank, D., Salihoglu, I., 2002. Pycnocline and deep mixing in the Black Sea: stable isotope and transient tracer measurements. Estuar. Coast. Shelf Sci. 54 (3), 621–629.

Peeters, F., Kipfer, R., Achermann, D., Hofer, M., Aeschbach-Hertig, W., Beyerle, U., Imboden, D.M., Rozanski, K., Fröhlich, K., 2000. Analysis of deep-water exchange in the Caspian Sea based on environmental tracers. Deep-Sea Res. I 47 (4), 621–654.

Reeburgh, W.S., Ward, B.B., Whalen, S.C., Sandbeck, K.A., Kilpatrick, K.A., Kerkhof, L.J., 1991. Black Sea methane geochemistry. Deep-Sea Res. 38 (Suppl. 2), S1189–S1210.

Rehder, G., Brewer, P.W., Peltzer, E.T., Friederich, G., 2002. Enhanced lifetime of methane bubble streams within the deep ocean. Geophys. Res. Lett. 29 (15), 1731.

Reichert, P., 1994. Aquasim — a tool for simulation and data analysis of aquatic systems. Wat. Sci. Tech. 30 (2), 21–30.

Ross, D.A., Neprochnov, Y.P., Scientific Party of DSDP Leg 42B, 1978. Initial reports of the Deep Sea Drilling Project, vol. 42, Part 2. U.S. Government Printing Office, Washington.

Schmale, O., Greinert, J., Rehder, G., 2005. Methane emission from high intensity marine gas seeps in the Black Sea into the atmosphere. Geophys. Res. Lett. 32, L07609.

Schubert, C.J., Durisch-Kaiser, E., Holzner, C.P., Klauser, L., Wehrli, B., Schmale, O., Greinert, J., McGinnis, D.F., De Batist, M., Kipfer, R., 2006a. Methanotrophic microbial communities associated with bubble plumes above gas seeps in the black sea. Geochem. Geophys. Geosyst. 7 (4), Q04002.

Schubert, C.J., Durisch-Kaiser, E., Klauser, L., Wehrli, B., Holzner, C.P., Kipfer, R., Schmale, O., Greinert, J., Kuypers, M., 2006b. Recent studies on sources and sinks of methane in the black sea. In: Neretin, L., Jørgensen, B., Murray, J.W. (Eds.), Past and Present Water Column Anoxia. NATO Science Series: Earth and Environmental Sciences. Kluwer-Springer, pp. 419–441.

Sorokin, Y.I., 2002. The Black Sea: Ecology and Oceanography. Biology of Inland Waters. Backhuys Publishers, Leiden.

Stanev, E.V., Staneva, J., Bullister, J.L., Murray, J.W., 2004. Ventilation of the Black Sea pycnocline. Parameterization of convection, numerical simulations and validations against observed chlorofluorocarbon data. Deep-Sea Res. I 51 (12), 2137–2169.

Strassmann, K.M., Brennwald, M.S., Peeters, F., Kipfer, R., 2005. Dissolved noble gases in porewater of lacustrine sediments as palaeolimnological proxies. Geochim. Cosmochim. Acta 69 (7), 1665–1674.

Top, Z., Clarke, W.B., 1983. Helium, neon and tritium in the Black Sea. J. Mar. Res. 41 (1), 1–17.

Top, Z., Izdar, E., Ergün, M., Kunok, T., 1990. Evidence of tectonism from ^{3}He and residence time of helium in the Black Sea. Eos 71, 1020–1021.

Top, Z., Östlund, G., Pope, L., Grall, C., 1991. Heluim isotopes, neon and tritium in Black Sea, a comparison with the 1975 observation. Deep-Sea Res. 38 (Suppl. 2), S747–S759.

Torgensen, T., Top, Z., Clarke, W.B., Jenkins, W.J., Broecker, W., 1977. A new method for physical limnology–tritium–helium-3 ages — results for Lakes Erie, Huron and Ontario. Limnol. Oceanogr. 22 (2), 181–193.

Walter, K.M., Zimov, S.A., Chanton, J.P., Chapin III, F.S., 2006. Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. Nature 443, 71–75.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. 97 (C5), 7373–7382.

Winckler, G., Aeschbach-Hertig, W., Holocher, J., Kipfer, R., Levin, I., Poss, C., Rehder, G., Suess, E., Schlosser, P., 2002. Noble gases and radiocarbon in natural gas hydrates. Geophys. Res. Lett. 29 (10), 1423.

Wüest, A., Brooks, N.H., Imboden, D.M., 1992. Bubble plume modeling for lake restoration. Water Resour. Res. 28 (12), 3235–3250.