

Interpretation of dissolved atmospheric noble gases in natural waters

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Abstract. Several studies have used the temperature dependence of gas solubilities in water to derive paleotemperatures from noble gases in groundwaters. We present a general method to infer environmental parameters from concentrations of dissolved atmospheric noble gases in water. Our approach incorporates statistical methods to quantify uncertainties of the deduced parameter values. The equilibration temperatures of water equilibrated with the atmosphere under controlled conditions could be inferred with a precision and accuracy of $\pm 0.2^\circ\text{C}$. The equilibration temperatures of lake and river samples were determined with a similar precision. Most of these samples were in agreement with atmospheric equilibrium at the water temperature. In groundwaters either recharge temperature or altitude could be determined with high precision ($\pm 0.3^\circ\text{C}$ and ± 60 m, respectively) despite the presence of excess air. However, typical errors increase to $\pm 3^\circ\text{C}$ and ± 700 m if both temperature and altitude are determined at the same time, because the two parameters are correlated. In some groundwater samples the composition of the excess air deviated significantly from atmospheric air, which was modeled by partial reequilibration. In this case the achievable precision of noble gas temperatures was significantly diminished (typical errors of $\pm 1^\circ\text{C}$).

1. Introduction

The behavior of noble gases in nature is governed by relatively simple and well-known physical processes such as diffusion, partition between different phases, or nuclear transformations. For this reason, noble gases are excellent geochemical tools to investigate a variety of physical parameters of environmental and geological systems.

Concentrations of noble gases in the hydrosphere are primarily governed by solution of atmospheric noble gases in surface waters. Equilibrium concentrations in surface waters depend on temperature (T) and salinity (S) of the water, as well as ambient atmospheric pressure (P). Thus the determination of the concentrations of the five stable noble gases (He, Ne, Ar, Kr, and Xe) in any water sample should enable a reconstruction of the T , S , and P conditions under which the water equilibrated with the atmosphere. Any body of originally meteoric water that has been sealed off from the atmosphere can be seen as a potential archive of past environmental conditions.

The most important of these potential archives are groundwaters, which cover a range of residence times from days to millions of years [Loosli *et al.*, 1998]. In a number of studies, noble gases dissolved in groundwater have been used to deduce paleotemperatures back to the last ice age [e.g., Mazor, 1972; Andrews and Lee, 1979; Stute and Schlosser, 1993]. Other archives could be sediment pore waters or deepwater bodies of lakes or the ocean, but they have not been explored so far.

In groundwater the interpretation of noble gas concentrations is complicated by the empirical finding of an ubiquitous excess of gases relative to solubility equilibrium with the atmo-

sphere [Heaton and Vogel, 1981]. In certain aquifer systems the composition of this excess air appears to deviate from that of atmospheric air. Partial loss of the excess air due to diffusive reequilibration has been proposed as a conceptual model to interpret the measured noble gas abundance pattern in such situations [Stute *et al.*, 1995b]. Thus two additional parameters, the amount of excess air (A) and the degree of reequilibration (R), may be needed to describe noble gas concentrations in groundwater.

Both A and R may provide valuable information about the environmental conditions during groundwater recharge. Several studies have discussed possible correlations of excess air with lithology, temperature, precipitation, or flooding [Herzberg and Mazor, 1979; Heaton and Vogel, 1981; Heaton *et al.*, 1983; Wilson and McNeill, 1997; Stute and Talma, 1998]. Little is known about the factors that influence the occurrence of partial reequilibration. Although the excess air in groundwater is incompletely understood, it appears to be a potential tool for hydrological and paleoclimatological studies [Loosli *et al.*, 1998].

Previous methods for the interpretation of noble gas concentrations in groundwaters focused on the calculation of the noble gas temperature [Rudolph, 1981; Stute, 1989; Pinti and Van Drom, 1998]. In principle, the problem is to determine the five parameters T , S , P , A , and R from five measured noble gas concentrations. In practice, however, helium often cannot be used for this inversion because of the presence of nonatmospheric helium from sources within Earth. Yet, in most practical cases some of the five parameters are well constrained (e.g., S and P). With only two or three unknown parameters and four measured concentrations the system is overdetermined. The model parameters can be solved for by an error-weighted nonlinear inverse technique, as first proposed by Hall and Ballentine [1996] and Ballentine and Hall [1998, 1999].

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Here we describe our completely independent development of a general weighted least squares method to determine subsets of the five model parameters from measured noble gas concentrations in natural waters. We apply this technique to the relatively simple case of lake and river waters, which provides a verification of the approach. Furthermore, several groundwater data sets and the effects of excess air and partial reequilibration are discussed.

2. Theory

The most important source of noble gases in natural waters is the solution of atmospheric gases according to Henry's law:

$$p_i = k_i(T, S)x_i \quad (1)$$

Thus the equilibrium concentration of the dissolved gas i in the solution (here expressed as mole fraction x_i) is proportional to its partial pressure p_i in the gas phase, with a coefficient of proportionality (Henry coefficient) k_i which depends on temperature and salinity.

Noble gas concentrations in water are usually reported in cm^3 STP g^{-1} . It is reasonable to assume that equilibration occurred with moist (water vapor saturated) air. Therefore gas solubilities are most conveniently expressed by the moist air equilibrium concentration C^* , which is the gas volume (STP) per unit weight of solution in equilibrium with moist air at a total atmospheric pressure of 1 atm. Equilibrium concentrations of this form have been reported for He, Ne, Ar, and Kr by Weiss [1970, 1971] and Weiss and Kyser [1978], both for freshwater and seawater. Benson and Krause [1976] gave Henry coefficients for all noble gases in pure water and claimed a very high precision (better than $\pm 0.2\%$). Critical evaluations of the literature on noble gas solubilities were published [Clever, 1979a, b, 1980].

The effect of salinity can be described by the Setchenow relation:

$$\ln \left(\frac{\beta_i(T, 0)}{\beta_i(T, S)} \right) = K_i S \quad (2)$$

where β_i is the Bunsen coefficient of gas i (volume of gas (STP) absorbed per unit volume of solution at a partial pressure of 1 atm) and K_i is its Setchenow or salting coefficient. Empirical salting coefficients for all noble gases in NaCl solutions have been reported by Smith and Kennedy [1983]. In applied studies involving all five noble gases [e.g., Stute and Schlosser, 1993], the data of Weiss [1970, 1971] for He, Ne, and Ar have usually been complemented by the solubilities of Kr and Xe as given by Clever [1979b] paired with the salt dependency of Smith and Kennedy [1983]. For this study we calculated three sets of solubilities: (1) the "Weiss solubilities," combining the data of Weiss [1970, 1971] and Weiss and Kyser [1978] for He, Ne, Ar, and Kr with those of Clever [1979b] and Smith and Kennedy [1983] for Xe; (2) the "Clever solubilities," combining the data of Clever [1979a, b, 1980] with Smith and Kennedy [1983]; and (3) the "Benson solubilities," combining the data of Benson and Krause [1976] with Smith and Kennedy [1983]. The first set is used as the default; the other two sets will only be discussed when the deviations appear relevant.

In the conversion of units a problem arises from the different parameterizations of salinity in the literature. Weiss [1970, 1971] and Weiss and Kyser [1978] use seawater salinity S , whereas Smith and Kennedy [1983] use the molar concentration

c_{NaCl} of pure NaCl solutions. We relate the two parameters S and c_{NaCl} by equating the mass of salt per unit volume:

$$c_{\text{NaCl}} M_{\text{NaCl}} = S \times \rho(T, S) \quad (3)$$

where M_{NaCl} is the molar mass of NaCl and $\rho(T, S)$ is the density of a sea-salt solution [Gill, 1982]. Justification for this simple approach is given by the results of Weiss and Price [1989], who showed that even for the hypersaline Dead Sea, water solubilities could be estimated from those in seawater with an error of less than 10% by assuming an equal salting-out effect by an equal mass of dissolved salt. For salinities up to 35‰ the use of (3) introduces less than 0.5% deviation between the Weiss and Clever or Benson solubilities, except for He (about 1.5%). In fresh waters, salinity may be estimated from κ_{20} , the electrical conductivity at 20°C according to the methods outlined by Wüest et al. [1996]. For small salinities any rough approximation of S is sufficient. We use the following relation established for CaHCO_3 -dominated waters:

$$S[\text{‰}] = 0.87 \times 10^{-3} \kappa_{20} [\mu\text{S cm}^{-1}] \quad (4)$$

In lakes, κ_{20} rarely exceeds 500 $\mu\text{S cm}^{-1}$; thus S is below 0.5‰, and the influence of S on the solubilities is less than 0.5%. In chemically evolved groundwaters, κ_{20} may be substantially higher, but relevant for the solution of noble gases is the salinity at the time of infiltration, which is usually close to zero.

To calculate moist air equilibrium concentrations $C_i^*(T, S, P)$, the literature values for k_i in pure water are first converted to Bunsen coefficients, and then (2) and (3) are used to introduce the salt dependence. We finally arrive at

$$C_i^*(T, S, P) = \frac{1}{k_i - 1} \frac{\rho(T, 0)}{\rho(T, S)} \frac{V_i}{M_w} \frac{[P - p^*(T)]}{P_0} z_i e^{-K_i c_{\text{NaCl}}(S)} \quad (5)$$

where M_w is the molar mass of water (18.016 g mol^{-1}), P_0 is the reference pressure (1 atm), $p^*(T)$ is the saturation water vapor pressure [Gill, 1982], z_i is the volume fraction of gas i in dry air [Ozima and Podosek, 1983], and V_i is the molar volume of the gas i . Real gas values of V_i are used, calculated from the van der Waals equation of state with constants as given by Lide [1994]. These real gas corrections are of minor importance in comparison to experimental uncertainties, even for Kr (0.3%) and Xe (0.6%).

There is one caveat in the calculation of the Weiss solubilities. Because of the water vapor pressure, the moist air equilibrium concentrations are not simply proportional to P . The correct pressure dependence is

$$C_i^*(T, S, P) = C_i^*(T, S, P_0) \frac{[P - p^*(T)]}{[P_0 - p^*(T)]} \quad (6)$$

The atmospheric pressure P is related to the altitude H of the water surface by a barometric altitude formula of the form:

$$P = P_S \times e^{-H/H_0} \quad (7)$$

where P_S is the pressure at sea level and H_0 is the scale height in meters. This conversion is not unique and should be adapted to local conditions, since H_0 is a function of temperature and humidity [e.g., Gill, 1982] and P_S can also deviate locally from the global average. For instance, in northern Switzerland the average atmospheric pressure reduced to sea level is 1.004 atm [Schüepf and Gisler, 1980]. For this region we used tabulated values of average pressure as a function of altitude. Otherwise,

the constant values $P_S = 1$ atm and $H_0 = 8300$ m were used. With these values, (7) deviates less than 1‰ from the U.S. standard atmosphere for altitudes up to 1800 m.

In addition to the equilibrium concentrations $C_i^*(T, S, P)$ an excess of atmospheric gases has been found in many natural waters. The elemental composition of the excess air is usually assumed to be atmospheric. It can be described by the volume A of dry air injected per gram of water:

$$C_i^{ex} = Az_i \quad (8)$$

Because the excess air is best detectable with Ne, it is often expressed as a relative Ne excess ΔNe , that is, the percentage of the Ne excess relative to the Ne equilibrium concentration. As a rule of thumb, 1% ΔNe corresponds to $A \approx 10^{-4}$ cm³ STP g⁻¹ (this is exact for $T = 22.4^\circ\text{C}$, $P = 1$ atm, and $S = 0\%$). In the ocean a small air excess equivalent to a few percent ΔNe is very common and attributed to injection of bubbles by breaking waves [Craig and Weiss, 1971; Bieri, 1971]. In groundwater an even larger "excess air" component is ubiquitous [Heaton and Vogel, 1981] and attributed to dissolution of air trapped in the pore space. However, a comprehensive description of the processes that lead to the formation of excess air is still lacking.

In some groundwaters the assumption of a purely atmospheric composition of the excess air cannot describe the measured noble gas patterns. Possible explanations could be incomplete dissolution of trapped bubbles or partial loss of the excess air across the water table [Stute *et al.*, 1995a]. Both processes result in an enrichment of the heavy noble gases in the excess air component relative to atmospheric air. Equilibration of the water with a large air reservoir at hydrostatically increased pressure would be equivalent to a rise in pressure and would therefore not require an additional parameter. However, the interpretation of the pressure as directly related to altitude would become questionable. Stute *et al.* [1995b] introduced a model of partial loss of the initial excess air by diffusive reequilibration, which also approximates complicated scenarios involving partial dissolution of bubbles. Note that the degassing in this model happens shortly after infiltration, close to the water table. It should not be confused with possible degassing during sampling. The model requires a new parameter which Stute *et al.* [1995b] expressed as the remaining fraction of the initial Ne excess:

$$\frac{C_i^{ex}}{C_i^{ex}(0)} = \left(\frac{C_{\text{Ne}}^{ex}}{C_{\text{Ne}}^{ex}(0)} \right)^{D_i/D_{\text{Ne}}} \quad (9)$$

where C_i^{ex} is the remaining excess of gas i after partial reequilibration, $C_i^{ex}(0)$ is the initial excess, and D_i is the molecular diffusion coefficient, which governs the degassing process. We prefer to write the degassing term in a way which more directly refers to the underlying physical process, by defining the reequilibration parameter $R = -\ln [C_{\text{Ne}}^{ex}/C_{\text{Ne}}^{ex}(0)]$:

$$C_i^{ex} = C_i^{ex}(0)e^{-R(D_i/D_{\text{Ne}})} \quad (10)$$

Values for D_i were taken from Jähne *et al.* [1987] except for Ar. D_{Ar} was interpolated from the diffusion coefficients of the other noble gases assuming that D is inversely proportional to the square root of the atomic mass.

In addition to noble gases derived from the atmosphere, some noble gas isotopes can originate from other sources [Ozima and Podosek, 1983]. Most prominently, ⁴He is produced in the α -decay series of U and Th in crustal rocks. In

deep groundwaters this radiogenic ⁴He component is often many orders of magnitude larger than the atmospheric equilibrium concentration. Hence ⁴He cannot be used for the determination of infiltration conditions but can be used as a qualitative indication of groundwater residence time. ³He is rarely an alternative to ⁴He, because nonatmospheric ³He can originate from nucleogenic production in the crust, from a migration of mantle gases characterized by a high ³He/⁴He ratio, or from tritium decay, which can again be used as a dating tool. Radiogenic ⁴⁰Ar produced by decay of ⁴⁰K is masked by the large atmospheric Ar concentration in near-surface waters but may be found in deep waters and brines. In such cases, ³⁶Ar can be used to calculate the atmospheric Ar component. Other nonatmospheric noble gas isotopes are irrelevant for this study.

In summary, a complete model for atmospheric noble gases in water is given by

$$C_i = C_i^*(T, S, P) + Az_i e^{-R(D_i/D_{\text{Ne}})} \quad i = \text{Ne, Ar, Kr, Xe} \quad (11)$$

This equation can be applied for He only if the presence of nonatmospheric He components can be excluded. Otherwise, the difference between the measured He concentration and the result of (11) evaluated for He yields the best estimate of the nonatmospheric He component.

The nonlinear equation system (11) contains five unknown parameters and one equation for each of the four or five applicable noble gases. Because of the errors of the measured concentrations, it is not advisable to look for exact solutions of (11) but for parameter combinations that provide model predictions which agree with the measured data within experimental error. If some parameters are known or prescribed, such that the number of free parameters becomes smaller than the number of applicable measured gases, (11) is overdetermined and can be solved by least squares techniques. Different conceptual submodels can be derived from (11). For instance, in surface waters it appears reasonable to set A and R to zero thus reducing the model to atmospheric equilibrium. In groundwaters, at least A has to be included. Often, S and P are well known, and T is searched for. In some situations, such as systems with large salinity gradients or altitude variations, S or P may become the wanted parameters.

3. Methods

3.1. Experimental Methods

Details on our experimental methods for the mass-spectrometric determination of noble gas concentrations in water samples will be published elsewhere (U. Beyerle *et al.*, A mass spectrometric system for the analysis of noble gases from water samples, submitted to *Environmental Science and Technology*, 1999). Sampling and extraction procedures are essentially identical to those used for the analysis of the light noble gases He and Ne only [Kipfer *et al.*, 1994]. Here only the derivation of experimental uncertainties is discussed because they play a decisive role in the parameter fitting described in this work.

Calibration is regularly performed with aliquots of an air standard, which are known with an accuracy of about 0.3%. This systematic source of error is of minor importance compared to statistical fluctuations of the instrument sensitivity, which typically are $\pm 1\%$. Therefore the assumption of independent, normally distributed errors is a reasonable approxi-

mation. The statistical errors are estimated from the standard deviation of the calibrations within a measurement run. For the 111 samples used for this study, the average errors were 0.6% for He, 0.9% for Ne, 0.7% for Ar, 1.0% for Kr, and 1.3% for Xe. The consistency of the error estimate is continuously checked by analysis of aliquots of a water standard. The reproducibility of 12 water standard measurements made so far is in good agreement with the long-term mean errors and is consistent with longer time series of standards for He and Ne only [Aeschbach-Hertig, 1994; Aeschbach-Hertig et al., 1996].

3.2. Numerical Methods

Any subset of up to three of the five parameters in (11) can be determined such that the sum of the weighted squared deviations between the modeled and measured concentrations is minimized. The goal function is

$$\chi^2 = \sum_i \frac{(C_i - C_i^{\text{mod}})^2}{\sigma_i^2} \quad (12)$$

where C_i^{mod} are the modeled concentrations, C_i are the measured concentrations, and σ_i are their experimental 1σ errors.

Standard methods of least squares fitting can be applied to solve the minimization problem (12). We employed the Levenberg-Marquardt method [Press et al., 1986] to minimize χ^2 . The code used for this work was developed based on the standard mathematical software MATLAB®. It includes tools for the statistical and graphical analysis of the output data. It allows one to select any combination of up to three free parameters and to choose whether He shall be used as a fit target or not. The user may also choose to restrict the range of possible parameter values, although this option should be used with caution. Solutions with unphysical values (e.g., negative values of any parameter) may indicate that the applied conceptual model is not appropriate.

The approach described here to derive environmental parameters from noble gas concentrations in waters is essentially identical to the method used by Ballentine and Hall [1999] but has been developed completely independently. The method is, however, quite different from the traditional approach to determine recharge temperatures from noble gases in groundwaters [Rudolph, 1981; Stute, 1989; Pinti and Van Drom, 1998]. The latter method uses the temperature as fit target; that is, it looks for parameter values of A and R (P and S are prescribed) such that the spread of the temperatures calculated individually from Ne, Ar, Kr, and Xe is minimized. The measured concentrations are corrected for (fractionated) excess air, and a temperature is calculated from the corrected concentration of each noble gas. This process is iteratively repeated with varying amounts of excess air until optimum agreement between the four temperatures is reached. The standard deviation of the individual temperatures may then be used to estimate the error of the mean noble gas temperature. In addition, Monte Carlo simulations have been carried out to determine the uncertainty of noble gas temperatures [Stute, 1989; Stute et al., 1995b].

The inverse approach has a number of advantages compared to the traditional iterative method. First, it treats all physical parameters in the same way, rather than focusing on temperature alone. Thus several subsets of the parameters, corresponding to different conceptual models as to how to describe the measured noble gas concentrations, can be calculated and compared.

Second, the contribution of each noble gas to the goal function is weighted with the individual experimental errors. In the iterative approach the experimental errors are not considered, and the temperature derived from each gas has equal weight. However, because the sensitivity to temperature increases with molecular weight, the temperatures derived from the heavy noble gases should have the highest weight if all gases were determined with the same precision. In the inverse approach the contributions of the heavy gases to χ^2 in (12) react more sensitively to variations of the temperature parameter than those of the light gases. Therefore temperature is mainly restricted by the Kr and Xe concentrations. Because of the different weighting, the temperatures derived from the two approaches differ slightly. However, if there is no systematical bias between the temperatures derived from the individual noble gases, we should not expect a systematical deviation between the two approaches.

A third advantage is that the experimental errors can be used to judge the goodness of the fit, that is, the validity of the conceptual model that was adopted to describe the data. The model selection is based on the χ^2 test. The expected minimum value of χ^2 is the number of degrees of freedom $\nu = n - m$, where n is the number of data points (4 or 5) and m is the number of free parameters (1 to 3). The probability for χ^2 to be higher than a given value can be obtained from the χ^2 distribution with ν degrees of freedom. If this probability is lower than some cutoff value, the model has to be rejected. In this study we reject models with probability $p < 0.05$. If a model has to be rejected, a different model, possibly with an additional parameter, should be used. If for any sample no model yields an acceptable χ^2 value, its noble gas abundance pattern cannot be interpreted in the framework of (11). Very low χ^2 values, corresponding to very high probabilities, also indicate a problem. Possible reasons could be overestimated or correlated experimental errors, which we expect to be only minor effects in our data (see section 3.1). In view of the small number of degrees of freedom, overparameterization may also be a reason for low χ^2 values. As a consequence, we argue for the use of the simplest model that yields acceptable χ^2 values.

The χ^2 test can be generalized to assess the applicability of a conceptual model to a whole data set consisting of N samples. Applying the same model to each sample of the data set may be interpreted as fitting one model with Nm free parameters to Nn data points. The χ^2 value for the whole data set is then the sum of the χ^2 values of the individual samples, and the number of degrees of freedom is $N\nu$. This data set χ^2 value also follows a χ^2 distribution but with a much larger number of degrees of freedom than for each individual sample. Therefore a conceptual model may not be consistent with a whole data set, although it cannot be rejected based on any single sample.

The fourth advantage of the inverse approach is that confidence intervals for the derived parameters can be calculated, and the correlation between the parameters can be studied. In the theory of least squares fitting, uncertainties of the estimated parameters are derived from the covariance matrix [Press et al., 1986]. These errors correspond to a rigorous propagation of the experimental uncertainties if the latter are independent and normally distributed. If this condition is not fulfilled, the errors may be propagated numerically by a Monte Carlo simulation. We implemented this possibility in our program. However, the errors obtained from the covariance matrix or from Monte Carlo simulations do not take into account how well the model actually fits the data. Thus standard least

Table 1. Synthetic Data Sets for $T = 10^\circ\text{C}$, $S = 0\%$, $P = 1 \text{ atm}$, $A = 3 \times 10^{-3} \text{ cm}^3 \text{ STP}^{-1} \text{ g}^{-1}$, and $R = 0$

Solubility	He, $\text{cm}^3 \text{ STP g}^{-1}$	Ne, $\text{cm}^3 \text{ STP g}^{-1}$	Ar, $\text{cm}^3 \text{ STP g}^{-1}$	Kr, $\text{cm}^3 \text{ STP g}^{-1}$	Xe, $\text{cm}^3 \text{ STP g}^{-1}$
Weiss*	6.217×10^{-8}	2.563×10^{-7}	4.141×10^{-4}	9.445×10^{-8}	1.344×10^{-8}
Clever†	6.237×10^{-8}	2.576×10^{-7}	4.134×10^{-7}	9.440×10^{-8}	1.344×10^{-8}
Benson‡	6.271×10^{-8}	2.586×10^{-7}	4.123×10^{-7}	9.465×10^{-8}	1.343×10^{-8}

*Weiss [1970, 1971], Weiss and Kyser [1978], and Clever [1979b] for Xe.

†Clever [1979a, 1979b, 1980].

‡Benson and Krause [1976].

square algorithms often scale the experimental errors as well as those of the parameters with the factor $(\chi^2/\nu)^{1/2}$ [Rosenfeld *et al.*, 1967]. The philosophy behind this scale factor is that one has more confidence in the applied model than the stated experimental errors. Therefore the experimental errors are estimated from the observed deviations between modeled and measured values by using the condition that the expected value of χ^2 is ν .

Although this scaling method has no strict mathematical foundation [Brandt, 1992], it may give a more realistic estimate of the uncertainty of the parameters in cases when χ^2 is significantly larger than ν . For this reason we chose to state conservative uncertainties for the parameters by using the scaled error estimate whenever it is larger than the error obtained from the covariance matrix. However, given the good control on experimental errors (see section 3.1), large values of

χ^2/ν are more likely to indicate that the chosen conceptual model is inappropriate than that the experimental errors were underestimated. Therefore, for data sets that cannot be satisfactorily described by (11), new conceptual models should be sought.

Besides the uncertainties of the parameters, their mutual correlation can also be obtained from the covariance matrix. High correlations between two or more parameters occur when a change in one parameter can be almost compensated by corresponding changes in the others. Thus such combinations of parameters are poorly identifiable. Since the noble gas solubilities exhibit systematic dependencies on the parameters, it is likely that some parameters are indeed correlated.

4. Testing of the Methods

4.1. Synthetic Data

Great effort was made to verify the applied numerical procedures. Synthetic data were calculated from (11) with varying parameter values (T from 0° to 30°C , P from 0.5 to 1 atm, S from 0 to 35%, A from 0 to $10^{-2} \text{ cm}^3 \text{ STP g}^{-1}$, and R from 0 to 1). Errors of 1% were assigned to each noble gas concentration, and fits of Ne through Xe were performed with different choices of free parameters. With initial parameter values varying in the above range, the least squares routine almost always returned the exact solutions within numerical precision. Only in one case with T , S , and P as free parameters (T - S - P model), did the solver converge to a local minimum (with negative S). Thus, in general, the numerical procedure appears to be stable.

The synthetic data sets were used to explore some general properties of the problem. For example, consider a hypothetical groundwater sample that equilibrated at $T = 10^\circ\text{C}$ and $P = 1 \text{ atm}$, has a contribution of excess air of $A = 3 \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$ ($\Delta\text{Ne} = 27\%$), and $S = R = 0$ (Table 1). The T - A model yields accurate results, with errors of 0.22°C for T and $0.15 \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$ for A (Figure 1a). This result was cross-checked with Monte Carlo simulations by generating realizations of concentrations that were normally distributed around the original values within the assigned error of 1%. For each generated data set the optimal parameter values were calculated, and their distribution was analyzed. Since the distribution of the parameters is not necessarily normal, its median and the width which contains 68.3% of the values were calculated. For example, a Monte Carlo run with 1000 realizations yielded approximately normal parameter distributions with $T = (10.007 \pm 0.216)^\circ\text{C}$ and $A = (2.995 \pm 0.147) \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$. With only 100 realizations, similar results were obtained. Thus the Monte Carlo errors closely correspond to the errors calculated from the covariance matrix, as

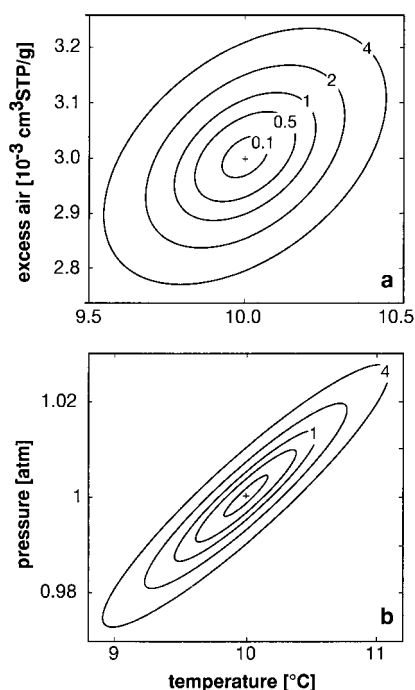


Figure 1. Contours of the χ^2 surface in the parameter space, calculated for the first synthetic data set of Table 1 with the Weiss solubilities. Contours for $\chi^2 = 0.1, 0.5, 1, 2,$ and 4 are shown in both plots. (a) T - A model. T and A are not correlated, the χ^2 surface is nearly circular, and the minimum is well defined. (b) T - P - A model, with a two-dimensional-section in the T - P plain. Note the larger T scale compared to Figure 1a. T and P are correlated, and the χ^2 surface is strongly elliptical, which increases the parameter errors [see Press *et al.*, 1986].

Table 2. Concentration Changes Induced by Specified Small Changes of the Parameters Relative to the First Data Set of Table 1

Parameter Changes	ΔHe , %	ΔNe , %	ΔAr , %	ΔKr , %	ΔXe , %
$\Delta T = 1^\circ\text{C}$	-0.32	-0.74	-2.12	-2.71	-3.35
$\Delta S = 1\%$	-0.42	-0.48	-0.67	-0.72	-0.77
$\Delta P = 0.01 \text{ atm}$	0.76	0.80	0.94	0.98	0.99
$\Delta A = 10^{-4} \text{ cm}^3 \text{ STP g}^{-1}$	0.84	0.71	0.23	0.12	0.06
$\Delta R = 0.1$	-4.44	-2.03	-0.42	-0.14	-0.06

expected from theory in the case of normally distributed errors [Press *et al.*, 1986]. These errors thus represent the optimal precision of the parameters that can be expected for the assigned precision of the concentrations.

However, if in our example we fit S or P as the third free parameter, the temperature error increases to 2.0°C . The reason for this problem can be made evident by a plot of the χ^2 surface in the parameter space, for example, the T - P plain (Figure 1b). The region of small χ^2 values is a long ellipse oriented along the diagonal. This means that for each variation of T , there is a corresponding value of P , which keeps the change of χ^2 small. An equivalent statement is that T and P are strongly correlated. In fact, the correlation coefficient between T and P , r_{TP} , is 0.994 and so is r_{TS} . Although the uncertainties for both T and P individually are small, they become large if both parameters are varied at the same time. Thus, for groundwaters it is essential to have a good control on S and P if the temperature is to be determined with high accuracy. Fortunately, this is usually no problem. However, if S or P shall be determined, then T should be known.

In order to investigate both the sensitivity of the concentrations with respect to the parameters and the correlations among the parameters, the relative changes of the concentrations for standard changes of the parameters were calculated (Table 2). Obviously, the dependence of noble gas concentrations on the parameters follows some systematic trends. The effects of T and S increase with molar mass of the gas, whereas the effect of excess air decreases, because the solubilities strongly increase with the molar mass. Degassing also affects preferentially the light noble gases, particularly He, because of their higher diffusivities. Pressure has a uniform effect relative to equilibrium concentrations, but in the presence of excess air it is relatively more important for the heavy noble gases. From Table 2 it can easily be seen which parameter combinations are clearly identifiable, because they have very different patterns of effects (e.g., T and A), and which are hard to separate, because they have almost identical effects (e.g., S and P).

As a further test, synthetic data generated with the alternative solubility data were evaluated with the standard choice of solubilities. The corresponding synthetic data sets are listed in Table 1. The three sets agree very well for Kr and Xe. However, the solubilities of Benson are about 0.5% lower than those of Weiss for Ar and are about 1% higher than those of Weiss for He and Ne. The data of Clever, which are, in part, based on the other two sets, lie in between. For instance, fitting the Benson data set of Table 1 with the Weiss solubilities and a T - A model yields $T = (10.07 \pm 0.21)^\circ\text{C}$ and $A = (3.12 \pm 0.15) \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$. For the Clever data set the deviations from the true parameter values are only about half as big. The choice of solubilities does not significantly affect

the parameters because the largest differences between the three sets of solubilities are of the same magnitude as the experimental uncertainties (1%). However, in contrast to random errors the switch of solubilities introduces systematical deviations.

4.2. Air-Equilibrated Water

As an overall test of the method including the experimental and numerical methods as well as the literature solubilities, samples of air-equilibrated water at several different temperatures were produced. Three large ($\sim 30 \text{ L}$) containers three-quarter filled with tap water and open to ambient air were placed in temperature stabilized rooms at temperatures of about 4° , 15° , and 30°C (samples C1–C3). A fourth container was placed in our noble gas laboratory, where the temperature is relatively stable near 20°C (sample L1). The water was very gently stirred to accelerate gas exchange while avoiding any occurrence of bubbles. The water was exposed for approximately 10 days, since we estimated that it may take several days to reach complete equilibrium (height of the water column about 0.5 m and gas exchange velocities of the order of 1 m d^{-1}). Both water temperature and ambient atmospheric pressure were monitored over the entire period. Whereas temperature soon became stable within the precision of measurement ($\pm 0.1^\circ\text{C}$), the pressures varied typically by a few mbar over the time of exposure. The average pressure of the last 7 days before sampling was used. A few measurements of electrical conductivity were made in order to estimate salinity (except for sample L1). Samples were drawn from a bottom outlet of the containers with the usual techniques.

Surprisingly, it is not possible to fit all five noble gases with the assumption of atmospheric equilibrium, because of an excess of He. The Ne concentrations show that this excess cannot be of atmospheric origin, except for sample L1. We suspect that the He partial pressure in the air-conditioned rooms, located below ground level and vented only artificially, was slightly enhanced relative to air, because of the presence of radiogenic He. Indeed, the $^3\text{He}/^4\text{He}$ ratios of samples C1–C3 are slightly below the atmospheric equilibrium value given by Benson and Krause [1980]. Thus, for these samples, He was excluded from the fit for T as the only free parameter. Sample L1 can be fitted in the same way. However, only the T - A model fits the measured concentrations of all five gases.¹ This interpretation of sample L1 appears more likely and yields the better agreement with the measured water temperature.

Figure 2 shows the difference between the actual water temperature and the noble gas temperatures calculated with all three sets of solubilities. All solubilities yield very similar temperatures, which agree with the measured temperatures within error. Note that the error of the noble gas temperatures slightly increases with temperature (from $\pm 0.2^\circ$ to $\pm 0.3^\circ\text{C}$), because of the decreasing temperature sensitivity of the solubilities. On average, the noble gas temperatures are about 0.1°C lower than the directly measured temperatures. The excess air in sample L1 can be accurately determined by using He as additional constraint. However, the result depends on the choice of solubilities and varies from $(1.4 \pm 0.3) \times 10^{-4} \text{ cm}^3$

¹ Supporting tables are available on diskette or via Anonymous FTP from kosmos.agu.org, directory APEND (Username = anonymous, Password = guest). Diskette may be ordered from American Geophysical Union, 2000 Florida Avenue, N.W., Washington, DC 20009 or by phone at 800-966-2481; \$15.00. Payment must accompany order.

STP g^{-1} (Benson) to $(2.3 \pm 0.3) \times 10^{-4} \text{ cm}^3 \text{ STP g}^{-1}$ (Weiss). For the other three samples the solubilities of Clever and Benson do not favor the presence of any excess air, whereas the Weiss solubilities tend toward positive values of excess air. In fact, the Weiss solubilities always yield the highest values for excess air, because they are about 1% lower than those of Benson for He and Ne. Therefore care should be taken in the interpretation of very small amounts of excess air, for example, in lakes or the ocean. Overall, the equilibrated samples confirm the consistency of the experimental and numerical methods, although slight systematical deviations cannot be excluded.

4.3. Comparison With the Iterative Technique

For comparison, 43 samples from a shallow alluvial aquifer which contains unfractionated excess air (see section 6.1) were evaluated with the iterative technique and solubilities as used by *Stute* [1989], as well as with our inverse procedure, using all three sets of solubility data. The resulting noble gas temperatures of all samples agree within error, independent of the choice of solubility data (Figure 3). Furthermore, the errors estimated from the standard deviation of the individual noble gas temperatures in the iterative technique are, on average, in good agreement with the rigorous error estimates obtained with the error-weighted inverse method.

The noble gas temperatures calculated with our procedure and the Weiss solubilities are, on average, 0.07°C higher than those calculated with the iterative technique, although the same solubilities were used except for Kr. The deviation is a result of the fact that for this data set the Xe temperature calculated with the iterative approach is, on average, 0.17°C higher than the mean noble gas temperature. Because the Xe concentration has the largest influence on the temperature in the inverse approach, this small systematic bias leads to a difference between the two methods. However, this is a feature of this particular data set and does not indicate a general offset

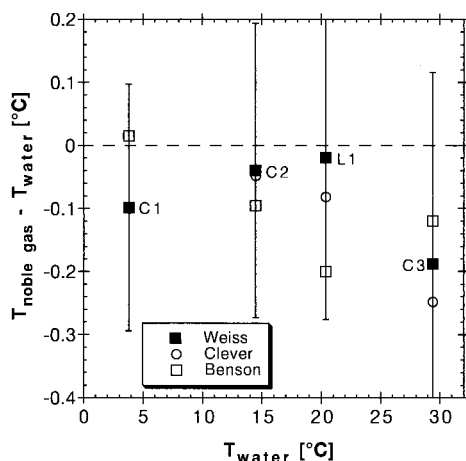


Figure 2. Deviations of calculated noble gas temperatures from directly measured water temperature of artificially equilibrated water samples. Calculations were performed with the solubilities of *Weiss* [1970, 1971] and *Weiss and Kyser* [1978], *Clever* [1979a, b, 1980], and *Benson and Krause* [1976]. The 1σ errors are given for the values calculated with the Weiss solubilities. Samples C1–C3 were evaluated with T as the only free parameter and without the He concentration. For sample L1, He was included and a T - A model was fitted.

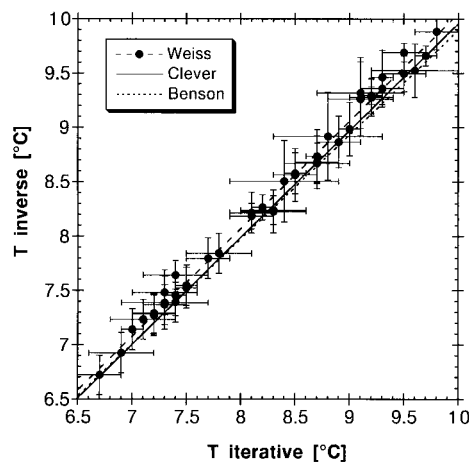


Figure 3. Comparison of noble gas temperatures calculated with the iterative method according to *Stute* [1989] and with our inverse procedure for 43 groundwater samples from the Töss Valley with unfractionated excess air. Points show the results obtained with the Weiss solubilities in the inverse calculations, which is the same database as used in the iterative method, except for Kr. Errors for the iterative technique were estimated from the spread of the individual noble gas temperatures. The lines represent linear regressions through the data obtained with the three different sets of solubility data used in the inverse calculations. The temperatures derived from the two methods closely agree, irrespective of the solubility database.

between the two methods. The strength of the inverse approach is not that it yields more accurate noble gas temperatures but that it allows one to estimate all parameters and that it provides rigorous statistical tools.

5. Lake and River Samples

To our knowledge, no measurements of all five noble gases in lakes have been published, although a number of tritium-He-Ne studies have been performed in lakes [*Torgersen et al.*, 1977; *Kipfer et al.*, 1994; *Aeschbach-Hertig et al.*, 1996]. Yet noble gases are of use for the study of several processes in lakes. For instance, gas exchange and its dependency on diffusivity can be addressed [*Torgersen et al.*, 1982]. Excess air may be less important for lakes than for the ocean, because breaking waves are less frequent, but this remains to be shown. The importance of bubble inclusion in rivers is even more uncertain. Excess air due to inflow of groundwater has been observed in some small alpine lakes [*Aeschbach-Hertig*, 1994]. Thus the interaction of groundwater with rivers or lakes could potentially be studied with noble gases. Furthermore, questions related to the thermal structure of lakes and processes of their deepwater renewal may be addressed by noble gas measurements. Deepwater temperatures in some lakes are significantly affected by the geothermal heat flux [e.g., *Wüest et al.*, 1992], which should lead to a deviation between noble gas and in situ temperature.

In most cases, however, lake and river waters can be expected to be or have been in close equilibrium with the atmosphere at their in situ temperature. Because all relevant parameters related to the calculation of equilibrium concentrations, that is, temperature, salinity, and altitude, can be measured easily and accurately in lakes, they provide a further test of the noble

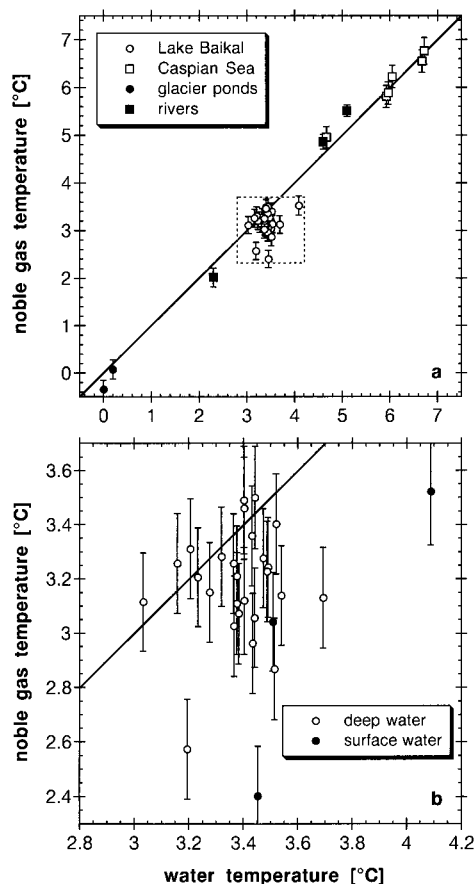


Figure 4. Noble gas temperature of lake and river samples versus in situ measured water temperature. (a) All 40 samples in the temperature range between 0° and 7°C lie close to the line which indicates equal noble gas and water temperatures. The dashed square indicates the position of the enlargement shown in Figure 4b. (b) Detail of Figure 4a showing the 29 samples from Lake Baikal taken in June 1996. Samples from the mixed layer (20 m depth) show relatively large deviations between noble gas and water temperature during this period of rapid warming.

gas method. We present here noble gas results from a large range of surface water systems. A summary of the results is given in Figure 4a, showing the comparison between the calculated noble gas temperatures and directly measured water temperatures. A very good agreement was obtained for 40 samples within a temperature range between 0° and 7°C. One additional sample at about 14°C also gave a reasonable agreement.

5.1. Lake Baikal

In Lake Baikal, the world's deepest lake, the temperature during periods of deepwater renewal in the different basins was of interest. The deep water temperature in Lake Baikal is very uniform, varying only between 3.2° and 3.6°C over a depth range of more than 1000 m [Hohmann *et al.*, 1997]. Salinity is also uniform and very low; a constant value of 0.095‰ was used here. The noble gas concentrations measured in 29 samples in three different profiles, one in each of the three basins of the lake, are also very uniform, with the exception of radiogenic ^4He and tritogenic ^3He excesses increasing with depth [Kipfer *et al.*, 1996; Hohmann *et al.*, 1998]. Thus He cannot be

used as a constraint. Least square fits with T as free parameter yield acceptable fits except for the sample from 20 m depth in the South Basin, which has excess air. Noble gas temperatures of the 20 m samples from all basins are between 0.5° and 1°C lower than water temperatures (Figure 4b), presumably because the profiles were taken in early June during a period of rapid warming of the surface layer, when the noble gases had not yet attained equilibrium at the present water temperature. The noble gas temperatures of the 26 samples from depths greater than 200 m are on average 0.20°C below the in situ temperature. We see several possible reasons for this deviation: (1) A very small part (0.01°C at most) is explained by the neglected difference between in situ and potential temperature because of adiabatic warming; (2) the noble gases may not be in equilibrium in newly forming deep water, as observed in the surface water in spring; (3) diffusive downward fluxes may affect the temperature more strongly than the noble gases; and (4) the noble gas temperatures may be systematically slightly too low, as observed with the equilibrated samples.

An interesting observation is that only the Weiss and Clever solubilities yield acceptable fits of the Lake Baikal data. This can be shown by applying the χ^2 test to the whole data set of 26 deepwater samples. For the T model we have three degrees of freedom for each sample, thus $\nu = 78$ for the whole data set. The sum of the χ^2 values for the Weiss solubilities is 67; thus χ^2/ν is 0.86, indicating an entirely satisfying fit ($p = 0.81$). For the Clever solubilities we obtain a whole data set χ^2 value of 90 which is equally fine ($p = 0.16$). In contrast, the Benson solubilities yield $\chi^2 = 132$ ($\chi^2/\nu = 1.69$), which is highly improbable ($p < 0.001$). On a sample to sample basis, four samples cannot be fitted ($p < 0.05$) with the Benson solubilities. If excess air is introduced as additional free parameter, only the Weiss solubilities yield a good fit ($\nu = 52$, $\chi^2 = 38$, and $p = 0.92$), with an average excess air of 1% ΔNe . For the T - A fit the Clever solubilities yield a χ^2 value of 81 ($p < 0.01$), and those of Benson give $\chi^2 = 120$ ($p < 0.001$). Very similar results are obtained if P is used as second parameter instead of A .

The conclusion for Lake Baikal is that the noble gases are essentially in equilibrium at the water temperature. There are only weak indications of excess air or of warming of the deep water during its residence time of around 10 years [Peeters *et al.*, 1997].

5.2. Caspian Sea

In the Caspian Sea, the world's largest inland water body, the fit with only T as free parameter does not yield acceptable χ^2 values ($p < 0.05$ in four out of six samples and $p < 0.001$ for the whole data set). The T - A model works fine ($\nu = 12$, $\chi^2 = 15$, and $p = 0.24$) and yields a significant excess air component (on average $(3.2 \pm 1.0) \times 10^{-4}$ cm³ STP g⁻¹ or 3% ΔNe). Unfortunately, an excess of radiogenic He, although small, precludes the use of He to better constrain the excess air. The Caspian Sea has a much larger surface area than Lake Baikal and thus has a larger wind fetch, which more frequently gives rise to breaking waves. It appears likely that the Caspian Sea exhibits the same phenomenon of excess air due to bubble injection as observed on the open oceans. All six samples show an excellent agreement of the noble gas temperatures and the in situ temperatures (Figure 4). If the Clever or Benson solubilities are used, the temperatures are slightly lower and the air excess is considerably smaller (mean 2.0×10^{-4} and 1.6×10^{-4} cm³ STP g⁻¹, respectively), but the whole data set χ^2 values are unacceptably high ($\nu = 12$, $\chi^2 = 22$ and 30, respec-

tively, and $p = 0.04$ and 0.003 , respectively). Thus the data from Lake Baikal and the Caspian Sea appear to justify the use of the Weiss solubilities as standard choice.

The Caspian Sea has a mean salinity of approximately 12.5‰ [Peeters *et al.*, 1999]. The good agreement of noble gas and in situ temperatures demonstrates the validity of our salinity parameterization (3), although the ion composition of Caspian Sea water differs from both ocean water and NaCl brines. Vice versa, the salinity of Caspian Sea water can be determined from the noble gas data with a precision of about $\pm 1\%$ if temperature is prescribed. This precision, however, is not sufficient to address questions related to the role of salinity in the physics of the Caspian Sea.

5.3. Ponds and Rivers

Two noble gas samples from small ponds that often form at the ends of alpine glaciers were analyzed in connection with studies of glacial meltwater. The ponds were open to the atmosphere, although some ice was floating in them. Therefore they were expected to be in atmospheric equilibrium at a temperature close to the freezing point and an atmospheric pressure of about 0.72 atm (2700 m altitude). However, the concentrations of Ne through Xe fit these assumptions rather poorly. Better fits are obtained if excess air is taken into account. Excess air in glacial meltwaters may originate from air trapped in the ice. Because there is no reason to expect radiogenic He in the meltwater ponds, He can be used to check the hypothesis of an excess air component, which renders the results conclusive. The model without excess air must be rejected because of very high χ^2 values (32 and 62, respectively, $\nu = 4$, and $p < 0.001$). With excess air the model fits the data nicely (χ^2 of 2.5 and 3.7, respectively, and $\nu = 3$), the noble gas temperatures are in reasonable agreement with the measured temperatures (Figure 4), and the excess air is 1.8×10^{-4} cm³ STP g⁻¹ on average. By inclusion of He as fit constraint, the errors of A are reduced from $\pm 1.0 \times 10^{-4}$ cm³ STP g⁻¹ to $\pm 0.3 \times 10^{-4}$ cm³ STP g⁻¹.

In the course of studies of riverbank infiltration to the groundwater, two small rivers were sampled for noble gases to check the assumption of atmospheric equilibrium. As with the glacial ponds, the equilibrium is expected to hold also for He. Indeed, all three samples from the Töss river in northern Switzerland can be fitted with a simple T model for all five noble gases. The noble gas and measured river temperatures agree within $\pm 0.5^\circ\text{C}$ (Figure 4). The three samples cover a range from 4° to 15°C . However, the equilibrium assumption clearly does not hold for the sample from a tributary of the Brenno River in southern Switzerland. There, a significant air excess of $(3.6 \pm 1.3) \times 10^{-4}$ cm³ STP g⁻¹ results even without including He. The noble gas temperature agrees reasonably well with the measured value. Including He changes the results for both T and A very little but drastically reduces the uncertainty of the excess air to $\pm 0.4 \times 10^{-4}$ cm³ STP g⁻¹.

In summary, the possibility of small amounts of excess air cannot be excluded in ponds and rivers. He is of great value for the study of the excess air, because of its sensitivity to this parameter. Unfortunately, the use of He as a purely atmospheric gas appears possible only in shallow surface water, whereas deep lakes often contain significant amounts of radiogenic ⁴He and tritiogenic ³He.

6. Groundwater Samples

Stute and Schlosser [1993] showed that noble gases in groundwater measure the mean annual ground temperature, which in most cases is closely related to the mean annual air temperature. However, noble gases in groundwater may serve also other purposes than paleotemperature reconstruction. In mountainous areas a determination of the recharge altitude could help to locate the origin of spring water or groundwater. Moreover, the excess air component in groundwaters may carry information which is at present only poorly understood. The conditions and processes that lead to the formation of excess air need more study in order to learn how to model and interpret this component. We present noble gas data from a broad spectrum of aquifers to illustrate the range of conditions that may be encountered.

6.1. Alluvial Aquifers in Switzerland

Our first example is a shallow, unconfined alluvial aquifer near Glattfelden in northern Switzerland, fed by infiltration from the Glatt River. Five samples were taken from boreholes in the immediate vicinity of the river where according to investigations with ²²²Rn [Hoehn and von Gunten, 1989] the age of the groundwater is only a few days. Our ³H/³He dating confirmed these very small ages. The samples from Glattfelden lie between typical surface and groundwater samples, because they have both low excess air and radiogenic He. Their interpretation is not unique. If He is excluded, three of the five samples can be fitted with T as the only free parameter. All samples are consistent with a T - A model, with A ranging between 0 and 8×10^{-4} cm³ STP g⁻¹. If He is included, only the T - A model is applicable. The minimum value of A is then constrained to 2.5×10^{-4} cm³ STP g⁻¹. Apparently, at this site the residence time of the groundwater is so short that the process of excess air formation can actually be observed. It seems to take place within days after infiltration. With all models the resulting temperatures are in close agreement with the temperature of the groundwater measured during sampling, except for one sample.

The second groundwater example is from a nearby and hydrogeologically very similar site, where the Töss River feeds an alluvial gravel and sand aquifer. Samples were taken at different times of the year to investigate the influence of different river water levels on infiltration, mainly by means of ³H/³He dating [Beyerle *et al.*, 1999]. ³H/³He ages range between 0 and 1 year for most of the samples from shallow boreholes and between 1 and 2 years for most of the deeper samples. Noble gases of 48 samples were analyzed to determine the recharge temperature and to study the formation of excess air. In fact, although the river water is close to equilibrium (see section 5.3), all groundwater samples contain appreciable amounts of excess air, even those from wells within meters of the river bank and with vanishing ³H/³He ages within the error of at least a month. Thus a T - A model was used to fit the data, yielding excess air amounts from 3×10^{-4} to 3×10^{-3} cm³ STP g⁻¹. Although there is only little radiogenic excess He, inclusion of He as fit target is not possible for most samples. However, the results of the fits based on the other noble gases can be used to determine the atmospheric ³He component needed for the calculation of the ³H/³He ages.

It is useful to evaluate the χ^2 test for this whole data set of 48 samples. With the T - A model we have two degrees of freedom for each sample thus $\nu = 96$ for the whole data set.

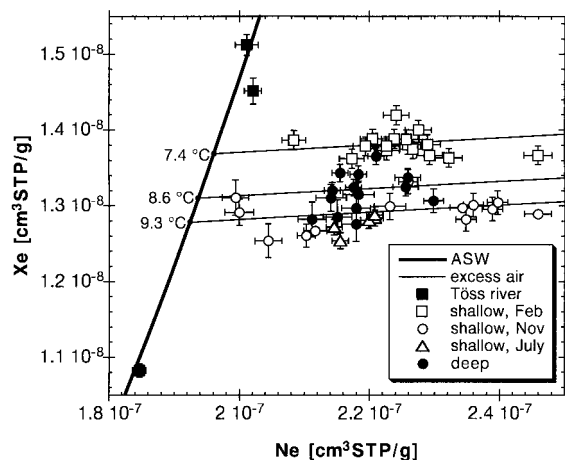


Figure 5. Ne versus Xe concentrations from the Töss River and the adjacent aquifer. The solid line to the left represents the composition of air-saturated water (ASW) as a function of temperature. The fine lines indicate addition of excess air. Groundwater samples are explained by small variations of the recharge temperature and varying amounts of excess air. Samples from shallow boreholes taken in February 1996 (open squares) have the highest Xe concentrations, corresponding to the lowest temperatures (7.4°C). Shallow samples from November 1995–1997 (open circles) and July 1996 (open triangles) indicate warmer recharge temperatures (9.3°C in November). The samples from deeper boreholes (solid circles) lie in between (8.6°C).

The sum of the χ^2 values using the Weiss solubilities is 138 ($\chi^2/\nu = 1.44$), which indicates a poor fit ($p = 0.003$). Therefore one might try to include R as an additional parameter. In that case, ν is 48 and the sum of the χ^2 values is reduced to 27 ($\chi^2/\nu = 0.56$). This, however, is an improbably close fit (χ^2 should be larger than 27 with a probability of 0.994). Including P instead of R as third parameter has the same effect ($\nu = 48$, $\chi^2 = 21$, and $p > 0.999$). We therefore interpret the inclusion of P or R as an overparameterization. Closer inspection of the data shows that the T - A model fails for only six out of the 48 samples ($p < 0.05$ for an individual sample), five of which are the shallow samples taken in July 1996. We therefore assume that these five samples, the only ones taken in summer, constitute a different sample population. By splitting the data set in this way, the χ^2 test for the two subsets yields satisfying results. The five summer samples can be fitted with fractionated excess air ($\nu = 5$, $\chi^2 = 3.6$, and $p = 0.61$), whereas the other 43 samples are consistent with pure excess air ($\nu = 86$, $\chi^2 = 65$, and $p = 0.95$). Interestingly, the T - P - A model still yields unrealistically good fits for both subsets.

We used the 43 unfractionated samples to assess the consistency of our data with the different sets of solubility data. The Clever solubilities yield a perfect fit ($\nu = 86$ and $\chi^2 = 87$). In contrast, the Benson solubilities yield $\chi^2 = 143$ ($\chi^2/\nu = 1.67$) which is not acceptable ($p < 0.001$). On a sample to sample basis, eight samples cannot be satisfactorily fitted ($p < 0.05$) with the Benson solubilities. The Benson solubilities also fail for the five fractionated samples ($\nu = 5$, $\chi^2 = 20$, and $p = 0.001$). As for the lake samples, only the Weiss and Clever solubilities appear to be consistent with our data.

For the 43 samples with unfractionated excess air, temperature can be determined with a precision of $\pm 0.2^\circ\text{C}$. The temperatures range from 6.7° to 9.9°C (Figure 3), with an average

of 8.4°C. Given the rigorous propagation of errors, the scatter of the noble gas temperatures must indicate real temperature variations. The effects of temperature and excess air on noble gas concentrations can be visualized in a graph of Xe versus Ne concentrations (Figure 5). Xe reacts most sensitively to temperature, whereas Ne represents the effect of excess air. The noble gas data form clusters which are separated from each other mainly by different Xe concentrations. These concentration clusters indicate various regimes of groundwater recharge at different temperatures. Samples from shallow depth exhibit a seasonal variation. The samples taken in February 1996 have the highest Xe concentrations, corresponding to the lowest temperatures. They yield, on average, 7.4°C with a standard deviation of only 0.3°C. The shallow samples taken in November of the years 1995, 1996, and 1997 have low Xe concentrations, and they yield an average noble gas temperature of $9.3 \pm 0.4^\circ\text{C}$.

The Xe concentrations of the deep aquifer lie between these extremes, representing the mean recharge temperature of the Töss Valley aquifer of $8.6 \pm 0.5^\circ\text{C}$. This temperature is identical with the measured mean annual temperature of the Töss River [Beyerle *et al.*, 1999] and closely corresponds to the mean annual air temperature in the region [Schüepf, 1981]. The variation of the calculated temperatures of the shallow boreholes is small compared to the seasonal variation of the river water temperature (between 0° and 18°C) and indicates a considerable attenuation of the seasonal temperature amplitude within the first meters of the soil. It is known that the amplitude of temperature oscillations exponentially decreases with depth [e.g., Stute and Schlosser, 1993].

The five shallow samples from July 1996 have similar Xe concentrations as the November samples (Figure 5). However, because these samples were fitted with the T - A - R model, they yield higher temperatures (10.5°C, on average). The parameters A and R are highly correlated ($r_{AR} \approx 0.994$) and therefore have large errors. Temperature is somewhat more weakly correlated to the other parameters ($r \approx 0.96$), but still the uncertainty of T is considerably increased compared to the T - A model. The average temperature error for the five July samples is 0.6°C, although all noble gas concentrations were determined with a precision better than $\pm 1\%$. A peculiarity of the reequilibration model is that it involves high initial air excesses, which are subsequently diminished by degassing to values typical for this aquifer. For the five samples from July 1996 the T - A - R model predicts a mean initial air excess of $10^{-2} \text{ cm}^3 \text{ STP g}^{-1}$ (100% ΔNe), 3 times higher than the largest excess observed in the unfractionated samples. The degassing parameter R is, on average, 1.8, corresponding to a loss of more than 80% of the initial Ne excess. Thus the remaining Ne excess is close to the average of the unfractionated samples (15%).

Major conclusions of the studies of the Glatt and Töss valley groundwaters are that excess air is formed within days after infiltration and within meters from the rivers and that this excess air is mainly unfractionated. If this is the case, infiltration temperatures can be determined with high precision ($\pm 0.2^\circ\text{C}$), allowing one to easily detect seasonal variations of only about $\pm 1^\circ\text{C}$.

6.2. Sandstone Aquifer in Botswana

From a partially confined sandstone aquifer in Botswana we obtained five samples that all exhibit a signature of fractionated excess air. The T - A fit clearly fails for this data set ($\nu =$

10, $\chi^2 = 75$, and $p < 0.001$). Both the T - P and the T - P - A models yield rather low χ^2 values ($\nu = 10$, $\chi^2 = 4.9$, and $p = 0.90$ for T - P and $\nu = 5$, $\chi^2 = 1.2$, and $p = 0.95$ for T - P - A) and clearly unreasonable solutions, with temperatures around 35°C and pressures of about 1.3 atm, although the local mean annual air temperature is 21°C and the atmospheric pressure is less than 0.9 atm (altitude 980 m). Thus, of the conceptual models given by (11), only the partial reequilibration model (T - A - R) is applicable ($\nu = 5$, $\chi^2 = 6.8$, and $p = 0.24$). He cannot be used to verify this choice, because of high concentrations of radiogenic ^4He , although the residence time of the groundwater is only some 50 years according to hydraulic models [Siegfried, 1997].

The T - A - R model yields reasonable temperatures (average 25.2°C), however, with large errors due to the high correlation of the parameters. This problem is aggravated for the Botswana samples compared to the Töss Valley by relatively large experimental errors, high absolute temperatures, and the fact that the average χ^2/ν is larger than 1. The mean error obtained from the propagation of the experimental uncertainties is 2.3°C; scaled by the factor $(\chi^2/\nu)^{1/2}$, it increases to 2.6°C. Even the smaller error estimate is sufficient to explain the standard deviation of the calculated noble gas temperatures of 2.1°C. It is thus consistent to assume that the five samples measure the same recharge temperature ($25^\circ \pm 2^\circ\text{C}$), which is apparently somewhat higher than the mean annual air temperature in the region (21°C).

As in the case of the Töss Valley, the reequilibration model involves very high initial air excesses, which are subsequently diminished by degassing by about a factor of 5. The average initial excess air is $25 \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$ (290% ΔNe) for the Botswana samples. We find it astonishing that the model predicts initial air excesses of a magnitude that is rarely observed, whereas the remaining Ne excesses fall in the range typically found in groundwaters. It is certainly one of the major challenges of the noble gas method to verify this model or to find alternative models to describe the observation of fractionated excess air.

Despite its problems the reequilibration model is the best currently available model to describe noble gas signatures found in some groundwaters. It appears to yield approximately correct temperatures, when compared to mean annual ground temperatures [Stute *et al.*, 1995b]. Because the uncertainty of noble gas temperatures increases when reequilibration is present, care should be taken with experimental precision in such cases. Furthermore, the precision of the temperature estimates in paleoclimate studies may be increased by averaging the results of several samples from each climate stage.

6.3. Recharge Altitude of Alpine Groundwaters

The last set of groundwater samples is used to investigate the potential of the method for the determination of recharge altitude in mountainous areas. Four samples from a shallow aquifer in the alpine valley Engadin were taken at an altitude of about 1800 m. Three samples were obtained from a shallow aquifer in the Val Roseg at an altitude of about 2000 m and a distance of some 2 km from a glacier. One sample was taken from a thermal spring near Bad Ragaz at an altitude of about 700 m. In all cases the water may have infiltrated at altitudes substantially higher than at the place of sampling.

Therefore we have to treat pressure as a free parameter, and a logical approach would be to fit the T - P - A model. However, owing to the high correlations in this model, quite erratic

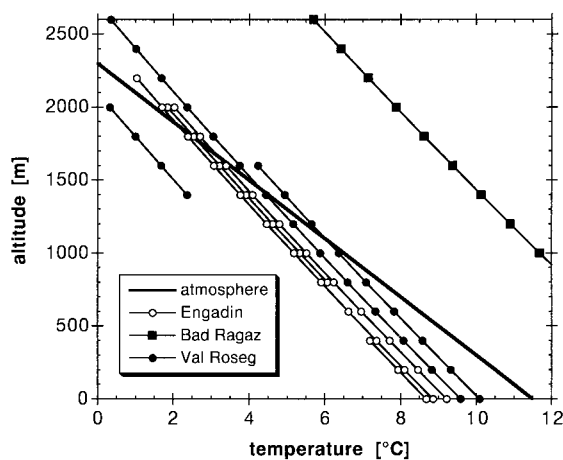


Figure 6. Noble gas temperatures of alpine groundwaters in dependence of the assumed recharge altitude. The results of T - A fits for a series of prescribed altitudes are shown as points. The points obtained from each sample are connected by lines, illustrating the pressure dependence of the calculated noble gas temperatures. Only results from statistically significant and physically reasonable T - A fits are shown ($p \geq 0.05$ and $A \geq 0$). The bold line represents equation (13), the local relationship between mean annual air temperature and altitude. If the recharge temperature was equal to the mean annual air temperature, the intersection of each sample line with the bold line would indicate the recharge altitude. This appears to be approximately true for the Engadin samples, whereas the other samples must have infiltrated at temperatures higher than the mean annual air temperature.

results and large errors are obtained for P or altitude H . In this discussion, P and H are always related by (7). Three of the four Engadin samples give relatively uniform altitudes between 800 and 1000 m, whereas one yields -500 m, with uncertainties of about ± 500 m. Obviously, all these altitudes are too low, since the samples were taken at 1800 m. For the Val Roseg samples the altitude can be estimated with an uncertainty of ± 700 m, but the results scatter greatly, between 100 and 2800 m. The thermal water from Bad Ragaz yields an altitude of 1600 ± 700 m, and a temperature of $9.3^\circ \pm 2.7^\circ\text{C}$. However, mean annual temperatures at 1600 m altitude in the Swiss Alps are only about 3°C; thus the T and H results are inconsistent.

Hence we tried to determine the recharge altitude by looking for pairs of T and H that are consistent with the local relationship between air temperature and altitude. From the climate data given by Schüep [1981], the following approximate relation was derived:

$$T[^\circ\text{C}] = 11.5 - 0.005 \times H[\text{m}] \quad (13)$$

For this approach a series of altitudes between 0 and 3000 m were prescribed and a T - A model was then solved for each altitude. The results are nearly straight lines in the T - H plain (Figure 6). Consistent T - H pairs are those which intersect the straight line given by (13). Unfortunately, the lines intersect at a small angle, and the solutions are therefore not precisely defined. For three of the four Engadin samples, there are intersections close to the sampling altitude of 1800 m. These samples may therefore be interpreted as water which infiltrated locally at the mean annual temperature of about 2.5°C. For the samples from Val Roseg the intersections lie at too low altitudes. Or, since we know that recharge must have taken

place at altitudes higher than 2000 m, they indicate noble gas temperatures above the local mean annual air temperature. In fact, this is not so surprising, since mean annual temperatures at these altitudes are close to the freezing point. Thus recharge can only take place during the warm season. Moreover, *Smith et al.* [1964] showed that in cold regions with long periods of snow cover, ground temperatures can be several degrees above the mean annual air temperatures.

These arguments appear insufficient to explain the high noble gas temperature of the thermal water from Bad Ragaz. Nevertheless, this water probably infiltrated as meteoric water at high altitude and later picked up heat (spring temperature is 36°C) and radiogenic gases during deep circulation. It has by far the highest amount of radiogenic He of the samples used in this study, and it is the only sample with significant radiogenic ^{40}Ar ($^{40}\text{Ar}/^{36}\text{Ar} = 300 \pm 1$). Thus ^{36}Ar was used to calculate the atmospheric Ar concentration.

A last attempt to determine the recharge altitude can be made for the samples from Engadin and Val Roseg. Since these are shallow, young groundwaters, it is reasonable to assume that their temperature has not greatly changed since the time of infiltration. Hence the temperature measured during sampling can serve as an approximation of the recharge temperature. Then, only P and A have to be fitted, yielding much better defined altitude estimates. Unfortunately, the water temperatures were not precisely measured for all the alpine samples. With the approximate temperature of 3°C, three of the four Engadin samples yield altitudes between 1600 and 1700 m, with an uncertainty of ± 60 m. One sample cannot be fitted with the P - A model. These altitudes are consistent with local infiltration at around 1800 m if the uncertainty of the estimate of the recharge temperature is taken into account (compare Figure 6). Of the three Val Roseg samples, two are from very shallow boreholes and had temperatures of about 1° and 2°C. They yield reasonable recharge altitudes of 1800 and 2100 m, respectively. The third well was deeper and had warmer water (4.5°C). With this temperature prescribed, an altitude of only 1500 m is obtained. Of course, the water must have infiltrated at a higher altitude and lower temperature.

To summarize, the determination of recharge altitude is hampered by two independent problems. First, the model parameters T and P are highly correlated, especially if excess air is present. Second, the relationship between the two model parameters resembles strongly the meteorological temperature-altitude relation thus limiting the use of the latter as an additional constraint. The only way to obtain well-defined altitude estimates is to prescribe the recharge temperature, if it can be accurately estimated.

7. Conclusions

The numerical method discussed in this study provides a general and flexible tool for the interpretation of dissolved noble gases in natural waters. In particular, it allows one to decide on statistical grounds between different conceptual models to explain the observed concentrations, for example, with or without excess air or partial reequilibration. Furthermore, it yields quantitative error estimates for the derived environmental parameters. Both the potential and the limitations of the use of noble gases to infer environmental parameters can be investigated.

The results from artificially equilibrated water, lakes, rivers,

and groundwaters demonstrate the strength of noble gases as temperature indicators. With a state of the art experimental precision of about $\pm 1\%$ on noble gas concentrations, temperature can be determined with a precision and accuracy of $\pm 0.2^\circ\text{C}$ to $\pm 0.3^\circ\text{C}$ (depending on temperature) if all other parameters are known. Similarly, the altitude (atmospheric pressure) or salinity at the time of equilibration can be determined accurately (± 40 m or $\pm 0.7\%$, respectively). Purely atmospheric excess air can easily be fitted in addition to any one of the parameters T , S , or P (errors increase slightly to typically $\pm 0.3^\circ\text{C}$, ± 60 m, and $\pm 1.2\%$). However, there are inherent limitations to the simultaneous determination of pairs of the parameters T , S , and P , particularly if excess air is present. The systematic dependency of the noble gas solubilities on these parameters causes an effective correlation between them. For the same reason, fractionation of the excess air component according to the partial reequilibration model of *Stute et al.* [1995b] diminishes the precision of the noble gas thermometer. Nevertheless, there are groundwaters for which the reequilibration model is at present the only conceptual model that yields reasonable and robust temperature estimates. Further study of the formation and evolution of the excess air component in groundwaters is needed to improve the interpretation of dissolved noble gases in such cases.

Application of the method to several case studies in different natural aquatic systems was successful. Lake Baikal water appears to be in atmospheric equilibrium at a temperature only slightly below the in situ temperature, except for radiogenic and tritiogenic He excesses in the deep water. In contrast, the Caspian Sea exhibits a small excess of atmospheric air, similar to the open ocean. River samples were mostly in equilibrium with the atmosphere. Nevertheless, shallow groundwater that infiltrated from the Töss River in Switzerland to an alluvial aquifer contains mostly unfractionated excess air, with a Ne excess of up to 30%. Seasonal variations of recharge temperature could be resolved in this young groundwater. Noble gas patterns of some samples from the Töss Valley, as well as all samples from a sandstone aquifer in Botswana, could only be modeled with the assumption of partial reequilibration. As a consequence, the uncertainty of the derived recharge temperatures increased to between $\pm 0.5^\circ$ and $\pm 3^\circ\text{C}$. The recharge altitude of groundwater from several locations in the Swiss Alps could only be accurately determined if the recharge temperature could be estimated.

Although the differences between literature data for the noble gas solubilities are small, the best fits to our data of 107 samples from natural aquatic systems were obtained with the solubilities of *Weiss* [1971, 1971] and *Weiss and Kyser* [1978]. For all samples, reasonable models to explain the observed noble gas concentrations could be found. The noble gases provide a robust, reliable, and precise tool to infer certain environmental parameters from natural waters.

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