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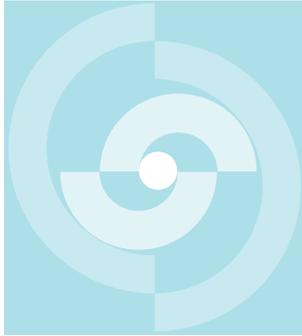
Nationale
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für die Lagerung
radioaktiver Abfälle

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pour l'entreposage
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TECHNICAL REPORT 88-36

HYDROGEOCHEMICAL ASSESSMENT OF CRYSTALLINE ROCK FOR RADIOACTIVE WASTE DISPOSAL: THE STRIPA EXPERIENCE

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AUGUST 1988

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(present address: GSF, Neuherberg, FRG.)

⁴⁾ US Geological Survey, USA
(Chairman of the Geochemical Advisory Group, Stripa)

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Der vorliegende Bericht betrifft eine Studie, die für das Stripa-Projekt ausgeführt wurde. Die Autoren haben ihre eigenen Ansichten und Schlussfolgerungen dargestellt. Diese müssen nicht unbedingt mit denjenigen des Auftraggebers übereinstimmen.

Le présent rapport a été préparé pour le projet de Stripa. Les opinions et conclusions présentées sont celles des auteurs et ne correspondent pas nécessairement à ceux du client.

This report concerns a study which was conducted for the Stripa Project. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

Das Stripa-Projekt ist ein Projekt der Nuklearagentur der OECD. Unter internationaler Beteiligung werden von 1980-86 Forschungsarbeiten in einem unterirdischen Felslabor in Schweden durchgeführt. Diese sollen die Kenntnisse auf folgenden Gebieten erweitern:

- hydrogeologische und geochemische Messungen in Bohrlöchern
 - Ausbreitung des Grundwassers und Transport von Radionukliden durch Klüfte im Gestein
 - Verhalten von Materialien, welche zur Verfüllung und Versiegelung von Endlagern eingesetzt werden sollen
 - Methoden zur zerstörungsfreien Ortung von Störzonen im Fels
- Seitens der Schweiz beteiligt sich die Nagra an diesen Untersuchungen. Die technischen Berichte aus dem Stripa-Projekt erscheinen gleichzeitig in der NTB-Serie der Nagra.

The Stripa Project is organised as an autonomous project of the Nuclear Energy Agency of the OECD. In the period from 1980-86, an international cooperative programme of investigations is being carried out in an underground rock laboratory in Sweden. The aim of the work is to improve our knowledge in the following areas:

- hydrogeological and geochemical measurement methods in boreholes
- flow of groundwater and transport of radionuclides in fissured rock
- behaviour of backfilling and sealing materials in a real geological environment
- non-destructive methods for location of disturbed zones in the rock

Switzerland is represented in the Stripa Project by Nagra and the Stripa Project technical reports appear in the Nagra NTB series.

Le projet Stripa est un projet autonome de l'Agence de l'OCDE pour l'Energie Nucléaire. Il s'agit d'un programme de recherche avec participation internationale, qui sera réalisé entre 1980 et 1986 dans un laboratoire souterrain, en Suède. Le but de ces travaux est d'améliorer et d'étendre les connaissances dans les domaines suivants:

- mesures hydrogéologiques et géochimiques dans les puits de forage
- chimie des eaux souterraines à grande profondeur
- écoulement des eaux souterraines et transport des radionucléides dans les roches fracturées
- comportement des matériaux de colmatage et de scellement des dépôts finals
- méthodes de localisation non destructive des zones de perturbation de la roche

La Suisse est représentée dans le projet Stripa par la Cédra. Les rapports techniques du projet Stripa sont publiés dans la série des rapports techniques de la Cédra (NTB).

ABSTRACT

This report presents a programme for the hydro-geochemical assessment of a crystalline rock site for radioactive waste disposal. It is based upon experience gained during the international programme of hydrochemical work at the Stripa mine. The important results of this work are summarised in this report and fuller details may be found in the separate final reports of the Phase 1 and Phase 2 geochemical investigations of the Stripa groundwaters.

The present report summarises the general sampling requirements for a successful hydrochemical investigation; the isotopic and chemical parameters which should be determined and the geochemical characterisation of the rock matrix necessary for the interpretation of hydrochemistry. A general strategy for site evaluation by geochemical methods is presented.

RESUME

Ce rapport présente un programme d'évaluation hydrogéochimique d'un site de dépôt pour déchets radioactifs situé dans des roches cristallines. Il se fonde sur les expériences acquises lors du programme international de recherches hydrochimiques dans la mine de Stripa. Les résultats importants de ces travaux sont résumés dans le présent rapport et des détails plus complets peuvent être trouvés dans les rapports finals distincts des phases 1 et 2 des investigations géochimiques des eaux souterraines de Stripa.

Le présent rapport résume les exigences générales concernant la prise d'échantillons assurant des investigations hydrochimiques fructueuses; les paramètres isotopiques et chimiques qui devraient être déterminés et la caractérisation géochimique de la matrice rocheuse nécessaire à l'interprétation de l'hydrochimie. Une stratégie générale pour l'évaluation d'un site par des méthodes géochimiques est présentée.

ZUSAMMENFASSUNG

In diesem Bericht wird ein Programm für die hydrogeochemische Beurteilung eines potentiellen Standorts für das Endlager radioaktiver Abfälle im Kristallin beschrieben. Das Programm beruht auf der Erfahrung, die bei der Durchführung eines internationalen hydrochemischen Forschungsprojekts im Felslabor Stripa gewonnen wurde. Im vorliegenden Text werden die wichtigsten Ergebnisse dieser Arbeit resümiert - detailliertere Angaben können separaten Abschlussberichten der Phasen I und II der geochemischen Untersuchungen an Stripa-Grundwässern entnommen werden.

Der vorliegende Bericht fasst folgende Punkte zusammen: allgemeine Anforderungen an eine für aussagefähige hydrochemische Untersuchung erforderliche Wasserbeprobung; zu bestimmende chemische und Isotopen-Parameter; geochemische Charakterisierung der Gesteinsmatrix, die für die Interpretation der Hydrochemie benötigt wird. Schliesslich wird die allgemeine Strategie der Standortevaluation nach geochemischen Gesichtspunkten dargestellt.

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SUMMARY

The aim of these investigations within the International Stripa project was to develop and evaluate geochemical concepts and techniques suitable for the assessment of crystalline rock as an ultimate barrier to the movement of radioactive materials in nuclear waste repositories. The movement of groundwater in fractured crystalline rock systems is very complex and is not readily assessed using classical hydrological concepts. Geochemical parameters can be very sensitive indicators of changing stress fields, thermal effects on the repository and consequent changes in flow patterns so that geochemical monitoring can also provide an on-going safety assessment of a developed repository site. The hydrogeochemical investigations at Stripa have resulted in entirely new results and hypotheses about granite-groundwater interactions and their relevance to repository site characterisation.

The Stripa granite has a high radioelement content with a U-content of 10 - 15 times the world average for granites. Consequently, the in-situ neutron flux causes significant neutron-induced reactions which produce isotopes that are normally used for groundwater age-dating. Such in-situ production places limitations on the application of these groundwater dating methods.

The shallow groundwaters at Stripa are of the Ca-HCO₃ type with total dissolved solids (TDS) less than 300 ppm whereas the deeper minewaters have TDS up to 1300 ppm and are of the Na-Ca-Cl-SO₄ type. Groundwater pH increases with depth to values between 9 and 10 and the total alkalinity (as HCO₃⁻) of the deep groundwaters decreases to less than 10 ppm compared with about 200 ppm in the shallow groundwaters.

The presence of saline waters at depth in the Stripa granite and the change in the chemical character of the solutes at depth is clear evidence of either water-rock interaction or of the presence of migrating saline fluids of a regional origin. However, development of salinity is only to a limited degree associated with granite leaching as ³⁶Cl/Cl isotopic measurements have convincingly demonstrated.

Stable isotope analyses (^2H and ^{18}O) permit the recognition of different groundwater regimes and demonstrate the general lack of interconnectivity between fracture systems. All waters sampled in boreholes drilled within the granite are normal, meteoric waters for which the isotopic composition has not been measurably affected by rock-water interaction. However, the deeper groundwaters are isotopically lighter than the local modern groundwaters in which seasonal variations have been smoothed out. A comparison of chemical and stable isotope data show that local groundwater mixes with an isotopically lighter saline water at depth.

Stable carbon isotope analyses reveal the dominating influence of ^{13}C -depleted carbon. Biogenic carbon is added in the recharge environment of these waters through soil carbon dioxide. Its presence is recognised in all shallow and intermediate-depth groundwaters. The deep waters, however, receive an additional input of "organic carbon" either through bacterial action on dissolved organic carbon (DOC) or the oxidation of methane.

Bacterial action is also indicated by the isotopic compositions of aqueous sulphate. In the shallow groundwater at Stripa, all sulphate originates in the surface environment from atmospheric fallout and the oxidation of sulphides in the rock matrix. In the deep groundwaters, however, sulphide oxidation does not proceed and, instead, both ^{18}O and ^{34}S concentrations are typical of sedimentary sulphates and implicate a sedimentary brine in the formation of the deep saline waters. However, sulphates in magmatic and metamorphic environments have similar ^{34}S values and the origin of the deep sulphate remains ambiguous.

Isotope analyses on fracture calcites and comparisons with chemical and mineralogical data permitted the recognition of at least four calcite precipitation events which range in age from modern to contemporaneous with the granite emplacement.

Strontium isotope analyses ($^{87}\text{Sr}/^{86}\text{Sr}$) on aqueous and mineral Sr suggest that several events of fluid movement were involved in secondary mineral formation and that most of this alteration took place during late stage

cooling of the pluton.

The ^{222}Rn content of the deep groundwaters is remarkably high and is evidence for the close proximity of natural uranium to the fracture porosity of the granite. Measurements of the ^{222}Rn flux from the surfaces of Stripa granite samples have been used to calculate the fracture widths. The mean fracture width so derived is about 100 μm and hydraulic considerations show that infiltration of shallow groundwaters to the deeper system along such fractures is possible within 1 to 10 years.

Natural uranium is strongly mobilised in the shallow groundwater zone; these waters have U contents of up to 90 ppb. In the deeper zone, U content decreases because of changing redox conditions to <1 ppb for the deepest groundwaters sampled. The uranium isotope activity ratio, $^{234}\text{U}/^{238}\text{U}$, generally increases as the U content decreases.

The residence time of ^{234}Th and ^{210}Po are less than 12 days and 2 hours respectively. These nuclides are natural analogues which are a guide to the expected residence times of the long-lived actinide components of nuclear wastes, for example, ^{239}Pu and ^{241}Am . This suggests that the saline groundwaters at depth in the Stripa granite would be an effective barrier against actinide migration.

The ratio of the rare radioisotope ^{36}Cl to stable isotopes of chlorine has shown that in-situ production within or in contact with the rock matrix is a dominant source of ^{36}Cl . The $^{36}\text{Cl}/\text{Cl}$ ratio observed in the deepest groundwaters is less than that expected for in-situ production within the granite so that some of the dissolved chloride must have been derived outside the granite. The surrounding leptite is a possible site in which saline fluids could have been stored.

The ^3H contents of the minewaters show clearly that surface waters can rapidly penetrate the fracture system to all mining levels. Waters which were sampled from boreholes which extended below the open mine galleries, initially had low ^3H contents but these have generally increased over the period of study. The stored groundwater within the granite begins to mix

with more superficial waters as soon as flow is induced.

The lowest ^{14}C content measured in the DIC in Stripa groundwaters is below about 3% of modern carbon. These values were found in borehole M3 (330m level) and deeper boreholes tend to have somewhat lower measured values. Estimated groundwater "ages" correspond to about 25,000 years.

For the deep groundwater zone where reducing conditions for uranium have been established, the rate of $^{234}\text{U}/^{238}\text{U}$ enhancement due to recoil solution of ^{234}U was estimated. The time for this ratio to increase from that typical of chemical dissolution to the observed ratios in V2 groundwaters is in the range 1000 to 30,000 years.

The $^{36}\text{Cl}/\text{Cl}$ ratio is generally lies between that typical of the leptite and that typical of the granite. If the fluids entered the granite with ^{36}Cl typical of the leptite, it would require residence times of up to 300,000 years to produce the observed amounts of ^{36}Cl unless there is further solution of chloride.

The Stripa investigations have demonstrated that for geochemical studies it is essential to have dedicated drillholes which are carefully packed off so that individual fracture zones can be isolated and monitored for long periods of time. For the interpretation of isotopic and geochemical techniques, an integrated study involving various simultaneously determined parameters is necessary to optimise the information obtained.

Groundwater chemistry is the result of water-rock interaction and for the interpretation of groundwater analyses it is essential that both the physical and chemical properties of the rock matrix be determined.

A general strategy for geochemical investigation of a repository site should involve three distinct phases. The first phase, which may require up to 2 years to complete should be a geochemical survey of regional groundwaters. The second phase would be repository construction and the third phase would involve geochemical monitoring of groundwater sources during deposition of radioactive waste and after closure.

1. THE PURPOSE OF HYDROGEOCHEMICAL INVESTIGATIONS

The purpose of the hydrogeochemical investigations within the International Stripa Project was to develop and evaluate geochemical concepts and techniques suitable for the assessment of crystalline rock as an ultimate barrier to the movement of radioactive and toxic materials from nuclear fuel wastes.

In the case of an actual disposal site such investigations would also provide background data prior to site development and could also be used to monitor any induced changes in the hydrochemical regime during waste disposal as well as the re-establishment of stable hydrogeochemical conditions after closure of the repository.

Geochemical investigations provide valuable information on groundwater conditions that often cannot be determined by other methods. Such geochemical characterisation of groundwaters can aid in the evaluation of the following parameters and processes:

- I. The regional groundwater characteristics and its relationship to groundwaters at the repository site.
- II. The identification of different groundwaters at the repository site.
- III. The dominant geochemical processes which affect groundwater chemistry.
- IV. Geochemical constraints upon any hydrogeological model of the groundwater system.
- V. Long-term and long-distance (far-field) transport of solutes and groundwater and possibilities for radionuclide migration.
- VI. The corrosion potential of waste canisters in contact with the groundwater of the repository.
- VII. The potential reactivity and migration of leaking

radionuclides, and the retardation of such migration in the repository.

- VIII. The thermal effects of radioactive waste disposal and the effects of consequent stress relief on the groundwater flow regime.

The chemical and isotopic characteristics of a groundwater are an integral part of its hydrological and geological properties. Any hydrogeological model that claims to reflect the actual groundwater conditions and to predict future scenarios must be consistent with all available geochemical data or it will be unrealistic. When such consistency is obtained, the reliability of the safety analysis is considerably enhanced. Furthermore, geochemical parameters can be very sensitive indicators of changing stress fields, thermal effects on the repository and consequent changes in flow patterns. Geochemical monitoring can therefore provide an on-going safety assessment of a developed repository site.

A hydrogeological programme to meet these objectives requires an assessment of groundwater movement and its interactions with the rock mass under natural and disturbed conditions. The movement of groundwater in fractured crystalline rock systems is very complex and is not readily assessed using classical hydrological concepts. For example, bulk-permeabilities are several orders of magnitude lower than for porous media and are very heterogeneous in nature. The bulk permeability in a given volume may be almost entirely accounted for by a single fracture. Flow paths are also very tortuous and although the fracture system is the main cause of rock permeability, it represents a small proportion of the total porosity. The porosity of a fractured crystalline rock is mainly due to micropores and microcracks which are partially isolated from the main flow system.

2. DEVELOPMENT OF A HYDROGEOCHEMICAL PROGRAMME AT STRIPA

In the spring of 1977, an agreement was reached between the Swedish State Power Board and the Lawrence Berkeley Laboratories (University of California) for a joint project "Waste Storage in Mined Caverns".

It was decided that an ..."abandoned iron ore mine at Stripa (Sweden) can be used for a cooperative work program on the problem of terminal storage of radioactive waste in mined caverns."

This project had the following tasks as its principal objectives:

- Task 1 Full scale heater experiment to investigate effects of temperature increases on crystalline rocks.
- Task 2 Time-scaled heater experiments to assess long-term effects of the thermal-mechanical loading on a repository in crystalline rock.
- Task 3 Assessment of the fracture hydrology.
- Task 4 Geophysical assessment of fractured rock masses.
- Task 5 Laboratory measurement of material properties.
- Task 6 Mass transfer of water to the ventilation system.
- Task 7 Measurement of in-situ stresses caused by hydraulic fracturing.

Thus, no provision for a specific geochemical programme was made, possibly because it was implicitly assumed that it would be possible to select "a rock mass where the only practical pathways for fluid movement are through fractures in the rock system. The basic problem is to demonstrate that movements through such fractures will be essentially nil." Task 3 had as its aim to "define the surface and subsurface hydrological conditions of the fractured granite rock mass at Stripa... using various borehole tests." A small isotope/geochemical program was foreseen, however, within the Task 3 activities:

"In addition to the borehole tests, an attempt will be made to obtain two uncontaminated water samples per borehole plus three samples from the pumping-out testing program from a total of seven samples for age determinations and chemical analysis. Several

additional water samples will be collected from the surface water system to provide appropriate background data. An attempt will also be made to obtain water samples in the subsurface excavations."

These modest plans changed very quickly, however, into a major task because it was soon realized that fracture systems in crystalline rocks were far from impermeable and in addition, it was found that salinity gradients existed in waters encountered within the first deep borehole drilled by the Swedish Geological Survey (borehole V2). Increasing salinities with depth suggested the possible presence of different flow systems. An environmental isotope programme was designed based on ^2H and ^{18}O to characterise these waters and samples were collected for tritium, radiocarbon and uranium series analyses in an attempt to develop models which would permit the age dating of the groundwaters as an aid to the safety assessment of the site.

The outcome of these studies was highly successful because they resulted in not only the recognition and chemical characterisation of different groundwaters at Stripa but also in the clear documentation of the value of isotope geochemical data within hydrological studies at crystalline sites. This, in turn, had consequences for similar projects elsewhere. Furthermore, these studies set the stage for much more refined investigations which were to follow in a subsequent phase. In 1980 the Stripa project was transformed into an international cooperation between Canada, Finland, Japan, Sweden, Switzerland and USA. France, West Germany and the United Kingdom were also associated with the project. Two principal project orientations were chosen: a buffer mass test and hydrogeological studies in boreholes. Hydrogeochemistry was now a very major component of these projects. Emphasis was no longer placed solely on the chemical characterisation of different groundwaters but the program was seen as an integral part of crystalline rock investigations. It involved analysis of rock-water interactions which controlled the geochemical evolution of these groundwaters, descriptions of geochemical regimes as well as the testing and development of potential groundwater dating tools. The principal findings of the Phase 1 studies are summarised in the Stripa Report 85-06.

The present report at the end of the Phase 2 investigations summarises not only additional data obtained but also attempts to evaluate the various tools employed in terms of their importance for future site characterisation. The ultimate aim of a physical hydrology program must be to develop a 3-dimensional picture in terms of fluid flow through the Stripa rock mass, because it is essential to know from where and to where groundwater moves. It is here that the geochemical programme contributed most directly to the hydrogeological studies because the isotope/geochemical data clearly document the existence of distinct flow regimes in different fracture systems. The results also suggest that a component of regional groundwater flow is present, suggesting that site investigations cannot be limited to the local environment.

3. SPECIFIC RESULTS FROM STRIPA

Several of the hydrogeochemical investigations at Stripa have resulted in entirely new results and hypotheses about granite-groundwater interactions and their relevance to repository site characterisation. The major highlights are summarised below followed by a general assessment of hydrogeochemical parameters that provide some guidelines for future site investigations.

3.1 Documentation of in-situ production of radionuclides

The Stripa granite has a high radioelement content with a U-content of 10 - 15 times the world average for granites. Consequently, the in-situ neutron flux which arises from alpha-particle reactions with light elements of the rock matrix is much greater than in other granites. This makes Stripa an ideal site for the investigation of neutron-induced reactions which produce isotopes that can normally be used for groundwater age-dating. Such in-situ production places limitations on the application of these groundwater dating methods. The investigations at Stripa have provided the most fully documented case study for in-situ production reactions.

The in-situ production of ^3H , ^{14}C , ^{36}Cl , ^{129}I , ^{37}Ar , ^{39}Ar , ^{81}Kr and ^{85}Kr by neutron-induced reactions and spontaneous nuclear decay

processes has been estimated within the Stripa granite, its associated fracture minerals and surrounding leptite. Experimental measurements of the neutron flux ($3.3 \pm 0.5 \times 10^{-4} \text{ cm}^{-2} \text{ s}^{-1}$) in the Stripa granite are within 15% of theoretical values and were used to calculate production rates for neutron-induced reaction products. The in-situ produced activities of ^3H and ^{14}C which enter fracture fluids from the rock matrix are close to present detection limits. For ^3H , the most significant production is within the rock matrix whilst for ^{14}C it is within the circulating fracture fluids. Chlorine-36 production by neutron-capture within the granite is much more significant than inputs from cosmogenic and nuclear fallout sources. The $^{36}\text{Cl}/\text{Cl}$ ratio may be used to evaluate Cl^- sources in saline groundwaters. In-situ production of ^{129}I by spontaneous fission of ^{238}U is an important source of ^{129}I in the highly radioactive Stripa granite. Argon-37, ^{39}Ar and ^{85}Kr are produced by in-situ reactions within the rock matrix, fracture mineralisation and at the sites of U-mineralisation, respectively.

3.1.1 Stripa rock and fracture fluid composition The theoretical calculation of the in-situ neutron flux and isotope production within the rock matrix or its groundwaters requires a knowledge of the geochemical composition of the rock, its fracture mineralisation and typical fluids in the fracture flow system. These data are summarised for the Stripa granite (and the surrounding leptite) in Table 1. Those elements which are most significant for in-situ production estimations are indicated by an asterisk.

3.2 Increased salinity found at depth

Whereas the shallow groundwaters at Stripa are of the Ca-HCO_3 type with total dissolved solids (TDS) less than 300 ppm, the deeper minewaters have TDS up to 1300 ppm and are of the Na-Ca-Cl-SO_4 type. Groundwater pH increases with depth to values between 9 and 10 and the total alkalinity (as HCO_3^-) of the deep groundwaters decreases to less than 10 ppm compared with about 200 ppm in the shallow groundwaters.

The finding of saline waters at depth and the complexity of hydrochemical systems in the Stripa granite was unexpected and the change in the chemical character of the solutes at depth is clear

Table 1. Element compositions ($\mu\text{g/g}$) of the Stripa granite, its fracture infills, fracture fluids and leptite.

Element	Granite	Fracture Infill (5)	Fracture Fluid (1)	Leptite (6)
H	423.(3)	423.(3)	110,000.	423.(3)
Li*	1.8 - 28	0.5	0.18	14.
Be	5.	-	<0.003	6.
B*	3.0 - 33(8)	-	0.24	5.9
C	300.(2)	60,000.	2.56	-
N	20.(2)	20.(2)	31.(4)	20.(2)
O*	480,000.	455,000.	890,000.	485,000.
F	440.	-	4.4	800.(2)
Na*	30,200.	-	304.	10,200.
Mg*	1,570.	29,450.	0.32	9,200.
Al*	74,100.	53,950.	<0.005	60,500.
Si*	359,000.	63,800.	6.4	350,500.
P	390.	-	<0.007	-
S	<300.	-	8.0	-
Cl*	160.	-	700.	105.
Ar	-	-	1.42(4)	-
K*	38,400.	1,615.	2.5	33,750.
Ca*	5,150.	201,000.	170.	13,500.
Sc	4.8	-	-	-
Ti*	480.	325	-	1,260.
Cr*	1.7	-	<0.005	-
Mn*	460.	3,100	<0.1	155.
Fe*	9,300.	129,600	0.008	19,850.
Co*	0.71	-	<0.005	-
Ni*	8.	-	<0.005	-
Zn	19.	-	<0.01	-
Kr	-	-	0.0006(4)	-
Rb	200.	-	<0.005	-
Sr	300.(2)	-	1.8	-
Sb	0.19	-	-	-
Cs	4.3	-	-	-
Ba	545.	-	0.014	-
La	30.	-	-	-
Ce	72.	-	-	-
Nd	41.	-	-	-
Sm*	11.4	-	-	7.9
Eu	0.42	-	-	-
Gd*	12.9	-	-	7.5
Tb	2.2	-	-	-
Tm	1.0	-	-	-
Yb	8.1	-	-	-
Lu	1.3	-	-	-
Hf	3.8	-	-	-
Ta	7.9	-	-	-
U*	44.1	1,000	<0.001	5.4(7)
Th*	33.0	-	<0.0002	17.9(7)

- (1) All analytical data from NORDSTROM et al.(1985) unless otherwise stated. A density of 2.6 g cm^{-3} has been used for all rock types.
- (2) Average granitic values from PARKER (1967).
- (3) For 1% bound or intergranular fluids.
- (4) Dissolved gases and ionic species.
- (5) For a 50/50 calcite/chlorite fracture filling. [Based on fracture mineral analyses by S.K. FRAPE (personal communication)].
- (6) Analytical data from S.N. DAVIS (personal communication).
- (7) WOLLENBERG et al.(1980).
- (8) Value of 33 ppm from analysis of V2 core sample by B. SMITH.

evidence of either water-rock interaction (which could include fluid inclusion leakage from crystalline rock) or the presence of migrating saline fluids of a regional origin. The salinity/depth profile is heterogeneous and documents a lack of simple interconnection between fractures. Individual fractures produce waters with a characteristic salinity which during the observation period was constant in time. However development of salinity is only to a limited degree associated with granite leaching as has been convincingly demonstrated by the $^{36}\text{Cl}/\text{Cl}$ isotopic measurements. The basic geochemical character of the deep groundwaters has been established as a basis for hydrogeological interpretations, although some aspects of the origin of the groundwater salinity are still unresolved.

3.3 Stable Isotope Analyses

3.3.1 Deuterium and Oxygen-18 The determination of ^{18}O and ^2H concentrations in groundwaters of the Stripa granite provided the backbone of environmental isotope investigations. Close to 300 samples were collected and analysed during the eight year project for both oxygen and hydrogen isotope contents.

Results of these analyses permitted the recognition of different groundwater regimes and emphasized the lack of interconnectivity in several parallel or subparallel fracture systems. All waters sampled in boreholes drilled within the granite are normal, meteoric waters for which the isotopic composition has not been measurably affected by rock-water interaction. However, the deeper groundwaters contain a saline component whose origin is as yet unknown and they are isotopically lighter than the local modern groundwaters in which seasonal variations have been smoothed out.

A comparison of chemical and stable isotope data points towards a three component system for the deep waters whereby local groundwater mixes with an isotopically lighter saline water. The latter most likely acquired its salinity by admixture of small amounts of a brine whose geochemistry reflects crystalline rock-water interaction but which also has some sedimentary characteristics which suggest

the presence of a third component. It is unlikely that the latter can be recognised in the isotopic composition of the deep waters.

- 3.3.2 Carbon-13 Stable carbon isotope analyses were initially undertaken primarily in support of the radiocarbon studies and as an aid to understand the geochemical processes which determine the geochemistry of the different groundwaters. However, a wide range of isotopic compositions in the dissolved inorganic carbon (DIC) necessitated further analyses. The most important finding was the dominating influence of ^{13}C -depleted carbon. Biogenic carbon is added in the recharge environment of these waters through soil carbon dioxide. Its presence is recognised in all shallow and intermediate-depth groundwaters. The deep waters, however, receive an additional input of "organic carbon" either through bacterial action on dissolved organic carbon (DOC) as food-source or the oxidation of methane, possibly of inorganic origin.

The existence of bacterial activities is indicated by the isotopic compositions of aqueous sulphate; by the presence of minor amounts of methane in the deep waters and was confirmed by direct sampling and culturing. Little is yet known about the age and origin of DOC and methane in the deep groundwater. The DOC could have the "age" of the water if it originated in the recharge environment but could also be "old" carbon if it has been produced by oxidation of inorganic methane. Similarly methane could be produced from DOC or, as appears more likely on the basis of preliminary ^{13}C measurements, it could have a thermocatalytic origin. Thus, the addition of such carbon to the DIC can result in the addition of old carbon and the dilution of the radiocarbon concentrations.

Isotope analyses on fracture calcites and comparisons with chemical and mineralogical data permitted the recognition of at least four events of fluid movements which caused calcite precipitation. The older calcites are related to magmatic and hydrothermal events which may have been in part contemporaneous with the granite emplacement. The youngest calcites have $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values similar to those expected for calcite deposited from present groundwaters. This includes calcites with $\delta^{13}\text{C}$ (relative to the PDB standard) similar to values for the DIC of deep groundwaters. Values of $\delta^{13}\text{C}$ below

-40‰ occur in some calcites. This is lower than that of biogenic organic compounds but is typical for both thermocatalytic and biogenic methane, suggesting that methane oxidation may have been the carbon source for these calcites.

- 3.3.3 Sulphur-34 and Oxygen-18 in Sulphate Isotope analyses on aqueous sulphate were undertaken to contribute to the discussion on the origin and flowpaths of the Stripa groundwaters and to obtain information on the origin of the sulphur (magmatic or sedimentary).

In the shallow groundwater at Stripa, all sulphate originates in the surface environment from atmospheric fallout and the oxidation of sulphides in the rock matrix. In the deep groundwaters, however, sulphide oxidation does not proceed and, instead, both ^{18}O and ^{34}S concentrations are typical of sedimentary sulphates. (However, sulphates in magmatic/metamorphic environments are also known to fall into a similar range of ^{34}S values). Although this supports the hypothesis of the participation of a sedimentary brine in the formation of the deep saline waters, the origin of the deep sulphate remains ambiguous. The recognition of bacterial activities which reduce the aqueous sulphate and cause isotopic enrichments for both ^{18}O and ^{34}S is an important result of these isotope analyses.

- 3.3.4 Nitrogen-15 Nitrogen gas was separated from seven shallow and deep groundwaters. All results indicate that the nitrogen has an atmospheric origin. No indication exists that nitrogenous organic matter is being decomposed in significant amounts.

- 3.3.5 Strontium-87/strontium-86 Strontium isotope analyses on aqueous and mineral Sr permits discussion on rock-water interactions, the importance of clay mineral formation and - under favourable circumstances - age dating of fracture minerals. Results support the conclusion that several events of fluid movement were involved in secondary mineral formation and that most of this alteration took place during late stage cooling of the pluton.

3.4 Radioisotope analyses

- 3.4.1 Radon-222 The ^{222}Rn content of the deep groundwaters is remarkably

high (up to 10^5 Bq/kg) and is evidence for the close proximity of natural uranium to the fracture porosity of the granite. Measurements of the ^{222}Rn flux from the surfaces of Stripa granite samples have been used to calculate the fracture widths which are required in the deep system to support these high ^{222}Rn contents. The mean fracture width so derived is about 100 μm and hydraulic considerations show that infiltration of shallow groundwaters to the deeper system along such fractures is possible within 1 to 10 years. Such infiltration can only occur if a pathway to depth exists with a hydraulic gradient which is due to the presence of the Stripa mine itself. It is expected that much slower infiltration would occur in a repository excavation after it had been closed and backfilled so that more natural hydraulic gradients are re-established.

- 3.4.2 Uranium isotopes Natural uranium is strongly mobilised in the shallow groundwater zone; these waters have U contents of up to 90 ppb. In the deeper zone, U content decreases to <1 ppb for the deepest groundwaters sampled. The uranium isotope activity ratio, $^{234}\text{U}/^{238}\text{U}$, generally increases as the U content decreases, due to either preferential solution of ^{234}U or to alpha-recoil induced solution of ^{234}U .
- 3.4.3 Thorium-234 and Polonium-210 Measurements of the ^{234}Th and ^{210}Po contents of the V2 groundwaters have been used to derive the residence times of these radionuclides in solution. These residence times have been found to be very short, less than 12 days and 2 hours respectively. Since these nuclides are 4 and 3-valent actinides, they provide natural analogues which are a guide to the expected residence times of the long-lived actinide components of nuclear wastes, for example, ^{239}Pu and ^{241}Am . This suggests that the saline groundwaters at depth in the Stripa granite would provide a barrier against migration of these nuclides.
- 3.4.4 Chlorine Isotopes The ratio of the rare radioisotope ^{36}Cl to stable isotopes of chlorine has been determined in an extensive survey of groundwaters associated with the Stripa mine. Although there is a natural input of cosmic-ray produced ^{36}Cl at recharge, the admixture of chlorine during groundwater migration adds ^{36}Cl which has been formed by in-situ production within or in contact

with the rock matrix. The latter has been shown to be the dominant source of ^{36}Cl in the Stripa groundwaters. The $^{36}\text{Cl}/\text{Cl}$ ratio observed in the deepest groundwaters is less than that expected for in-situ production within the granite, demonstrating that some of the dissolved chloride must have been derived outside the granite. The surrounding leptite is a possible site in which saline fluids could have been stored and which would account for the observed isotopic ratios.

3.5 Groundwater residence time

3.5.1 Tritium, ^3H Thermonuclear tritium is present in all groundwaters which have been recharged later than 1954. It has been much used for estimating the extent of mixing of such waters with older groundwaters. At Stripa, the ^3H contents of drip-waters range from 60 - 160 tritium units (T.U.), even at the deepest mine level (410 m). Clearly, surface waters can rapidly penetrate the fracture system to all mining levels. Waters which were sampled from boreholes which extended below the open mine galleries, initially had low ^3H contents but these have generally increased over the period of study. The stored groundwater within the granite begins to mix with more superficial waters as soon as flow is induced in the borehole. For the deepest boreholes (V1 and V2), low levels of ^3H are now present in their groundwaters. It is now clear that these are above the amounts which could be due to in-situ production of ^3H and must be attributed to some admixture of recent groundwater. These rapid groundwater movements are most likely to have been caused by the hydraulic gradients induced by the mine excavations.

3.5.2 Carbon-14 Carbon-14 has been widely applied for estimating groundwater residence times up to about 30,000 years. At Stripa, calcite precipitation removes most of the DIC and hence also the ^{14}C , from the groundwaters as they migrate into the deeper zone. This is not necessarily fatal to the use of carbon-14 for groundwater "dating", but the resulting very low amounts of ^{14}C that remain in solution in the deeper groundwaters make sampling and/or measurements difficult and subject to contamination, either by admixture of younger groundwaters or directly from the atmosphere

during sampling. The lowest ^{14}C content measured in the DIC in Stripa groundwaters is below about 3% of modern carbon. These values were found in borehole M3 (330m level) and deeper boreholes tend to have somewhat lower measured values. Groundwater "ages" correspond to the lowest ^{14}C contents are about 25,000 years. This estimate is a maximum because ^{14}C -loss by exchange or diffusion and by dilution with other inputs (eg DOC oxidation) cannot be quantified. Such loss could be substantial so that even relatively young waters attain very low ^{14}C contents.

Radiocarbon measurements on the DOC have been attempted. As well as being of value for determining the origin of the organic carbon these measurements may form the basis of a radiochronometer if the DOC can be shown to have a surface (soil) origin.

The in-situ production of ^{14}C by neutron-induced reactions is unlikely to be able to contribute a ^{14}C activity of more than about 0.5% modern in the fracture fluids and so would not appreciably affect this time estimate. In-situ production of ^{14}C due to the recently discovered direct decay mode of radium isotopes is less well defined but if the ^{14}C so produced were readily transferred to the fracture fluids their ^{14}C content could be significantly increased.

3.5.3 Uranium Isotopes In the deep groundwater zone where reducing conditions for uranium have been established, the rate of $^{234}\text{U}/^{238}\text{U}$ enhancement due to recoil solution of ^{234}U could be estimated. The time for this ratio to be increased from that typical of chemical dissolution (about 2.5) to the observed ratios in V2 groundwaters was calculated to be in the range 1000 to 30,000 years.

3.5.4 Chlorine-36 It was observed above that the $^{36}\text{Cl}/\text{Cl}$ ratio was less than that which corresponds to the ratio within the granitic rock matrix. Consequently, at least some of the dissolved chloride must have been derived from outside the granite fracture system. In this case, subsequent storage of the saline fluid in the granite fracture system would subject the dissolved chloride to the neutron flux due to the rock matrix and its $^{36}\text{Cl}/\text{Cl}$ ratio would increase according to radioactive ingrowth relationships. Thus, if the fluids entered the

granite with ^{36}Cl typical of the leptite, it would require residence times of up to 300,000 years to produce the present observed amounts of ^{36}Cl or less if there were some further dissolution of chloride from the granite. A detailed regional survey is required to establish possible chloride (brine) sources.

4. HYDROGEOCHEMICAL RECOMMENDATIONS FOR SITE CHARACTERISATION

4.1 General sampling procedures

The Stripa investigations have demonstrated that for geochemical studies it is essential to have dedicated drillholes which are carefully packed off so that individual fracture zones can be isolated and monitored for long periods of time (six months to several years). These drillholes must not be tampered with during the course of the investigations. Furthermore, the design, materials and constructions of the sampling system (whether a system of packers, or downhole collection devices) must be carefully planned and executed. The sampling lines and containers must be teflon or teflon-coated if DOC or trace elements are to be analysed. Contact of groundwaters with any metallic, nylon or porous or leachable plastic must be avoided. The point of sample collection, preservation and in-situ measurements are, as mentioned before, critical to the integrity of the sample analysis.

4.2 Isotopic parameters

The Stripa experience has clearly demonstrated that for the interpretation of isotopic and geochemical techniques, an integrated study involving various simultaneously determined parameters is necessary to optimise the information obtained. The results of these investigations will be site-specific and will therefore need to be applied for each proposed repository location. This will require the coordinated efforts of specialist teams for planning, implementation and interpretation of site assessments.

The isotopic parameters listed in Table 2 were considered for the Stripa programme but for technical reasons not all of these were appropriate or could be used. The following general comments on

Table 2. Stable and naturally radioactive isotopes for groundwater tracing.

ISOTOPE	HALF-LIFE	APPLICATIONS	ADVANTAGES	CONSTRAINTS	CATEGORY	UNIT COST \$ (1987)
^{18}O , ^2H	Stable	GW origin, diagenetic reactions	Ideal 'tracers', simple sampling	Local/regional GW & rainfall records	XXX	80
^3H	12.4 a	Recognition of young GW	Conclusive if > 1 T.U.	Recognition of post 1957 GW only	XX	100
^{14}C	5740 a	Age dating, WRI, carbon	Time range 0-30 ka	Chemistry, sampling, analysis (AMS)	XX	250
^{13}C	Stable	Carbon origin, WRI, ^{14}C correction	solid-liquid equilibria	Precautions during sampling	XXX	50
^{34}S (SO_4^{2-} , S^{2-})	Stable	Sulphur origin, redox processes, mixing, WRI	Constraint upon origin of SO_4	Precautions during sampling	XX	70
^{18}O (SO_4^{2-})	Stable	Origin of sulphates, redox processes	Constraint upon origin of SO_4	Precautions during sampling	XX	80
^{85}Kr	10.8 a	Recognition of young GW	No chemical interactions	Large sample volume, limitation by in-situ production	X	1600
$^{40}\text{Ar}/^{36}\text{Ar}$	Stable	Recognition of alteration reactions	No chemical interactions	Special sampling conditions	XXX	80
^{39}Ar	269 a	Age dating	No chemical interactions	Large sample volume, limitation by in-situ production	X	6300
^{36}Cl	3.01 ka	Age dating, chloride origin, WRI	Time range 10^5 - 10^6 a	Interpretation, in-situ production, analytical (AMS)	XX	1500
^{37}Cl	Stable	Chloride origin		Small natural variations	-	200
^{87}Sr	Stable	Sr origin, WRI, mixing		Detailed mineralogy required, lack of kinetic data	XX	300
^{129}I	1.57×10^7 a	Age dating	Long time range, 10^7 a	In-situ production	-	1500
^{222}Rn	3.8 days	Porosity and fracture width estimates	No chemical interactions	Short half-life, time limit for analysis	XXX	80
$^{234}\text{U}/^{238}\text{U}$	4.5×10^9 a	Redox, age dating	Analogue for radioactive wastes	Special sampling conditions	XX	225
$^3\text{He}/^4\text{He}$	Stable	Origin of radiogenic He		Special sampling conditions	XX	250
^4He , noble gases	Stable	Identification of flow direction, gas migration, WRI recharge temperature	No chemical interactions	Special sampling conditions	XX	225
$^{15}\text{N}/^{14}\text{N}$	Stable	Origin dissolved N_2		Special sampling conditions	X	100
^{32}Si	104 a	Age dating	WRI	Geochemical interactions	-	500

Abbreviations: GW, groundwaters; WRI, water rock interaction; AMS, Accelerator Mass Spectroscopy
Unit analytical costs exclude field costs; ^{39}Ar measurements include ^{85}Kr .

CATEGORY

(Recommendation for use): XXX always required; XX required for selected samples; X useful in exceptional cases; - not considered useful at present stage of development

these methods may be made:

- (1) It is essential to recognise that the solvent and solutes may be of different origin and it is therefore crucially important that the isotopic composition of the water molecule itself, ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) must be included in any study. Tritium measurements are absolutely essential because it is still the most reliable tool to recognise groundwaters of post-nuclear origin.
- (2) Isotopic studies of solute species should be determined after the chemical reconnaissance has been completed. Carbon isotopic analysis is of special importance because of the major role that the DIC/DOC systems play in most aquifers and because C-14, may be used for estimating groundwater residence times and/or "age" relationships for different groundwater systems provided that the appropriate corrections for ^{14}C loss or dilution can be made.
- (3) Isotope analysis of aqueous sulphur-bearing compounds can greatly assist in the interpretation of flow paths and the bio-geochemical evolution of different groundwater systems. These analyses should be included.
- (4) Nitrogen and helium isotope analyses on dissolved gases are important where the presence of gases from the lower crust or mantle is suspected. The interpretation of such data also requires a knowledge of the in-situ production reactions in the groundwater host rocks.
- (5) Radon (^{222}Rn) contents of groundwaters are directly related to hydrological parameters such as porosity, fracture frequency and width, and should be included in any hydrochemical study. It is essential for interpretation that concurrent ^{222}Rn release studies should be made on the bulk rock matrix.
- (6) Uranium contents of groundwaters are controlled by its redox character and are related to the radioelement content of the

aquifer. In systems where reducing conditions have been established, uranium isotopic analyses may be used for age dating.

- (7) Chlorine-36 determinations combined with neutron flux measurements (or calculations) provide a unique method for identifying possible origins for the dissolved chloride in saline groundwaters.

4.3 Hydrochemical parameters

- 4.3.1 Field measurements Some measurements must be carefully made in the field in a closed-line flow-through cell to avoid irreversible chemical changes in the sample caused by gas exchange through air equilibration, thermal gradients, pressure gradients, microbial contamination and particle contamination. These measurements include pH, temperature, specific conductance and dissolved oxygen.
- 4.3.2 Field preservation Some constituents are unstable in aqueous solution and must be carefully preserved in the field for subsequent laboratory analyses. It is often preferable (though not essential) to determine some of these constituents in the field if facilities are available. Each constituent often has its own preservation procedure which must be carefully followed.
- 4.3.3 Chemical constituents The major ions and trace elements from a water analysis contain signatures of the whole history of that groundwater and its reactions with the surrounding mineral assemblages over the course of long periods of time. Hence, the groundwater chemistry reflects important aspects of the hydrogeological system that are not evident from hydraulic or geologic properties alone. It also indicates, through appropriate computations, whether minerals are likely to be dissolving or precipitating along a flowpath and this can have an important impact on permeability and porosity.

Chemical constituents that undergo redox reactions, such as Fe(II/III), S(II/VI) and As(III,V), can indicate the redox condition of the groundwater which is essential for determining the potential

mobility of radionuclides.

Table 3 lists the hydrochemical parameters that were considered for the Stripa programme although many of them were not found to be significant. For example, most trace metals were found to be below the limit of detection (5-10 ppb).

4.4 Rock characterisation

Groundwater chemistry is the result of water-rock interaction and for the interpretation of groundwater analyses it is essential that both the physical and chemical properties of the rock matrix be determined. Geochemical variability generally requires that a minimum of about 10 samples of each rock type which is implicated in the groundwater flow system should be analysed. Table 4 lists the properties which should be determined to enable rock-water interaction and in-situ production of radioisotopes to be assessed.

5. GENERAL RECOMMENDATIONS FOR SITE CHARACTERISATION

Many factors might influence the origin, evolution, reactive processes and flow characteristics of groundwaters in crystalline rocks, including recent or ancient marine sources, recent or ancient meteoric sources, sedimentary basin fluids, residual metamorphic/magmatic fluids (fluid inclusions) and hydrothermal fluids. Any combination of these may occur and they may be modified in composition by interaction with the local rock mass.

The main purpose of the geochemical site characterisation is to identify different groundwater types, relate them to groundwater flow patterns and to explain their differences within the framework of mean residence times, their relationship to the various lithologies, the possible mixing of groundwaters within the site and the dominant reactions which control their chemical and isotopic compositions. These objectives can only be achieved if good quality geochemical data can be obtained and this requires that the following general recommendations are fulfilled:

- I. A geochemical team leader should be involved at the earliest

 Table 3. Hydrochemical parameters for site characterisation

- (1) To be included in reconnaissance and detailed/monitoring programmes
 Major constituents: Ca, Mg, Na, K, Cl, F, SO₄, HCO₃, CO₃,
 Minor constituents: SiO₂, Br, NO₃, H₂S, U, I, NH₄, Fe (total).
 Physical parameters: temperature, pH, Eh, conductivity, dissolved
 oxygen and discharge.
 Isotopic parameters: ¹⁸O, ²H, ³H, ¹³C, ¹⁴C, ³⁴S, ²²²Rn.
- (2) Additional parameters to be included in detailed/monitoring programmes
⁴He, ²³⁴U/²³⁸U, ²²⁶Ra, ³⁶Cl and neutron flux, ¹⁸O and ³⁴S in sulphate
³⁴S in reduced S species, Li, Sr, Ba, Al, B, Fe (II/III), Mn,
 As (III/IV), Cu, Zn, Cr, Rb, PO₄
- (3) Parameters which are generally of low significance or below the
 detection limit.
 NO₂, NH₄, Cd, Pb, Co, Ni, V, Mo, Be.
-

 Table 4. Parameters required for rock characterisation

- a) Density, porosity and permeability
 b) Mineralogical description and modal composition
 c) Fluid inclusion studies
 d) Major element composition
 O, Na, Mg, Al, Si, K, Ca
 e) Minor element composition
 U, Th, Li, B, C, P, S, Cl, Ti, Cr, Mn, Fe,
 Co, Ni, Sm, Gd
 f) Radon-222 flux from rock matrix
 g) Age dating
-

stages of planning and design. This geochemist must work closely and co-operatively with a geological (or geophysical) team leader and a hydrological team leader. The geochemical data must ultimately be integrated with the existing hydrological and geological data (and vice versa).

- II. All existing background data on groundwater and surface water quality data should be compiled and interpreted on both a regional scale and a local scale.
- III. Groundwaters from wells, boreholes, springs, seeps or other sources should be sampled on both a local and a regional scale.
- IV. Analyses should begin with major chemical constituents and selected minor and isotopic species in a reconnaissance study.
- V. The reconnaissance study should be followed by analyses for a wider range of isotopic and trace elements for a selected number of locations.

The geochemical parameters which should be determined in the various parts of the site characterisation are detailed in table 2.

5.1 **A general strategy for investigation of a repository site.**

It is envisaged that any geochemical investigation of a proposed site for a nuclear waste repository should be broken into three phases as outlined below:

PHASE 1. Preliminary investigations (Estimated time 2 years)

- a) Work plan derived by cooperative efforts of geologists, hydrologists and geochemists.
- b) Compile and evaluate pre-existing hydrological, geochemical and geological data.
- c) Carry out regional survey including chemical/isotopic characterisation of both rock and existing groundwater sources.

- d) Drill at least two deep drillholes to investigate deeper systems
- e) Report on first evaluation of regional data

PHASE 2 Construction phase (Timetable will be dictated by engineering of the excavation.)

- a) Continue monitoring of sources examined in PHASE 1
- b) During or immediately after repository evacuation, drill dedicated boreholes for geochemical studies; sample all significant drillhole and tunnel inflows; continue to monitor these inflows.
- c) Report on second evaluation of regional data and first evaluation of sub-surface excavation data.

PHASE 3. Repository supervision (Timescale will be indefinite)

A detailed programme of hydrogeochemical monitoring of groundwater sources during deposition of radioactive waste and after closure of the repository.

5.2 Detailed guidelines for the hydrochemical investigations

A description or model of the regional scale groundwater system should be developed based on all the available data (geological, hydrological and geochemical). The regional patterns of groundwater movement must include identification of recharge areas, discharge areas, direction and length of flow paths, flow velocities and residence times, extent of regional flow and groundwater mixing, man-made induced perturbations on the regional flow pattern and potential disturbances induced by site development.

Deep drilling for either the regional or local studies must be carefully planned and executed to achieve any meaningful hydrochemical results. Too frequently a drilling programme has been carried out without the necessary pre-planning to obtain useful water analyses. There are at least six general problems related to groundwater analyses that must be carefully attended.

5.2.1 Drilling fluid contamination of an aquifer This problem is difficult to overcome entirely but it can be minimised by using

deionised water as the drilling fluid. The next best results would be achieved by using a filtered local surface or shallow groundwater. In either situation, the oxygen-18, deuterium and tritium concentrations of the drilling fluid should be carefully measured so that its distinct isotopic character can be used as a natural tracer. Such a natural tracer is preferable to a synthetic tracer because no changes are induced in the water chemistry and there are no doubts regarding the inertness of the tracer.

- 5.2.2 Pumping rates that are too high It is quite easy to pump groundwaters from drillholes at rates that cause leakage around packers either directly at the packer/rock interface or through interconnected fractures which bridge the packers. To avoid such contamination of deep groundwaters, pump rates should be minimal, perhaps just slightly greater than the flow rates under any hydrostatic head.
- 5.2.3 Interference by other studies If insertion and withdrawal of drillhole equipment for purposes other than hydrochemical sampling is allowed, then contamination of deep aquifers by shallow groundwaters is likely to occur and mixing between different horizons within the borehole will also take place. After such disturbances, it may take several months to again achieve a composition representative of the undisturbed system. Therefore, the provision of "dedicated" drillholes that are operated solely for the hydrogeochemical investigations is extremely important.
- 5.2.4 Contamination by the sampling system Several sources of contamination may make water samples collected from drillholes unsuitable for detailed geochemical analysis. It should be especially noted that organics may be leached from sampling lines and that oxidation, hydrolysis and precipitation of dissolved iron in the sampling lines frequently occurs. For sampling systems using downhole packers the sampling lines should be teflon tubing and the packers and accessories should be coated with metal-free epoxy paint or teflon. For downhole sampling vessels, the vessel walls should be teflon-coated. In this regard, it is also important to avoid significant changes in temperature and pressure of the groundwater sample because this may also induce precipitation of solids and

outgasing that can irreversibly change the water chemistry.

5.2.5 The sample collection system The Stripa results have clearly shown that small sampling intervals at the scale of two metres, reveal fracture zones which bear waters of different salinity. Whether or not smaller intervals are necessary has not been ascertained since two metres is the resolution of the current equipment. The sample collection system must be able to collect samples from a single fracture zone.

5.2.6 Supervision of sampling, analyses and hydrogeochemical interpretation It is crucial to the organisation of a meaningful geochemical programme to appoint a groundwater geochemist to supervise and co-ordinate the programme. The useful interpretation of geochemical results depends strongly on the degree to which sampling continuity and correlation with hydrological testing can be maintained throughout the whole programme. This person must be experienced in field sampling, preservation techniques, analytical procedures and their evaluation, and in the interpretation of chemical and isotopic data.

6. CONCLUSION

Experience at the Stripa project has demonstrated that a well-planned hydrogeochemical investigation of both regional and local groundwater systems is an essential requirement for the safety assessment of a nuclear waste repository. Groundwater movement in a fractured system cannot be predicted from hydrological criteria and an experimental investigation is required. The authors recommend that for future site investigations, the Stripa experience can form the basis of a geochemical programme which would enable the extent of any natural barrier to radionuclide migration to be better understood. The project demonstrated the extreme difficulties that may be encountered in the application of conventional isotopic techniques for dating groundwaters in an environment where more than one groundwater source may be present. The combined chemical and isotopic investigations enabled possible salinity sources to be identified and placed constraints upon the possible age relationships of the groundwaters.

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