

**36Cl IN GROUNDWATERS OF OXFORDIAN AND DOGGER LIMESTONES OF THE EASTERN PARIS BASIN: IMPLICATIONS FOR OLD GROUNDWATER DATING**

C. Le Gal La Salle¹, L. Benedetti², J. Lancelot¹, D. Bourlès², B. Hamelin²

1. GIS, Université de Nîmes, UMR 6635 CNRS, Parc Scientifique Georges Besse, 150 rue Georges Besse, 30035 Nîmes cedex, France (corinne.legallasalle@unimes.fr, joel.lancelot@unimes.fr)

2. CEREGE, Université d’Aix-Marseille 3, UMR 6635 CNRS, Europôle Méditerranéen de l’Arbois - BP 80 - 13545 AIX EN PROVENCE cedex 04, France (benedetti@cerge.fr, bourles@cerge.fr, hamelin@cerge.fr)

**INTRODUCTION**

In the eventuality of containment barrier failure in deep underground nuclear waste storage scheme, the estimation of groundwater residence time is essential to evaluate the time scale of radionuclide dispersion by advection. Diffusive vertical transfer of anions out of the clay layer in the Oxfordian limestones of the Paris Basin was shown (Lavastre et al, 2005) and the superimposed advective transfer in limestones surrounding the clay layer would contribute to a potential dispersion of the radionuclides as anions. Beyond 30 ka, the limit of 14C dating, groundwater residence time is rather difficult to estimate. With a half-life of 301 ka, 36Cl is particularly appealing for dating groundwaters on the time scale of 10⁴ to 10⁶ years. 36Cl is produced in the atmosphere by spallation of argon nuclei by cosmic rays. After entering the hydrologic cycle by dissolution in precipitation and infiltration, groundwater residence time can be estimated on the basis of cosmogenic 36Cl radioactive decay. Chloride being a conservative ion in solution, changes in 36Cl signal due to water rock interaction is limited and decreasing 36Cl concentration may be attributed to radioactive decay (Phillips 2000). However the cosmogenic origin of groundwater 36Cl has to be ascertained, the input ratio quantified, and potential contribution of deep chlorine-36 needs to be accounted for. This study investigates old groundwaters from the confined Oxfordian and Dogger limestone formations surrounding Callovo-Oxfordian clay layer in the vicinity of the Andra Underground Research Laboratory (URL), east of the Paris Basin.

**RESULTS AND INTERPRETATION**

Dogger and Oxfordian formation waters were collected during the Andra 2003-2004 sampling campaign. Groundwaters of 7 Porous Horizons (PH) in the Oxfordian limestones were sampled during the excavation of the URL main shaft. Another 15 groundwaters were sampled in additional 8 boreholes in the Oxfordian and Dogger formations in the vicinity of the URL, either by slow pumping rate at the depth of porous horizons during borehole excavation (‘Diapo’), or as long term pumping (LTP) after completion of the borehole. The AgCl precipitate was prepared at CEREGE and 36Cl/Cl ratio was determined by accelerator mass spectrometry at the Lawrence Livermore National Laboratory CAMS while stable chlorine concentrations were determined by ion chromatographer at CEREGE. AMS blanks were approximately one order of magnitude lower than the samples and precision on stable chlorine concentrations reach 3% precision.

Dogger groundwater 36Cl/Cl ratio (1 to 5 × 10¹⁵ at.at⁻¹), similar to that at secular equilibrium in this formation (2.3 to 6.5 × 10¹⁵ at.at⁻¹), can be explained either by i) mixing with “old” chloride in equilibrium with the matrix or by ii) chlorine-36 decay. The later hypothesis, while unlikely, would suggest groundwater with age over 1.2 to 1.5 Ma (i.e. 4 to 5 times the 36Cl half-life).

Most Oxfordian groundwaters seem to follow a mixing trend on a 36Cl/Cl ratio vs chlorine plot, between a low Cl and high 36Cl/Cl end-member and a high chloride end-member with low 36Cl/Cl ratio tending toward the 36Cl/Cl ratio at secular equilibrium (6 to 10 × 10¹⁵ at.at⁻¹) (Fig. 1). Mixing could occur i) with
Figure 1: $^{36}$Cl/Cl versus Cl (a), and $^{37}$Cl versus $^{36}$Cl/Cl (b) showing groundwaters sampled in the Oxfordian and Dogger limestones. PH refers to Porous Horizons in the Oxfordian limestones intercepted by the URL main shaft. For other groundwaters, sampled as “diapo” or long term pumping after bore completion, the depth or “LTP” is indicated below the bore number.

chlorine from either Dogger or even Triassic groundwaters by advection through fractures, ii) either with chlorine diffusing from the underlying Callovian-Oxfordian clay layer separating both limestone formations, and/or iii) between groundwaters from several porous horizons (PH) in the Oxfordian limestone presenting varying $^{36}$Cl signature. Chlorine-37, which fractionates during chloride diffusion, provides further information on the mixing process. Oxfordian groundwater $^{37}$Cl ranging between -2,13 and -0,07 %e vs SMOC supports the hypothesis of chlorine diffusion from the underlying Callovian-Oxfordian clay layer (Lavastre et al, 2005). However on a $^{37}$Cl vs $^{36}$Cl/Cl ratio graph (Fig 1b), two of the high $^{36}$Cl/Cl ratio and low chloride concentration groundwaters, EST 351 and EST 321, show little $^{37}$Cl fractionation, with $^{37}$Cl similar to that of the shallow Tithonian groundwaters (-0.7 to +0.3 %e vs SMOC), suggesting that they are not or little affected by chlorine diffusion and might still be considered for dating.

In the hypothesis of mixing with deep $^{37}$Cl, no groundwater ages can be calculated. In the hypothesis that EST321 is not affected by mixing and if we can assume that EST321 is representative of the input signal, straight radioactive decay between EST321 and EST351 can be considered. Taking into account the $^{37}$Cl in situ production, ages in the order of 400±70 ka and 450±70 ka can be calculated for EST351 393m and “LTP” respectively. However EST321 does not necessarily represent the input signal. Considering a theoretical $^{37}$Cl input signal in the precipitations, based on calculated $^{36}$Cl fallout (Philips 2000), leads to ages ranging between 200±80 to 570±160 ka depending on the considered initial conditions including the rate of evapotranspiration and potential variations of the $^{37}$Cl/Cl cosmogenic production. All these emphasize that it is essential to i) better define the input signal to the system through the investigation of groundwater chlorine-36 signal toward the recharge area and ii) identify additional groundwater sample not or little affected by mixing. Measurement of chlorine-36 concentration in modern precipitations in the studied area would also contribute to assist in better defining the input signal.

References: