CHEMICAL EVOLUTION OF DEEP GROUNDWATERS IN GRANITES, INFORMATION ACQUIRED FROM NATURAL SYSTEMS.

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Abstract

A research program has been carried out for five years, concerning a major aspect of deep radioactive waste disposals : groundwaters in the host-rock. The following items have been examined: the exact composition of confined waters, excluding those which are found in highly conductive (even deep) fractures; evolution path from surface waters to confined waters; possible influence of the repository on the composition of groundwaters; possible influence of groundwaters on the elements which could escape the repository (major elements, trace elements, radioactive elements). The following methodology is used : groundwater sampling and analysis, identification of the major phenomena controlling element concentration in groundwaters, modelling, modelling validation.

Introduction

Our study has been devoted to deep groundwaters in both hot (100°C) and cold (20°C) conditions in order to have a precise idea of their composition and variation; to understand the regulation mechanisms of trace and major elements to be able - in fine - to forecast their behaviour in the environment of a deep radioactive waste repository.

More than 200 groundwaters in granitic areas have been collected. Most confined and aged granitic groundwaters are alkaline and chemically reduced. These features are progressively acquired through the course of water-rock interaction, in systems where water/rock ratios are very small, which should be the reference case for radioactive waste repositories. The composition of superficial and intermediate waters has been also examined to evaluate the progressive acquisition of solutes.

1. What problems should be adressed in priority

1) one needs a complete description resulting in a database of deep groundwaters. This database should not be organized randomly, but with major "guidelines", which are somewhat "a priori " ideas of the origin and evolution mechanisms of analyzed groundwaters,

2) as the aim is to understand and predict what would happen around a deep radioactive waste repository, we have to understand and model the present data, and we must predict the evolution of the water/rock system after some eventual changes of key parameters,

We can now list some important questions we have to answer in order to be able to make some predictions :

- What is the ultimate composition of confined waters when water-rock interaction is a dominant process, and what is its duration?
- What elements are controlled by secondary mineral precipitation?
- What elements are not controlled by precipitation and might be introduced as parameters in the prediction?
- What are the effects of some parameters such as temperature, total amount of mobile elements, CO_2 partial pressure (if it is externally imposed to the system)?
- What is the range of these parameters in natural systems that could be selected for possible repository sites?
- What is the behaviour of minor and trace elements? Are they controlled by the same mechanisms, and can their concentration be predicted in deep groundwaters?

2. Some general features of deep and confined groundwaters in granitic areas

variability : granitic groundwaters are not unvariable and cannot be replaced by a "mean granitic water". Confined waters may be very dilute, although they have a tendancy to have a higher TDS content with progressive confinement.

dynamics : granitic waters participate to dynamic systems closely related to the hydrodynamical properties of the host rock. It must be noted that mixing processes cannot explain everything and are rarely evidenced by hydrodynamics, particularly in low porosity fractured reservoirs. In our opinion, the most efficient approach is to consider in priority the progressive evolution of the same fluid through the course of its interaction with the rocks or fractures in which it flows. Mixing must be clearly and unambiguously evidenced by converging arguments (isotopes, mobile element ratios).

chemistry : most confined granitic groundwaters are alkaline, whith pH up to 10 in some cases. Figure 1 shows the location of some well studied deep granitic alkaline groundwaters in Western Europe. We exclude of our study all systems with deep CO2 input, resulting in carbon-dioxide rich groundwaters, which should be carefully eliminated when selecting candidate sites for future repositories. pH generally increases with confinement, ie in most systems with depth (figure 2)
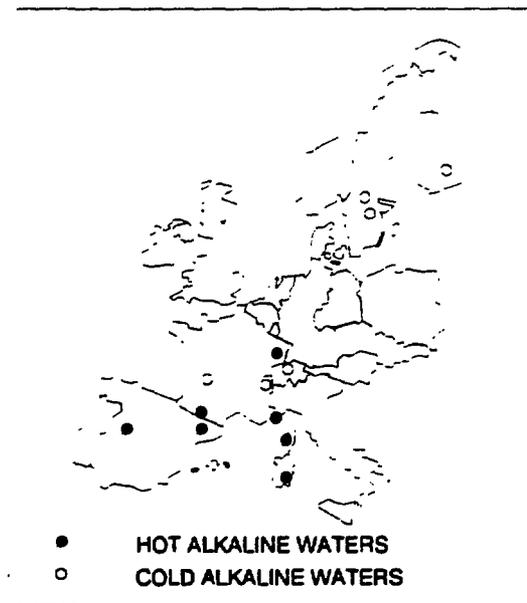

•   HOT ALKALINE WATERS
o   COLD ALKALINE WATERS

Figure 1. Emplacement of well documented granitic alkaline
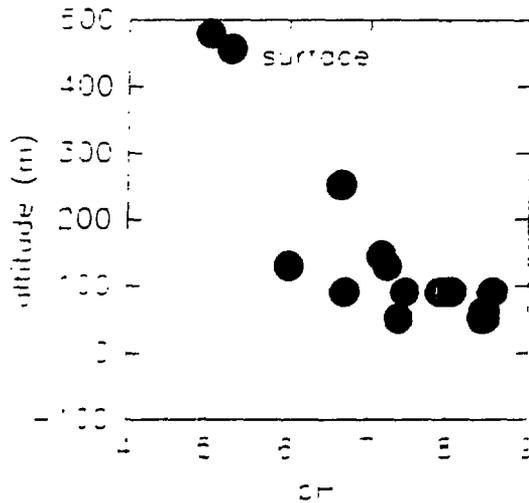groundwaters in western Europe

Figure 2. Evolution of pH with depth in granitic waters from Limousin (France)

Table 1. Typical deep groundwater compositions (concentrations in mmoles/l) High pH, low Eh, high Na/K, low Mg

	Low T° (Stripa)	High T° (Pyrénées)
pH field	10.06	9.00
T°	8.6°C	75°C
Eh	négative	-380mV
HS⁻	-	0.2
ALK.	0.29	1.77
Cl⁻	12.95	0.28
F⁻	0.6	0.32
SO_4^{2-}	0.6	0.24
SIO_2	0.3	1.39
Na^+	9.47	2.81
K^+	0.01	0.06
Ca^{2+}	2.35	0.04
Mg^{2+}	0.0025	0.0004

3. Controlled elements versus mobile elements

We have established that most major elements are controlled by secondary mineral precipitation in confined waters, and moreover, by a complete paragenesis that corresponds to the isochemical recrystallization of the host rock (Michard, 1985, 1987). An example of a controlling paragenesis is given below:

|		
Na	:	Low T° albite
K	:	adularia
Ca	:	laumontite or prehnite
Mg	:	chlorite
Al	:	kaolinite (or kaolinite-like clay)
Si	:	calcedony (or quartz above 100°C)
HCO_3^-	:	calcite

this assumption can be validated by the following methods :

- comparison of computed equilibrium compositions to field data : *generally good fitting, lack of accurate data at low temperature*

- examination of late alteration mineral assemblages and fracture fillings : *it is difficult to identify the last assemblage, some minerals can be present in tiny amounts*

- examination of colloidal mineral particles, which can be inherited or newly formed : *this is promising, inherited particles are easily distinguished, a complete trend from poorly crystalline allophanes to well crystallised minerals can be sampled (Beaucaire and Magonthier, 1992)*

Mobile elements are not controlled by secondary mineral precipitation, the solubility of which is far too high (NaCl, for instance). Consequently, they tend to accumulate in groundwaters as far as they are released in the system by the dissolution of mobile element-bearing minerals. Cl is the most important, although sulfates can be mobile if the solubility of gypsum is not reached. This is of course true for every element which minimum solubility is not reached.

controlled cations equilibria :

As a consequence of previous statements, the following equation can be established for any controlled element M. Na is controlled by a paragenesis that includes albite, kaolinite and silica. At equilibrium, we have:

$$NaAlSi_3O_8 + H^+ + \frac{1}{2}H_2O \leftrightarrow Na^+ + \frac{1}{2}Al_2Si_2O_5(OH)_4 + 2SiO_2$$
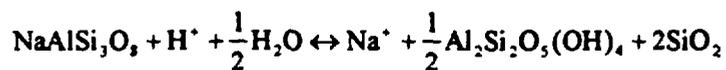
$$K = \frac{(Na^+)}{(H^+)}$$

This can be generalized for every controlled element M

$$(M^{z+}) = K \cdot (H^+)^z$$

The charge balance equation can the be written:

$$\sum_i \frac{z_i K_i (H^+)^{z_i}}{\gamma_i} - [A^-] = 0$$

Consequently, for a given temperature T° and for a given total mobile ion concentration A, all controlled elements can be predicted (table 2), provided that equilibrium is attained with respect to a suitable paragenesis. The agreement between computed and measured concentrations is very good. Similar results have been obtained in low temperature systems by Grimaud et al. (1990).

Table 2. Comparison between computed and measured groundwater composition : Thuès les Bains, Pyrénées, France (after Michard, 1989)

mobile element concentration : $\Sigma A^- = 1.37$ mmoles/l
computed deep equilibrium temperature 115°C
measured emergence temperature 78°C
equilibrium paragenesis :
Quartz, Kaolinite, Albite, Adularia, Chrysotile, Laumontite, Calcite
concentrations in mmoles/l

	Computed	Measured
pH(115°C)	8.46	
pH(78°C)	8.92	8.79
Na+	2.82	2.81
K+	0.057	0.065
Ca2+	0.022	0.035
Mg2+	< 1e-3	< 1e-3
Σ CO2	0.88	0.80
Σ SiO2	1.32	1.48
Σ A-	1.37	1.37

4. Expected ranges of external parameters

Temperature and the sum of mobile ions can be introduced as external parameters in predictive calculations. In addition, the partial pressure of carbon dioxide must be evaluated or predicted.

Temperature

In order to predict the composition of deep groundwaters, one must be able to evaluate the temperature evolution around the repository. It will be determined by :
- the geothermal gradient,
- the heat production induced by nuclear waste cannisters, which effect on temperature will depend on the thermal conductivity of host rocks and near field components.

Both can be predicted at each stage of the evolution of the repository, although difficulties may arise from coupling between thermics, mechanics and convection.

Carbon dioxide partial pressure

In some cases, pCO2 must be considered, as some systems may be externally regulated as regards carbonates such as volcanic or tectonically active areas, which can induce deep CO2 inputs. However, in most deep groundwaters, carbonates and Ca are regulated by calcium alumino-silicates and calcite, which fixes the CO2 partial pressure for a given temperature. PCO2 increases in shallow waters due to biological activity, $\Sigma CO2$ evolves then in close system in deeper waters. As carbonates are removed from the solution by calcite precipitation (Ca is added by silicate dissolution), $\Sigma CO2$ progressively decreases, inducing a decrease of both alkalinity and PCO2. Deep granitic groundwaters have generally low alkalinities (less than 1mmole/l) and CO2 partial pressures (10^{-5} 10^{-6} atm.). In organic-rich systems, which is generally not the case in granitic rocks, an increase of CO2 pressure can be induced by organic matter oxidation, correlated with iron or sulphate reduction.

mobile elements

The amount of mobile elements which will be released in the system is far more difficult to establish. In a normal evolution scenario, wastes should not generate significant amounts of mobile elements. Mobile elements can be of internal origin, ie released during dissolution processes; or external origin (influence of connate waters inheritage or surrounding evaporitic formations). If significant amounts of chloride for instance are present in primary unaltered host rocks, Cl generally increases with reaction progress, which allows to use it as and index of reaction progress (Grimaud et al. 1990). A priori modelling is however difficult, as the repartition of chloride (minerals, grain boundaries, fluid

inclusions) is uneasy to evaluate. Our opinion is that the best way to estimate its maximum amount is to carefully examine the composition of deep equilibrated groundwaters during site characterization processes.

5. Behaviour of trace elements.

Minor and trace elements show contrasted behaviours depending on their chemical properties:

Alkali and alkali-earth trace elements are closely correlated to corresponding major elements, depending on the way they are incorporated in secondary mineral structure (Ouzounian et al., 1980, Beaucaire and Michard, 1982). Empirical correlations can be used for predictive evaluations (figure 3)

Some metals are controlled by limiting solubility equilibria. This is the case for most transition metals that are limited by sulphides, or uranium that is limited by uraninite in reducing confined groundwaters (Moulin et al., 1990, Alaux Négrel et al., 1992)

Trivalent and tetravalent metals are generally not solubility-limited and mostly carried by particles (REE, Zr, Hf, Sc, Th) in deep alkaline reducing groundwaters (Michard et al., 1991, Alaux Négrel et al., 1992). This may not be the case in CO_2-rich groundwaters in which carbonate complexation is very efficient (Michard et al., 1987). Such a behaviour explains the correlation that are oberved between trivalent and tetravalent metals (figure 4). The size range of particles is between 10nm and 450nm (table3)

Concerning this process, it is important to mention that :

* no chemical fractionation between source rocks and particles

* inorganic particles play a major role in the transport and retention of these metals. They are intensively studied. Preliminary results show a progressive range between poorly organized gels or allophanes and crystallized silico-aluminates (Beaucaire and Magonthier, 1992)

Conclusion

From these natural granitic geothermal and groundwater systems, we establish that major elements are controlled by secondary mineral precipitation (alumino-silicates). Regulation levels depend both on equilibration temperature and mobile anion concentration (mainly chloride). From empirical laws, the regulation levels with temperature of some trace elements (alkaline and most divalent) elements can be estimated, although a precise explanation accounting for the regulation mechanism is not yet available. Transition metals are controlled by sulphide precipitation; uranium is controlled by uraninite solubility. A reasonable prevision of the behaviour of the previous elements with temperature can be obtained, either using thermodynamic laws (major elements,

some transition elements) or empirical laws (alkaline and alkaline-earth trace elements). Trivalent and tetravalent metals are present in association with colloidal particles and their maximum regulation levels can be estimated, using thorium as a reference. The thermodynamical validation of major element control is currently achieved by identifying newly formed minerals in the particulate phase.

Table 3. Deep groundwater composition, Pyrénées, France

	< 450nm	<10 nm	
	moles/Kg	moles/Kg	
Ba	$8.0\ 10^{-8}$	$1.0\ 10^{-9}$	part.
Ca	$4.0\ 10^{-5}$	$4.0\ 10^{-5}$	diss.
Ce	$5.5\ 10^{-9}$	$<8.5\ 10^{-11}$	part.
Co	$5.0\ 10^{-10}$	$5.0\ 10^{-10}$	diss.
Cs	$1.0\ 10^{-7}$	$1.0\ 10^{-7}$	diss.
Eu	$3.5\ 10^{-11}$	$<1.5\ 10^{-12}$	part.
Hf	$7.7\ 10^{-9}$	$<4.7\ 10^{-12}$	part.
La	$3.0\ 10^{-9}$	$2.6\ 10^{-11}$	part.
Mo	$4.4\ 10^{-8}$	$4.0\ 10^{-8}$	diss.
Na	$2.5\ 10^{-3}$	$2.5\ 10^{-3}$	diss.
Nd	$7.1\ 10^{-9}$	$<6.1\ 10^{-10}$	part.
Rb	$3.0\ 10^{-7}$	$3.0\ 10^{-7}$	diss.
Sc	$1.0\ 10^{-9}$	$5.5\ 10^{-12}$	part.
Sm	$3.7\ 10^{-10}$	$5.6\ 10^{-12}$	part.
Sr	$2.8\ 10^{-7}$	$2.8\ 10^{-7}$	diss.
Ta	$1.1\ 10^{-10}$	$<2.3\ 10^{-12}$	part.
Tb	$6.3\ 10^{-11}$	$<2.2\ 10^{-12}$	part.
Th	$5.5\ 10^{-10}$	$<4.3\ 10^{-12}$	part.
Zr	$6.5\ 10^{-7}$	$<6.2\ 10^{-8}$	part.
Zn	$2.1\ 10^{-8}$	$1.2\ 10^{-8}$	diss.

part.:associated with particles
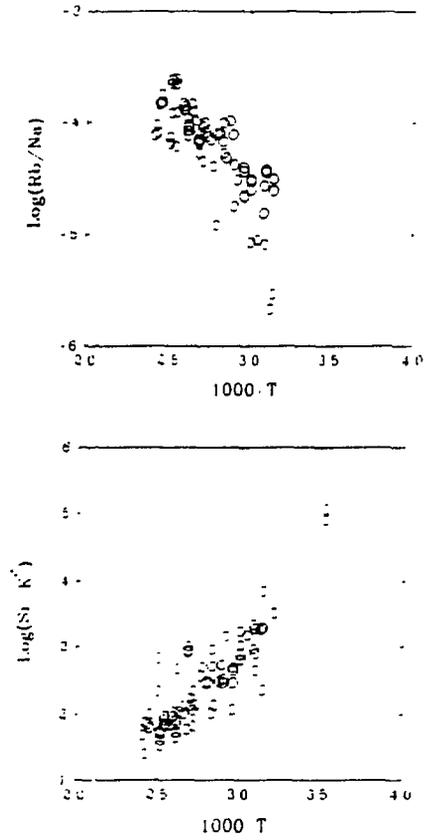diss. : present as dissolved species

Figure 3 : **Correlation between Rb/Na, Sr/K² and deep temperature in equilibrated thermal waters and groundwaters.**
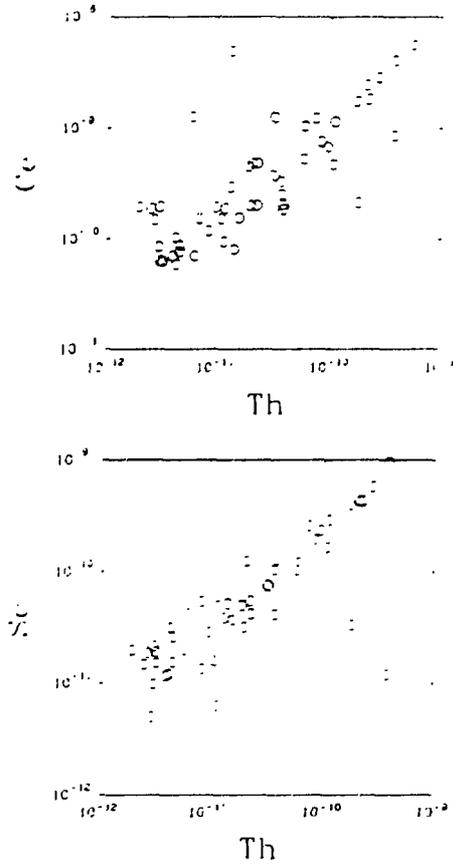
Figure 4 : Correlation between tetravalent and trivalent
metals in equilibrated thermal waters and groundwaters.
Log-Log slope is 1, that is interpreted by the presence of
variously diluted particles bearing these metals.

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