

# Stable and radiogenic isotope systematics in ground water and fracture fillings at Äspö, Sweden

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## Introduction

The island of Äspö on the Baltic coast in southeastern Sweden, 400 km south of Stockholm, has been selected as a site for the study of final nuclear fuel disposal in Precambrian bedrock. An underground laboratory is now being constructed (Äspö Hard Rock Laboratory-ÄHRL) as part of a program initiated by the SKB (Swedish Nuclear Fuel and Waste Management Company) in 1986. Preliminary results from one of many ongoing co-operative studies between SKB and DOE (United States Department of Energy) of the ground water and bedrock at the site is presented here. It is focused on stable and radiogenic isotope studies of the ground water and fracture filling minerals to facilitate a better understanding of the present and the past ground water situation at the site.

## Geological setting and hydrogeochemistry

The 1.8-Ga-basement rocks of the Äspö area are within the Svekokarelian belt and are composed granitic rocks of the serorogenic Småland-Värmland granites and acid volcanic rocks of Småland porphyries. The fracture frequency at Äspö is considered to be medium to high, whereas at Laxemar only 7 km to the east, fracture frequency is low. At least two different tectonic events are recorded in the horizontal and subhorizontal fractures developed in the area. The fracture mineralogy which seems to be similar at both sites, is dominated by calcite, hematite, Fe-oxyhydrite, chlorite, fluorite and minor proportions of sulphides. Three different ground waters are distinguished on the basis of isotopic and chemical compositions and concentrations of the dissolved component. There is an overall increase in chlorinity with depth, followed by Na, K, Ca,  $\text{SO}_4^{2-}$  and Br, whereas  $\text{HCO}_3^-$  decreases. The pH of the ground water increases slightly with depth and the partial pressure of  $\text{CO}_2$  decreases.

## Discussion

Ground water and calcite fracture fillings in Early

Proterozoic granite at the island of Äspö show wide ranges in stable and strontium isotopic compositions. None of the isotope signatures resemble those of modern Baltic Sea water although the possibility of mixing exists.  $\delta\text{D}$  values ranges between -112 and -55‰ and the  $\delta^{18}\text{O}$  values ranges between -7 and -15‰. The  $\delta^{13}\text{C}$  of the dissolved bicarbonate range between -16 and -6‰ and decrease systematically with depth suggesting a mixing between an organic and an inorganic carbon source. The  $\delta^{18}\text{O}$  is uniform (+18 and +22‰) and in equilibrium with the most of the ground water.  $\delta^{34}\text{S}$  values of the dissolved sulphate varies between +9.8 and +21‰.  $\delta^{87}\text{Sr}$  values ( $\delta^{87}\text{Sr}$  is defined as the per mil deviation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  value of the sample from the value for present-day sea water) of ground water define two populations.

Eighteen samples of ground water from depths of 15 to 800 m have  $\delta^{87}\text{Sr}$  values between +9.9 and +13‰. These large  $\delta^{87}\text{Sr}$  values contrast markedly with those of five samples of Baltic Sea water collected in the vicinity of Äspö with values between +0.2 and +0.4‰ or only slightly larger than the open ocean water. The 1.8-Ga host rock at Äspö is a high-Sr granodiorite characterized by low Rb/Sr ratios. Its estimated present-day  $\delta^{87}\text{Sr}$  of +2.5‰ illustrates the lack of Sr isotopic equilibrium between the ground water and the host rock at the bulk-rock scale. Preferential dissolution of biotite, which has much larger  $\delta^{87}\text{Sr}$ , could explain the radiogenic character of Sr in the ground water but not its high chlorinity and very large Na/K ratios. In contrast with the ground water, calcite fissure fillings (20 samples) have smaller  $\delta^{87}\text{Sr}$  values ranging from -3.6 to +9.9‰. Only those with the largest  $\delta^{87}\text{Sr}$  values could have precipitated from present-day ground water.  $\delta^{87}\text{Sr}$  values generally decrease with increasing depth and correlate crudely with reciprocal Sr concentrations. The latter relationship is commonly attributed to mixing of two end-members, but it more likely represents a progressive interaction with ground water isotopically similar to that which presently exists in the rock mass, with plagioclase (large Sr concentra-

tions and small  $\delta^{87}\text{Sr}$  values) (Wallin and Peterman, 1994).

$\delta^{13}\text{C}$  values in the calcite fissure fillings range between  $-48$  and  $-3\text{‰}$  and the  $\delta^{18}\text{O}$  values range between  $+15$  and  $+26\text{‰}$ . The large range in  $\delta^{13}\text{C}$  values is indicative of multiple sources for the carbon, including atmospheric, organic and methane derived carbon (Wallin and Peterman, 1994). The  $\delta^{18}\text{O}$  signatures suggest a mixing of meteoric and possibly marine waters, although some of the calcites could be in equilibrium with the modern ground water.

The stable isotope data from the calcite fissure fillings and the dissolved species suggest three different water layers at Äspö: (1) a shallow ground water (0–150m) characterized by a mixture of meteoric water and minor proportions of Baltic Sea water (according to the seasonal variation of the isotopic signature ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) of the rain water the recharge of this water lens takes place during the autumn and the winter), (2) an intermediate water (150–500m) characterized by a mixture of marine and meteoric isotope signatures, and (3) a deep ground water body (>500m) which is highly saline with nonmarine signatures of the dissolved species.

The  $\delta^{13}\text{C}$  signatures of the dissolved carbonate in the shallow ground water fall within a narrow range of  $-15.8$  to  $-17.4\text{‰}$ , indicative of an organic carbon source. The low  $\delta^{13}\text{C}$  values suggest that input of soil- $\text{CO}_2$  is the dominating carbon source for that system. This is supported by the high TOC concentrations (up to 20 mg/L) in the shallow ground water body. Degradation of organic matter is coupled with inorganic oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and subsequent hematite formation.

The intermediate water layer is characterized by a considerable drop in the  $\delta^{34}\text{S}$  values of the dissolved sulphate which indicates an in-mixing of a non-marine component. This suggests a contribution of reduced sulphur from the fracture sulphides. Therefore the sulphur and oxygen data combined for that water suggest that it originates from an early injection of a highly oxygenated Baltic Sea water, presumably after the latest ice recession in the area. The deep ground water contains a stable isotope assembly with overall typically non-marine signatures. However, the spread in  $\delta^{34}\text{S}$  of the dissolved sulphate in combination with the sulphide sulphur signatures suggest that considerable bacterial sulphate reduction takes place in the upper part of this water body.

The Baltic Sea may have undergone a substantial decrease in  $\delta^{87}\text{Sr}$  during the Holocene. Strontium in the modern Baltic is derived through runoff from surrounding terranes and perhaps from some influx of sea water from the north Sea

(Andersson *et al.*, 1992). Studies by Löfvendahl (1990) and others have shown that the  $\delta^{87}\text{Sr}$  in runoff from the Precambrian terranes averages about  $+29\text{‰}$ . During the retreat of the ice sheet, finely ground Precambrian material would have been exposed to weathering and transport into Baltic Basin dramatically increasing influx of Sr from the Precambrian shield areas and thus raising the  $\delta^{87}\text{Sr}$  in Baltic Sea water. Accordingly the early post glacial melt waters formed during the ice recession of the latest glacial period could be responsible for the  $\delta^{18}\text{O}$  depletion observed in the saline ground waters at Äspö. In addition, the sulphate  $\delta^{34}\text{S}$  values ( $+14$  and  $+15\text{‰}$  observed at intermediate depth at Äspö) are significantly lower than those of modern marine water sulphates. This could indicate contribution of reduced sulphur due to water/rock interaction to the marine or brackish waters which was residing in the Baltic area after the ice recession. The discrepancy of the observed  $\delta^{18}\text{O}$  and  $\delta^{87}\text{Sr}$  values in the ground water at Äspö, could hence reflect an accumulation of post-glacial runoff waters as well as injections of early marine post glacial stages of the Baltic Sea.

### Conclusions

Several waters have been involved in the precipitation of calcite fissure fillings, other than present-day water at Äspö. The isotopes  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{87}\text{Sr}$  provide evidence of meteoric waters and/or glacial melt waters as well as fossil marine waters with depleted  $\delta^{18}\text{O}$  signatures and high Cl concentrations.  $\delta^{87}\text{Sr}$  values of calcite fracture fillings which are crudely correlative with reciprocal Sr concentrations could record progressive and preferential water/rock reaction.  $\delta^{34}\text{S}$  values of the dissolved sulphate show a multiple source, including marine sulphur, biologically reduced sulphur. This study demonstrates that the combination of stable and radiogenic isotopes is particularly productive in providing constraints for modelling the source and evolution of ground water and hydrogenic deposits in such terranes.

### References

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