

# Modelling of hydrochemical evolution in coastal regression area in Finland: a mass balance approach

P. Pitkänen

Technical Research Centre of Finland, P.O.Box 19041, FIN-02044 VTT, Finland.

M. Snellman

Imatran Voima Oy, P.O. Box 112, FIN-01019 IVO, Finland.

## Introduction

Evolutionary processes of the groundwater at the nuclear waste investigation site Olkiluoto are interpreted. The hydrogeological characterization is based on measurements and interpretations from surface and boreholes drilled down to a 1,000-m depth into granite migmatized mica gneiss bedrock (TVO 1992, Pitkänen *et al.*, 1994). The Olkiluoto site is an island off the coast of the Gulf of Bothnia (Baltic Sea). The site is situated in that part of the Fennoscandian shield, where the modern postglacial land uplift is moderate, about 6 mm per year. The elevation on the island is mostly less than 10 m above the mean sea level.

The groundwater types encountered at the site are (1) a diluted recharge Ca-Mg-Na-SO<sub>4</sub>-HCO<sub>3</sub> water, (2) a shallow fresh Na-Cl-HCO<sub>3</sub> type, (3) a brackish Na-Cl type resembling modern Baltic seawater (3,250 mg/l in Cl) with increasing salinity, and (4) a deep saline Ca-Na-Cl type that reaches 22,000 mg/l in Cl. In general, the salinity and Na, Ca, Cl, and Br concentrations increase with depth, whereas Mg, K, HCO<sub>3</sub> and SO<sub>4</sub> show varying trends. Fe, Al, HS and dissolved silica concentrations are low, max. few mg/l. Pitkänen *et al.* (1994) has pointed out that chloride is the most sensitive and conservative indicator for compositional changes in the water chemistry at low temperatures which have prevailed at least hundreds of thousands of years according to fracture calcite studies (Blomqvist *et al.*, 1992, Frapé *et al.*, 1992), probably even longer since the Precambrian. Bromide was also considered to show conservative behaviour. Na, Ca, SO<sub>4</sub> and Br follow the seawater dilution line in low and moderate Cl concentrations, up to 1,000 mg/l. With higher Cl concentrations they show trends towards deep saline groundwater. Mg and K are depleted compared with seawater dilution. HCO<sub>3</sub> shows a great increase in fresh groundwater until the concentration decreases steeply in brackish groundwater. The pH increases immediately from 5–6 of the recharging water to the level of 8–9 in bedrock groundwater. The redox conditions are sulphidic in the bedrock groundwater, even methanic in saline groundwater.

The purpose is to determine the processes which can explain the changes during the evolution of the groundwater system which has been affected by for example coastal regression, and to what extent these processes have taken place.

## Method

The problem was approached by mass balance calculations with the NETPATH program (Plummer *et al.*, 1991). A set of four analyses was selected, representing the chemical changes from recharge water via fresh groundwater and low saline brackish groundwater to the most saline brackish groundwater. The selected processes which can explain the changes between the initial and final water of the modelling steps are based on the observations in chemical, isotopic, mineralogical and hydrological data and the results of speciation calculations. Modern seawater and the most saline deep groundwater sample from Olkiluoto were used as mixing end-members and Cl and Br as mixing parameters.

## Results

The calculated results show that Na and Ca in brackish water and SO<sub>4</sub> in fresh and low saline brackish water are produced mainly (> 80%) by the mixing of fresh recharging groundwater descending into the bedrock with Baltic-type seawater and saline deep groundwater. The same principal sources were expected for these ions, because Na, Ca, SO<sub>4</sub>, and Br compared with Cl show linear increase of same kind from fresh to brackish groundwater. Stable isotope compositions (<sup>2</sup>H, <sup>18</sup>O, <sup>34</sup>S/<sup>32</sup>S, <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>18</sup>O(SO<sub>4</sub>) of groundwaters (Blomqvist *et al.*, 1992, Pitkänen *et al.* 1994) also support the conclusion. However, Na, Ca and SO<sub>4</sub> also take part in chemical interaction. Cation exchange was considered a probable process in the coastal regression area, where seawater has first intruded into an originally Ca-rich saline aquifer. Later seawater has been replaced by recharging Ca-dominated diluted water. The calculated results also indicate these

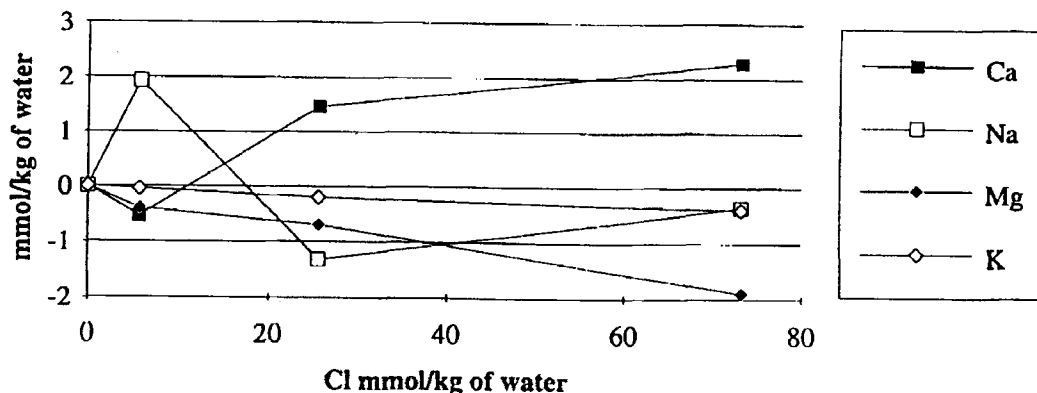


FIG. 1. Cation exchange of mass transfer model results. The points in succession to the right from the origin (recharge water) represent the needed ion exchange of the evolution of fresh groundwater, low saline brackish water and the most saline brackish groundwater. A positive value means release of ion into the solution and a negative value, uptake of ion.

replacement processes (Fig. 1). Ca is released in the brackish groundwater layer, representing the seawater-type intrusion. In the shallow fresh aquifer, where brackish groundwater is diluted, Na is released. The depletion of Mg and K seem to result from ion exchange.

The slightly basic conditions of the bedrock groundwater at all depths seem to result from the buffering of pH by calcite dissolution, which is limited to very shallow depths according to fracture mineralogy, and precipitation coupled with silicate hydrolysis being calculated as plagioclase weathering to kaolinite and silica according to fracture mineralogy. The release and consumption of protons is conserved reasonably in these reactions. The calcite precipitation reaction also consumes a significant part of the dissolved bicarbonate in the brackish groundwater. However, calcite dissolution does not seem to play a major role in the steep increase in bicarbonate of the fresh groundwater at shallow depths. The high calculated  $p_{\text{CO}_2}$  values ( $-3.5 < \log p_{\text{CO}_2} < -2.6$ ) in fresh and brackish groundwater and available data on  $\delta^{13}\text{C}$  (DIC) content ( $-17\text{‰}_{\text{PDB}}$ ) of brackish groundwater indicate an organic source for the bicarbonate. The mass-balance calculations emphasize silicate hydrolysis, which is promoted by carbonic acid (aerobic respiration) in the recharge water, to be the main bicarbonate-producing reaction. The calculations also indicate anaerobic respiration of organic matter, coupled with microbially catalyzed sulphate and ferric iron reduction leading to pyrite precipitation, to be an important bicarbonate source in fresh and brackish groundwater. These also seem to be plausible redox-controlling processes in Olkiluoto. Pyrite coatings on low-

temperature fracture calcites (Blomqvist *et al.*, 1992), lack of ferric precipitates, comparable amounts of measured and calculated organic carbon in groundwater and sulphidic redox-conditions already even at shallow depths in bedrock support the calculated results.

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