A new software tool for the analysis of noble gas data sets from (ground)water

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ABSTRACT

In this article we present the software *PANGA* which is a new open-source tool for the evaluation of noble gas data from (ground)water samples. In addition to most of the features of traditionally used software like *NOBLE*, it includes among others easy-to-use methods for Monte Carlo simulations and analyses, as well as support for newer excess air models and ensemble fits. We verify *PANGA's* results for two data sets by comparing them with the results of *NOBLE*, using different excess air models. We conclude this study with a set of recommendations for the evaluation of noble gas data sets, giving detailed step-by-step instructions, including descriptions of the Monte Carlo patterns most commonly observed.

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Software availability

Name of software: PANGA ("Program for the Analysis of Noble GAs data")
Developer: Michael Jung, E-mail: panga@mjung.org
Year first available: 2013
Software required: Operating systems Windows XP or newer, MacOS 10.8 or newer, or Linux
Hardware required: Any hardware that runs one of the above operating systems
Program language: C++
Program size: about 9 MB
Availability and cost: Compiled binaries are available freely for download on http://www.iup.uni-heidelberg.de/tools/PANGA. A link to the GitHub repository of the source code is also provided there
PANGA is free software: It can be redistributed and/or modified under the terms of the *GNU General Public License* version 3 as published by the *Free Software Foundation* (http://www.gnu.org/licenses/gpl-3.0.en.html)

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1. Introduction

Noble gases, being chemically inert and having a well-known atmospheric source, are useful tracers in many geochemical, environmental and in particular aquatic systems (Burnard, 2013). Dissolved noble gases in water have become widely used tools in environmental systems such as oceans, lakes, groundwater, sediment pore water, or even speleothem fluid inclusions (Stanley and Jenkins, 2013; Brennwald et al., 2013; Kluge et al., 2008), with two main applications. The first concerns age dating of the water, where several methods based on noble gases are available, including the accumulation of tritiogenic ^{3}He (^{3}H-^{3}He method) and radiogenic ^{4}He (Kipfer et al., 2002). The second major application is noble gas thermometry (Stute and Schlosser, 1993; Aeschbach-Hertig and Solomon, 2013), where the concentrations of dissolved atmospheric noble gases provide a thermometer via the temperature dependence of gas solubilities in water.

These applications require an accurate separation of the noble gas components originating from equilibration with the atmosphere and radiogenic production. Further complications may arise in some environmental systems from the presence of additional phases such as ice, hydrocarbons, or other gases (Utting et al., 2013; Visser et al., 2007). The quantitative interpretation of noble gases in water must thus be based on an accurate model of their partitioning between air, water, and possible additional phases. This

applies in particular for the noble gas paleothermometer in groundwater.

It has long been recognized that the entrapment of air bubbles during infiltration of groundwater leads to an additional dissolved noble gas component of atmospheric origin, the so-called excess air (Heaton and Vogel, 1981). Correctly accounting for this component is crucial for the determination of reliable noble gas paleotemperature records. Therefore, various models for the origin and composition of excess air and numerical tools to evaluate the resulting noble gas concentrations in groundwater have been developed in the field of noble gas thermometry in groundwater hydrology (Aeschbach-Hertig and Solomon, 2013). Some of these models can also describe the less frequently encountered case of degassed samples, which exhibit dissolved gas concentrations below atmospheric equilibrium (Aeschbach-Hertig et al., 2008).

In 1999, two groups independently presented an inverse modeling approach for the interpretation of dissolved noble gas concentrations in natural waters (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999). This approach consists of a minimization of the error-weighted deviation (denoted as χ^2) between observed noble gas concentrations and those derived from models designed to describe these concentrations with few parameters, such as the equilibration temperature, the excess air content, or the extent of degassing, for example. The goal is to derive quantitative estimates of the model parameters, in particular the equilibration or recharge temperature, and their uncertainties.

In principle, the inverse approach is applicable to noble gas concentrations in any aquatic system, as long as a model for the expected concentrations with few parameters (less than the number of measured gases) is available. In practice, it has mainly been applied to interpret atmospheric noble gas (Ne, Ar, Kr, Xe) data sets from groundwater in terms of past recharge temperatures (Aeschbach-Hertig and Solomon, 2013). Noble gases in lake sediment porewater have been used to reconstruct paleosalinity (Brennwald et al., 2004). In a recent study by Chatton et al. (2016), the inverse approach has been adapted to a reduced set of noble gases (Ne, Ar) combined with nitrogen as an additional quasi-conservative gas for groundwater recharge temperature estimation. Another recent study has extended the principle of the noble gas thermometer to estimate recharge properties of the deep ocean (Loose et al., 2016).

At the time when the inverse approach was introduced, only few models for the atmospheric noble gas components in groundwater were available and implemented in the first fitting tools. These were the unfractionated excess air (UA), partial re-equilibration (PR), and partial degassing (PD) models (see, e.g., Kipfer et al., 2002; Aeschbach-Hertig and Solomon, 2013). Shortly thereafter, the closed-system equilibration (CE) model was developed (Aeschbach-Hertig et al., 2000). This new model along with other extensions was implemented in the software *NOBLE* presented by Peeters et al. (2003), which became widely used for the purpose of parameter estimation from noble gas data sets derived from groundwater and sometimes also other systems.

In the meantime, several new models for atmospheric noble gas components in groundwater have been presented in the literature, most notably the oxygen-depletion (OD, Hall et al., 2005) and the gas diffusion relaxation (GR, Sun et al., 2008) models. Furthermore, the reliability and numerical stability of the different models has been critically evaluated (Sun et al., 2010), raising some questions with regard to a possible bias of the temperature estimates obtained from the CE model. Jung et al. (2013) have shown the usefulness of Monte Carlo simulations in assessing and resolving such problems that sometimes afflict the parameter estimation based on the CE model using the *NOBLE* software.

In this study, we present *PANGA*, a new, stand-alone software for the analysis of noble gas data from (ground)water samples. It updates on *NOBLE* by including newer excess air models and it is flexibly designed to enable easy incorporation of new models as they may be developed in the future. It furthermore provides user-friendly tools to conduct and evaluate Monte Carlo simulations and thus apply the procedures suggested by Jung et al. (2013).

2. Physical background

Noble gas concentrations in groundwater are assumed to consist of two components: the equilibrium component, i.e., the gas concentrations in water when it is in equilibrium with the atmosphere, and the so-called "excess air", which is an additional component caused by air entrapment during water table fluctuations in groundwater (Holocher et al., 2002). In addition, interaction of the groundwater with a gas phase may lead to a loss of dissolved gases, usually referred to as degassing (Aeschbach-Hertig et al., 2008). If degassing occurs, the dissolved noble gas concentrations are lowered and may fall below the equilibrium concentrations.

A comprehensive review of the currently available models to describe the effects of excess air and degassing has recently been provided by Aeschbach-Hertig and Solomon (2013). In the following, we only give a short summary of the different models. However, in contrast to Aeschbach-Hertig and Solomon (2013), throughout this article and in the software we do not use molar units for concentrations even though they lead to more elegant equations. Instead we use cm³ STP/g for dissolved noble gas concentrations and express gas phase concentrations as partial pressures. Choosing these units is consistent with the model equations as given by Kipfer et al. (2002) and as used in the software *NOBLE*. This choice also avoids problems with unit conversion, since most laboratories report their noble gas results in cm³ STP/g, which is an absolute and experimentally easily accessible measure for gas concentrations per water amount. Similarly, partial pressures in the gas phase can directly be related to known atmospheric abundances. Expressing concentrations in mol/l in both phases is advantageous for formal calculations, but the conversion from these units to the experimentally accessible forms used here depends on environmental conditions like temperature, pressure and salinity.

The equilibrium components of He, Ne, Ar and Kr are calculated using the solubilities determined by Weiss (1970, 1971); Weiss and Kyser (1978). The equations given by Clever (1979) were used for Xe. The implementation follows the recommendations of Kipfer et al. (2002). So far, these are the only solubility equations implemented. The program can, however, easily be extended to include others as well.

The following section provides a list of all available excess air or degassing models and their equations. They all share three parameters, which are needed to calculate the equilibrium component: the temperature T, measured in °C, the salinity S in g/kg and the pressure P in atm. Another quantity used in all formulas is z_i which stands for the volume or mole fraction of the specific noble gas in dry air.

Unfractionated excess air (UA) model This traditional and most simple model of pure air addition can be expressed as follows:

$$C_i(T, S, P, A) = C_i^{eq}(T, S, P) + Az_i$$

A denotes the concentration of dissolved excess air in cm³ STP/g.

Partial re-equilibration (PR) model This model assuming diffusive loss of excess air has been introduced by Stute et al. (1995) and can be written as: