Dissolved Gases in Groundwaters at Olkiluoto

Mel Gascoyne

October 2005
Dear Mia,

Please note that you have my permission for you to print my report on dissolved gases.

Yours sincerely,

M. Gascoyne

29 September 2005
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October 2005
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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.
ABSTRACT

The database for dissolved gases in groundwaters, sampled during 1997-2004 from boreholes at the Olkiluoto site, south-west Finland, has been examined. Gas samples taken at the surface have previously been shown to have suffered gas loss and gas fractionation by comparison with the down-borehole PAVE data. Lower-than-expected volumes of groundwater are sometimes recovered from the PAVE sampler possibly due to 1) the existence of a gas phase at sampling depth, 2) to a high pressure of back-fill gas in the sampler or 3) loss of hydrostatic pressure due to pumping and vessel opening (with corresponding ex-solution of dissolved gases).

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. The use of N₂ as a back-pressure gas gives more reliable values of Ar concentrations.

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, efforts to further investigate this possibility by obtaining additional reliable dissolved gas samples from deep boreholes at Olkiluoto.

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

TIIVISTELMÄ

Tässä työssä on tarkasteltu Olkiluodon pohjavesinäytteenä otetuista kaasutuloksista vuosilta 1997-2004. Maan pinnalta otettujen kaasunäytteiden on todettu sisältävän vähemmän kaasuja kuin PAVE-laitteistolla kairanreiässä vallitsevasta paineesta otetut näytteet. PAVE laitteistolla otettujen vesinäytteen määrät ovat olleet toisinaan oletettua pienempiä, mikä saattaa johtua 1) näytteenottosyvyydellä olevasta kaasufaasista, 2) näytteenottosääliöissä käytetystä liian korkeasta vastapaineesta tai 3) hydrostaattisen paineen pienemistä pumpauksen ja sääliöiden avaamisen seurauksena.

PAVE-laitteella otettujen vesinäytteiden N2/Ar suhteet vaihtelevat huomattavasti laajemmin kuin olisi oletettavaa kaasuille, jotka ovat pääosin peräisin ilmakehästä. Argo- nin lievä rikastuminen on tavallista syvissä pohjavesissä, mutta tämän tutkimuksen korkeat Argon pitoisuudet ovat todennäköisimmin peräisin Argonista, jota käytetään painesäiliöiden tuhkimisen aikana männän liikuttamiseen. Realistisemmat Argon tulokset saadaan painesäiliöistä, joissa on käytetty vastapainekasua tyyppää.

Syvistä pohjavesistä (< 300 m) on analysoitu korkeita metaanipitoisuuksia, joihin usein liittyy myös korkeita H2-pitoisuuksia. Syväältä otettujen näytteiden metaanin liukuisuuden liittyvät tarkastelut osoittavat, että näytteet ovat kyllästymistasolla tai sen alapuolella. Tämän perusteella on mahdollista, että syvällä (800-1000 m) kallioperässä on olemassa metaanista muodostunut kaasufaasi. Muut kaasut ovat kyllästymistason alapuolella ja on epä todennäköistä, että ne kykenisivät muodostamaan kaasufaasin kallioperässä. Koska kaasufaasin muodostuminen ja sen vaikutus kairotulostumiseen on erittäin tärkeää turvallisuusanalyysin kannalta, on kaasunäytteenottoja jatkettava syvistä kairanreiä luotettavan datan saannin varmistamiseksi.

Avainsanat: liuennet kaasut, jalokaasut, pohjavesikemia, vesinäytteenotto, suolaisuus
PREFACE

This study is part of the research programme for disposal of spent nuclear fuel in crystalline bedrock in Finland and builds on an earlier, preliminary assessment by Gascoyne (2000).

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, Margit Snellman and Mia Mäntynen.

The work has been funded by Posiva Oy and I am grateful for the support of Mia Mäntynen in this study.
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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, 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 (mainly collection in glass vessels or Al bags). This work has been described by Lampén & Snellman (1993), Snellman et al. (1995), Ruotsalainen and Snellman (1996), and Pitkänen et al. (1994, 1996). Later work, up to the present, used a down-borehole sampler (PAVE) in various configurations to obtain dissolved gas samples from depth (300-1000 m). Results of recent sampling, using PAVE, have been reported by Pitkänen et al. (1999, 2003), Gascoyne (2000) and Hatanpää et al. (2005). A detailed examination of the representativity of PAVE samples has been reported by Hatanpää et al (2005).

This report describes the status of the dissolved gas sampling program, examines new downhole gas concentration data obtained in 1998-2004, calculates gas solubilities for the deeper sampled zones, and compares these data with earlier Olkiluoto results and data from other Shield environments.

Figure 1-1. The Olkiluoto study site showing location and trend direction of the deep boreholes KR1-KR23.
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. M\(^{-1}\)) 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

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

where \( \rho \) 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).
\[
\ln \left( \frac{\beta_0}{\beta_s} \right) = M k_s
\]  

(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 CH₄ and, therefore, all CH₄ 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 2-3. Maximum solubilities of CH₄ for depths of 10, 500 and 1000 m in groundwaters of different salinities at 0 °C (solid lines) and 30 °C (data from 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 groundwater samples at in-situ pressures, 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, from 2 to 20 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). 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 44 dissolved gases in groundwaters at Olkiluoto are given in Table 4-1. This table has been obtained from the Olkiluoto database spreadsheet (PARVIOL5) and includes only samples collected by the PAVE system. Of these data, only the most representative set is selected from each borehole zone. Selection criteria include minimal amount of O₂ (see section 4.3.1), highest water volume for the vessel size used and minimal amount of back-fill gas content (N₂ or Ar). Two samples in Table 4-1 show significant O₂ contamination (>5 mL/L) and these were not used in calculations of individual gas concentrations in this chapter. Their data were used, however, in measurements of total gas content and relation to water volume in the sampling vessel.

4.1 Gas and water volumes

Previous work on the PAVE data (Gascoyne 2000) has shown that gas concentrations are an order of magnitude higher when collected by the PAVE system, at depth in the borehole, rather than the Al-bag or glass vessel methods, at the surface. The down-hole PAVE 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.

A further, more detailed study of the representativity of down-borehole samples collected by PAVE has been recently performed by Hatanpää et al. (2005). Correlation was sought between volume of gas collected, volume of water in sampling vessel, depth of sampling, size of sampling vessel, and location of vessel in the sampling string. It was found that these parameters were unrelated to each other except that gas concentration increased with depth of sampling. This relationship is shown in Figure 4-1.

The data in Table 4-1 indicate that Olkiluoto groundwaters are typically gas-rich below 400 m depth 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.
<table>
<thead>
<tr>
<th>Borehole</th>
<th>Sampling interval (m)</th>
<th>Date (ddmmyy)</th>
<th>Filling gas</th>
<th>PACE size of vessel</th>
<th>Diss. Gas (mL/L)</th>
<th>Vol. Water (g)</th>
<th>Uncorr'd Q2 (mL/L)</th>
<th>Corr'd Q2 (mL/L)</th>
<th>CO2 (mL/L)</th>
<th>R2 (mL/L)</th>
<th>Uncorr'd CH4 (mL/L)</th>
<th>Corr'd CH4 (mL/L)</th>
<th>No (mL/L)</th>
<th>CH4 (uL/L)</th>
<th>C2H6 (uL/L)</th>
<th>C3H8 (uL/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KR1_612_3</td>
<td>612 - 615</td>
<td>130203</td>
<td>N2</td>
<td>middle/small</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KR2_596_1</td>
<td>596.5 - 596.5</td>
<td>180302</td>
<td>N2</td>
<td>upper/big</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KR2_876_2</td>
<td>876 - 876</td>
<td>171103</td>
<td>Ar</td>
<td>lower/small</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KR2_950_1</td>
<td>950 - 950</td>
<td>301003</td>
<td>Ar</td>
<td>lower/small</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>KR2_1039_1*</td>
<td>1030 - 1030</td>
<td>240697</td>
<td>Ar</td>
<td>big</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KR3_343_1*</td>
<td>343 - 343</td>
<td>271486</td>
<td>Ar</td>
<td>big</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>KR4_818_1</td>
<td>818 - 818</td>
<td>180304</td>
<td>N2</td>
<td>upper/small</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>KR4_864_1*</td>
<td>864 - 864</td>
<td>202708</td>
<td>Ar</td>
<td>big</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KR4_864_2*</td>
<td>864 - 864</td>
<td>140262</td>
<td>N2</td>
<td>lower/small</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KR4_864_1*</td>
<td>864 - 864</td>
<td>301597</td>
<td>Ar</td>
<td>big</td>
<td></td>
<td></td>
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* indicates data reported in Gascoyne (2000)

Table 4A. Summary of P4E-sampled dissolved gas concentrations for Okitoho
Two gas vessel sizes (100 mL and 250 mL) were used in post-1999 PAVE sampling (prior to this date only 250 mL vessels were used). The size used in the later sampling is indicated in Table 4-1. It might be expected that the volume of water collected by the PAVE sampler would be constant and equal to the internal volume of the PAVE sample vessel. The volume of water sampled by PAVE varies somewhat, however, as shown in Figure 4-2. Nevertheless, over 200 mL of water was obtained in most cases for the large vessels (~ 250 mL volume) and over 70 mL for the small vessels (~ 100 mL). However, two samples taken from depth in large vessels, had high gas volumes, but recovered less than 50 mL of water.

The anomalously low water volumes in these deep samples have previously been ascribed to 1) leakage of the PAVE sampler, 2) limitation on the amount of water that can enter the sampler because of a gas phase present at these depths, and 3) back-pressure of the inert filling gas, coupled with the low pumping rate used, causing inadequate filling of the sampler.

Figure 4-1. Variation of dissolved gas content with depth of PAVE-sampled groundwaters.
Leakage of the PAVE sampler has been ruled out by weighing the vessels on recovering from the borehole and again at the laboratory. The second explanation would indicate that there must be a gas phase existing at those depths and that the borehole was possibly venting gas. However, if a gas phase exists at those depths, 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. The third possibility has been examined in detail by Hatanpää et al. (2005) and, while contamination of the sample by filling gas is believed to occur occasionally, it is small in comparison to the volume of dissolved gases and, therefore, unlikely to be the cause of incomplete filling of the vessel. Incomplete filling of the vessels may be due to back-pressure, however.

Another possible explanation could be that pumping of the groundwater to the surface from the down-hole PAVE sampler will cause a pressure drop in the zone being pumped, particularly in zones with low permeability. In cases where gas content is high, this would allow gases to exsolve and thus cause incomplete filling of the gas vessel.

Figure 4-2. Variation of volume of water collected with dissolved gas concentration and vessel size in PAVE samples.
4.2 Gas concentrations

Individual gas concentrations are plotted as a histogram in Figure 4-3. 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 4-4). Nitrogen and CH₄ are the most abundant gases below 400 m but concentrations of CH₄ are highly variable over the depth range 100 - 400 m.

Figure 4-3. Concentrations of dissolved gases in PAVE-sampled groundwaters (numbered axis refers to sequence in Table 4-1).
4.3 Atmospheric gases

4.3.1 O$_2$

Groundwaters at Olkiluoto are believed to be anoxic, as shown by redox and dissolved 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 O$_2$.

Modern analytical techniques for O$_2$ have a detection limit of about 1 µL/L in groundwater and any amount greater than this will give rise to positive Eh values (Gascoyne 1997). Therefore, the measured O$_2$ concentrations in the dissolved gas samples (Table 4-1) are probably due to contamination from the atmosphere as a result of 1) not adequately purging the sample vessel before filling with groundwater, 2) leakage of air into the pump, tubing or sample vessel during sampling and analysis or 3) contamination in the laboratory. The PAVE samples show detectable O$_2$ to be present in all samples, ranging from concentrations of 30 to 35,000 µL/L although, in most cases, the O$_2$ content is low enough to be of little consequence.

If there has been no gas fractionation, the gas data may be corrected for air contamination (principally the N$_2$ and Ar content) using the standard abundances of O$_2$,...
N\textsubscript{2} and 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 a few samples, as can be seen by comparing corrected and uncorrected N\textsubscript{2} and Ar concentrations.

### 4.3.2 N\textsubscript{2}-Ar

The N\textsubscript{2} content of Olkiluoto groundwaters is shown in Table 4-1 and in Figure 4-4 as a function of depth, for PAVE samples only. In general, N\textsubscript{2} concentrations are independent of depth except for the 1997 sampling of zone OL-KR4 (~860 m), which had large quantities of N\textsubscript{2} (480 mL/L) in association with high H\textsubscript{2}, He and CH\textsubscript{4} concentrations. This is one of the deepest borehole zones sampled. The zone was re-sampled in 1998 and, although high concentrations of H\textsubscript{2}, He and CH\textsubscript{4} were again observed, N\textsubscript{2} was much lower (167 mL/L) (although still higher than most other groundwaters), and there was a significant contamination by O\textsubscript{2}. Recent sampling in 2002 gave essentially the same results but with no O\textsubscript{2} contamination.

Based on only the available data at the time (from 1997 PAVE samplings), Pitkänen et al. (1999) believed that the N\textsubscript{2} was derived from a deep natural source such as ancient hydrothermal fluids. Re-sampling of the zone suggests that the first analysis of N\textsubscript{2} was anomalously high but N\textsubscript{2} concentrations are still elevated (>100 mL/L) compared to shallower waters. The zone at about 1030 m in borehole OL-KR2 also shows slightly elevated N\textsubscript{2} concentrations (137 mL/L) and so it would appear that, pending more data from other deep zones, the high N\textsubscript{2} concentration of OL-KR4 may be derived from a deeper source.

Argon concentrations in Olkiluoto groundwaters are shown in Table 4-1 and range from 0.5 to 7 mL/L for PAVE-sampled groundwaters except for two samples (from KR4-861 and KR15-449 (34 and 62 mL/L, respectively). The ratio of N\textsubscript{2} to Ar in the atmosphere is 83.54. However, because Ar is more soluble than N\textsubscript{2}, 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 N\textsubscript{2}/Ar ratios for Olkiluoto groundwater sampled by the PAVE system range between 1.2 and 182 (Figure 4-5), values that are well outside of the expected range. It is possible that the high Ar samples could be contaminated with Ar used as a back-pressure gas in the operation of the PAVE sampler except that N\textsubscript{2} was used in sampling KR15-499. This aspect was recognised by Karttunen et al. (2000) and has recently been examined in detail by Mäntynen et al. (2005). It was found that Ar, when used as a back-fill gas, could contaminate the sample on occasions and so the samples with high Ar were not reliable for determining the real Ar content of deep groundwaters. Possible contamination by the Ar back-fill gas has also been recognised in groundwaters samples taken by PAVE at the Hästholmen site in eastern Finland (Pitkänen et al. 2000). However, reliable Ar concentrations can be obtained from the samples where N\textsubscript{2} was used as a back-pressure gas.
Samples from depths less than about 600 m, using N₂ as back-fill gas, contained between 0.5 and 1.5 mL/L of Ar. Many are also below the level of atmospheric equilibration (as shown in Figure 4-5) 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 4-5. Variation of N₂/Ar ratio in dissolved gases at Olkiluoto, in comparison to values of the ratio in air and in water equilibrated with air.](image)

### 4.4 H₂-CH₄

The variation of H₂ and CH₄ with depth in the PAVE-sampled groundwaters is shown in Figure 4-6. High concentrations of both gases are found in the deepest groundwaters but significant amounts of the gases, particularly CH₄, may also occur in some of the 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).
Methane is the most abundant gas below 400 m but concentrations of CH$_4$ are highly variable over the depth range 100 - 400 m possibly due to the varying redox conditions associated with the presence of Litorina seawater in this interval (Pitkänen et al. 2004).

Hydrogen is also present at depth and shows a general increase in concentration as CH$_4$ increases (Figure 4-6). However, it is noteworthy that many groundwaters contain CH$_4$ with practically no H$_2$ whereas the reverse (containing H$_2$ with no CH$_4$) is not found. This relationship may indicate that the waters containing CH$_4$ with little H$_2$ may have undergone some degassing and gas loss.

**Figure 4-6.** Variation of H$_2$ and CH$_4$ concentrations with depth in Olkiluoto groundwaters.
Figure 4-7. Relationship between $H_2$ and $CH_4$ concentrations in Olkiluoto groundwaters.

during sampling because $H_2$ is lost more readily than $CH_4$ (as described in section 3).

The close association of $H_2$ and $CH_4$ in the deeper Olkiluoto groundwaters is clearly shown in Figure 4-7. Although the $CH_4/H_2$ ratio varies widely over four orders of magnitude, there appears to be a zone at about 400-600 m depth (Figure 4-8) where $CH_4$ greatly exceeds $H_2$ concentrations 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.

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 4-8. Variation of $\text{CH}_4/\text{H}_2$ ratio with depth in Olkiluoto groundwaters.

4.5 $\text{CH}_4$ - $\text{SO}_4$

The relationship between dissolved $\text{CH}_4$ and $\text{SO}_4$ gases in Olkiluoto groundwaters is shown in Figure 4-9. The generally inverse relationship between $\text{CH}_4$ and $\text{SO}_4$ has been noted before in Olkiluoto groundwaters (Pitkänen et al. 1996) and it has been argued that bacterial reduction (and, therefore, removal of $\text{SO}_4$) is the key control over the concentration of each species.
Figure 4-9. Relationship between CH₄ and SO₄ in Olkiluoto groundwaters.

4.6 Gas saturation pressures

Estimations of the concentration of gases such as N₂, He and H₂ 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-KR4-861-1 at a depth of 860 m. These concentrations are 480, 154 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 CH₄, however.

The levels at which groundwaters become saturated with CH₄ have been described in Table 2-2, based on data reported by Duan et al. (1992), for various temperatures and salinities. The CH₄ data for Olkiluoto groundwaters are compared to the predicted solubilities in Figure 4-10. 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-KR4-861-1, TDS = 69126 mg/L). The highest CH₄ analyses in Figure 4-10 are comparable with the location of the CH₄ saturation levels for 1 to 2 M solutions, predicted by Duan et al. (1992) at 30 °C.

Additional groundwater samples have been taken from this zone in KR4 since the results given by Gascoyne (2000), including the deep zones in KR2 and in other boreholes and they confirm that while most groundwaters are undersaturated with respect to CH₄, those below 800 m have high CH₄ concentrations and suggest that a gas phase may exist at those depths.

The effects of reduced solubility of gases due to the presence of other gases may be important in further causing CH₄ 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 4-10. Comparison of CH$_4$ concentrations with predicted CH$_4$ solubilities over the depth range 0 to 1 km for 30 °C.
5 SUMMARY AND CONCLUSIONS

This report has examined data on dissolved gases from the Olkiluoto site in south-west Finland collected over the period 1997 to 2004 inclusive. Gas samples taken at the surface have been shown to be suspect and suffered gas loss and fractionation by comparison with PAVE data. Examination of the N₂ and Ar contents of the PAVE samples indicates that there may be some contamination by back-filling gases 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 several samples are close to saturation levels and, therefore, a gas phase may exist at depths below 800 m.

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 more data is obtained from deep samples in boreholes at Olkiluoto. The cause of incomplete filling of the PAVE sample vessels needs to be identified more clearly. The possibility of replacing the piston gas filling with a vacuum are suggested as possible improvements to the system. Incomplete vessel filling and reproducible results may to be due to the pressure drop (and associated degassing) due to pumping on the zone and opening of sample valves to fill the chambers. Another alternative is to fill the vessels at the beginning with deionised, degassed water. Water is incompressible and non-expandable so there would be no pressure drop or bubble formation when the valves are opened. This water would be gradually replaced by borehole zone groundwater during the pumping afterwards to flush the vessels.
REFERENCES


