Dissolved gases in groundwaters at Olkiluoto

Mel Gascoyne

December 2000
Margit Snellman,
POSIVA OY,
Toolonkatu 4,
FIN-00100 Helsinki,
Finland.
Fax: 358-9-2280-3719

SUBMISSION OF REPORT

P.O. Box 141
6 Tupper Place
Pinawa, MB R0E 1L0
Canada
Phone 1-204-753-8879
Fax 1-204-753-2292
e-mail: gascoyne@granite.mb.ca

13 December 2000

For Expert Review and Assistance in Hydrogeochemistry Studies (P.O. Number 9746/99/MVS): Report on Dissolved Gas Data from Olkiluoto

Dear Margit,

Please find enclosed the final copy of the report defined above. The report has been reviewed and approved according to the requirements of my company, Gascoyne GeoProjects Inc. and meets all quality assurance requirements of Posiva.

Yours sincerely,

M. Gascoyne
(President and CEO, Gascoyne GeoProjects Inc.)
Dissolved gases in groundwaters at Olkiluoto

Mel Gascoyne

December 2000
Working Report 2000-49

Dissolved gases in groundwaters at Olkiluoto

Mel Gascoyne
Gascoyne GeoProjects Inc.
Pinawa, Manitoba, Canada

December 2000

Working Reports contain information on work in progress or pending completion.

The conclusions and viewpoints presented in the report are those of author(s) and do not necessarily coincide with those of Posiva.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>DISSOLVED GASES IN GROUNDWATER</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Sources of gas</td>
<td>3</td>
</tr>
<tr>
<td>2.2</td>
<td>Solubility of gases</td>
<td>3</td>
</tr>
<tr>
<td>2.3</td>
<td>Influence of pressure and salinity</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>SAMPLING METHODS</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>RESULTS AND DISCUSSION</td>
<td>13</td>
</tr>
<tr>
<td>4.1</td>
<td>Gas volumes</td>
<td>13</td>
</tr>
<tr>
<td>4.2</td>
<td>Gas concentrations</td>
<td>20</td>
</tr>
<tr>
<td>4.3</td>
<td>Atmospheric gases</td>
<td>20</td>
</tr>
<tr>
<td>4.3.1</td>
<td>$O_2$</td>
<td>20</td>
</tr>
<tr>
<td>4.3.2</td>
<td>$N_2$-Ar</td>
<td>25</td>
</tr>
<tr>
<td>4.4</td>
<td>$H_2$-$CH_4$</td>
<td>27</td>
</tr>
<tr>
<td>4.5</td>
<td>$CH_4$-SO$_4$</td>
<td>31</td>
</tr>
<tr>
<td>4.6</td>
<td>Gas saturation pressures</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>SUMMARY AND CONCLUSIONS</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>REFERENCES</td>
<td>37</td>
</tr>
</tbody>
</table>
DISSOLVED GASES IN GROUNDWATERS AT OLKILUOTO

ABSTRACT

The current database for dissolved gases in groundwaters sampled from boreholes at the Olkiluoto site, south-west Finland, has been examined. Gas samples taken at the surface are shown to have suffered gas loss and gas fractionation by comparison with the later-sampled PAVE data and the greater depletion of the lighter gases. Lower-than-expected volumes of groundwater were recovered from the PAVE sampler for two high gas-content groundwaters could be due to the existence of a gas phase at sampling depth.

The N₂/Ar ratios of the PAVE samples show a wider range than expected for groundwaters whose main source of these gases is the atmosphere. Some enrichment in Ar is common in deep groundwaters but the high Ar values seen are more likely due to contamination by Ar used to drive the piston of the PAVE sampler.

High concentrations of CH₄ have been observed, often with high H₂ levels, in deeper (> 300 m) groundwaters where there is an inverse relationship with dissolved SO₄. Calculation of CH₄ solubility in the few deeper samples shows that these samples are at or below saturation levels indicating the possibility of a gas phase existing in the depth range 800-1000 m. Other gases are below their saturation solubility and are unlikely to form a gas phase. Because of the importance of gas-phase formation and its migration to the safety and performance assessment of a nuclear fuel waste repository, more efforts should be made to obtain reliable dissolved gas samples from deep boreholes at Olkiluoto.

Keywords: dissolved gases, noble gases, groundwater chemistry, groundwater sampling, salinity, isotopes
OLKILUODON POHJAVESINÄYTTEIDEN LIUENNEET KAASUT

TIIVISTELMÄ

Tässä työssä on tarkastettu Olkiluodon pohjavesinäytteisiin perustuva liuennuksen kaasujen tietoaineistot. Paikkatutkimusten alkuvaiheessa käytetty tekniikka, jossa näytteet ovat kerätty maan pinnalla, on aiheuttanut kaasujen vapautumista ja fraktioitumista sekä erityisesti kaasujen vapautumista verrattuna uusimpaan PAVElla (paineellinen vesinäytteenottolaitteisto) otettuihin näytteisiin. PAVElla kerätyistä näytteistä kahdessa runsaasti kaasua sisältävissä näytteessä oli selvästi otettua pienempi vesitilavuus mikä saattaa johtua kaasufaasin esiintymisestä näytteenottosyyvyydellä.

PAVE-näytteiden N2/Ar suhteessa on ollut vaihtelun suurempi verrattuna pohjavesiin, joissa nämä ovat pääosin atmosfääristä alkuperäällä. Argon on jonkin verran rikastunut syvissä pohjavesissä mutta korkeat Ar-pitoisuudet ovat todennäköisesti PAVE sähällön vastapainevesien kontaminaatiota.

Korkeita CH4-pitoisuuksia, usein kohonneiden H2-pitoisuuksien kanssa, on tavattu syvissä ( > 300 m) pohjavesissä. Näsissä vesissä metaanin ja sulfaatin väliillä on käänteinen korrelaatio. Metaanin liukuisuustarkastelujen perusteella vesinäytteet ovat lähes kylläätä tai hieman alikylläätä metaanin suhteen, mikä voi merkitä kaasufaasista esiintymistä 800-1000 m syvyydessä. Vesi on alikylläinen muiden kaasujen suhteen eivätkä muut tutkimut kaasut näinollen todennäköisesti muodosta kaasufaasia. Kaasufaasin mahdollinen muodostuminen ja kaasun kulkeutuminen on tärkeää selvittää käytetyn polttainesyyn loppusijoituksen toimintakykyarvon kannalta. Erityisen tärkeää on riittävien ja edustavien kaasunnäytteiden kerääminen syvistä pohjavesinäytteistä.

Avainsanat: Liuennet kaasut, jalokaasut, pohjavesikemia, pohjaveden näytteenotto, sulaisuus, isotootit
PREFACE

This study is part of the research programme for disposal of spent nuclear fuel in crystalline bedrock in Finland.

This work uses the data obtained on groundwater samples from the OL-KR series boreholes at Olkiluoto by numerous researchers including Petteri Pitkänen, Paula Ruotsalainen and Margit Snellman.

The work has been funded by Posiva Oy and I am grateful for the support of Margit Snellman in this study.
1 INTRODUCTION

The sampling and analysis of dissolved gases in groundwaters from bedrock boreholes at the Olkiluoto site, Eurajoki, (Figure 1-1) has been performed as part of the site characterisation activities of Posiva’s nuclear fuel waste management program since 1991. Several methods, each with improved sophistication, have been used to obtain samples of groundwaters and their dissolved gas component from boreholes up to 1000 m deep in the fractured crystalline rock at the site.

Early work (1991-1995) was based on sampling groundwater from boreholes KR1-KR5 using surface-based methods. This work has been described by Lampén & Snellman (1993), Snellman et al. (1995), Ruotsalainen and Snellman (1996), and Pitkanen et al. (1994, 1996). Preliminary results of a more recent sampling, of boreholes KR3-KR10, using a downhole geochemical sampler, have been reported by Pitkänen et al. (1999).

This report describes the status of the dissolved gas sampling program, examines new downhole gas concentration data obtained in 1998-2000, calculates gas solubilities for the deeper sampled zones, and makes a preliminary comparison with earlier Olkiluoto results and data from other Shield environments.
Figure 1-1. The Olkiluoto study site showing the geology and location and trend direction of the deep boreholes KR1-KR12 (Figure provided by Hanna Malmlund from Saanio & Riekkola Oy).
2 DISSOLVED GASES IN GROUNDWATER

2.1 Sources of gas

The major sources of dissolved gases in groundwaters are 1) equilibration with the atmosphere during recharge at the surface, 2) inclusion of additional ('excess') air by entrainment during migration through the unsaturated zone, and 3) uptake of gases produced by radiogenic, thermogenic and biological processes in the saturated zone. These sources are summarised in Figure 2-1 (from Andrews 1992).

2.2 Solubility of gases

The dissolution of gases by groundwater is dependent upon pressure, temperature and groundwater composition. The amount of gas dissolved upon equilibration of water with the atmosphere is given by Henry's Law:

\[ n = \frac{p}{k} \]  

where \( n \) is the number of moles of a gas dissolved in one mole of water at partial pressure, \( p \), and \( k \) is the Henry's Law constant (atm\(^{-1}\)) at that temperature.

The solubility of a gas is usually defined in terms of the volume that has dissolved in a given volume of water. The Bunsen coefficient \( \beta \) is defined as the volume of gas (at standard temperature and pressure, S.T.P.) that is dissolved by a unit volume of solvent (water) at a given temperature under a partial pressure of 1 atmosphere. For atmospheric gases, Bunsen coefficients range in value from 0.009 for He to 0.88 for \( CO_2 \) at 20°C and coefficient values (i.e. gas solubilities) decrease as temperature increases.

For ease of use, Henry's law and the Bunsen coefficient are combined in the following equation:

\[ V = \frac{\beta p}{1000} \]  

where \( V \) is the volume of gas dissolved at STP and \( \beta \) and \( k \) are related by

\[ \beta = 1.244 \times 10^6 \times \frac{p}{k} \]  

where \( p \) is the groundwater density at its ambient temperature.

Equation (3) indicates that the Bunsen coefficient varies with groundwater salinity. The coefficient, \( \beta_s \), for a saline groundwater is related to that for pure water, \( \beta_0 \), by the equation
Figure 2-1. Schematic diagram of sources of noble gases and their isotopes and their pathways of migration (from Andrews 1992)
\[ \ln \left( \frac{\beta_0}{\beta_s} \right) = M k_s \quad (4) \]

where \( M \) is the Cl concentration of the groundwater (as moles) and \( k_s \) is the 'salting coefficient'. Values of \( k_s \) are given in Andrews (1992). For groundwater salinity less than 1 g/L, gas solubility is reduced by \(< 1\%\), whereas at sea water salinity (35 g/L TDS), argon solubility, for instance, decreases by up to 25\% (Figure 2-2).

The concentration of atmospheric gases in groundwater has been used as an indicator of paleotemperature (i.e. the temperature at which recharge at the surface occurred) because the partial pressure of each gas is a function of its solubility, which is temperature-controlled (Mazor 1972, Andrews 1992).

**Figure 2-2.** Solubility of Ar in a) fresh water and b) sea water for equilibration with the atmosphere at temperatures up to 40 °C (from Andrews 1992)
2.3 Influence of pressure and salinity

Groundwaters that circulate to considerable depths often release gases as they return to atmospheric pressure on discharging at the surface. These gases are held in solution by hydrostatic pressure during sub-surface flow and they tend to accumulate by dissolution of air entrained in bubbles during recharge ('excess air') and by dissolution of gases produced in the bedrock by radioactive decay (He, Ar, Rn), crustal degassing (He, N₂, CH₄, H₂) and thermogenic or biogenic decomposition (CH₄, H₂S).

The amounts of these gases may be such that very high hydrostatic pressures may be needed to retain all gases in solution. If gas accumulation goes on for a prolonged time, then, at a stable hydrostatic pressure, gas phases could form at depth and these would tend to migrate rapidly upward, as microbubbles, mainly through fractures and fault zones. Evidence for this process has been reported by Malmqvist and Kristiansson (1984) for crystalline rocks in Scandinavia. They believe that this could be a mechanism for transporting radionuclides and other contaminants (e.g. Hg) rapidly to the surface from considerable depth.

Henry's Law (equation 1) describes the relationship between the amount of gas dissolved and the hydrostatic pressure of a groundwater. Provided the pressures are not too high or the temperatures too low, most gases obey Henry's Law, especially if they are not very soluble. In other words, the maximum amount of gas that may be dissolved in a groundwater is directly proportional to the pressure. For example, the solubility of pure Ar in water is 56 mL/L. At a depth of 100 m (i.e. hydrostatic pressure of ~ 10 atmospheres or 1 MPa) the solubility increases to 560 mL/L if Ar can be assumed to behave as an ideal gas under these conditions.

When gases dissolve from a mixture, the solubility of each gas is proportional to its partial pressure and Henry's Law applies to each gas independent of the partial pressure of the other gases. However, at high pressures and high concentrations of other, more abundant gases, a 'salting out' effect can occur, thereby reducing the solubility of the lower abundance gases. An example might be the reduced solubility of He in the presence of large amounts of CH₄.

Experimental data providing information on the non-ideal characteristics of dissolved gases at increased pressure and gas concentrations and for various salinities at temperatures below 25 °C are very limited in availability but some examples have been reported in the literature for specific situations (e.g. CH₄ solubility in sea water).

For instance, Haas (1978) has constructed an empirical equation describing the solubility of CH₄ in pure water and salt-waters (up to 250 gm/L NaCl) for temperatures up to 360 °C and depths up to an equivalent pressure of 138 MPa. Sherwood Lollar et al. (1993) has used this equation to determine whether CH₄ is
close to saturation in several mine groundwaters in the Fennoscandian Shield (Table 2-1). In all cases, the groundwaters were well-undersaturated with respect to CH$_4$ and, therefore, all CH$_4$ was fully dissolved at the depth of sampling.

**Table 2-1.** Comparison of measured CH$_4$ concentrations in Fennoscandian Shield groundwaters with estimates of CH$_4$ solubility under similar temperature-pressure-salinity conditions (from Sherwood Lollar et al. 1993).

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Depth (m)</th>
<th>Measured CH$_4$ (mL/L STP)</th>
<th>CH$_4$ solubility (mL/L STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pori</td>
<td>151</td>
<td>0.03</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>0.15</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>0.26</td>
<td>&gt;350</td>
</tr>
<tr>
<td></td>
<td>351</td>
<td>5.27</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Ylistaro</td>
<td>102</td>
<td>0.63</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>8.33</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>301</td>
<td>40.4</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>407</td>
<td>157</td>
<td>&gt;800</td>
</tr>
<tr>
<td>Ylivieska</td>
<td>249</td>
<td>3.59</td>
<td>&gt;500</td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>190</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Enonkoski</td>
<td>204</td>
<td>374</td>
<td>&gt;450</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>126</td>
<td>&gt;450</td>
</tr>
</tbody>
</table>

Since the initial calculations by Haas (1978), and because of the economic importance of CH$_4$, there have been numerous detailed attempts to define the CH$_4$-salt-water system in terms of temperature, pressure and water. Controversy over the reliability of experimental data and the lack of an equation of state for the gas phase has prevented the development of quantitatively reliable models (Duan et al. 1992).

In a careful collection and examination of CH$_4$ solubility data at various pressures, temperatures and salinities, Duan et al. (1992) derived an equation of state for CH$_4$ under these conditions and expressed CH$_4$ solubilities in tabular form from which the data for low-temperature (0 – 30 °C), low- pressure (0 – 100 bar), and various salinities (0 – 234 g/L as NaCl) conditions are shown in Table 2-2.

The data in Table 2-2 indicate that the maximum solubility of CH$_4$ ranges from about 680 mL/L in saline water (~ 230 g/L) at 30 °C to 2600 mL/L in fresh water
Table 2-2. Summary of CH$_4$ solubility (mL/L) under various conditions of temperature, pressure and salinity as might be found in Fennoscandian Shield groundwaters (after Duan et al. 1992).

<table>
<thead>
<tr>
<th>Groundwater Salinity (Mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press. (bars)</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

at 0 °C. The data are plotted for 0 and 30 °C in Figures 2-3a and b, respectively. These data are used to interpret Olkiluoto dissolved gas results below.

Unfortunately, except for CH$_4$, most geoscience studies of gas solubility look at the variation with temperature, not pressure. This is because they are largely concerned with equilibration with atmospheric abundances of gases, rather than the solubility of a gas phase at high pressure, a far larger value. Data can be found, however, in reports from the oceanographic, industrial chemical, and nuclear power literature. Summary tables for most gases are in Perry (1984).

Goodman and Krase (1931) determined the solubility of N$_2$ in water at pressures from 10 to 30 MPa and calculated coefficients in Henry's Law for the temperature range 0 to 170 °C. At 10 MPa (equivalent to a depth of 1 km in freshwater) and 25 °C, N$_2$ solubility is 1070 mL/L. This is somewhat less than that of an ideal gas assuming 14 mL/L at 1 atmosphere (i.e. 1400 mL/L at 10 MPa, Horne 1969), probably due to non-ideal behaviour of N$_2$ at high pressures. Battino et al. (1984) have used data from Goodman and Krase (1931) and numerous other sources, to give a comprehensive description of air and N$_2$ solubility in various liquids.

Hydrogen solubility at 1 km depth in freshwater at 0 °C is about 2140 mL/L (Baranenko and Kirov 1989) compared with a theoretical value of 2120 mL/L (based on a solubility of 21.2 mL/L at 1 atmosphere). Of all the atmospheric gases, H$_2$, therefore, behaves closest to that of an ideal gas.

None of the sources examined give data for He. However, because it is a low molecular weight noble gas, it will likely behave like H$_2$ and closely follow Henry's Law. This means that, at 1 km depth in freshwater, the saturation solubility of He will be about 1 L/L assuming a solubility of 10 mL/L at 1 atmosphere pressure.
Figure 2-3a. Maximum solubilities of CH₄ for depths of 10, 500 and 1000 m in groundwaters of different salinities at 0 °C (after Duan et al. 1992)
Figure 2-3b. Maximum solubilities of CH$_4$ for depths of 10, 500 and 1000 m in groundwaters of different salinities at 30 °C (after Duan et al. 1992)
3 SAMPLING METHODS

Two main methods have been used to sample dissolved gases in groundwater that has been pumped to the surface from packer-isolated zones in boreholes at Olkiluoto. An earlier technique for a few of the samples obtained prior to 1995, was to collect gas and pumped groundwater in an aluminum-laminated bag which was impermeable to gas diffusion. Subsequently, a glass vessel was used, fitted with ground glass taps to sample dissolved gases from most of the available borehole zones.

These techniques suffered from two main problems: 1) groundwater was being sampled at surface pressures (~1 atmosphere) and so gas would exsolve and could be lost from the sampling equipment during travel to the surface, and 2) gases analysed in the collection vessel (the Al or glass vessels) did not necessarily originate from the volume of water that was collected in the vessel because of the exsolution of, and resulting phase separations in, the sample tubing.

The latter problem prevents any quantitative assessment being made of dissolved gas concentrations in the fully pressurized groundwater at zone depths. Some estimate of relative abundances can be made but even these may be distorted because the different solubilities of each gas would cause them to fractionate as they exsolve. Degassing of the groundwater results in a depletion of the lighter (less soluble) gases because they tend to diffuse faster into the forming bubbles. The resulting fractionation of the gases can be approximated by a Rayleigh-type distillation equation.

To address these problems, the PAVE sampler was constructed to take pressurized groundwater samples, at depth in the borehole (Ruotsalainen et al. 1996). The PAVE sampler consists of a gas-inflatable membrane to pump groundwaters to the surface for sampling and monitoring, a chamber with a moving piston for sample collection and isolation, and two inflatable packers, nominally 5 to 10 m apart, to isolate the permeable zone from the rest of the borehole. Groundwater from the zone of interest is first pumped to the surface to remove contamination from the zone and allow the composition to stabilize. Valves on the PAVE sampler are then activated to allow groundwater to enter the sample chamber and displace the piston. Argon (and later N₂) gas is used in the chamber behind the piston to reduce the pressure drop when activating the sampler. The valves are then closed pneumatically, the packers deflated, and the sampler brought to surface.

It has been observed that the filling gas (Ar or N₂) could diffuse past the piston in the sample vessel (Helenius et al. 1998). Also, on occasions, two sample cylinders in series (one above the other), have been used in the gas sampling at Olkiluoto. The upper was back-filled with Ar and the lower with N₂. Because the
vessels are not separately isolated downhole, some gas transport might have occurred from the lower to the upper cylinder during the lift to the surface, before the manual valve separating the two can be closed. These aspects are considered further in this review of Olkiluoto dissolved gas data.
4 RESULTS AND DISCUSSION

The results of sampling and analysis of dissolved gases in groundwaters at Olkiluoto are given in Table 4-1. This table has been obtained from the Olkiluoto database spreadsheet (PARVIOL5) by removing most of the dissolved ion data and reorganising the table so that all results (glass vessel and PAVE) for a given borehole are grouped together. This allows easier visual comparison of the data from one zone to another in a borehole and between the glass vessel and PAVE samplings of a given zone. Only three dissolved gas samplings using the AI bag method were listed in PARVIOL5 and, because these are given as percent volume only, they have not been included in Table 4-1.

4.1 Gas volumes

The volume of gas obtained by sampling at the surface (in glass vessels) is compared in Figure 4-1 with that for sampling at zone pressure in the borehole (PAVE). Typically 10 to 50 mL/L of gas is collected at the surface in glass vessels whereas an order of magnitude more gas (100 to 2000 mL/L) is collected downhole using the PAVE system. The downhole samples are believed to be more accurate because 1) the PAVE samples are sealed and maintained at in situ pressure until analysis, whereas the glass samples store the groundwater at ~1 atmosphere, and 2) the glass samples will have experienced degassing in the pumping line to the surface and thus the collected groundwaters will have been stripped of much of their gas content. Therefore, Olkiluoto groundwaters are typically believed to be gas-rich and contain over 100 mL/L of total dissolved gas. As shown in Figure 4-1, the gas content increases with depth to 2000 mL/L at about 1 km depth.

A similar correlation is found when gas volume is compared with Cl concentration in the groundwater (Figure 4-2). This correlation is not because gases are more soluble in saline waters (in fact, the opposite is true, as described below) but because Cl concentration is itself depth related. As shown in Section 4.6, large gas concentrations are able to be maintained by the high hydrostatic pressures and are not significantly limited by the lower solubility of gases in increasingly saline water.

Because gases fractionate from each other as they exsolve and the lighter gases tend to fractionate more than the heavier gases, a pattern of lower He/N₂ ratios should be seen for groundwaters that have undergone depressurisation and gas loss. Evidence for the loss of gas from the glass samples is clearly indicated by the low He/N₂ ratios for glass samples as compared with PAVE samples (Figure 4-3). This information, plus the order-of-magnitude lower total gas concentrations renders the data for the glass vessel samples of minimal use and so reference to these data is minimised in the remainder of this report.
### TABLE 4.1. Summary of Dissolved Gas Concentrations for Okikuuto Groundwaters

| A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y |
| 1 | **Boldface** | **Date** | **Interval (m)** | **Pump** | **T** | **O2** | **Eh (mV)** | **Inh (s)** | **Sampling Method** | **Vol. Gas** | **MA** | **N2** | **O2** | **CO2** | **H2** | **He** | **CH4** | **C2H6** | **C3H8** | **C4H10** | **C5H12** | **C6H14** | **C7H16** |
| 2 | **(mm/year)** | **Top Bottom Length (m)** | **(m/s)** | **V** | **(mg/L)** | **ppm** | **(m/s)** | **(m/s)** | **Volume** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** | **(m/s)** |
| 3 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 8 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 9 | | | | | | | | | | | | | | | | | | | | | | | | | | |
Figure 4-1. Relationship between volume of dissolved gas and depth of permeable zone for glass- and PAVE-sampled groundwaters.
Figure 4-2. Relationship between volume of dissolved gas and Cl concentration for glass- and PAVE-sampled groundwaters
Figure 4-3. Variation of He/N₂ ratio with depth for glass- and PAVE-sampled groundwaters
Careful examination of the PAVE data, however, indicates that the PAVE system is not without problems. Figure 4-4 shows how the volume of sampled water by PAVE varies somewhat, although over 200 mL of water was obtained in most cases. The two samples with high gas volumes, however, recovered less than 50 mL of water. It might be expected that the volume of water present in PAVE would be constant and equal to the internal volume of the PAVE sampler. The anomalously low water volumes in the two deep samples may be due to either 1) a limitation on the amount of water that can enter the sampler because the rest is gas (i.e. the gas is not fully in solution at these depths) or 2) the back-pressure of the inert filling gas, coupled with the low pumping rate used, is causing inadequate filling of the sampler. Leakage of the PAVE sampler can be ruled out as the system was carefully checked each time during use and no evidence of leaking was found. The former explanation would indicate that there must be a gas phase existing at those depths and that the borehole was possibly 'blowing' (i.e. venting gas). An additional problem arises out of 1) above, if a gas phase can exist at those depths, because the volumetric calculations of gas concentration (mL/L water) will not be accurate (even for PAVE samples) as the gases will have already fractionated in the borehole zone according to their relative solubilities.

This aspect of the results is re-examined more closely in Section 4.6 when the saturation levels of gases are determined.
Figure 4-4. Variation of volumes of water and gas collected in the PAVE sampler
4.2 Gas concentrations

Individual gas concentrations are plotted as a histogram in Figures 4-5 (glass samples) and 4-6 (PAVE samples). The glass data are shown here so that the difference between the glass and PAVE data (caused by preferential loss of the lighter gases, $\text{H}_2$, $\text{He}$ and $\text{CH}_4$, from the glass samples) can be seen.

As described above, the total dissolved gas content of groundwater at Olkiluoto increases with depth. In most cases, individual gas concentrations also increase with depth (Figure 4-7) and with increasing $\text{Cl}$ concentration (Figure 4-8).

4.3 Atmospheric gases

4.3.1 $\text{O}_2$

Groundwaters at Olkiluoto are believed to be anoxic, as shown by redox and dissolved $\text{O}_2$ measurements in the field, the existence of fracture-filling minerals such as pyrite and a lack of iron oxyhydroxides, and presence of sulphide in the groundwater together with sulphur-reducing, iron-related and methanogenic bacteria. The groundwaters, therefore, should not contain any detectable $\text{O}_2$.

Modern analytical techniques for $\text{O}_2$ have a detection limit of about 1 $\mu\text{L}/\text{L}$ in groundwater and any amount greater than this will give rise to positive Eh values (Gascoyne 1997). Therefore, the measured $\text{O}_2$ concentrations in the dissolved gas samples (Table 4-1) are probably due to contamination from the atmosphere as a result of either not adequately purging the sample vessel before filling with groundwater or leakage of air into the pump, tubing or sample vessel during sampling and analysis. The PAVE samples show detectable $\text{O}_2$ to be present in all samples, ranging from concentrations of 70 to 35,000 $\mu\text{L}/\text{L}$ although, in most cases, the $\text{O}_2$ content is low enough to be of little consequence. This $\text{O}_2$ is most probably due to contamination during improper purging and evacuation of PAVE prior to sampling or during the analysis of gas in the laboratory.

If there has been no gas fractionation, the gas data may be corrected for air contamination (principally the $\text{N}_2$ and $\text{Ar}$ content) using the standard abundances of $\text{O}_2$, $\text{N}_2$ and $\text{Ar}$ in air. This has been done for the individual gas concentrations in Table 4-1 and only makes a significant difference in total gas volume and relative gas concentrations for sample OL-KR7.
Figure 4-5. Concentrations of various dissolved gases measured in glass-sampled groundwaters (numbered axis refers to sequence in Table 4-1)
Figure 4-6. Concentrations of various dissolved gases measured in PAVE-sampled groundwaters (numbered axis refers to sequence in Table 4-1)
Figure 4-7. Variation of individual gas concentrations with depth for PAVE samples
Figure 4-8. Variation of individual gas concentrations with Cl concentration for PAVE samples
4.3.2 N₂-Ar

The N₂ content of Olkiluoto groundwaters is shown in Table 4-1 and in Figure 4-9 as a function of depth, for PAVE samples only. In general, N₂ concentrations are independent of depth except for the 1997 sampling of zone OL-KR4/P1, which has large quantities of N₂ (480 mL/L) in association with high H₂, He and CH₄ concentrations. This is one of the deepest borehole zones sampled. The zone was re-sampled in 1998 (OL-KR4) and, although high concentrations of H₂, He and CH₄ were again observed, N₂ was much lower (167 mL/L). Based on only the available data at the time (from 1997 PAVE samplings), Pitkanen et al. (1999) believed that the N₂ was derived from a deep natural source such as ancient hydrothermal fluids. The zone at about 1030 m in borehole OL-KR2 does not show high N₂ concentrations and so it would appear that, pending more data from other deep zones, the high N₂ concentration of OL-KR4 may be a purely local feature.

Argon concentrations in Olkiluoto groundwaters are shown in Table 4-1 and range from 0.7 to 35.5 mL/L for PAVE-sampled groundwaters. The ratio of N₂ to Ar in the atmosphere is 83.54. However, because Ar is more soluble than N₂, the ratio in a groundwater that has been equilibrated with air at 10°C, for instance, is 37.33. Groundwaters might be expected, therefore, to lie between these two values depending on how much additional air has been dissolved during recharge and bubble entrainment. The N₂/Ar ratios for Olkiluoto groundwater sampled by the PAVE system range between 1.5 and 182, values that are well outside of the expected range. It is possible that the high Ar samples are contaminated with Ar used as a back-pressure gas in the operation of the PAVE sampler. Contamination by the Ar back-pressure gas has also recently been recognised in the evaluation of the representativity of the gas samples taken by the PAVE -sampler (Karttunen et al. 2000). There are only three samplings (when N₂ was used as a back-pressure gas) that can be used to determine the Ar content of deep groundwaters. These are indicated in Table 4-1.

These three analyses show very low Ar concentrations (0.5 to 0.76 mL/L) and are also below the level of atmospheric equilibration and are, therefore, comparable to results of other studies showing slight N₂ enrichment due to entrainment of air during recharge.

Because of the extremely wide variability of N₂ and Ar concentrations and their ratios for Olkiluoto groundwaters, it is unlikely that any reliable palaeotemperature data could be obtained for the time of recharge of these waters based on the differential gas solubilities of N₂ and Ar.
Figure 4-9. Relationship between dissolved $N_2$ content and depth of zone
4.4 H$_2$-CH$_4$

The variation of H$_2$ and CH$_4$ with Cl concentration in the PAVE-sampled groundwaters is shown in Figures 4-10a and 4-10b, respectively. High concentrations of both gases are found in the most saline groundwaters but significant amounts of the gases, particularly CH$_4$, may also occur in some of the less saline (and shallower) groundwaters. The occurrence of these gases in deeper groundwaters supports the interpretation of strongly reducing conditions at depth at Olkiluoto that has previously been made by Lampen and Snellman (1993) and Pitkänen et al. (1996).

The close association of H$_2$ and CH$_4$ in the deeper Olkiluoto groundwaters is clearly shown in Figure 4-11. Although the CH$_4$/H$_2$ ratio varies widely over four orders of magnitude, there appears to be a zone at about 400-500 m depth where CH$_4$ greatly exceeds H$_2$ concentrations (Figure 4-12) suggesting that this might be a zone of CH$_4$ production or, conversely, H$_2$ consumption. This approximately correlates with the depth at which SO$_4$ concentration decreases rapidly (see Section 4.5).

The relationship between H$_2$ and CH$_4$ has also been observed at several sites on the Fennoscandian and Canadian Shields. For instance, at Pori and Ylistaro in Finland and Sudbury in Canada, the concentrations of both gases are positively correlated (Sherwood et al. 1988, Sherwood Lollar et al. 1993). However, in Enonkoski and Vammala (Finland) and Yellowknife (Canada), CH$_4$ is found in abundance but without significant H$_2$. This suggests that the processes forming CH$_4$ and H$_2$ are different and operate to varying extents depending on locality, geologic and geochemical setting, etc.
Figure 4-10a. Variation of $H_2$ concentration with $Cl$ concentration
Figure 4-10b. Variation of CH₄ concentration with Cl concentration
Figure 4-11. Relationship between $H_2$ and $CH_4$ concentrations
Figure 4-12. Variation of CH₄/H₂ ratio with depth

4.5 CH₄-SO₄

The relationship between dissolved CH₄ and SO₄ gases in Olkiluoto groundwaters is shown in Figure 4-13. All groundwater samples (PAVE and glass samples) are included here to show the coherence of the data irrespective of the method of sampling. The inverse relationship between CH₄ and SO₄ has been noted before in Olkiluoto groundwaters (Pitkänen et al. 1996) and it has been argued that bacterial reduction (and, therefore, removal of SO₄) is the key control over the concentration of each species. The lack of coexistence of SO₄ and CH₄ is shown clearly in Figure 4-14 where, below about 300 m, SO₄ concentration sharply decreases while CH₄ concentration increases strongly.
Figure 4-13. Relationship between $CH_4$ and $SO_4$ for all groundwater samples
Figure 4-14. Diagram showing the lack of coexistence of CH₄ and SO₄ in groundwaters over the sampling depth.
4.6  Gas saturation pressures

Estimations of the concentration of gases such as N\textsubscript{2}, He and H\textsubscript{2} at saturation levels has been described in section 2.3 for depths up to 1 km. The maximum concentrations of these gases in Olkiluoto groundwaters are found in sample OL-KR4/P1 at a depth of 865 m. These concentrations are 480, 164 and 268 mL/L, respectively. The concentrations are well below both the theoretical estimates (determined by linear projection of Henry’s Law for atmospheric pressure solubility of the pure gas phase to pressures of 10 MPa, assuming a freshwater composition) and the experimental measurements, of the solubility of each gas under these conditions. These estimates and measurements range from 1000 to over 2000 mL/L for these gases (section 2.3).

In some literature studies, the effects of salinity on gas solubility have been determined, typically using seawater (35 g/L) as the liquid phase. Although these experiments have indicated a depression in gas solubility, there is no indication that saturation levels are being achieved although the data are insufficient to state this categorically, at present. The situation is somewhat different for CH\textsubscript{4}, however.

The levels at which groundwaters become saturated with CH\textsubscript{4} have been described in Table 2-2, based on data reported by Duan et al. (1992), for various temperatures and salinities. The CH\textsubscript{4} data for Olkiluoto groundwaters are compared to the predicted solubilities in Figure 4-15. Since the most saline groundwater at Olkiluoto, for which dissolved gas data has been collected, has a salinity a little over 1 M, as NaCl, (sample OL-KR4/P1, TDS = 69126 mg/L), the data in Figure 4-15 are compared only to the 0 and 1 M solutions of Duan et al. (1992).

It can be seen from Figure 4-15 that all Olkiluoto groundwaters contain CH\textsubscript{4} at pressures less than the maximum solubility although some of the most saline samples approach the limit for solubility at 30 °C. In particular, the sample from 865 m in borehole OL-KR4 appears to be very close to saturation with CH\textsubscript{4}. More groundwater samples need to be taken to confirm the fact that the groundwaters are all undersaturated with respect to CH\textsubscript{4} and to demonstrate that a gas phase does not exist at those depths. The second sampling of the 865 m zone in borehole OL-KR4 (Table 4-1) appears to indicate this.

The effects of reduced solubility of gases due to the presence of other gases has also not been examined in detail but may be important in causing CH\textsubscript{4} to exceed its solubility limit. Data for these applications may not exist in the literature for these pressure and temperatures conditions and experimental determinations may need to be performed.
Figure 4-15. Comparison of CH₄ concentrations with predicted solubilities over the depth range 0 to 1 km for different temperatures.
5 SUMMARY AND CONCLUSIONS

This report has examined the currently available data on dissolved gases from the Olkiluoto site in south-west Finland. Difficulties in interpreting data for gas samples taken at the surface have been identified and the samples have been clearly shown to have suffered gas loss and gas fractionation by comparison with the later-sampled PAVE data and the depletion of lighter, less-soluble gases relative to the heavier, more-soluble gases. Two high gas-content groundwaters have been sampled from deep borehole zones. In these cases, lower than expected volumes of groundwater were recovered from the sampler due, possibly, to the presence of a gas phase at the depth of sampling.

Examination of the N₂ and Ar contents of the PAVE samples indicates that there may be some contamination by Ar (the principal back-filling gas) that could have leaked past the piston seal in the sampler.

High concentrations of CH₄ have been observed, often with high H₂ levels, in the deeper (> 300 m) groundwaters. Methane concentrations show an inverse relationship to dissolved SO₄ concentrations for these groundwaters, as has been noted previously.

Measured concentrations of the gases N₂, He and H₂ all show values that are well below the theoretical and measured determinations of solubility at pressures up to 10 MPa (equivalent to a depth of 1 km in freshwater). Calculations of CH₄ solubility in the deeper samples show that most samples are below saturation levels and, therefore, a gas phase should not exist in the depth range 300-800 m. However, few data are available for depths below 800 m, where CH₄ contents appear to approach saturation limits, and so more groundwater samples need to be taken to confirm the fact that they are undersaturated with respect to CH₄ and to demonstrate that a gas phase does not exist at those depths.

Because of the importance of gas-phase formation and migration to safety assessment and performance calculations for a nuclear fuel waste repository, it is essential that efforts are made to obtain more reliable dissolved gas samples from deep boreholes at Olkiluoto. The possibility of improving seals on the PAVE sampler and replacing the piston gas filling with a vacuum are suggested as possible improvements to the system.
6 REFERENCES


