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Sub sea floor boiling of Red Sea Brines: New indication from noble gas data

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Abstract—Hydrothermal brines from the Atlantis II Deep, Red Sea, have been sampled in situ and analyzed for noble gases. The atmospheric noble gas concentrations (Ne, Ar_{atm}, Kr, Xe) in the deepest layer (LCL) are depleted by 20 to 30% relative to the initial concentrations in ambient Red Sea Deep Water without a systematic mass fractionation between the different noble gases. Sub surface boiling during the hydrothermal circulation and subsequent phase separation is shown to be a consistent explanation for the observed depletion pattern. Using a conceptual model of phase separation under sub-critical conditions, in which gases are partitioned according to Henry's Law, we reconstruct the fluid history before injection into the Atlantis II Deep: after having circulated through evaporites and young oceanic crust, where it becomes enriched in He_{MORB} and Ar_{MORB}, the ascending fluid boils, and the residual liquid becomes depleted in noble gas concentrations. The depleted fluid rises to the sediment surface and feeds the Atlantis II basin. The relatively low boiling degree of about 3% (i.e., the percentage of fluid removed as vapor) derived from the model indicates that the Atlantis II system represents an early stage of boiling with relatively small gas loss, in contrast to hydrothermal systems at sediment-free mid-ocean ridges. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

Since the discovery of oceanic hydrothermal activity and its impact on global cycling of chemical species, much attention has been focused on the processes that control the chemistry of hydrothermal vents. However, it is still one of the major challenges to create a model of the sub sea floor circulation and the physical processes occurring before injection of the hydrothermal fluid into the ocean.

The first hydrothermal field was discovered in the central rift zone of the Red Sea (Miller et al., 1966), which is presently known to contain more than 20 morphological depressions filled by highly saline brines (Hartmann et al., 1998a). The Atlantis II Deep, located on the axial zone at around 21°20'N (Fig. 1), is the most prominent depression within this unique geological environment of present submarine hydrothermal activity (Degens and Ross, 1969). Below 1900 m, it encloses a volume of about 17 km³ and its maximum depth is 2200 m. Recently, Blanc and Anschutz (1995) have shown that the brine pool consists of four well-mixed layers, named, from bottom to top, the lower convective layer (LCL) and upper convective layers 1, 2, and 3 (UCL1, UCL2, UCL3). The hottest and saltiest brine is found in the LCL (up to 67°C, 270 g/kg), which is separated from the successively colder and fresher layers above by extremely sharp vertical salt and temperature gradients.

The Atlantis II brine system is interpreted as a special case of a hydrothermal field at a mid-ocean ridge. In contrast to most hydrothermal areas, its hydrothermal fluid is not only the result of seawater reacting with basalts, but it also interacts with

another geochemical reservoir, the Miocene evaporites underlying the entire Red Sea. According to a generally accepted model, sea water of normal salinity penetrates into the sub surface and circulates downward through evaporites, where it becomes strongly enriched in salt. The fluid moves horizontally along fissures through the newly formed oceanic crust and interacts with the young basalts. This model is consistent with various isotopic and chemical studies (e.g., Zierenberg and Shanks III, 1986; Anschutz et al., 1995). First evidence for interaction with basalts was the strong ³He-MORB-excess transported by the discharging brines (Lupton et al., 1977). Subsequently, the hot fluid rises through fractures in the crust and is injected directly into the bottom of the southwest Atlantis basin (e.g., Hartmann, 1980; Monin et al., 1981).

However, despite numerous investigations of the hydrographic structure and its changes (e.g., Hartmann, 1980; Anschutz and Blanc, 1996; Anschutz et al., 1998; Hartmann et al., 1998a), little is known about the fluid history during hydrothermal sub sea floor circulation. In contrast to other hydrothermal systems, the hot fluid has never been sampled directly at the discharge site. Consequently, only indirectly derived information regarding the temperature and the formation of the brines venting into the Atlantis II Deep is available. Whereas a wide range of discharge temperatures (200°–400°C) is reported, most authors estimate venting temperatures in excess of 330°C (e.g., Monin and Plakhin, 1982; Oudin et al., 1984; Ramboz et al., 1988; Ramboz and Danis, 1990).

In recent years, boiling and phase separation have been verified as basic processes at mid-ocean ridge hydrothermal systems, e.g., at the Juan de Fuca Ridge (Butterfield et al., 1990; Butterfield et al., 1994; Butterfield et al., 1997; Von Damm et al., 1997). Evidence comes mainly from observation

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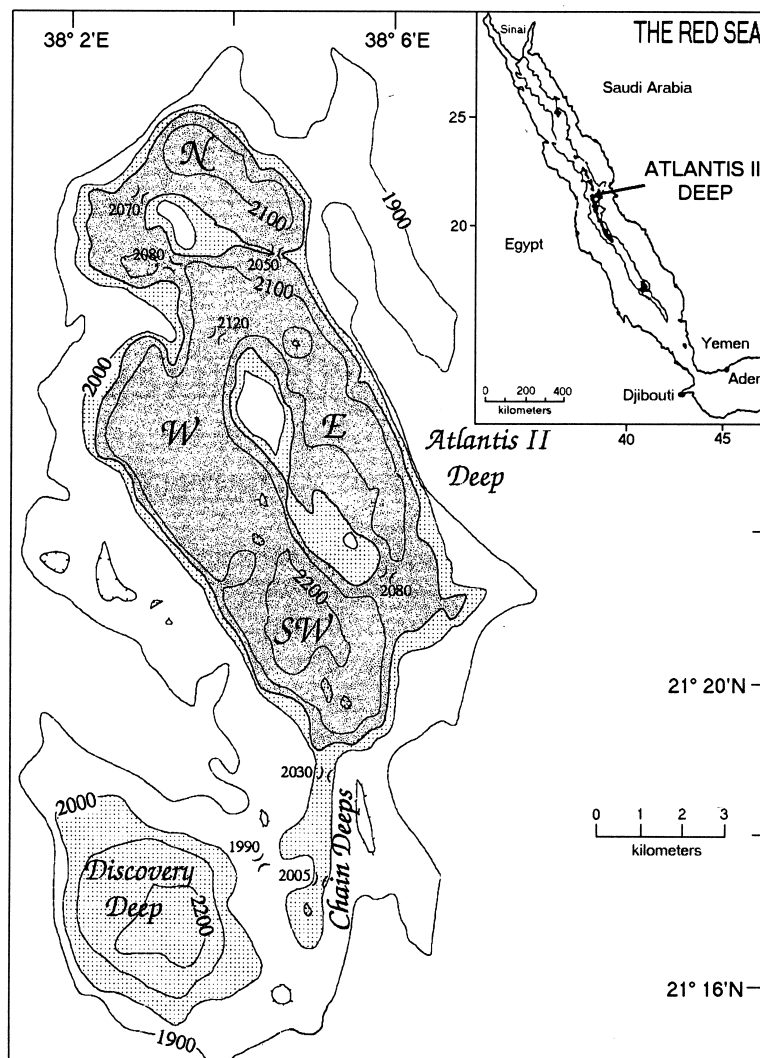


Fig. 1. Location and bathymetric map of the Atlantis II Deep area after Anschutz and Blanc (1996).

of nonvolatile components, primarily large salinity variations, which are assumed to be the result of boiling (e.g., Delaney and Cosens, 1982; Bischoff and Pitzer, 1985). This approach is not feasible for the Atlantis II system, because a potential chloride variation due to boiling is masked by the extremely high salt concentration of the brine which is caused by the interaction with the evaporites.

For the Atlantis II system, fluid inclusions in anhydrite recovered from a sediment core provide mineralogical evidence for boiling within the sea floor (Ramboz et al., 1988). The fluid inclusions are interpreted to be precipitated from "successive boiling brine pulses" at trapping temperatures of 390 to 403°C. However, the value of this method is limited as fluid inclusions are only secondary products of hydrothermal circulation.

Here, we present a more direct approach based on noble gas data from the brine itself offering the possibility to reevaluate the hypothesis of Ramboz et al. (1988). Due to their conservative nature in geochemical systems, noble gases represent an extremely useful tool to detect processes such as phase separation and to assess their effects on the gas composition of the

hydrothermal fluid. Despite their great potential, only one study applied atmospheric noble gases as tracers to hydrothermal vents (Kennedy, 1988).

For this study, water samples taken in situ in the Atlantis II brine were analyzed for their noble gas composition. The data provide a unique opportunity to directly study the sub sea floor processes associated with the formation of the Atlantis II brine and to develop a conceptual model of the evolution of the hydrothermal fluid prior to injection into the Atlantis II basin.

2. METHODS

During cruise 121 of RV SONNE in 1997 water samples for noble gas analysis were collected in copper tubes using a newly developed device to seal samples under in situ conditions for post-cruise tracer analysis. The new sampler (Fig. 2) is based on the construction previously described by Weiss (1968) and Jean-Baptiste et al. (1994).

The sampler is directly attached to a standard Niskin bottle (piggy-back method) and recovers water samples isolated at in situ pressure in copper tubing. Closing of the sampler by two tampered pins at each end of the copper tube is activated when the Niskin bottle is triggered. After the closed Niskin bottle and sampler have been recovered on board the

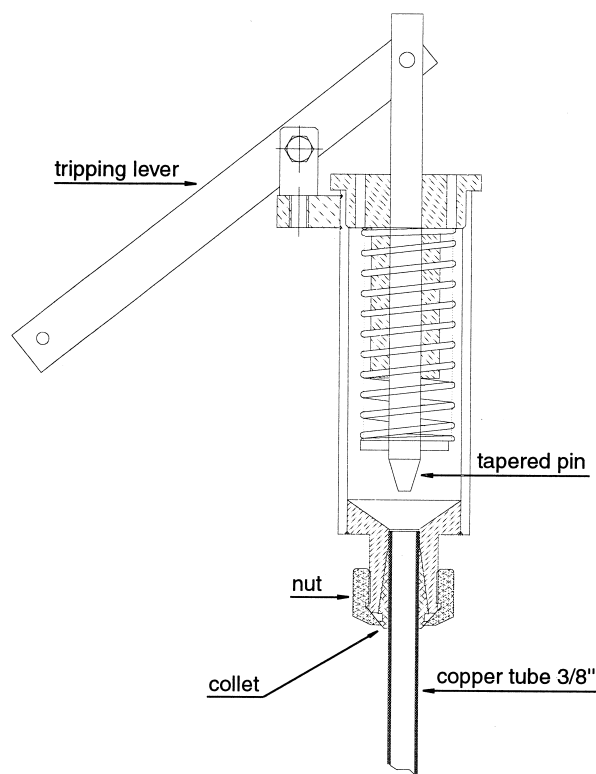


Fig. 2. Schematic drawing of one closing mechanism of the newly developed in situ sampler. The spring is tensioned by a tripping lever that is connected to the trigger of the Niskin bottle. When the lever is tripped, the spring is released and the tapered pin seals the copper tube tightly. After recovery of the in situ sample, the copper tube is finally sealed by standard pinch-off clamps.

copper tube is finally sealed by closing the standard pinch-off clamps on both ends of the sampler. This procedure of sampling under in situ conditions avoids degassing losses and fractionation due to pressure relaxation on the up-cast. Therefore, the data presented here reflect the undisturbed composition of the sampled brine layers.

For the noble gas mass spectrometric analysis, the samples were

quantitatively degassed on a vacuum line. After purification and separation, the noble gases were measured in two statically operated 90° sector mass spectrometers. Experimental details of the analytical procedures can be found in Beyerle et al. (1999).

3. RESULTS

The noble gas concentrations of the brine samples are summarized in Table 1. We assume that the initial noble gas composition of the circulating fluid is that of ambient Red Sea Deep Water (RSDW, $T = 21.5^{\circ}\text{C}$, $S = 40.6$) in solubility equilibrium with the atmosphere (Weiss, 1970; Weiss, 1971; Weiss and Kyser, 1978; Smith and Kennedy, 1983) because it is commonly assumed that the overlying water column acts as the source for fluid recharge.

All the atmospheric noble gas concentrations (except Ne of sample #67) are depleted relative to RSDW. To discuss their depletion, Figure 3 shows the obtained noble gas signatures expressed as ratio of observed and RSDW concentrations (i.e., $C/C_0 = 1$ represents RSDW). Sample #407, drawn from the uppermost brine layer, closely resembles RSDW, whereas #261 from UCL1 shows a moderate depletion of about 10% compared to RSDW. The noble gas concentrations of the second sample from UCL1, #67, are significantly higher than those of #261, probably indicating a contamination by a small amount of air during the analytical procedure. The strongest depletion was observed for the three LCL samples #399, #357, and #385 obtained from different sub-basins of the Atlantis II Deep. Here, the noble gas concentrations were found to be 70 to 82% of those expected for RSDW.

Accompanying helium and argon isotope analyses show extremely high helium enrichments as well as elevated $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios which reflect the acquisition of a strong MORB signal. The strongest ^3He enrichment (up to a factor of 3200 with respect to RSDW) and highest argon isotope anomaly were observed in the LCL. The implications of these data in relation to mantle geochemistry will be discussed elsewhere.

Table 1. Noble gas composition of the brine samples.

| Sample | Layer | Depth | T ^a | Salinity ^a | N | He | Ne | Ar ^{*b} | Kr | Xe |
|--------|--------------------------------|-------|----------------|-----------------------|------|---|---------------------|---------------------|---------------------|---------------------|
| | | m | °C | | | [10 ⁻⁸] | [10 ⁻⁷] | [10 ⁻⁴] | [10 ⁻⁸] | [10 ⁻⁹] |
| | | | | | | cm ³ · g ⁻¹ (STP) | | | | |
| 407 | Atlantis UCL3 | 2005 | 45.1 | 90 | 0.95 | 315 | 1.34 | 2.28 | 4.95 | 6.61 |
| 261 | Atlantis UCL1 | 2024 | 56.4 | 147 | 0.89 | 626 | 1.32 | 2.19 | 4.82 | 6.53 |
| 67 | Atlantis UCL1 | 2042 | 56.4 | 147 | 0.89 | 655 | 1.54 | 2.33 | 5.01 | 6.45 |
| 385 | Atlantis LCL | 2070 | 67.2 | 260 | 0.78 | 1240 | 1.01 | 1.79 | 3.98 | 5.44 |
| 357 | Discovery LCL | 2085 | 45 | 260 | 0.78 | 1210 | 1.07 | 1.81 | 3.94 | 5.28 |
| 399 | Atlantis LCL | 2145 | 67.2 | 260 | 0.78 | 1260 | 1.12 | 1.85 | 4.02 | 5.47 |
| | RSDW ^c | | 21.5 | 40.6 | 1 | 3.613 | 1.458 | 2.316 | 5.069 | 6.645 |
| | LCL _{eq} ^c | | 67 | 260 | 0.78 | 1.143 | 0.412 | 0.355 | 0.566 | 0.553 |

To correct for the large salinity variation between the individual brine layers, the noble gas concentrations are reported as cm³ STP per g RSDW. The measured noble gas concentrations in cm³ STP per g brine were divided by the layer specific normalization factor N which is the mass fraction of RSDW in the brine. The accuracy of the noble gas concentrations is ± 1% for He, Ne, Ar, Kr, and ± 1.8% for Xe.

^a temperature and salinity data are from Hartmann et al. (1998a, b).

^b Ar* denotes the atmospheric Ar concentration after correcting for the amount of radiogenic Ar (≤3%) present as indicated by the enhanced $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (up to 305).

^c RSDW and LCL_{eq} concentrations are determined as equilibrium concentrations for given T and salinity.

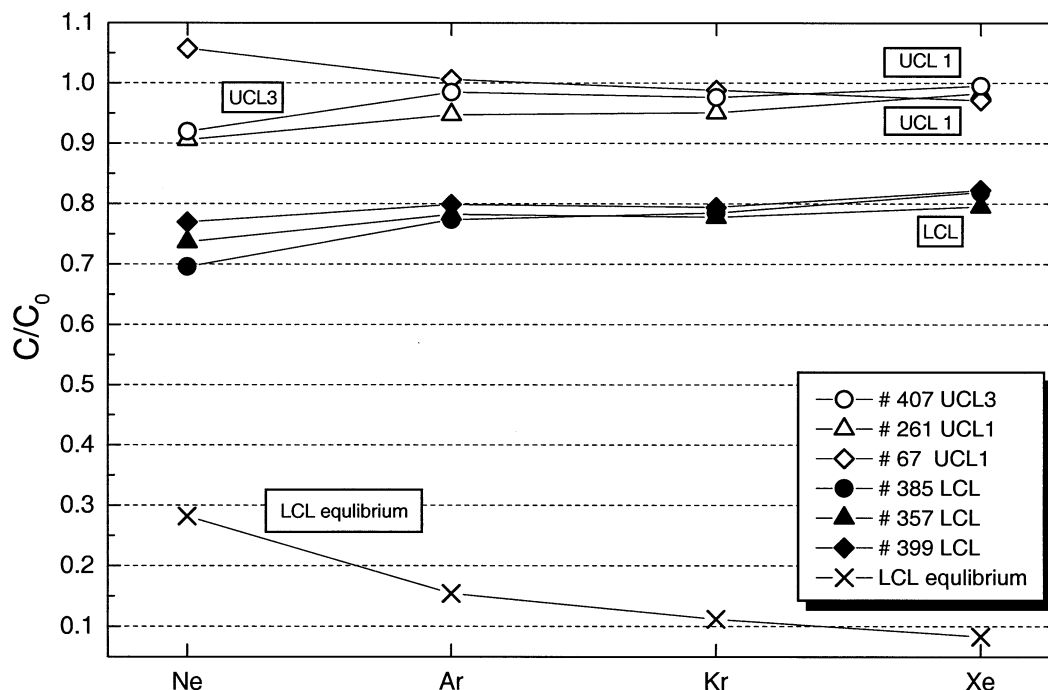


Fig. 3. Atmospheric noble gas composition (Ne, Ar_{atm}, Kr, Xe) normalized to noble gas concentrations C_0 in RSDW. The samples were taken in different brine layers of the Atlantis II system, the Lower Convective Layer (LCL), the Upper Convective Layer 1 (UCL1) and the Upper Convective Layer 3 (UCL3). All atmospheric noble gases are depleted with respect to RSDW (except Ne of #67) without significant fractionation. For comparison, the noble gas concentrations determined for equilibrium conditions with actual LCL temperature (67°C) and salinity (260 g/kg) are added. These concentrations are much lower than those observed and show a stronger fractionation.

4. DISCUSSION

We focus on the noble gases of atmospheric origin (Ne, Ar_{atm}, Kr, Xe) and on the depletion effect observed in the LCL that is thought to represent the hydrothermal fluid discharging into the Deep. The upper brine layers are generally explained as mixtures between the original hydrothermal fluid and RSDW (e.g., Hartmann, 1985). In the LCL, the noble gas concentrations were found to be ca. 70 to 82% of those expected for RSDW, without significant fractionation between the individual noble gases.

In the following, we discuss different processes which might have caused the observed depletion relative to the atmospheric signature of RSDW.

- 1) None of the observed noble gas signatures in the brine layers can be interpreted as resulting from solubility equilibration with the atmosphere. For illustration, the equilibrium noble gas concentrations for the actual LCL brine conditions (67°C, 260 g/kg) are given in Table 1 and plotted in Figure 3. They are significantly lower than the observed noble gas concentrations in the brine layers. Even more important, they show a significant fractionation relative to RSDW concentrations with the depletion increasing from Ne to Xe.
- 2) Salt induced diffusion (Suckow and Sonntag, 1993) cannot be responsible for the noble gas loss because diffusive processes would lead to significant fractionation between the noble gases which is not observed.

- 3) Degassing of the brines during sampling can be excluded as the copper tubes were closed under in situ conditions preventing any contact with the atmosphere (see Section 2).

As these three potential processes can be ruled out, another process must be responsible for the observed gas loss relative to RSDW.

4.1. The Boiling Hypothesis

We propose that the observed depletion is the result of a boiling process and associated phase separation between a gas and a liquid phase. Red Sea deep water penetrates into the sea floor and circulates through the hydrothermal system where it is heated and enriched in non-atmospheric noble gases, i.e., ^3He , ^4He , and ^{40}Ar of mantle origin. As the hot fluid ascends it gradually reaches depth levels of lower hydrostatic pressure, causing it to boil and separate into a vapor phase and a residual liquid phase. The noble gases will preferentially partition into the lower density phase and consequently, the residual liquid phase is expected to be depleted in absolute gas concentrations relative to the pre-boiling liquid.

4.2. The Boiling Model

To evaluate this boiling hypothesis, we make an attempt to reconstruct the fluid's history. We present a simple boiling model which describes the partitioning of gases between the

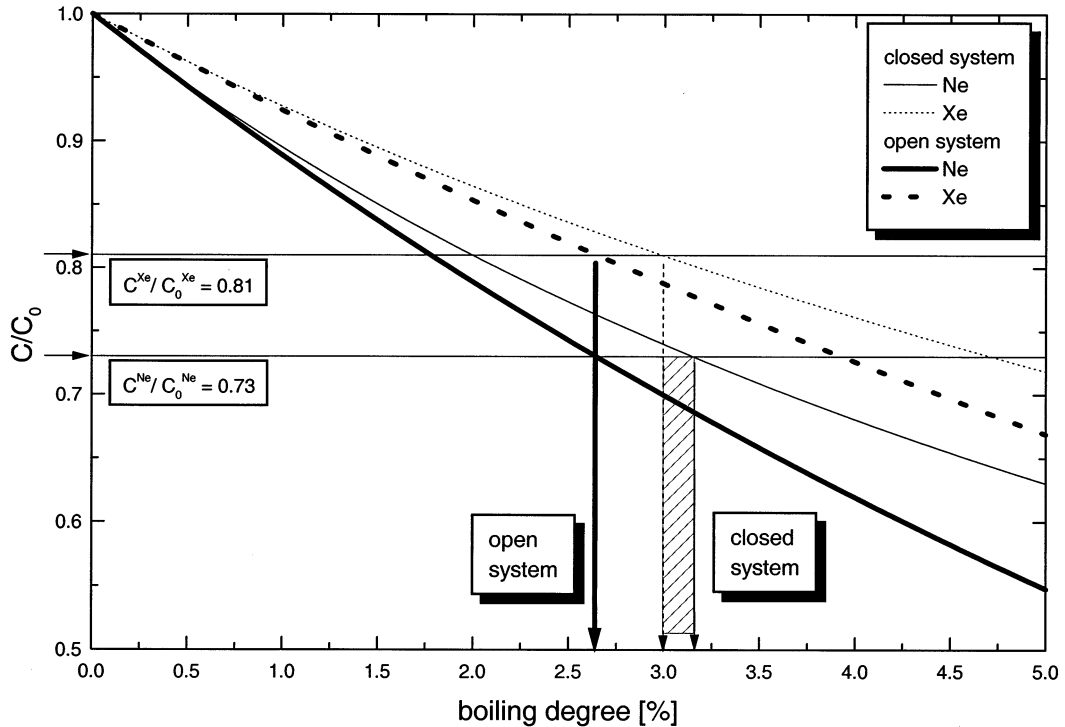


Fig. 4. Model results, ratio of noble gas concentration in the residual fluid to initial RSDW noble gas concentration as a function of the boiling degree; depletion curves are shown for Ne (solid line) and Xe (dashed line), and for the two different processes, closed system conditions (thin) and open system conditions (Rayleigh, bold). Horizontal lines give the Ne and Xe depletion of the LCL (determined as mean values of the three samples) and intersect the depletion curves at the boiling degree of about 3 to 3.2% for closed system conditions (thin) and 2.6% for open system conditions (bold) as indicated by the vertical arrows.

liquid and vapor phase and cross check its predictions with the data.

In principle, partitioning can be described by Henry's law. Two modes of phase separation may occur: 1) single-stage or 2) Rayleigh fractionation. Briefly, in a single-stage process, the vapor and liquid phases always remain in contact as the system evolves (closed system). In a Rayleigh process, the vapor is continuously removed from the liquid as boiling proceeds. The approach follows that of Mazor and Truesdell (1984) who applied these processes to a continental geothermal system.

For either system, the residual concentration of gas in the liquid phase can be calculated as a function of the boiling degree, for a single-stage separation

$$\frac{C_1}{C_0} = \frac{1}{F + \frac{1-F}{A}} \quad (1)$$

and for a continuous separation by

$$\frac{C_1}{C_0} = F^{(1/A-1)} \quad (2)$$

where C_1/C_0 is the ratio of the noble gas concentration in the remaining liquid to that in the initial one, F is the fraction of water remaining in the liquid phase after the fraction $B = 1 - F$ has been converted to vapor (in the following B is referred to as the degree of boiling), and A is the distribution coefficient

$C_{\text{liquid}}/C_{\text{vapor}}$. The distribution coefficients are calculated from the Henry's Law constants K_H using the equation given by Ellis and Mahon (1977)

$$A = \frac{RT}{K_H V_{sp}} \quad (3)$$

where R is the gas constant, T the absolute temperature and V_{sp} the specific volume of vapor.

This model requires the knowledge of the solubilities. As there are very little experimental data on noble gas solubilities at high temperatures and pressures (Himmelblau, 1960; Potter II and Clynne, 1978; Crovetto et al., 1982), the quantitative assessment of the degree and exact process of phase separation is limited. In this study, we used the solubility data as given by Crovetto et al. (1982) for the temperature range of 30 to 330°C. Solubilities for temperatures up to 390°C were obtained by extrapolating their empirical equations. This causes uncertainties in the Henry's Law constants of as much as 40%. An additional uncertainty arises because the "salting out effect" (i.e., lowering of the solubility due to addition of salt) is only known for temperatures below 60°C. According to Smith and Kennedy (1983) further extrapolation of the noble gas-brine solubility data is not feasible. Therefore, we refer to the extrapolated fresh water solubilities without corrections for salt effects.

It is important to state here that despite the uncertainties of

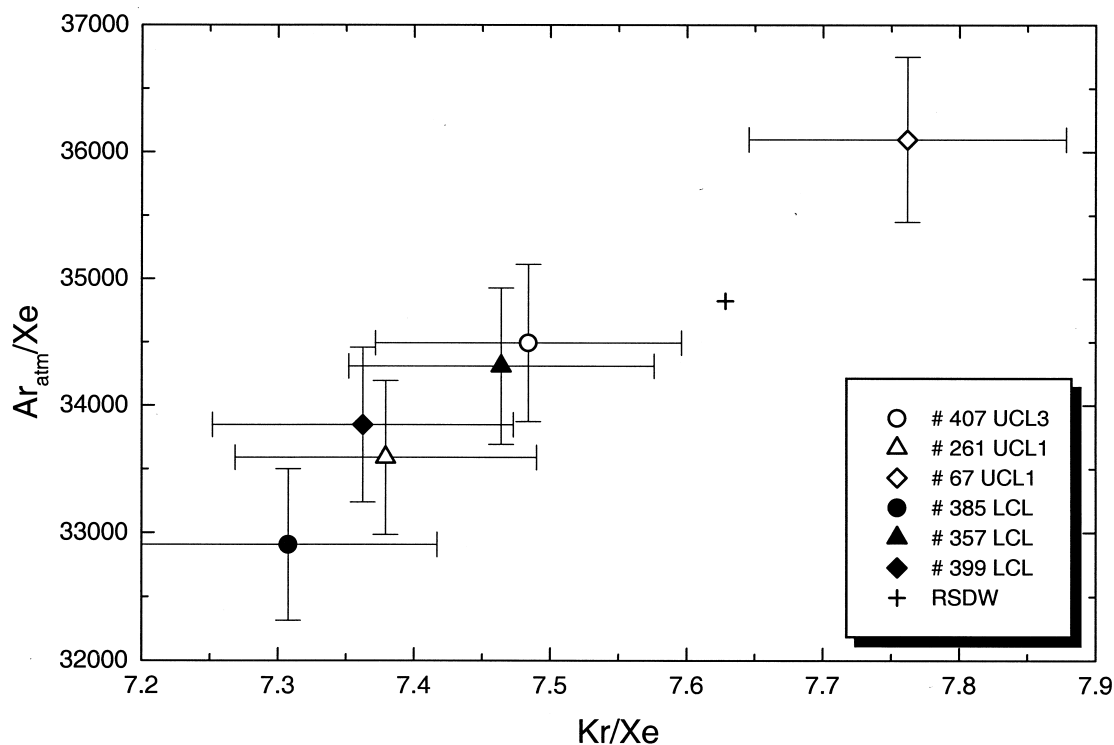


Fig. 5. Ar/Xe vs. Kr/Xe plot for the brine samples and RSDW. The linear correlation indicates a mixing trend of depleted LCL and RSDW.

noble gas solubility data at high temperatures the above cited experimental studies by Himmelblau (1960), Potter II and Clyne (1978), and Crovetto et al. (1982) agree in two main aspects:

- 1) whereas at low temperatures the noble gases are relatively insoluble, the noble gas solubilities increase (the Henry's Law constants decrease) rapidly with temperature by more than one order of magnitude
- 2) whereas at low temperatures the solubilities are strongly element dependent, the solubilities for the different noble gases converge at high temperatures (>550°C)

The initial boiling temperature can be estimated using the two-phase boundary curves for the system NaCl-H₂O derived by Bischoff and Pitzer (1985). In contrast to open ocean hydrothermal systems supercritical conditions do not have to be considered because the presence of large salt concentrations strongly elevates the critical point for the brine considered [540°C and 700 bar] relative to the critical point of pure sea water [407°C and 298.5 bar, (Bischoff and Rosenbauer, 1988)]. In our model, the boiling temperature is taken to be 390°C, in agreement with fluid inclusion data by Ramboz et al. (1988).

We are fully aware of the uncertainties of the input parameters of our conceptual model. Nevertheless, it allows us to determine the effect of phase separation and to study the basic features of the general trend of the noble gas evolution. By using Ne and Xe as examples, Figure 4 shows the depletion of the atmospheric noble gases relative to the initial RSDW composition as a function of the boiling degree B for phase separation

under closed and under open system conditions. Figure 4 clearly illustrates that there are—especially for low boiling degrees—only slight differences between the two scenarios and between the different noble gases, respectively.

4.3. Comparison of Model Results and Observed Noble Gas Patterns

4.3.1. Lack of mass-dependent fractionation

The model illustrates that the measured depletion pattern, namely the absence of a systematic mass-dependent fractionation pattern, is consistent with a boiling scenario at high temperatures where noble gas solubilities converge.

4.3.2. Extent of boiling

Our boiling model can be used to estimate the degree of boiling which is necessary to create the depletion observed in the LCL. The mean depletion of the Neon and Xenon concentration (C/C_0) of the three samples from the LCL is 0.73 and 0.81, respectively. In Figure 4 the degree of boiling is given by the intersection with the depletion curves obtained from the model. The consistency of the two noble gas species is striking. For closed system conditions a boiling degree of 3.2% (Ne) and 3% (Xe) is obtained, for open-system conditions we find a boiling degree of about 2.6% (Ne, Xe). This implies that a boiling process with about 3% of the fluid converted to vapor—regardless of the mode of boiling—produces a residual fluid

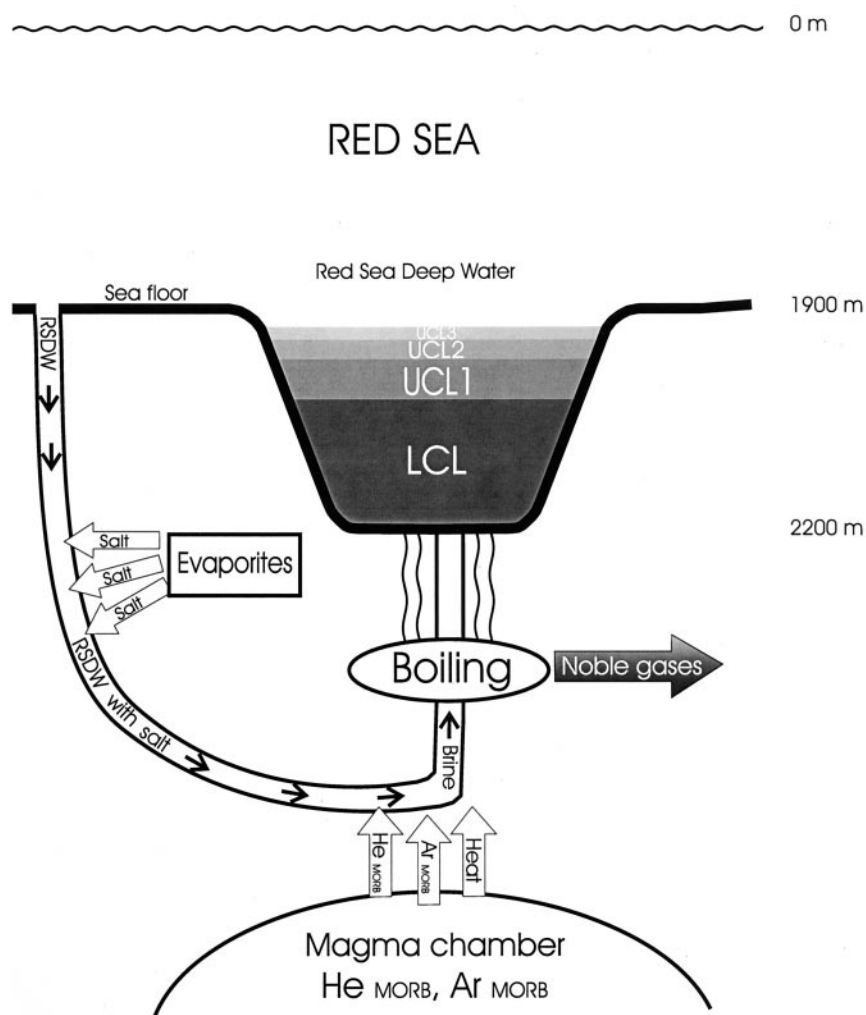


Fig. 6. Conceptual model of the evolution of the brine prior to injection into the Atlantis II Deep (see text).

with an atmospheric noble gas depletion of about 25% as observed in the LCL brine.

Compared to the 15 to 20% boiling which has been suggested for oceanic hydrothermal fields at the Juan de Fuca Ridge (Butterfield et al., 1990) the boiling degree of 3% reported here is significantly lower. Obviously, the Atlantis II brine system represents a relatively early stage of boiling, similar to those observed at continental geothermal systems of Wairakei, New Zealand (Mazor and Bosch, 1990), and in Mexico (Mazor and Truesdell, 1984).

4.3.3. Dilution trend

All noble gas ratios show a significant linear correlation indicating a mixture of two components. In Figure 5, the Ar/Xe versus Kr/Xe ratio is shown as an example. In addition, we observe an anti-correlation between the atmospheric noble gases (Ne, Ar_{atm}, Kr, Xe) and the MORB-derived He concentration as we move up the water column through the brine layers (see Table 1). Because the boiling process occurs subsequent to the accumulation of the non-atmospheric signal and

affects atmospheric and non-atmospheric noble gases alike, the observed anticorrelation excludes that the individual samples reflect different stages of boiling and also points to a two-component mixing: The residual liquid after boiling—the LCL endmember—which is still marked by a high MORB-⁴He signal and strong depletion of the atmospheric noble gases is subsequently diluted with a RSDW-type component.

4.4. Evolution of the Hydrothermal Brine

This scenario is illustrated in Figure 6: RSDW carrying atmospheric noble gases penetrates into the sediments. During the circulation through the Miocene evaporites it becomes strongly enriched in salt. Then the brine reaches a region of high temperatures, the hydrothermally active zone above the magma chamber, where it interacts with the hot young basalt and becomes enriched in MORB-components as He and Ar. As the fluid ascends, it progressively moves into regions of lower pressure and intersects the “boiling curve”: the fluid boils and separates into two phases, a residual noble gas-depleted liquid phase and a noble gas-enriched vapor phase. All noble gases,

the MORB–He excess as well as the atmospheric noble gases are depleted by boiling, but note that the residual fluid still shows a strong He excess. Due to only small differences in the solubilities at high temperatures the different noble gas species are depleted approximately to the same degree relative to the initial conditions. The depleted residual liquid ascends rapidly to the sea floor and discharges into the brine pool. Substantial sub surface mixing with cold percolating sea water can be largely excluded with respect to the high venting temperatures. Thus, the LCL seems to basically represent the boiled fluid, whereby the upper brine layers are formed by subsequent mixing with RSDW.

If boiling and phase separation affects the Atlantis II brine then the question arises where the noble gas-enriched phase produced by phase separation moves. In this study, we only found the depleted liquid residual to phase separation but did not observe a phase enriched in noble gases. This could be explained either by local or temporal variability. The enriched phase may be found apart from the region sampled or phase separation may be a process occurring only in episodes. Our noble gas data prove that phase separation does occur, but not if it is occurring presently.

5. CONCLUSIONS

Our data and the simulation by the model imply that atmospheric noble gases are useful in reconstructing dynamic processes like phase separation in hydrothermal systems. The mass-independent noble gas depletion pattern of the Atlantis II brine is shown to be consistent with a phase separation process occurring during the hydrothermal circulation of the brine. Our results are consistent with a boiling scenario and indicate that boiling may be an important step in the formation of the Atlantis II brine. The data confirm a previous hypothesis of boiling in the Atlantis II brine system that was based on fluid inclusions (Ramboz et al., 1988). Furthermore, we conclude that the Red Sea brines are another oceanic hydrothermal system, in addition to the vent systems at sediment-free ridges, where boiling and phase separation play a key role in controlling the hydrothermal chemistry.

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