

R-11-13

**Bacterial sulphate reduction and
mixing processes at the Äspö
Hard Rock Laboratory indicated
by groundwater $\delta^{34}\text{S}$ isotope
signatures**

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April 2011

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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Abstract

This report includes data mostly obtained from $\delta^{34}\text{S}$ isotope measurements of groundwater at the Äspö Island and one sampling from the Laxemar site, southeastern Sweden, during tunnel construction. Early sampling at Äspö (up to 1992), before tunnel excavation, indicates a groundwater system with multiple sulphur sources. The isotope changes over time in the dissolved sulphate were studied during a sampling campaign in the monitoring phase from 1993 to 1995. A total of 88 samples were collected by SKB between 1992 and 1995 from core-drilled surface boreholes and from boreholes drilled in the tunnel (34 of these samples were collected from the tunnel boreholes). The results of the analyses have been the focus of discussion of the isotope changes with time in the dissolved sulphate (SO_4^{2-}).

The results indicate that the sulphur isotope signatures in the dissolved sulphate of the groundwater and those from fracture-filling sulphides at Äspö originate from multiple sulphur sources in the groundwater at Äspö and Laxemar. The data may be grouped as follows: a) typically homogeneous marine signatures of dissolved SO_4^{2-} are observed, with $\delta^{34}\text{S}$ values of approximately +21‰ CDT at intermediate depths of approximately 100–250 m; b) dissolved sulphate in the groundwater at greater depths (below 600 m) with average values of approximately +10‰ CDT; and c) a dissolved SO_4^{2-} originating from a mixture of these sulphur sources (100 – 600m), although there is a difference between a mixture and modification by reduction. Reduced sulphur with low $\delta^{34}\text{S}$ values is also recorded in fracture-filling sulphides, with $\delta^{34}\text{S}$ values of approximately 0 to –10‰ CDT. This may contribute to small changes in the isotope signature of the dissolved SO_4^{2-} , probably by sulphide oxidation in the past.

The changes in the $\delta^{34}\text{S}$ isotope data for dissolved SO_4^{2-} over the 1992–1996 period suggest a complex situation, indicating both sulphate reduction by sulphate-reducing bacteria (SRB) and groundwater mixing from shallow marine and deeper, older groundwater sources during tunnel construction. These isotope changes were likely induced by the up-coning of deeper saline water and the inflow of Baltic Sea water to an intermediate depth (e.g., 200–400 m) at Äspö. The increase in $\delta^{34}\text{S}$ isotope values of dissolved SO_4^{2-} , peaking at +28‰ CDT (probably due to position of the tunnel below the Baltic Sea), was accompanied by a decrease in sulphate concentration in many places and, in some samples, also by changes in bicarbonate concentration, all of which are evidence of microbial sulphate reduction.

Contents

1	Background	7
2	Material	9
3	Methods	11
3.1	Sampling	11
3.2	Sample isotope preparation and measurement of sulphur isotopes	11
4	Results	13
5	Discussion	17
5.1	$\delta^{34}\text{S}$ isotopes as indicators	17
5.1.1	Indicators of sulphate reduction	17
5.1.2	Indicators of mixing	17
5.2	Origin of the sulphur source	19
5.3	Correlation between $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and Cl^-	22
5.4	$\delta^{34}\text{S}$ isotope changes in the dissolved sulphate over time observed in tunnel borehole water	23
5.4.1	Borehole SA1420A	24
5.4.2	Borehole SA2074A	27
5.4.3	Borehole SA1229A	28
5.4.4	Borehole SA1730A	30
5.4.5	Borehole SA2273A	31
5.4.6	Borehole SA2783A	32
5.4.7	Borehole SA0813A	33
5.5	Summary of observations concerning the tunnel boreholes	34
5.6	Processes that may be responsible for the observed changes in $\delta^{34}\text{S}$ over time	34
6	Conclusion	35
7	References	37

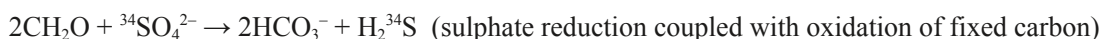
1 Background

Changes in the $\delta^{34}\text{S}$ isotope signatures are useful tools for monitoring microbial processes. Other chemical components, such as reactants (e.g. sulphates, C_{org} , HCO_3^-), are affected by the physical and biological processes which in turn enable the sulphur isotopes to be distinguished by producing distinct isotope ratios or “fingerprints” in various substances, such as reaction products (e.g. sulphides), integrated in time and space. However one needs to have a multiple parameter approach in order to fully delineate the various isotope signatures.

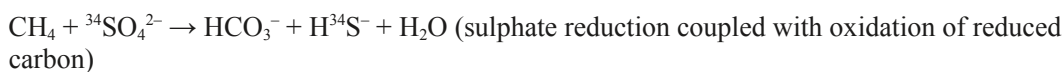
Sulphur isotopes can also be influenced by groundwater mixing, but one must be careful in delineating whether a change in isotope signature is due to mixing or to fractionation processes. However, if combined with conservative parameters such as groundwater $\delta^{18}\text{O}$ and Cl^- , the $\delta^{34}\text{S}$ isotope values of dissolved sulphate can be used to distinguish between mixing and, for example, microbial sulphate reduction of the sulphur sources.

During sulphate reduction, bacteria preferentially select the lighter isotope to save energy, so the residual sulphate becomes continuously enriched in the heavier isotope, ^{34}S . In contrast, the hydrogen sulphide produced is preferentially enriched in the lighter isotope, ^{32}S .

Given an accessible organic carbon substrate (or other electron donors such as H_2), bacteria such as *Desulfovibrio sulfuricans* will use the dissolved sulphate as an electron acceptor and produce sulphide and mineralised carbon according to the following basic reaction:



When CH_4 is present, a symbiosis of methanogenic and sulphate reduction bacteria will use this substrate as an electron donor according to the reaction below:



The reaction of ^{32}S during sulphate reduction is faster than that of ^{34}S , due to the lower energy needed to break $^{32}\text{S}-\text{O}$ bonds. As the reaction proceeds, ^{34}S gradually accumulates in the residual sulphate reservoir. The difference in ^{34}S between coexisting dissolved sulphate and sulphide ($\delta^{34}\text{S}_{\text{SO}_4-\text{H}_2\text{S}}$) has three controls: the $\delta^{34}\text{S}$ of the sulphate source (most often of marine origin, but also a potential contribution from the dissolution of, for example, gypsum and the oxidation of pyrite in the fractured host rock), the fractionation factor, and Rayleigh distillation effects.

An attempt is made here to use the observed changes of $\delta^{34}\text{S}$ in the dissolved sulphate over time to determine how much of the change is due to sulphate reduction and how much is due to mixing. Any changes in $\delta^{34}\text{S}$ in the dissolved sulphate due to mixing may be distinguished by use of corresponding observations of conservative parameters such as Cl^- and $\delta^{18}\text{O}$.

2 Material

Groundwater for $\delta^{34}\text{S}$ analysis of the dissolved sulphate was sampled at various depths from core-drilled surface boreholes, surface locations (i.e., Baltic Sea water or older marine water such as Littorina water), and tunnel boreholes in the Äspö Hard Rock Laboratory (HRL) tunnel. A total of 88 samples collected in 1992 and 1996 are examined in this report. All sampled boreholes and sites are listed in Table 2-1.

Table 2-1. All boreholes are listed along with data on water type, depth (m), and coordinates. The water types “SW” and “GW” indicate Baltic Sea water and groundwater, respectively. The (x, y, z) coordinates correspond to the Äspö 96 coordinate system. “Upper” and “lower” correspond to the borehole packer limits of the sampled section.

Sample	Water type	Upper (m)	Lower (m)	Elevation (m)	x	y	z
HAV 1 SW	SW	6.0	–	–6.0	–	–	–
HAV 2 SW	SW	3.0	–	–3.0	–	–	–
HBH 01	GW	31.0	50.6	–40.8	2,165.7	6,187.7	–39.7
HBH 02	GW	21.0	32.4	–26.7	2,160.0	6,194.5	–19.7
HBH E1 SW	SW	0.0	–	0.0	–	–	–
HBH V1 SW	SW	1.0	–	–1.0	–	–	–
KAS 02-2	GW	800.0	854.0	–827.0	2,111.9	7,327.4	–816.5
KAS 02-4	GW	309.0	345.0	–327.0	2,114.7	7,287.1	–318.2
KAS 03-2	GW	533.0	626.0	–579.5	1,781.6	7,825.3	–566.3
KAS 05-1	GW	440.0	549.0	–494.5	2,075.0	7,197.9	–483.0
KAS 06-1	GW	431.0	500.0	–465.5	2,225.8	7,311.0	–388.1
KAS 06-5	GW	191.0	249.0	–220.0	2,193.2	7,180.6	–182.7
KAS 07-1	GW	501.0	604.0	–552.5	2,043.8	6,994.8	–465.0
KAS 07-4	GW	191.0	290.0	–240.5	2,140.5	7,130.5	–201.3
KAS 08-1	GW	503.0	601.0	–552.0	2,324.0	7,189.4	–441.3
KAS 09-1	GW	116.0	150.0	–133.0	2,090.8	6,857.9	–110.6
KAS 12-4	GW	103.0	234.0	–168.5	2,174.6	7,509.4	–151.8
KAS 12-4	GW	103.0	234.0	–168.5	2,174.6	7,509.4	–151.8
KAS 13-1	GW	221.0	330.0	–275.5	2,039.6	7,288.8	–237.9
KAS 13-2	GW	191.0	220.0	–205.5	2,072.6	7,279.8	–176.9
KAS16	GW	40.0	–	–20.0	2,253.0	7,168.6	–35.54
KLX02	GW	315.0	–	–315.0	1,549,223.9	6,366,797.2	–331.2
KR0012B	GW	70.0	–	–35.0	2,171.3	6,161.7	–69.3
KR0013B	GW	70.0	–	–35.0	2,169.9	6,161.0	–69.3
KR0015B	GW	71.0	–	–71.0	2,068.0	6,159.9	–69.1
SA1062B	GW	151.7	–	–151.7	2,145.7	6,724.9	–147.7
SA0709B	GW	101.3	–	–101.3	2,161.8	6,364.8	–102.8
SA0776B(91)	GW	110.9	–	–110.9	2,155.2	6,443.7	–107.9
SA0776B(92)	GW	110.9	–	–110.9	2,155.2	6,443.7	–107.9
SA0982B	GW	140.3	–	–140.3	–	–	–
SA1229A	GW	175.6	–	–175.6	2,104.8	6,885.2	–172.0
SA1420A	GW	202.9	–	–202.9	2,079.7	7,092.6	–201.3
KA1639 (inner)	GW	234.1	–	–234.1	2,023.5	7,276.0	–224.4
KA1639 (middle)	GW	234.1	–	–234.1	2,023.5	7,276.0	–224.4
SA1730A	GW	247.1	–	–247.1	2,073.0	7,375.4	–237.8
KA1750A (inner)	GW	250.0	–	–250.0	2,073.0	7,375.4	–237.8
SA2074A	GW	296.3	–	–296.3	2,335.6	7,284.6	–282.4
SA2273A	GW	324.7	–	–324.7	2,221.2	7,151.1	–306.7
SA2600A	GW	371.4	–	–371.4	2,040.7	7,317.1	–345.8
SA2783A	GW	397.6	–	–397.6	2,160.7	7,444.0	–372.1
SA0813B	GW	116.1	–	–116.1	2,151.4	6,479.6	–113.7

During the monitoring phase between 1993 and 1996, a total of 34 samples were collected from the following boreholes in the HRL tunnel: SA0709B, SA1062B, SA0776B (91), SA0776B (92), SA0982B, SA1229A, SA1420A, SA1730A, SA2074A, SA2273A, SA2600A, SA2783A, and SA0813B (see Table 2-1 and Figure 2-1). This produced a time series from several boreholes from various depths in the tunnel.



Figure 2-1. A 3D projection of the tunnel at the Äspö HRL tunnel showing the positions of boreholes sampled for this study.

3 Methods

3.1 Sampling

Groundwater was collected by SKB from boreholes during the 1992–1996 monitoring campaign. The samples were filtered (45 microns), placed in acid-washed PVC containers, and precipitated as barium sulphate (BaSO_4) by adding BaCl_2 . The precipitation was performed at a controlled, low pH by acidification with HCl. The solution was filtered, and the precipitate was rinsed with distilled water before air drying. The samples were then shipped to the lab at the Institutt for Energiteknik (IFE; Oslo, Norway) for analysis. In addition to collecting groundwater for $\delta^{34}\text{S}$ isotope measurements, samples were collected for the analysis of major elements. In some cases, separate samples were taken for the $\delta^{18}\text{O}$, $\delta^2\text{H}$, and ^3H analyses.

Sulphides were sampled from fracture fillings from borehole cores by Geokema AB and subsequently leached using concentrated HNO_3 and precipitated as ZnS using Zn acetate in a reaction vessel. The samples were then decanted and the precipitate was sent to the IFE laboratory for isotope analysis.

3.2 Sample isotope preparation and measurement of sulphur isotopes

Further preparation and analysis of the BaSO_4 samples collected as precipitates (see Section 3.1 “Sampling”) were conducted at the IFE laboratory, where the first step was to prepare the samples for an NCS 2500 element analyser (Carlo Erba, Milan, Italy). The BaSO_4 precipitates were rinsed with warm, distilled water before air drying. Aliquots of the sample precipitates were mixed with V_2O_5 and transferred to tin capsules. The procedure continued with the flash combustion of the samples at approximately $1,700^\circ\text{C}$, reduction of SO_3 to SO_2 in the presence of Cu at $1,000^\circ\text{C}$, separation of combustion products by means of gas chromatography using a Poraplot Q column (Varian, Palo Alto, CA), and transfer of SO_2 to a Micromass Optima isotope mass spectrometer (Manchester, England) for determination of $\delta^{34}\text{S}$. The S-1 and S-2 standards from IAEA were used for calibration and the NBS-127 standard is analysed as unknown. The average analysed NBS-127 value in 2008–2009 was $\delta^{34}\text{S}_{\text{CDT}} = 20.51 \pm 0.31\text{‰}$ (one standard deviation); the “true” value /IAEA 1995/ is $20.315 \pm 0.357\text{‰}$ CDT.

The sulphide sample precipitates (i.e., ZnS) were prepared at the IFE lab as follows. AgNO_3 was added to the Zn acetate solution along with the ZnS precipitate and all sulphur was precipitated as Ag_2S . The solution was filtered and the filter, including Ag_2S precipitate, was washed with deionised water and dried in air. The precipitate was then weighed on a precision balance and mixed with V_2O_5 in a tin vessel. The vessel was closed and placed in the inlet system of an NCS 2500 element analyser (EuroVector, Milan, Italy). The samples were then combusted in an oven at $1,700^\circ\text{C}$ and the gas released (SO_3) was reduced to SO_2 using copper (Cu) at 650°C . The gas was separated in a column and introduced directly into a Micromass Optima isotope mass spectrometer (Manchester, England) for $\delta^{34}\text{S}$ determination.

Isotopic analyses of the SO_4^{2-} and sulphides (FeS) are expressed in per mil (‰) deviations (δ values) from the Canyon Diablo troilite standard (CDT) and calibrated to the IAEA and NBS standards given above; δ is defined as:

$$\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] * 1000$$

where R is $^{34}\text{S}/^{32}\text{S}$. Uncertainties (2 sigma) are $\pm 0.1\text{‰}$ or better.

All data from this study are available from the Sicada database.

4 Results

The results of the $\delta^{34}\text{S}$ analyses of the dissolved sulphate indicate a wide range in the isotope signature between +10 and +28‰ CDT. Overall, $\delta^{34}\text{S}$ decreases with depth from approximately +20‰ CDT in surface and shallow groundwaters to +10‰ CDT at depths greater than 800 m (Figure 4-1). This overall trend has been confirmed in later studies at Laxemar /Laaksoharju et al. 2009/. The elevated $\delta^{34}\text{S}$ values between +20 and 28‰ CDT are found at depths of 100–400 m (Figure 4-1). The $\delta^{34}\text{S}$ values observed in the time series from various boreholes in the tunnel indicate a change in isotope signature over time as described below.

In boreholes SA1420 at a depth of 202.9 m and A2273A at 324.7 m, an increase in $\delta^{34}\text{S}$ values with time was observed accompanied by a decrease in Cl^- and SO_4^{2-} . An even more pronounced increase in $\delta^{34}\text{S}$ values with time was observed in SA 2074A at a depth of 296.3. In contrast, the $\delta^{34}\text{S}$ values remained more or less constant between +14 and +15‰ CDT over time in borehole SA1730A at a depth of 247.1 m, though there was a large change in Cl concentration. The results of the $\delta^{34}\text{S}$ isotope measurements have been analysed together with the chemical parameters SO_4^{2-} , HCO_3^- , Cl^- , and $\delta^{18}\text{O}$ listed in Table 4-1 below.

Included in this study are sulphides (e.g., pyrite) collected from the fracture fillings at several depths for isotope analysis. The results are presented in Table 4-2. Though the sulphide data are not discussed in detail, they are reported here to indicate that there is considerable input of reduced sulphur into those sulphides.

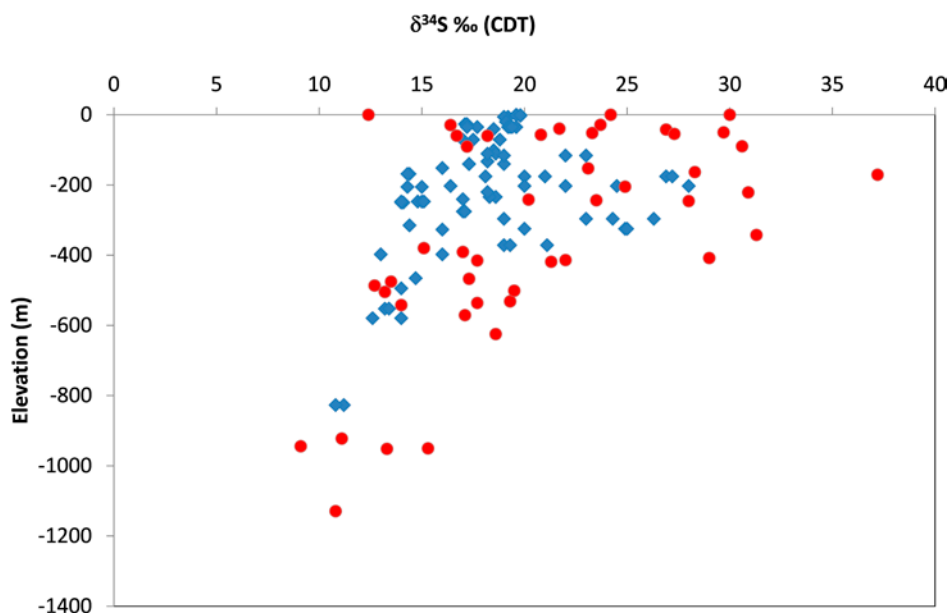


Figure 4-1. $\delta^{34}\text{S}$ of dissolved sulphate in Äspö groundwaters plotted versus depth. Blue diamonds: Äspö data collected up to 1996; red dots: data collected from borehole KLX02 in the Laxemar site investigation area /Laaksoharju et al. 2009/.

Table 4-1. Analysed dissolved sulphate $\delta^{34}\text{S}$ values in groundwater from core-drilled surface boreholes and tunnel boreholes together with some of the parameters used here. HAV 1 SW, HAV 2 SW, HBH E1 SW, and HBH V1 SW correspond to Baltic Sea water samples.

Sample	Sample ID (SKB)	Sampling date	Elevation (m)	$\delta^{34}\text{S}$ (‰) CDT	SO_4^{2-} (mg/L)	$1/\text{SO}_4^{2-}$ (L/mg)	$\delta^{18}\text{O}$ (‰) V-SMOW	Cl^- (mg/L)	HCO_3^- (mg/L)
HAV 1 SW	–	1992-09-01	–6.0	+19.2	–	–	–	–	–
HAV 1 SW	–	1992-09-01	–6.0	+19.0	–	–	–	–	–
HAV 2 SW	–	1992-09-01	–3.0	+19.8	–	–	–	–	–
HAV 2 SW	–	1992-09-01	–3.0	+19.8	–	–	–	–	–
HBH 01	2165	1993-09-08	–40.8	+18.5	–	–	–9.5	515	310
HBH 01	2165	1993-09-08	–40.8	+18.5	–	–	–9.5	515	310
HBH 02	2111	1993-06-12	–26.7	+17.1	20.9	0.04785	–9.4	13	74
HBH 02	2164	1993-09-08	–26.7	+17.2	–	–	–8.5	18	79
HBH 02	2164	1993-09-08	–26.7	+17.2	–	–	–8.5	18	79
HBH E1 SW	–	1992-09-01	0.0	+19.6	–	–	–	–	–
HBH E1 SW	–	1992-09-01	0.0	+19.6	–	–	–	–	–
HBH V1 SW	–	1992-09-01	–1.0	+19.6	–	–	–	–	–
HBH V1 SW	–	1992-09-01	–1.0	+19.8	–	–	–	–	–
KAS 02-2	1989	1992-08-19	–827.0	+11.2	–	–	–13.6	10,200	25
KAS 02-2	2163	1993-09-07	–827.0	+10.8	–	–	–13.4	10,800	8
KAS 02-4	1990	1992-08-19	–327.0	+16.0	200.0	0.00500	–13.3	3,250	138
KAS 03-2	1986	1992-08-19	–579.5	+14.0	–	–	–14.9	3,360	48
KAS 03-2	2162	1993-09-07	–579.5	+12.6	–	–	–14.3	4,230	38
KAS 05-1	2000	1992-09-01	–494.5	+14.0	576.0	0.00174	–12.9	7,290	12
KAS 06-1	1987	1992-08-19	–465.5	+14.7	357.0	0.00280	–9.2	5,670	52
KAS 06-5	1988	1992-08-19	–220.0	+18.2	117.0	0.00855	–12.0	2,450	135
KAS 07-1	1995	1992-08-31	–552.5	+13.4	486.0	0.00206	–12.1	6,060	18
KAS 07-1	1995	1992-08-31	–552.5	+13.2	486.0	0.00206	–12.1	6,060	18
KAS 07-4	2159	1993-09-06	–240.5	+17.0	–	–	–8.1	3,810	182
KAS 08-1	1997	1992-08-31	–552.0	+13.4	413.0	0.00242	–10.8	6,300	27
KAS 09-1	2002	1992-09-01	–133.0	+18.2	228.0	0.00439	–7.4	3,820	396
KAS 09-1	2002	1992-09-01	–133.0	+18.2	228.0	0.00439	–7.4	3,820	396
KAS 12-4	2003	1992-09-01	–168.5	+14.4	–	–	–11.4	–	–
KAS 12-4	2003	1992-09-01	–168.5	+14.3	–	–	–11.4	–	–
KAS 12-4	2161	1993-09-07	–168.5		–	–	–10.5	4,860	61
KAS 13-1	2004	1992-09-01	–275.5	+17.0	112.0	0.00893	–11.1	543	294
KAS 13-1	2004	1992-09-01	–275.5	+17.1	112.0	0.00893	–11.1	543	294
KAS 13-2	2005	1992-09-01	–205.5	+15.0	190.0	0.00526	–11.9	2,160	188
KAS 13-2	2005	1992-09-01	–205.5	+14.3	190.0	0.00526	–11.9	2,160	188
KAS16	13707	1992-08-20	–20.0	+19.1	–	–	–	–	–
KLX02	2738	1994-02-10	–315.0	+14.4	43.0	0.02326	–10.3	73	223
KR0012B	13218	1991-05-15	–35.0	+19.2	–	–	–11.4	677	200
KR0012B	13218	1991-05-15	–35.0	+19.6	–	–	–11.4	677	200
KR0013B	1984	1992-08-18	–35.0	+19.3	153.0	0.00654	–10.3	2,020	280
KR0013B	2108	1993-06-11	–35.0	+17.7	144.0	0.00694	–10.0	1,710	307
KR0013B	2277	1994-09-05	–35.0	+17.7	–	–	–9.4	1,737	291
KR0013B	2315	1995-05-17	–71.0	+17.5	–	–	–9.3	1,521	273
KR0013B	2315	1995-05-17	–71.0	+18.8	–	–	–9.3	1,521	273
KR0015B	13217	1991-05-07	–35.0	+19.4	89.0	0.01124	–11.6	3,050	122
KR0015B	13217	1991-05-07	–35.0	+19.4	89.0	0.01124	–11.6	3,050	122
KR0015B	2109	1993-06-11	–35.0	+17.2	134.0	0.00746	–10.1	805	415
KR0015B	2316	1995-05-17	–71.0	+17.0	–	–	–9.6	977	346
SA 1062B	17341	1992-08-18	–151.7	+16.0	187.0	0.00535	–7.3	4,350	403
SA 1062B	17341	1992-08-18	–151.7	+16.0	187.0	0.00535	–7.3	4,350	403

Sample	Sample ID (SKB)	Sampling date	Elevation (m)	$\delta^{34}\text{S}$ (‰) CDT	SO_4^{2-} (mg/L)	$1/\text{SO}_4^{2-}$ (L/mg)	$\delta^{18}\text{O}$ (‰) V-SMOW	Cl^- (mg/L)	HCO_3^- (mg/L)
SA0709B	17342	1994-08-18	-101.3	+18.5	-	-	-	-	-
SA0776B(91)	-	1991-06-28	-110.9	+18.6	-	-	-	-	-
SA0776B(92)	17343	1992-09-01	-110.9	+18.2	-	-	-	-	-
SA0982B	-	1992-08-18	-140.3	+17.3	-	-	-	-	-
SA0982B	-	1992-08-18	-140.3	+17.3	-	-	-	-	-
SA0982B	-	1994-09-05	-140.3	+19.0	-	-	-7.4	-	-
SA1229A	2147	1993-09-02	-175.6	+18.1	-	-	-7.4	4,105	-
SA1229A	2281	1994-09-05	-175.6	+20.0	242.0	0.00413	-7.1	3,687	242
SA1229A	2285	1994-09-07	-175.6	+21.0	224.0	0.00446	-7.1	3,872	224
SA1229A	2320	1995-05-18	-175.6	+26.9	-	-	-6.5	3,675	310
SA1229A	2329	1995-10-11	-175.6	+27.2	224.4	0.00446	-7.3	3,482	314
SA1420A	83	1992-08-18	-202.9	+16.4	200.0	0.00500	-11.2	4,610	830
SA1420A	2148	1993-09-07	-202.9	+20.0	308.8	0.00324	-7.2	3,435	212
SA1420A	2282	1994-09-05	-202.9	+22.0	280.0	0.00357	-7.1	2,950	199
SA1420A	2318	1995-05-18	-202.9	+28.0	253.0	0.00395	-7.1	2,900	199
SA1420A	2330	1995-10-11	-202.9	+24.5	267.4	0.00374	-7.3	2,721	204
KA1639 (inner)	-	1995-10-11	-234.1	+18.6	-	-	-	-	-
KA1639 (middle)	-	1995-10-11	-234.1	+18.3	-	-	-	-	-
SA1730A	2151	1993-09-07	-247.1	+14.8	470.8	0.00212	-11.7	6,065	40
SA1730A	2286	1994-09-07	-247.1	+15.0	549.0	0.00182	-12.4	8,500	31
SA1730A	2319	1995-05-18	-247.1	+14.0	540.0	-	-12.0	8,672	32
SA1730A	2331	1995-10-11	-247.1	+15.1	530.5	0.00189	-12.1	8,651	36
KA1750A (inner)	2331	1995-10-11	-250.0	+14.1	-	-	-	-	-
KA1750A (middle)	-	1995-10-11	-250.0	+14.0	-	-	-	-	-
SA2074A	2173	1993-09-07	-296.3	+19.0	277.0	0.00361	-8.4	4,670	79
SA2074A	2283	1994-09-06	-296.3	+23.0	263.0	0.00380	-8.4	3,967	103
SA2074A	2317	1995-05-18	-296.3	+24.3	-	-	-	-	-
SA2074A	2332	1995-10-11	-296.3	+26.3	251.3	0.00398	-8.4	3,239	140
SA2273A	2287	1994-09-06	-324.7	+20.0	203.0	0.00493	-7.9	4,921	205
SA2273A	2321	1995-05-18	-324.7	+24.9	-	-	-7.8	4,788	182
SA2273A	2326	1995-10-11	-324.7	+25.0	241.7	0.00414	-8.1	4,347	180
SA2600A	2284	1994-09-06	-371.4	+19.0	470.0	0.00213	-11.2	7,735	37
SA2600A	2312	1995-05-17	-371.4	+19.3	-	-	-	-	-
SA2600A	2327	1995-10-11	-371.4	+21.1	382.1	0.00262	-9.8	6,183	95
SA2783A	2288	1994-09-07	-397.6	+16.0	513.0	0.00195	-12.2	9,023	18
SA2783A	2322	1995-05-23	-397.6	+13.0	-	-	-12.0	10,944	14
SA0813B	2166	1993-09-07	-116.1	+19.0	-	-	-7.0	3,300	326
SA0813B	2275	1994-09-05	-116.1	+22.0	298.0	0.00336	-7.2	3,113	292
SA0813B	2311	1995-05-17	-116.1	+23.0	-	-	-	-	-
SA0813B	2336	1995-10-12	-116.1	+23.0	582.1	0.00172	-7.5	2,980	318

Table 4-2. Sulphide $\delta^{34}\text{S}$ values from pyrites collected in fracture fillings at Äspö.

Sample ID	Borehole	$\delta^{34}\text{S}$ (CDT)	Elevation (m)
PY2-70	KAS02	-2.2	-70
PY2-122	KAS02	-3.2	-122
PY2-433	KAS02	-9.1	-433
PY2-534	KAS02	-19.6	-534
PY2-597	KAS02	-7.2	-597
PY2-720	KAS02	-22	-720
PY3-223	KAS03	-2.4	-223
PY3-491	KAS03	-26.6	-491
PY3-520	KAS03	-6.4	-520
PY3-618	KAS03	0.4	-618
PY3-629	KAS03	-2.3	-629
PY6-102	KAS06	-9	-102
PY6-267	KAS06	-3.5	-267
PY6-412	KAS06	-8.3	-412
PY6-450	KAS06	-11	-450
PY6-495	KAS06	-13.4	-495

5 Discussion

5.1 $\delta^{34}\text{S}$ isotopes as indicators

The sulphur compounds from various sources participate in the geochemical evolution of groundwater. The $\delta^{34}\text{S}$ isotopes can therefore be used as a tool for monitoring changes in the groundwater. The fractionation of $\delta^{34}\text{S}$ isotopes in natural systems between sulphur compounds is an important tool to trace biological cycling and specifically sulphate reduction. On the other hand, in some systems $\delta^{34}\text{S}$ isotopes can contribute to the understanding of groundwater mixing, when used together with conservative parameters such as $\delta^{18}\text{O}$ and dissolved Cl^- .

5.1.1 Indicators of sulphate reduction

The most important process involved in the variation of sulphur (S) in the natural systems is the reduction of sulphate by anaerobic bacteria as mentioned above in the introduction section. However, the extent of fractionation is variable and depends on certain rate-controlling steps in the reactions by which S is metabolised /Faure 2005/. According to /Harrison and Thode 1958/ the fractionation associated with bacterial reduction of sulphate show fractionation effects up to 27 ‰ enrichment in the lighter isotope ^{32}S . Later /Kaplan and Ritterberg 1964/ obtained ^{32}S enrichments in H_2S of up to 46 ‰.

Another key observation is that the isotopic composition of H_2S liberated by bacteria also depends on the magnitude of the sulphate reservoir. At Äspö and Laxemar the dissolved sulphate concentrations are up to 400 to 500 mg/L in some waters (see Table 4-1). According to the previous observations these waters are referred to Baltic Sea and Littorina waters /Laaksoharju 1995, Laaksoharju et al. 2009/ and in this system are considered as a large source of sulphate, although not infinite. In principle, however, in a open system the $\delta^{34}\text{S}$ value of the H_2S produced by reduction of the sulphate should remain constant. This is not the case at Äspö and Laxemar and one can therefore assume that we are dealing of a semi-open system, based on the fact that the reservoir is limited. As a result the $\delta^{34}\text{S}$ value of the residual dissolved sulphate in the Äspö and Laxemar system appears to change as the fraction of the remaining sulphate decreases over time as seen e.g. in borehole SA1420 and SA0813A. This is a result even if the effective isotope fractionation factor remains constant.

5.1.2 Indicators of mixing

Using the $\delta^{34}\text{S}$ isotopes as indicators of mixing is also possible and several mixing models by use of $\delta^{34}\text{S}$ isotopes for open systems have been successful /Krause 1980/. In semi-closed to even closed systems similar to Äspö and Laxemar one has to be careful and need to combine the observations by use of the conserve parameters such as $\delta^{18}\text{O}$ and dissolved Cl^- as applied in this study. Still it can be hard to distinguish between the mixing and the sulphate reduction.

The methodology has to be used with caution, especially when mixing of low concentrations of dissolved sulphate in natural waters. However, at Äspö and Laxemar there are relatively high concentrations of dissolved sulphate (see Table 4-1). The complex groundwater system at Äspö suggests an overall multiple component mixing of different waters. In a few boreholes, however, by use of the $\delta^{34}\text{S}$ isotopes in combination with conservative parameters it seems to be a dominated two component mixing. This is exemplified e.g. in borehole SA2074A below. Also an in-mixing of a Deep Saline groundwater component (presumably up-coning) is observed in SA1730A.

To exemplify a two-component mixing result of the $\delta^{34}\text{S}$ value between a Baltic Sea water and a saline groundwater at Äspö, (e.g. by up-coning of Deep Saline groundwater) the following equation, modified from /Faure 2005/ can be used,

$$\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_M = \frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_A f_A S_A + \left(\frac{^{34}\text{S}}{^{32}\text{S}}\right)_B (1 - f_A) S_B}{S_A f_A + S_B (1 - f_A)}$$

Where, $(^{34}\text{S}/^{32}\text{S})$ is the isotopic ratio, M is the mixture, S_A is sulphate concentration of Baltic Sea water, S_B is sulphate concentration of the Deep Saline groundwater, f_A is the fraction of Baltic Sea water and f_B is the fraction of Deep Saline groundwater.

The change in $\delta^{34}\text{S}$ value in the different mixing fractions are seen in the Table 5-1 below.

The example in Figure 5-1 shows that in-mixing fractions of Baltic Sea water into Deep Saline groundwater, with high dissolved sulphate concentrations, give initially little changes in the $\delta^{34}\text{S}$ value. Hence, the isotope signature in the dissolved sulphate will show very small if any changes in $\delta^{34}\text{S}$ in the up-coning water as exemplified in some boreholes discussed below in Section 5-4.

Table 5-1. $\delta^{34}\text{S}$ values in a mixture of two components, Baltic Sea water (BSW) and Deep Saline groundwater (DSW) in relation to the in-mixed fraction (f) of Baltic Sea water. The average value of $\delta^{34}\text{S}$ is used for Baltic Sea water (+20 ‰) and Deep Saline groundwater (+10 ‰).

Fraction of BSW	[SO4]	[SO4]mix	$\delta^{34}\text{S}$	$\delta^{34}\text{S}$ in f
1	325	325	20	20.00000
0,9		383.1		17.63508
0,8		441.2		15.89302
0,7		499.3		14.55638
0,6		557.4		13.49839
0,5		615.5		12.64013
0,4		673.6		11.92993
0,3		731.7		11.33251
0,2		789.8		10.82299
0,1		847.9		10.38330
0,08		859.52		10.30249
0,06		871.14		10.22384
0,04		882.76		10.14727
0,02		894.38		10.07268
DSW	906	906	10	10.00000

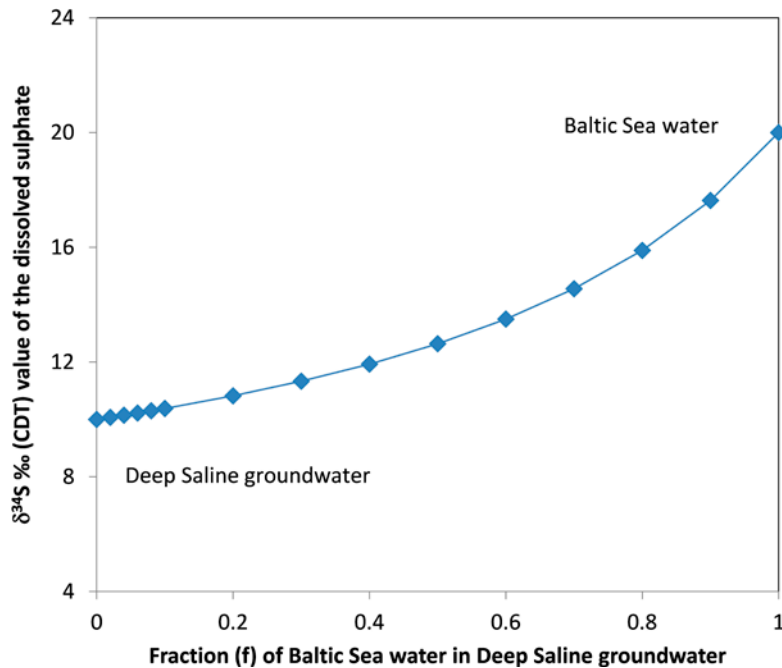


Figure 5-1. Diagram showing the change in $\delta^{34}\text{S}$ as a function of in-mixed Baltic Sea water into Deep Saline groundwater during e.g. up-coning.

5.2 Origin of the sulphur source

The $\delta^{34}\text{S}$ isotope signatures of the dissolved sulphate suggest multiple sources for the sulphur at Äspö, although two sulphur sources are dominant, namely, Baltic Sea water with a $\delta^{34}\text{S}$ value of approximately +19‰ to +20‰ CDT and Deep Saline groundwater with a $\delta^{34}\text{S}$ value of approximately +10‰ CDT. Early sampling from Äspö before tunnel construction revealed $\delta^{34}\text{S}$ signatures that decreased gradually with depth. This was also seen in groundwater sampled at Laxemar from boreholes KLX01 and KLX02 and has been confirmed during the site investigation programme at Laxemar /Laaksoharju et al. 2009/.

The Deep Saline groundwater has $\delta^{34}\text{S}$ values that are approximately +10‰ CDT, whereas the $\delta^{34}\text{S}$ of dissolved sulphate from a shallow depth of approximately 100 m at Äspö is approximately +19 to +20‰ CDT (Figure 5-2).

The origin of the low $\delta^{34}\text{S}$ values of the deep groundwater sulphur source is well understood with fracture gypsum of Palaeozoic age being the major source /Drake and Tullborg 2008, Gimeno et al. 2009, Laaksoharju et al. 2009/. The isotope values also correlate well with those of marine sulphate deposits from Permian and Trias /Claypool et al. 1980, Sakai 1972/ and similar $\delta^{34}\text{S}$ values are found for sulphates (e.g., barite and anhydrite) from fractures at Äspö and Laxemar /Drake and Tullborg 2008, Laaksoharju et al. 2009/. However, no evidence has so far been convincing and none of the possible explanations has been more convincing than the other.

The sulphur source with $\delta^{34}\text{S}$ values of approximately +19 to +21‰ CDT observed has typical present-day marine water signatures and likely reflects the presence of Baltic Sea water (Figure 5-2). This observation is supported by the Cl^- concentrations observed at a few sampling points previously described by /Laaksoharju 1995/. There are places in the basement that host groundwater of uncertain origin with chloride values slightly lower than those of the Baltic Sea. Those waters may represent remnants of old Meteoric water in-mixed with minor portions of saline water. The variation in the $\delta^{18}\text{O}$ of the shallow groundwater in what are considered discharge areas supports the possible mixing of Meteoric water with portions of in-mixed marine waters /Laaksoharju et al. 2009/. The overall mixing profile of the two sulphur sources mentioned above can be seen in the Figure 5-2.

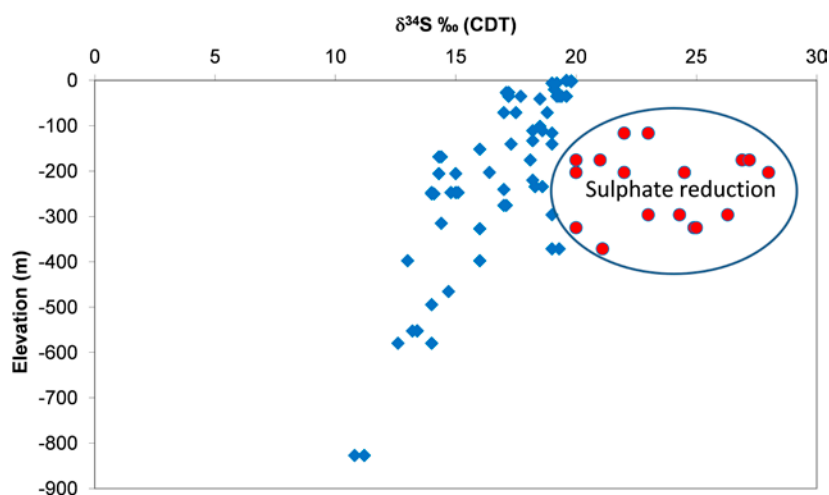


Figure 5-2. $\delta^{34}\text{S}$ of dissolved sulphate plotted versus depth in Äspö groundwaters collected up to 1996. There is an overall decrease of $\delta^{34}\text{S}$ with depth and a widely divergent and high $\delta^{34}\text{S}$ values at depths of 100–400 m are indicative of sulphate reduction (red dots).

In contrast to the two sulphur sources and $\delta^{34}\text{S}$ values discussed above, the $\delta^{34}\text{S}$ values (+19 to +28‰ CDT) found at depths of approximately 100–400 m are significantly higher and indicative of bacterial sulphate reduction (Figure 5-2). This is also supported by the presence of sulphides with reduced sulphur and low $\delta^{34}\text{S}$ signatures observed at these depths in the fracture fillings in the basement rocks in the tunnel area. Although, it is not fully clear if these sulphides were deposited during the pre-investigation and pre-tunnel construction phase. This has also been seen in Laxemar /Laaksoharju et al. 2009/. Measurements of a number of $\delta^{34}\text{S}$ signatures from pyrites and monosulphides in the fracture fillings indicate negative values of approximately –2 to –26‰ CDT, typical of bacterially reduced sulphur sources, as listed in Table 4-2, and reported in /Drake and Tullborg 2009/. Still one has to be cautious since these two types of sulphides may indicate a pyrite reduction under a long period of time and different origins. This is also what would be expected from a semi-open sulphur system affected by sulphate reduction. Presumably, the sulphides formed most recently in such a system would likely to have the highest $\delta^{34}\text{S}$ values of the dissolved sulphates. Most waters affected by the sulphate reduction are Baltic Sea water, typically containing relatively high Mg^{2+} concentrations of 140–150 mg/L (Figure 5-3).

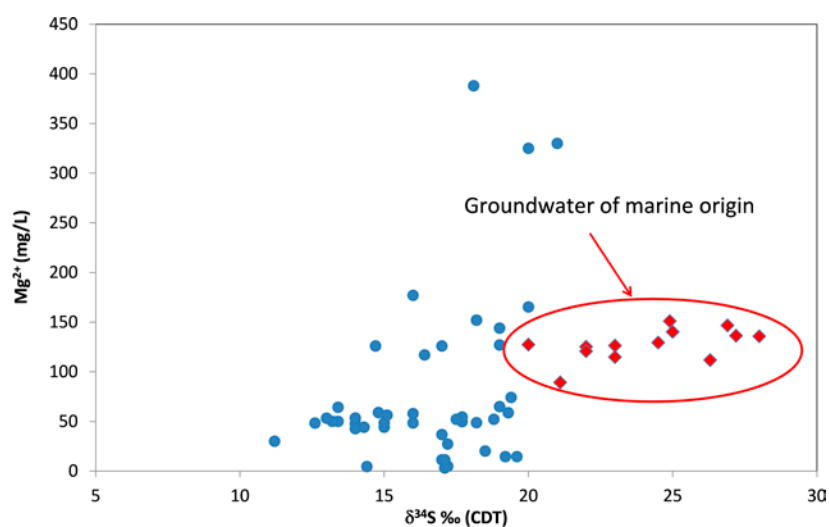


Figure 5-3. Mg^{2+} plotted versus $\delta^{34}\text{S}$ of dissolved sulphate in groundwaters from Äspö HRL tunnel boreholes. The high $\delta^{34}\text{S}$ values with Mg^{2+} concentrations of 100–150 mg/L, shown in the diagram by red dots, indicate that a large proportion of the groundwater of marine origin (as defined by the Cl^- and $\delta^{18}\text{O}$ observations) is affected by sulphate reduction.

Gradual changes in the flow system occurring after tunnel excavation, for example, due to the induction of extensive vertical/lateral flow of the recharging water, may oxidise the sulphides (pyrite) in the fractures. This is true if the waters are oxidising, though the large-scale redox experiment at Äspö demonstrated that oxygenated waters were quickly turned into reduced waters due to organic and inorganic processes during the penetration /Banwart et al. 1994/. The small amounts of these sulphides found in fractures at the Äspö (Table 4-2) and Laxemar /Drake and Tullborg 2009/ sites suggest that this sulphur source is a negligible contributor of groundwater sulphate. Notably, large amounts of sulphides are available in sea sediments outside Äspö, which is a relatively large solid-phase reservoir of sulphur. Although it is difficult to prove, this reduced sulphur source may obviously have had some impact on the infiltration of dissolved sulphate with Baltic Sea water into the basement rock. The various sulphur sources discussed are shown in the drawing in Figure 5-4.

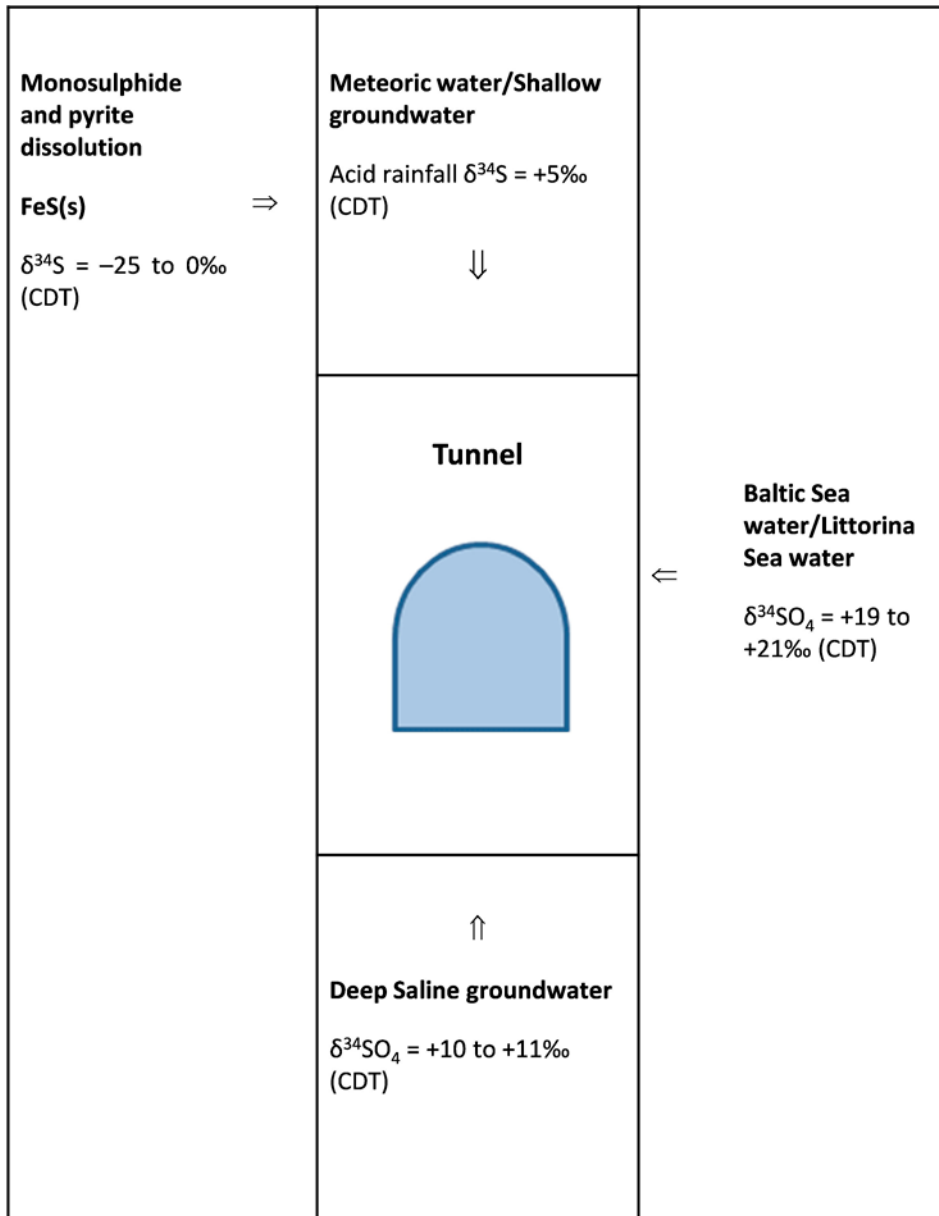


Figure 5-4. Schematic description of the various $\delta^{34}\text{S}$ sources observed in the groundwater at the Äspö HRL tunnel.

In conclusion, there are multiple sulphur sources at Äspö, including:

- a) marine sulphur (sulphate dissolved in the Baltic Sea and Littorina Sea water)
- b) deep sulphur (sulphate dissolved in the groundwater, likely from matrix pore water or possibly the dissolution of evaporites)
- c) reduced sulphur in the fracture fillings (i.e., pyrite and monosulphides)
- d) acid rainfall and sea spray – minor importance
- e) oxidation of sulphur in organic sediments such as sea sediments due to drawdown /Mossmark et al. 2008/.

The various sulphur sources reflect various water types that can be characterised by a combination of the conservative parameters Cl^- and $\delta^{18}\text{O}$, as examined in Section 5.3. The marine and deep sulphur sources are by far the two dominant sources in the water system, and input into the groundwater system from monosulphides and sea spray is negligible.

5.3 Correlation between $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and Cl^-

The increase in $\delta^{34}\text{S}$ values is commonly followed by an increase in $\delta^{18}\text{O}$ values (Figure 5-5). This likely in the first approximation signifies simple two-component mixing, as depicted in Figure 6-4, though this cannot be determined from the pattern seen in the plot between Cl^- and $\delta^{34}\text{S}$ (Figure 5-6). However, it is not as simple as that. There are other in-mixed water types as described by /Laaksoharju et al. 1995/. At least one more component or source seems to overlap this pattern, which is likely due to the sulphur source having undergone sulphate reduction. One may conclude from the plot in Figure 5-5 that the highest $\delta^{34}\text{S}$ values are dominant in waters with $\delta^{18}\text{O}$ signatures typical of the Baltic Sea water and with $\delta^{18}\text{O}$ values of approximately -7% V-SMOW. This observation is depicted in Figure 5-6, where most of the higher $\delta^{34}\text{S}$ values also correspond to Cl^- concentrations indicative of Baltic Sea water.

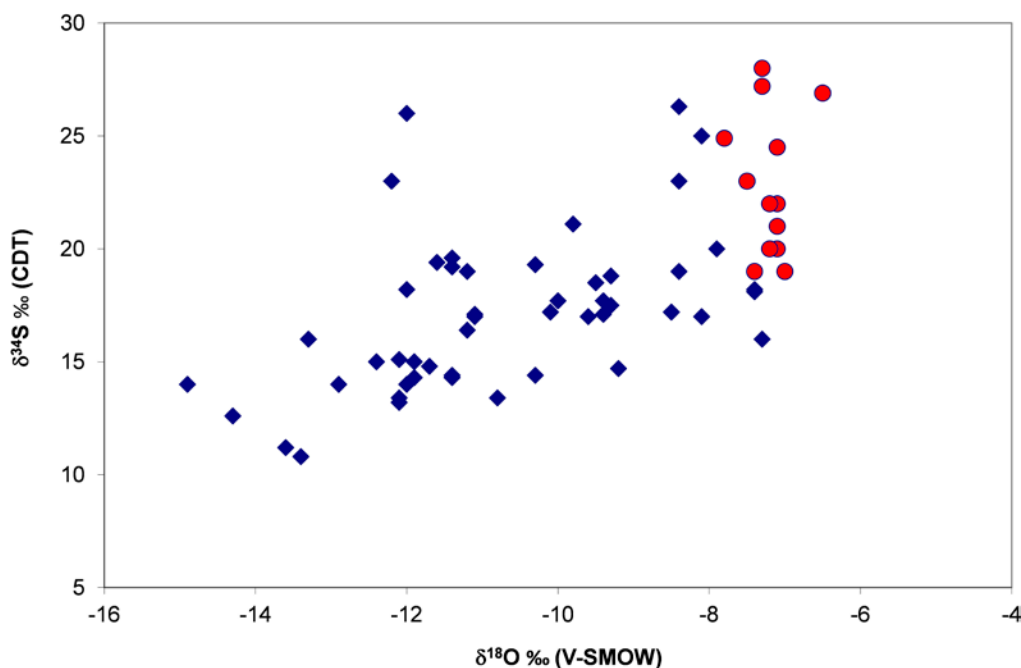


Figure 5-5. $\delta^{34}\text{S}$ of dissolved sulphate plotted versus $\delta^{18}\text{O}$ for groundwaters at Äspö HRL in 1996. The red dots represent groundwater of marine origin and the blue dots represent a mixture of other water types identified at Äspö, such as meteoric water, Deep Saline groundwater and possibly old Meteoric water. There is an overall decrease of $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ with depth.

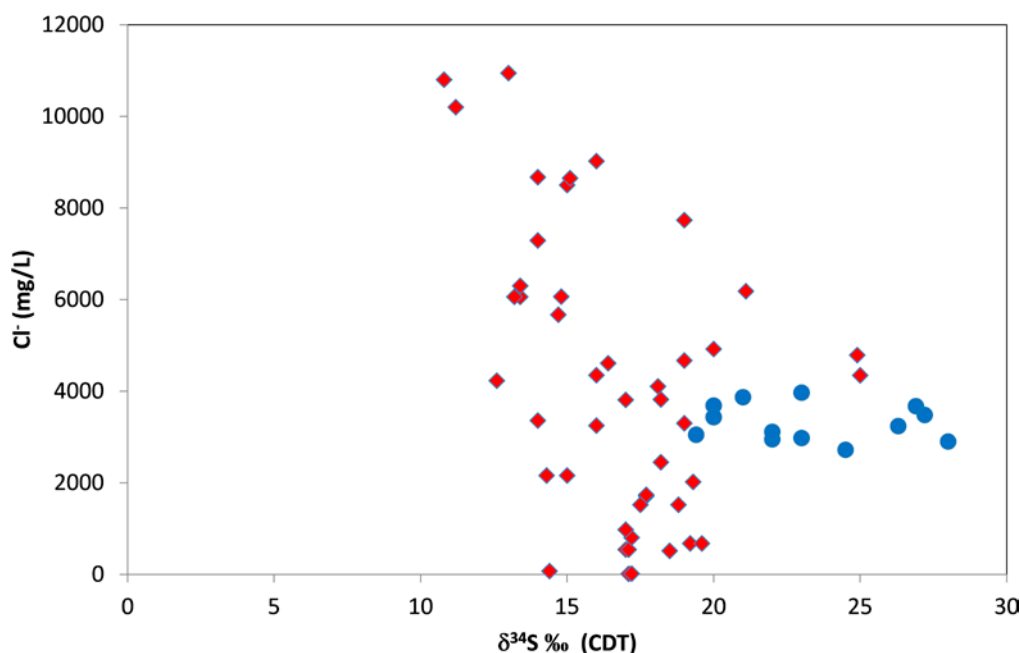


Figure 5-6. $\delta^{34}\text{S}$ of dissolved sulphate plotted versus Cl^- in groundwater samples collected from the tunnel and core-drilled boreholes at Äspö in 1996. The blue dots represent groundwater of marine origin. The three main water types (end-members) used in the discussion and the corresponding values of the parameters $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, SO_4^{2-} and Cl^- are listed below in Table 5-2.

Table 5-2. The main water types and their corresponding values of the parameters $\delta^{34}\text{S}$, Cl^- , SO_4^{2-} and $\delta^{18}\text{O}$.

Water type/Source	$\delta^{34}\text{S}$ (‰ CDT)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	$\delta^{18}\text{O}$ (‰ V-SMOW)
Meteoric water /Altered Meteoric water	± 0 to $+5$	0–5.4	0.5–6.92	–11
Reduced sulphur as pyrite, monosulphides, and acid rainfall	–25 to ± 0			
Baltic Sea water	+19 to +21	3,750	325	–6
Littorina Sea water	+19 to +21	6,500	890	–4.7
Deep Saline groundwater	+10 to +11	10,000–20,000	906	–10

5.4 $\delta^{34}\text{S}$ isotope changes in the dissolved sulphate over time observed in tunnel borehole water

Both the change in the $\delta^{34}\text{S}$ of the dissolved sulphate over the course of the monitoring phase and the groundwater system has been disturbed by various processes connected with tunnel excavation. Twelve boreholes were sampled for isotope analysis, though only seven boreholes were selected for discussion. This selection was made according to the criterion that a minimum of three observed $\delta^{34}\text{S}$ values in the time series were needed to confirm a trend over time (with the exception of borehole SA2783A). In five boreholes, namely, SA1229A, SA1420A, SA2074, SA2273A, and SA819A, the $\delta^{34}\text{S}$ values increased significantly with time. In borehole SA1730A, however, the $\delta^{34}\text{S}$ values changed only slightly or remained unchanged with time. A lowering in $\delta^{34}\text{S}$ values with time is observed in borehole SA2783A.

5.4.1 Borehole SA1420A

This borehole section is situated at a depth of 202.9 m in the tunnel (see Section 2, Figure 2-1). The $\delta^{34}\text{S}$ values recorded in the time series for borehole SA1420A (Figure 5-7) increased from +16 to +28‰ CDT and then dropped to +24.5‰ CDT by the last sampling occasion. The Cl^- concentration in SA1420A decreased over time from approximately 4,610 mg/L to 3,481 mg/L (Figure 5-8). Over the same sampling period, SO_4^{2-} concentration initially increased in concentration from 200 mg/L to 308 mg/L, after which it decreased steadily with time (Figure 5-9).

Assuming that the continuous increase in $\delta^{34}\text{S}$ values observed in SA1420A was a result of the bacterial reduction of sulphate (i.e., consumption of dissolved sulphate) from the same sulphur source, the initial $\delta^{34}\text{S}$ value of the dissolved sulphate should have the highest concentration. This was not the case, so the initial sample in the time series seems to reflect a slightly different water type from those of the last four samples. The SO_4^{2-} concentration of 200 mg/L, the Cl^- concentration of 4,600 mg/L, and a $\delta^{34}\text{S}$ value of 16‰ CDT of initial sampled groundwater in 1992 most likely reflect water with an in-mixed portion of Deep Saline groundwater.

It is certainly not Baltic Sea water as indicated by the Mg^{2+} concentrations over time (Figure 5-10), though it could very well be a mixture of deeper saline water and Baltic Sea water or even a mixture of deep saline water and glacial water.

This is also supported by the $\delta^{18}\text{O}$ value of the initial sample (Figure 5-11), which is approximately -11‰ V-SMOW. The last four samples in this series display relatively homogeneous $\delta^{18}\text{O}$ values of approximately -7‰ V-SMOW, coinciding with those of Baltic Sea water.

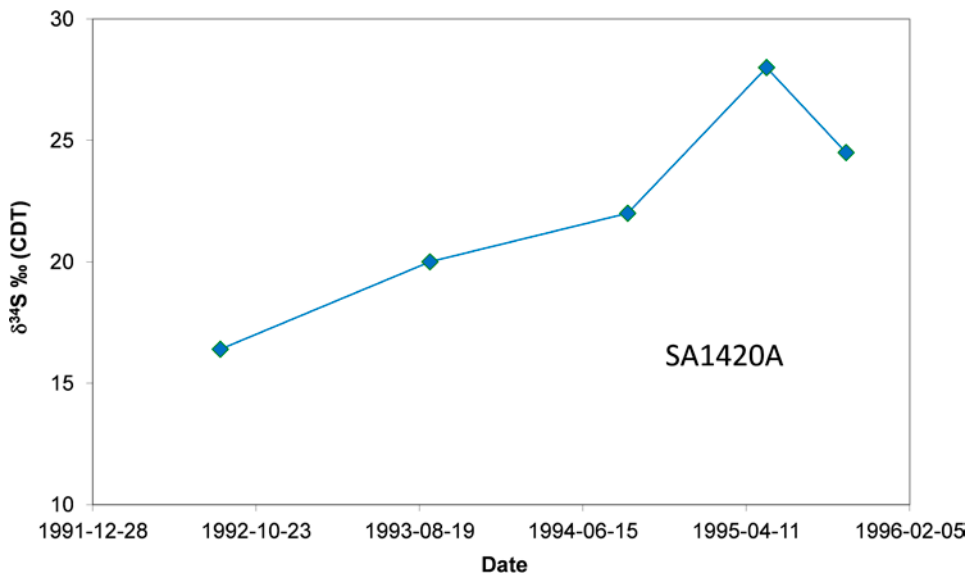


Figure 5-7. $\delta^{34}\text{S}$ values of dissolved sulphate plotted versus date (time) for borehole SA1420A at a depth of 202.9 m in the tunnel.

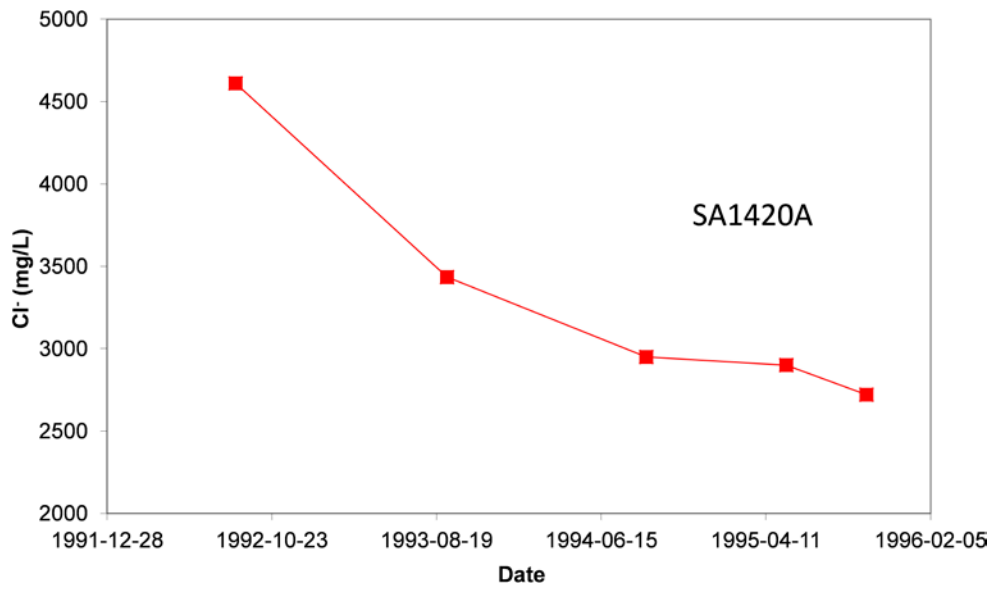


Figure 5-8. Cl⁻ plotted versus date (time) for borehole SA1420A at a depth of 202.9 m in the tunnel.

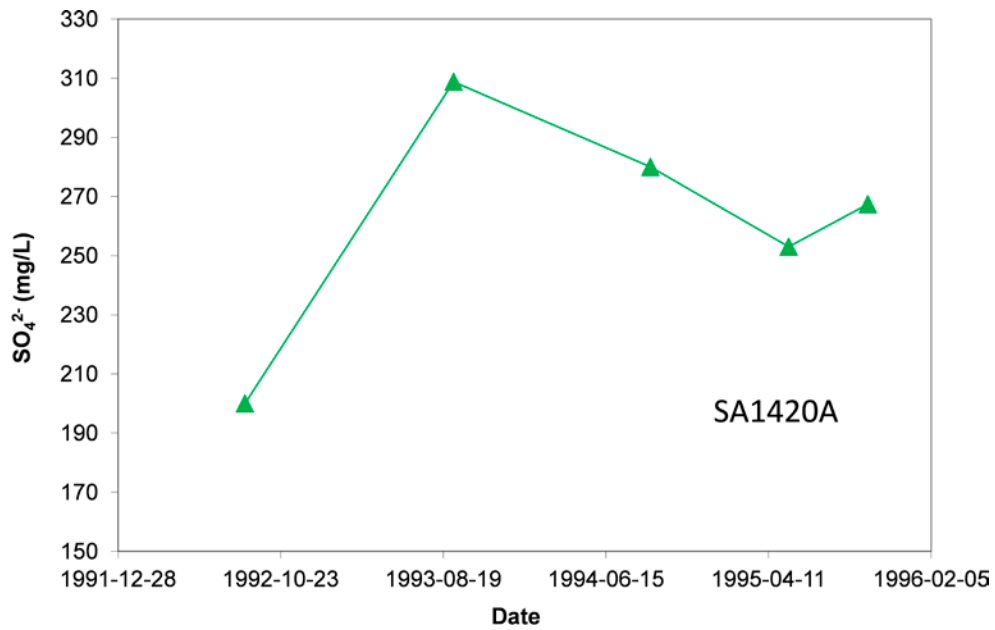


Figure 5-9. Dissolved sulphate concentration plotted versus date (time) for borehole SA1410A at a depth of 202.9 m in the tunnel.

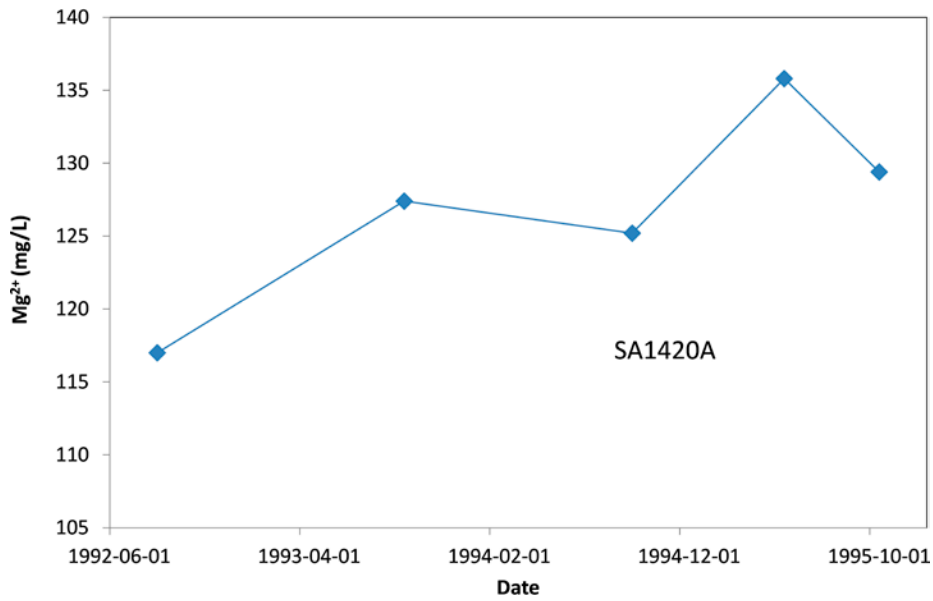


Figure 5-10. Mg²⁺ plotted versus date (time) for borehole SA1420A at a depth of 202.9 m in the tunnel.

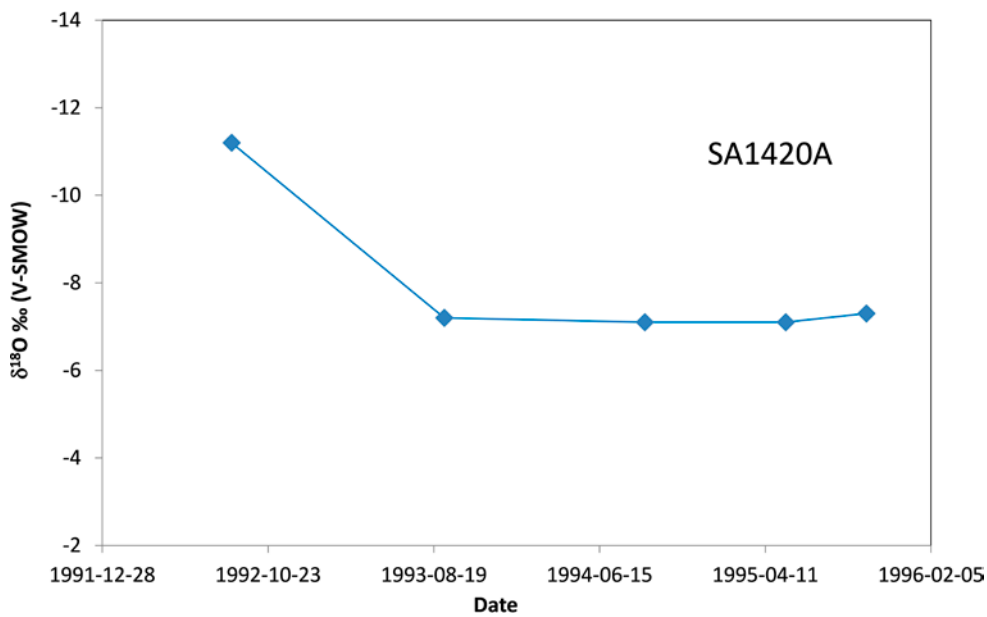


Figure 5-11. δ¹⁸O values plotted versus date (time) for borehole SA1410A at a depth of 202.9 m in the tunnel.

Therefore, the increase in δ³⁴S values likely reflects the inflow of Baltic Sea water into the borehole affected by sulphate reduction. Whether this reduction took place in the borehole or somewhere else in the basement rocks before the water reached the borehole entrance cannot be determined. Moreover, the drop in Cl⁻ concentration with time suggests that the groundwater underwent continuous dilution (Figure 5-8). The mechanism for this may have been the drawdown of less saline waters due to tunnel construction.

As suggested by /Mariotti et al. 1981/, the evidence of sulphate reduction is validated in the plot of the natural logarithm of sulphate versus the δ³⁴S values in Figure 5-12, where a typical negative straight line is projected.

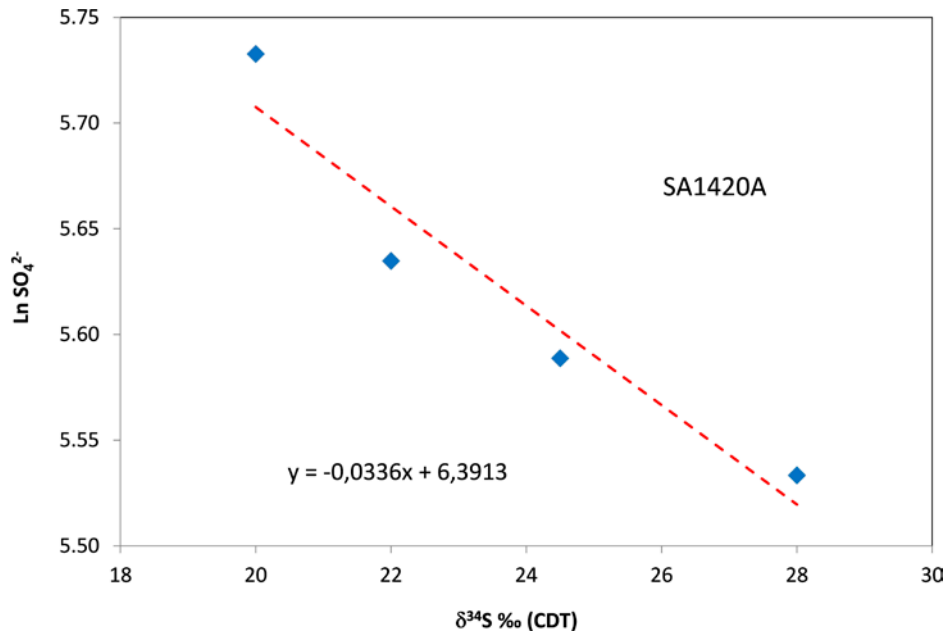


Figure 5-12. The natural logarithm (\ln) of SO_4^{2-} values plotted versus $\delta^{34}\text{S}$ in borehole SA 1420A at a depth of 202.9 m.

5.4.2 Borehole SA2074A

This borehole section is situated at a depth of 296.3 m in the tunnel (see Section 2, Figure 2-1). The data collected from borehole SA2074A mimic the pattern in borehole SA1420A, i.e., a constant increase in $\delta^{34}\text{S}$ values with time accompanied by a lowering in SO_4^{2-} concentration. The initial $\delta^{34}\text{S}$ value is +19‰ CDT and the final value is +26‰ CDT (Figure 5-13). Though only three samples have been collected for SO_4^{2-} analysis, the data indicate a drop in sulphate values over time (Figure 5-14). The $\delta^{34}\text{S}$ value of +19‰ CDT suggests a typical marine sulphur source.

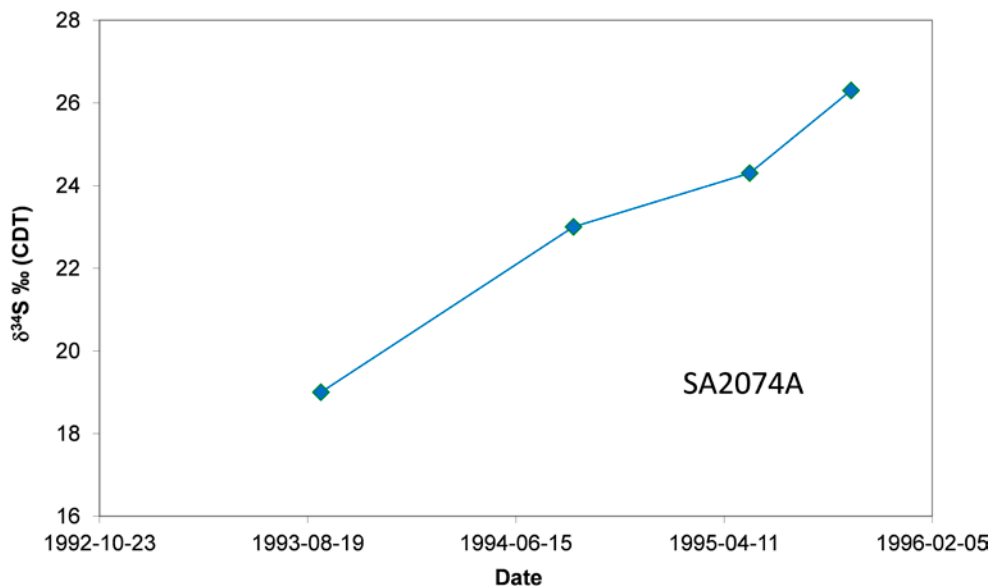


Figure 5-13. $\delta^{34}\text{S}$ values plotted versus date (time) for borehole SA2074A at a depth of 296 m in the tunnel.

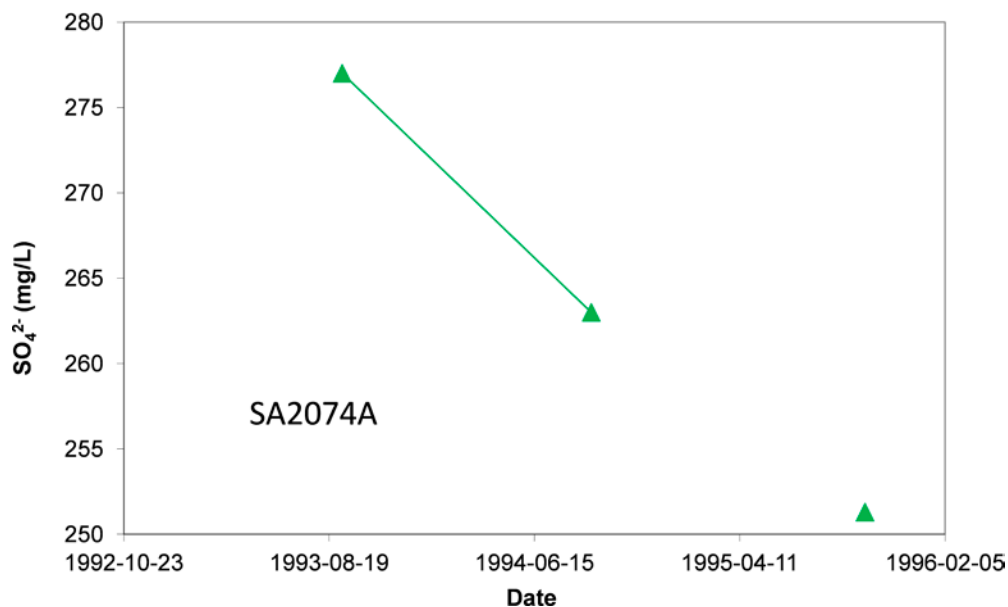


Figure 5-14. SO_4^{2-} values plotted versus date (time) for borehole SA2074A at a depth of 296 m in the tunnel.

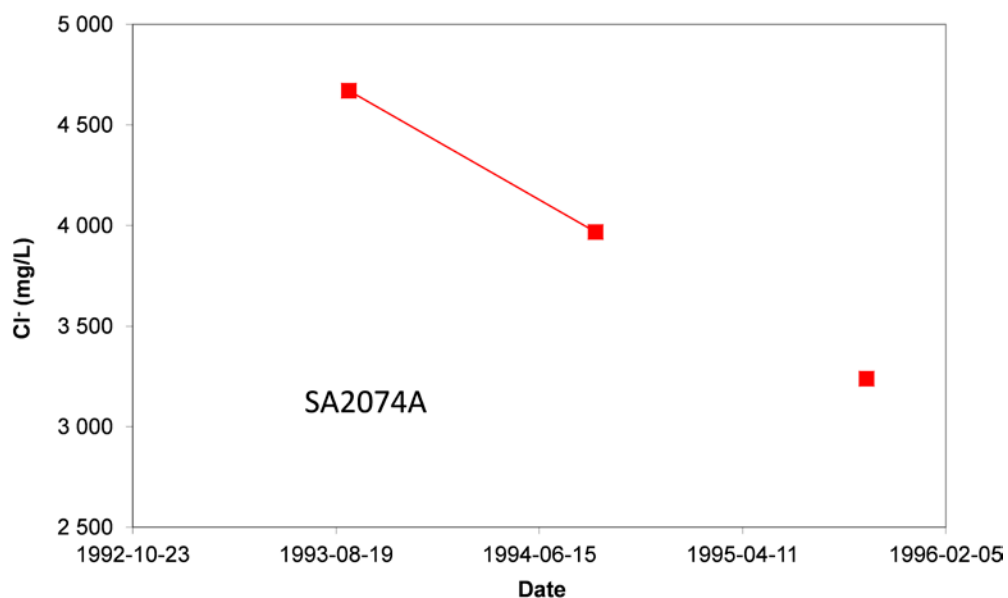


Figure 5-15. Cl^- plotted versus date (time) for borehole SA2074A at a depth of 296.3 m in the tunnel.

In this borehole, Cl^- concentration has changed continuously, decreasing with time, likely due to dilution by or in-mixing of water of lower Cl^- concentration (Figure 5-15). Furthermore, the Cl^- concentration in the first observation in this time series is higher than would be expected from Baltic Sea water possibly indicating a small portion of saline water or a remnant of Littorina Sea water, although this has not been confirmed. The constant value of $\delta^{18}O$ of -8.4% V-SMOW over time could either support a Baltic Sea or an altered mixed Littorina origin for the water.

5.4.3 Borehole SA1229A

A third example of time series collected from the tunnel is that of borehole SA1229A (see Section 2, Figure 2-1) at a depth of 175.6 m. Water sampled here displayed an increase in $\delta^{34}S$ with time, but with a slightly different pattern from that observed in boreholes SA1420A and SA2074A. There was a rapid increase in $\delta^{34}S$ from $+18$ to $+27\%$ CDT between the 1994 and 1995 samplings (Figure 5-16).

The $\delta^{18}\text{O}$ value remained homogeneous at approximately -7‰ V-SMOW, strongly indicative of a water with portions of Baltic Sea water or Littorina water (Figure 5-17). Chloride concentrations display little variation, remaining between 4,100 to 3,500 mg/L. The most likely scenario in this borehole is that a marine water type (Baltic Sea water or Littorina water) has been affected by sulphate reduction. The homogeneous pattern of $\delta^{18}\text{O}$ value over time suggests that this water has not become mixed, so the sulphate reduction presumably took place in or near of the borehole. However in contrast the decrease in Cl^- over time indicate a slight dilution of the water (Figure 5-18).

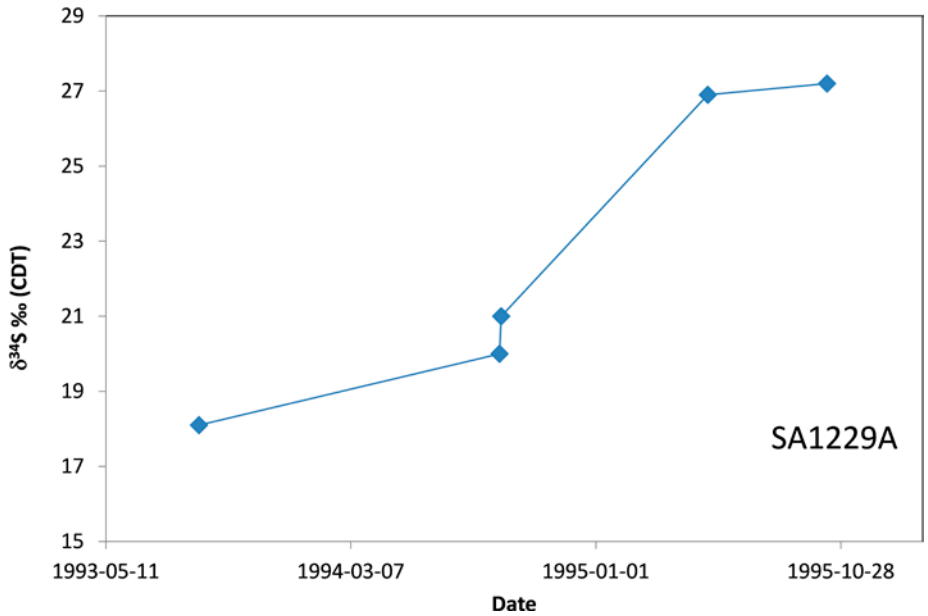


Figure 5-16. $\delta^{34}\text{S}$ values plotted versus date (time) for borehole SA1229A at a depth of 175.6 m in the tunnel.

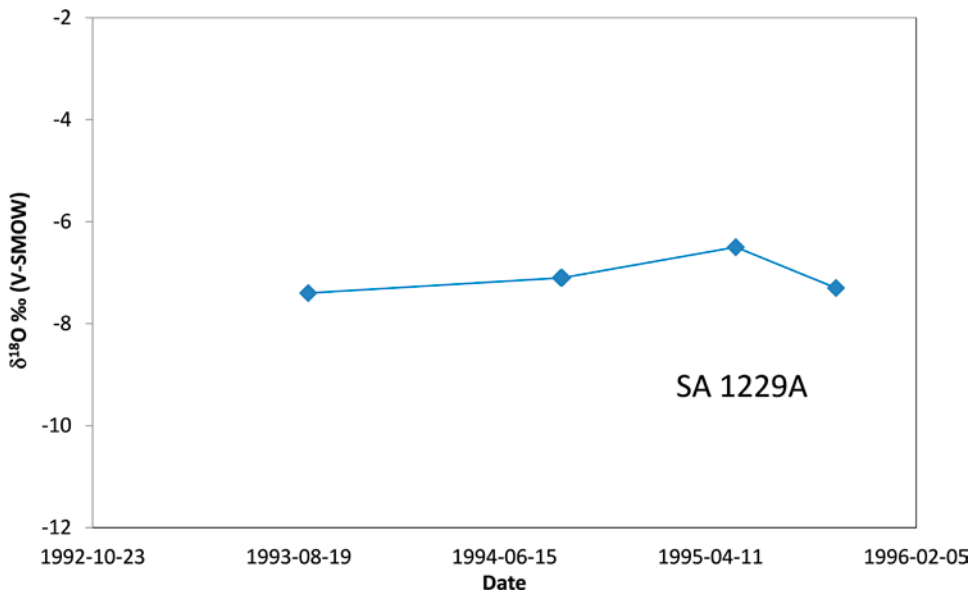


Figure 5-17. $\delta^{18}\text{O}$ values plotted versus date (time) for borehole SA1229A at a depth of 175.6 m in the tunnel.

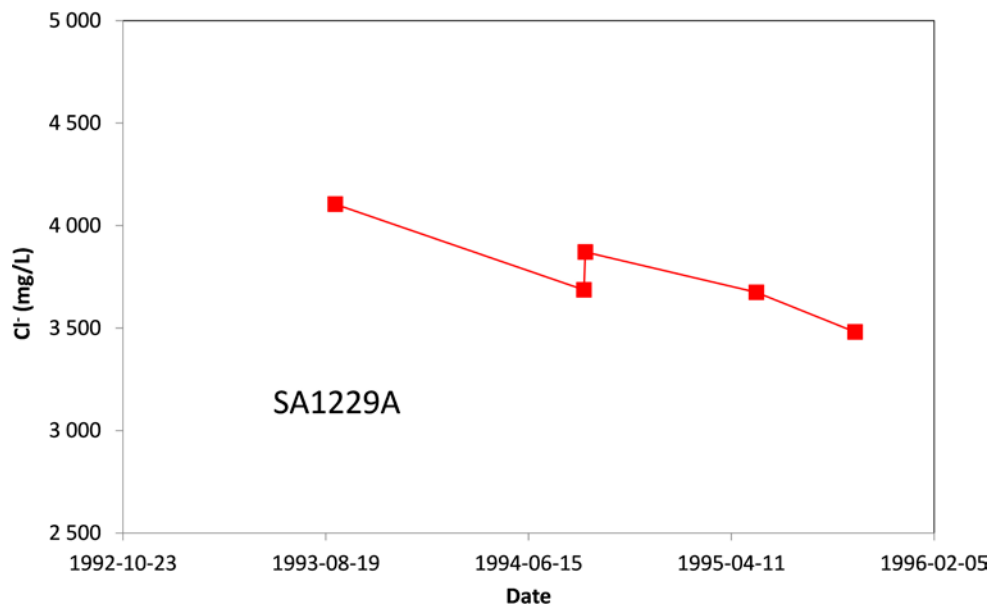


Figure 5-18. Cl⁻ values plotted versus date (time) for borehole SA1229A at a depth of 175.6 m in the tunnel.

5.4.4 Borehole SA1730A

In water from borehole SA1730A (see Section 2, Figure 2-1) at a depth of 247 m, the observed pattern differs completely from those seen in boreholes SA1420A, SA2074A, and SA1229A described above. The $\delta^{34}\text{S}$ values remained more or less constant at +14.1 to +15‰ CDT over the sampling period (Figure 5-19). However, a more dramatic change is observed in the Cl⁻ concentration, which increased from 6,000 mg/L in the first sample in 1993 to 8,500 mg/L in the second sample in 1994 (Figure 5-20).

Then the Cl⁻ concentration remained almost stable in the 1995 and 1996 samples (Figure 5-20). The more or less unchanged $\delta^{34}\text{S}$ values in the last three observations in this time series suggest a single sulphur source, likely the deep saline sulphur source recorded for this borehole. The dramatic increase in Cl⁻ from the 1993 to the 1994 sampling, resulting in high concentrations, may have resulted from the up-coning of deeper groundwater.

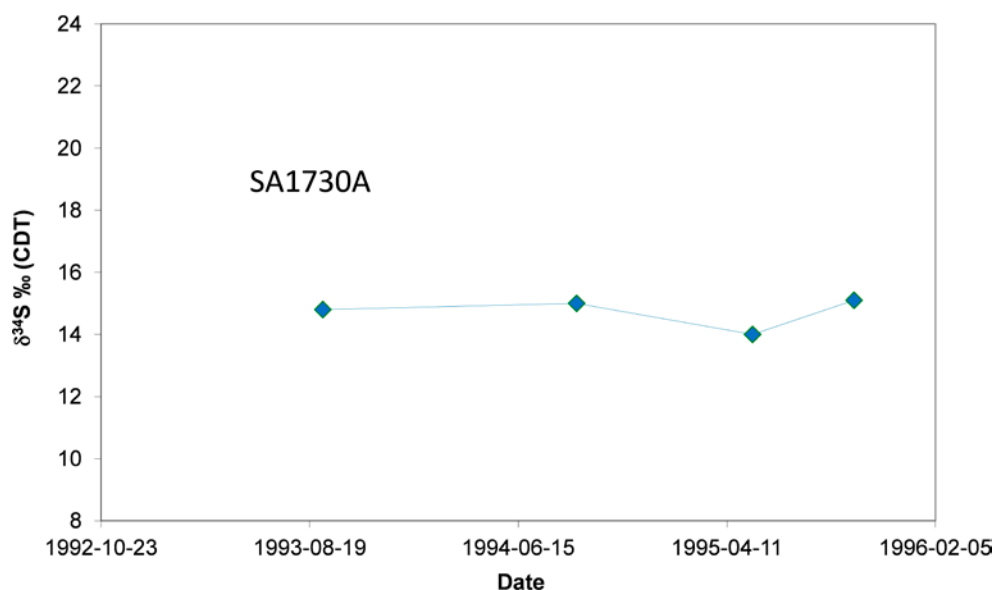


Figure 5-19. $\delta^{34}\text{S}$ values plotted versus date (time) for borehole SA1730A at a depth of 247.1 m in the tunnel.

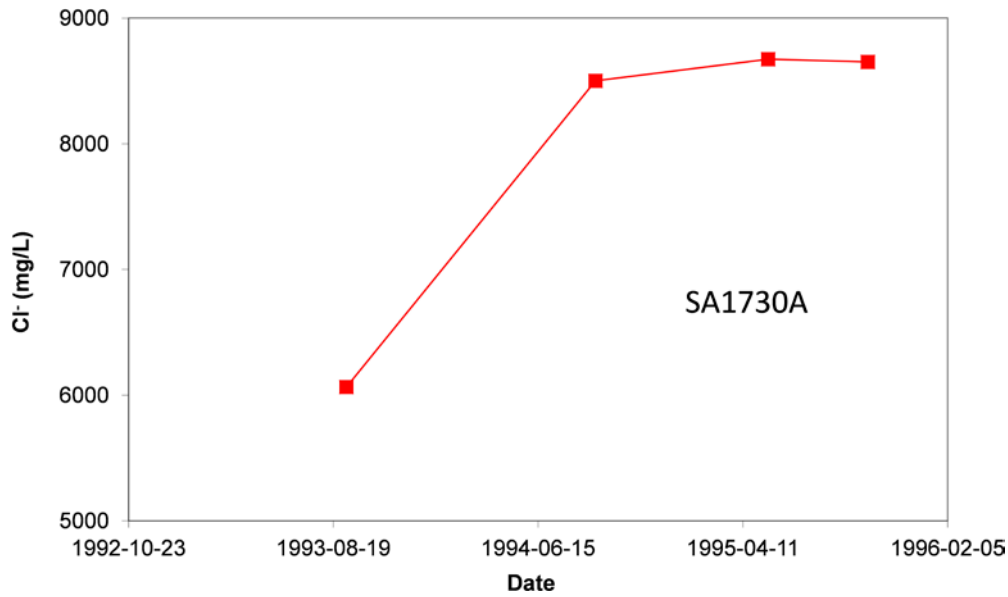


Figure 5-20. Cl⁻ plotted versus date (time) for borehole SA1730A at a depth of 247.1 m in the tunnel.

5.4.5 Borehole SA2273A

Borehole SA2273A at a depth of 296.3 m was sampled on three occasions in 1993, 1994, and 1995. The $\delta^{34}\text{S}$ values increased from +20 to +25‰ CDT from 1993 to 1994 (Figure 5-21), but remained almost unchanged one year later in the 1995 sample. The initial $\delta^{34}\text{S}$ value of +20‰ CDT suggests a marine sulphur source for the dissolved sulphate. The $\delta^{18}\text{O}$ values remain unchanged throughout the sampling period, suggesting that the same type of water resided in the borehole (Figure 5-22).

This observation is also supported by the Cl⁻ concentrations, which displayed relatively small changes, remaining between 4,900 and 4,300 mg/L over the sampling period (see Table 4-1). Interestingly, these high Cl⁻ concentrations are significantly higher than those of Baltic Sea water, and could indicate the presence of diluted or remnant Littorina Sea water at this depth in the tunnel. The constant $\delta^{18}\text{O}$ over time support a mixture of Baltic Sea water and Littorina water (Figure 5-22).

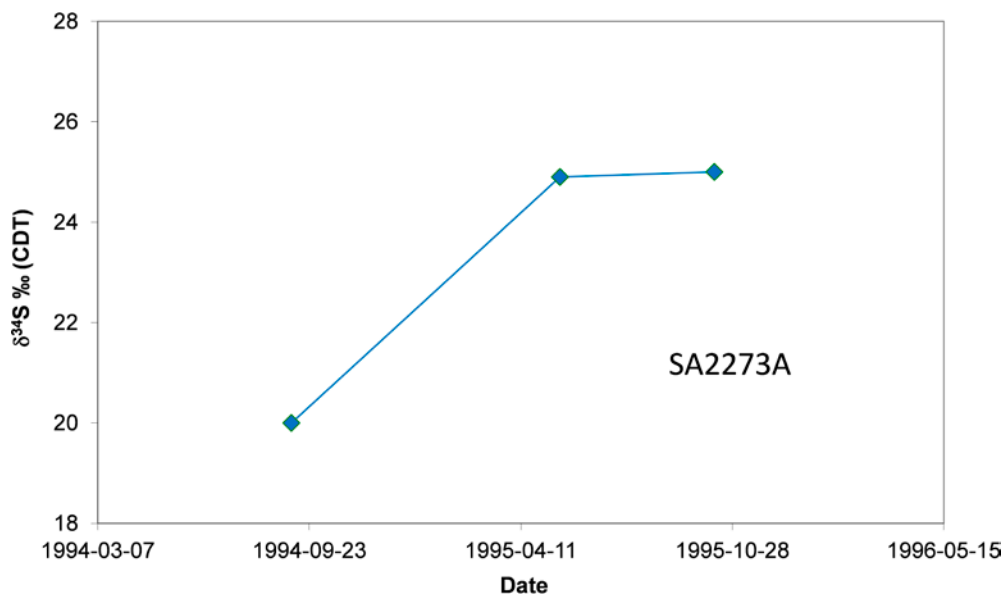


Figure 5-21. $\delta^{34}\text{S}$ values plotted versus date (time) for borehole SA2273A at a depth of 296.3 m in the tunnel.

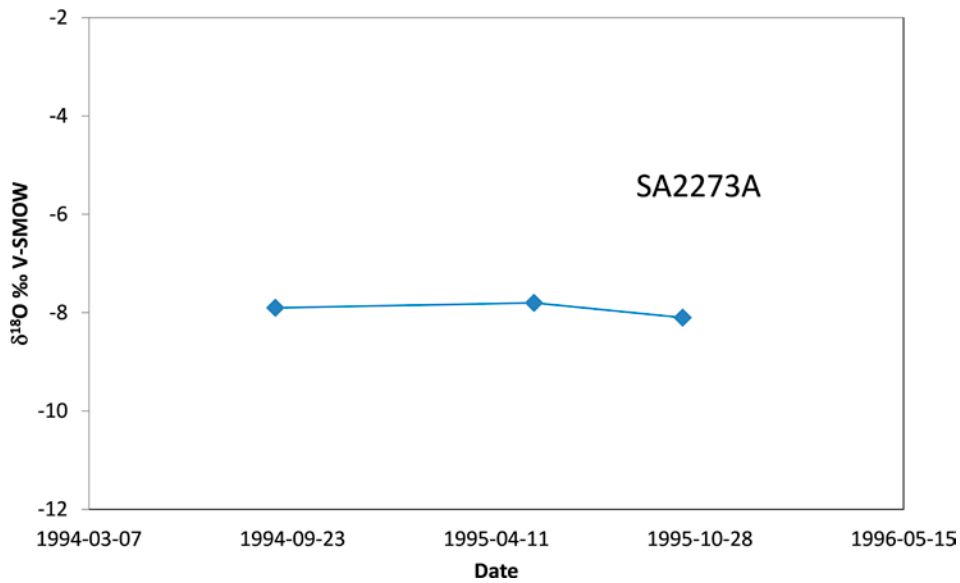


Figure 5-22. $\delta^{18}O$ values plotted versus date (time) for borehole SA2273A at a depth of 296.3 m in the tunnel.

5.4.6 Borehole SA2783A

In borehole SA2783A, the deepest borehole section sampled in the tunnel at a depth of 397 m, a decrease in the $\delta^{34}S$ was observed over time. The $\delta^{34}S$ value of the dissolved sulphate changed from +16 to +13‰ CDT (Figure 5-23) between the 1994 and 1995 samplings. Unfortunately, the $\delta^{34}S$ of the dissolved sulphate was analysed in only two samples, so the observed change may not be significant according to the statement in Section 5.3. However, the increase in Cl^- concentration (see Table 4-1) with time suggests an in-mixing of more saline groundwater. If so, the lowering of $\delta^{34}S$ with time supports the possibility of input from a deep saline sulphur source, possibly due to the up-coning of saline water in connection with tunnel construction.

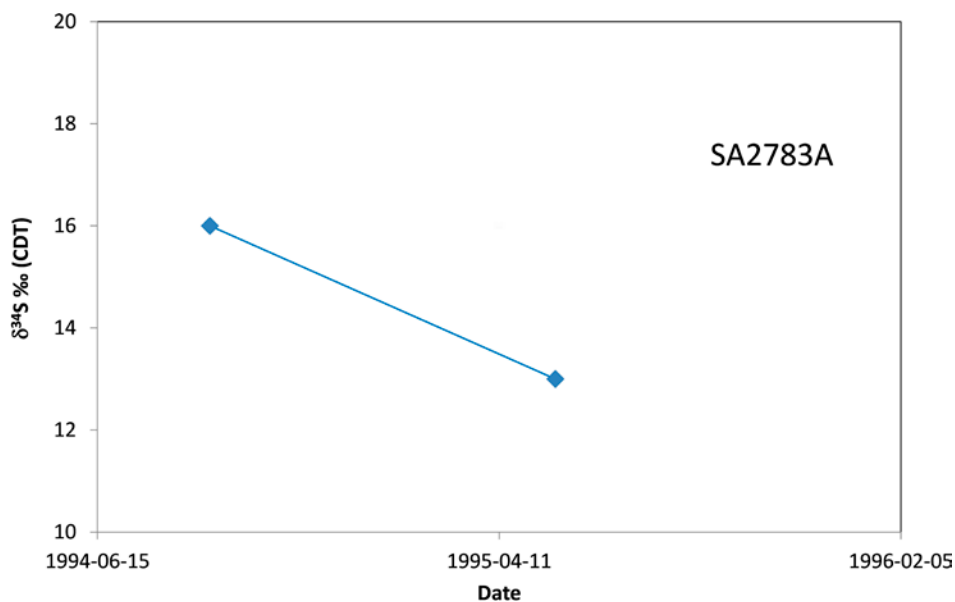


Figure 5-23. $\delta^{34}S$ values plotted versus date (time) for borehole SA2783A at a depth of 397 m in the tunnel.

5.4.7 Borehole SA0813A

The shallowest borehole section sampled in the tunnel is SA0813A at a depth of 119 m. The dissolved sulphate displayed a continuous increase $\delta^{34}\text{S}$ from an initial value of +19 to +23‰ CDT at the last sampling point in the time series (Figure 5-24). This increase in isotope signature is not as large as recorded in boreholes SA1420A and SA1229A, for example, suggesting that the sulphate reduction has not been very intense.

The $\delta^{18}\text{O}$ values remained stable at approximately -7% V-SMOW throughout the sampling period, coinciding with those observed in Baltic Sea water (Figure 5-25). In line with this, the Cl^- concentrations remained constant at approximately 3,000 mg/L throughout the sampling period. Based on the behaviour of these three parameters, it is concluded that Baltic Sea water that had undergone slight sulphate reduction is residing in borehole SA813A.

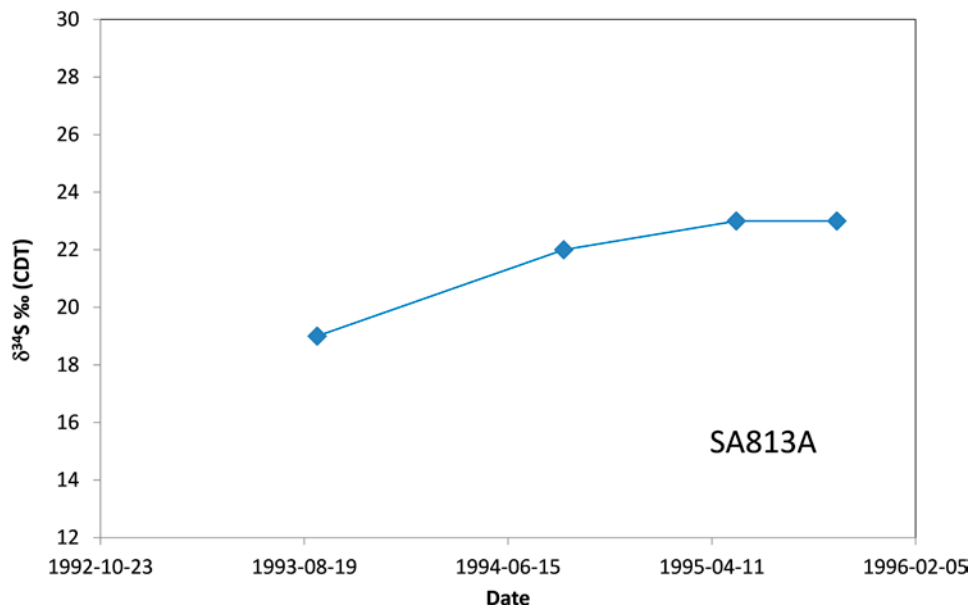


Figure 5-24. $\delta^{34}\text{S}$ values plotted versus date (time) for borehole SA0813A at a depth of 119 m in the tunnel.

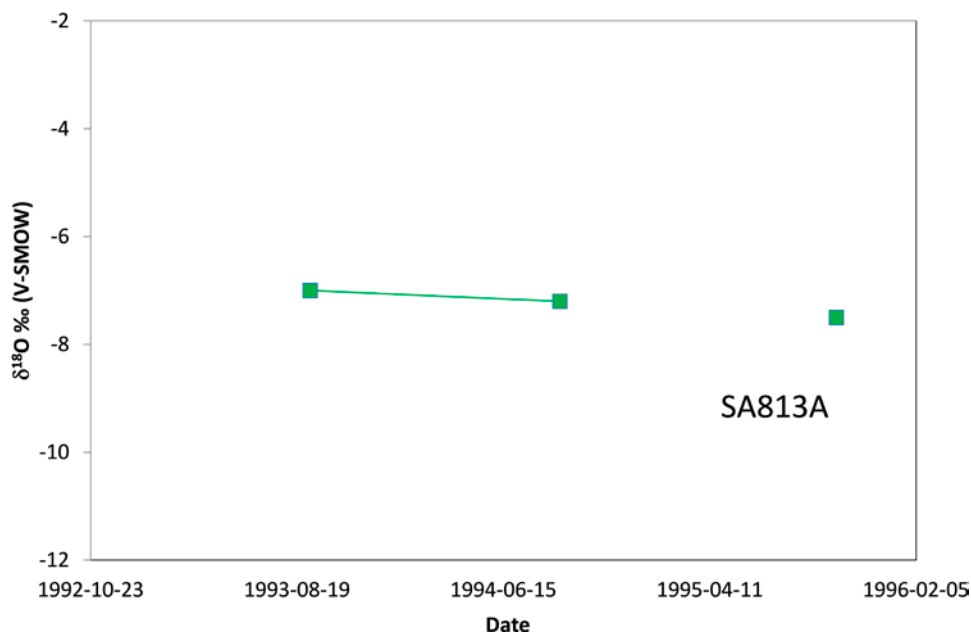


Figure 5-25. $\delta^{18}\text{O}$ values plotted versus date (time) for borehole SA0813A at a depth of 119 m in the tunnel.

5.5 Summary of observations concerning the tunnel boreholes

A significant increase over time in the $\delta^{34}\text{S}$ of the dissolved sulphate is observed in groundwater from boreholes SA1420A, SA2074A, SA1229A, SA819A, and SA2273A, likely strongly related to microbial sulphate reduction. In borehole SA1730A, the $\delta^{34}\text{S}$ values either changed slightly with time or remained unchanged, while lower $\delta^{34}\text{S}$ values with time were observed in borehole SA2783A. In several boreholes, the initially observed water had become mixed with portions of Baltic Sea water. The microbial sulphate reduction likely took place near the borehole, though some observations may indicate that the sulphate reduction was superimposed on the groundwater mixing process and the sulphate was already reduced before entering the borehole. Hence, in a few of those cases, this water has already been affected by sulphate reduction. Recent studies performed in drilled boreholes /Rosdahl et al. 2011/ and in tunnel boreholes has shown that the sulphate reduction is increased when boreholes sections is not being pumped and sampled. In contrast when the borehole section is pumped, groundwater from the surrounding fractures replaces the water in the borehole section and also the chemistry is changes due to microbial activity and corresponding sulphate reduction. It is most likely that some of the observations in this study are indicative of the same phenomenon. This may be exemplified in the borehole SA1420A. The replacement and /or in-mixing of water from surrounding fractures may also be indicative of the dramatic change in Cl^- pattern over time observed in e.g. SA1730A.

The change in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotope signatures was apparently induced by disturbed groundwater flow over time during tunnel excavation. The decrease in $\delta^{34}\text{S}$ of the dissolved sulphate over time in borehole SA2783A suggests the inflow of sulphur from a Deep Saline groundwater source due to up-coning. The in-mixing of Baltic Sea water and Deep Saline groundwater as can be seen in some boreholes. This is also most likely induced by up-coning of Deep Saline groundwater during the tunnel construction.

5.6 Processes that may be responsible for the observed changes in $\delta^{34}\text{S}$ over time

The overall significant increase over time of the $\delta^{34}\text{S}$ of the dissolved sulphate, which is recorded in several boreholes, is likely is due to the mixing of waters and resulting sulphate reduction that was intensified during tunnel construction. This conclusion is not based on tunnel data alone, but on a mixture of tunnel data and data collected from KAS boreholes. In any case, the plots may serve to indicate what has been recorded over time.

In several boreholes, the $\delta^{18}\text{O}$ isotope signature and Cl^- concentrations suggest that there has been an inflow of Baltic Sea water into the tunnel. This inflow was likely driven by the dynamic change in the flow system and by groundwater drawdown, as described by /Banwart et al. 1994, Laaksoharju 1995, Rhén et al. 1997/. In some of these cases, as mentioned earlier, a groundwater dilution effect was seen in the boreholes, accompanied by the change in $\delta^{34}\text{S}$ values.

In one borehole, SA 2283A, $\delta^{34}\text{S}$ values were observed to decline with time; unfortunately, only two samples were taken from that borehole, so the data must be interpreted with caution. In any case, the Cl^- concentrations in that borehole did increase considerably with time, suggesting that this was due to the up-coning and inflow of Deep Saline groundwaters.

6 Conclusion

The gradual increase in the $\delta^{34}\text{S}$ values of the dissolved sulphate recorded when sampling in the Äspö Hard Rock Laboratory (HRL) tunnel between 1992 and 1995 suggest the occurrence of groundwater mixing and sulphate reduction at several depths. Time series from boreholes at various depths all indicate changes in the $\delta^{34}\text{S}$ values. In most cases, increases in $\delta^{34}\text{S}$ isotope values are strongly related to sulphate reduction. In one borehole, no changes in $\delta^{34}\text{S}$ values were observed, while in another $\delta^{34}\text{S}$ values decreased with time.

This study complements a previous report on bacterial sulphate reduction at the Äspö HRL /Laaksoharju 1995/. The major approach used in the present study, as opposed to the previous one, is that bacterial sulphate reduction has been delineated using $\delta^{34}\text{S}$ signatures from the dissolved sulphate at various depths. In addition, the new dimension in the present work is the time series of data recorded from selected boreholes in the Äspö HRL tunnel.

It is also demonstrated that the approach presented here, and the use of $\delta^{34}\text{S}$ isotopes to indicate sulphate reduction in groundwater, may also be used to observe groundwater mixing.

In conclusion, the isotope data suggest that:

- $\delta^{34}\text{S}$ isotope data for the dissolved sulphate collected from boreholes at the time of tunnel construction indicate a significant change over time,
- $\delta^{34}\text{S}$ values observed in several boreholes indicate sulphate reduction in the groundwater during tunnel construction,
- the $\delta^{34}\text{S}$ data together with the $\delta^{18}\text{O}$ and Cl^- concentrations indicate that there has been a mixing of groundwaters over time in the boreholes, a mixing likely induced by tunnel construction,
- however, there is no way to judge whether groundwater mixing and microbial activity leading to sulphate reduction has occurred prior to entering the borehole section being sampled, or whether the reduction has taken place in the actual borehole section,
- drawdown of Baltic Sea water is observed in most examined boreholes, and
- mixing of different waters and up-coning of Deep Saline groundwater may be responsible for the decreased $\delta^{34}\text{S}$ isotopes signature recorded in one borehole.
- a slight increase $\delta^{34}\text{S}$ isotopes in other boreholes are most likely due to in-mixed Baltic Sea water superimposed on the sulphate reduction.

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