Journal of the Korean Society of Groundwater Environment, Vol. 1, No. 2, pp. 100~104, December, 1994

Limitation of Natural Analogue Studies on Rock Matrix Diffusion

기질내에서의 확산작용에 관한 자연유사연구의 한계

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Abstract : The rock matrix diffusion provides a retarding mechanism for sorbing and especially non-sorbing radionuclides. It has to be verified not only theoretically and experimentally but also from natural phenomena, before the mechanism can be incorporated fully into transport codes. The natural analogue studies, such as the concentration variation of radionuclides in profiles perpendicular to fluid-conducting fractures and to intrusive contact zones, have been believed to provide a validation. In thermal alteration zones of Naeduckri granite intruded by a pegmatite, large alkali and alkaline earth elements such as K, Rb, Sr, and Ba were moderately migrated during thermal alteration. Li, V, and Nb were also migrated about 9cm in width from the contact between the granite and the pegmatite. The concentration variation of these elements in thermally altered zones seems to be resulted from the local migration due to the re-equilibration among the elements released from the breakdown of primary minerals in the granite. Most of these natural analogue studies simply show only the concentration variation of elements without detailed informations on the diffusion time and other important data for interpreting the behaviour of radionuclides, because of the absence of appropriate minerals for age data. Despite this problem, natural analogue studies will be needed for transport models of radionuclides in safety assessment.

요 약 : 기질내에서의 원소의 확산현상은 흡착 및 비흡착성 방사성핵종의 지하매질내 이동을 지연시키는 특성때문에 처분장의 안전성평가에서 매우 중요한 현상으로 간주된다. 이 현상을 실제 안전성평가에 적용하기 위하여 확산현상이 인지되는 자연현상 중에서 자연방사성원소의 농도변화 및 붕괴사슬을 이용한 자연유사 연구가 많이 수행되고 있고 그 현상이 준정량적으로 확인된다. 기질내 원소의 확산현상은 액체상의 흐름에 수반되어 일어나거나 열적 영향에 의해 국부적으로 일어나기도 하는데 후자의 경우는 고준위 방사성폐기물 처분과 관련된 안정성평가에 그 중요성을 갖는다. 예를 들어 내덕리 화강암이 후기에 관입한 페그마타이트와 접촉하는 곳에서는 페그마타이트의 열적 영향에 의해 K, Rb, Sr 및 Ba과 같은 알카리 또는 알카리토 원소들과 Li, V 및 Nb 원소들이 접촉면으로부터 수직으로 약 9 cm 정도의 거리에 이르기까지 부화 또는 결핍된 이동현상이 관찰된다. 그러나 운반모델 설정을 위한 확산시간의 규모, 기질내 흡착된 핵종과 확산된핵종의 구분 등에 관한 연구는 필요한 시료의 취득이 불가능하여 이를 수행하지 못한 경우가 많다 이러한 문제점에도 불구하고 국내 처분장의 안전성 평가시에는 처분매질에 대하여 기질내 확산현상을 어느 정도 고려할 수 있는지를 자연유사 연구를 통해 규명되어야 할 것이다.

INTRODUCTION

One of major problems in radioactive waste disposal is the widespread lack of the public confidence in the prediction for the behavior of disposal system far into the future. To get over the problem, the following three key groups must have sufficient confidence: implementers, regulators and the public. The ideal procedure would be for implementers to illustrate, at a technical level, that predictive models for the migration process of radionuclides are perfect (in other word, validation), and for regulators to insist upon the validation of adequate quality for licensing purposes. Finally, the results obtained from the procedure would be admitted and accepted by the public. The current consensus is that the models are generally in advance of data. The predictive models can be based on the informations from laboratory experiments and natural systems. Laboratory experiments provide data obtained from well defined boundary conditions and geometries, which are their advantages and also their

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weakness. The data obtained from laboratory experiments over a few monthsora few years differ from those of actual processes occurring in repository over long periods.

NATURAL ANALOGUE STUDIES

Considering the time scale of the predictive models for a few hundred years to thousands of years, natural analogue studies provide realistic data relevant to the spatial and temporal scales similar to repository conditions. Nevertheless, quantitative data from natural analogue studies for safety assessment have been improved over the years. In an initial phase, large-scale analogues like Oklo uranium deposit in Gabon were studied in order to try to extract quantitative data on global consequences of a repository. Valuable indicative informations on the retention capability of geologic media were obtained.

However, boundary conditions concerning the behavior of radionuclides cannot be clearly characterized. Subsequently, more emphasis has to be placed upon analogues of specific processes. Some of the critical processes, from which the quantitative understanding has been improved by natural analogue studies, are as follows:

- Release from glass waste form
- Solubility and speciation in aqueous solution
- Redox front initiation and movement
- Matrix diffusion in clays and fractured media
- Colloidal transport of radionuclides

By numerous analogue studies which have been carried out to date, we expect more confidence of the public in our predictive abilities. However, as stated above, the physico-chemical boundary conditions of natural analogues are never identical with those of repositories. To increase the confidence of the public in the safety assessment based on the results obtained from natural analogue studies, McCombie (1991) suggested the following points:

- to continue to look for analogues of the highest quality
- to avoid irrelevant studies of natural systems under the "analogue label"
- to concentrate on issues revealed by safety analyses to be of greatest impact on repository behavior.

ROCK MATRIX DIFFUSION

Dissolved radionuclides in an aqueous solution are transported by two mechanisms: advection and diffusion. The radionuclides in advection process are transported along fractures by a fluid pressure gradient, whereas in diffusion process they are transported toward lower concentration parts through intergranular pores or microfractures by their chemical potential gradients.

According to the current concept for the disposal of radioactive waste, the emplacement of radioactive wastes in deep-seated rock formations will ensure that only negligible concentrations of radionuclides will reach the surface and so enter into the biosphere. The radionuclides released from a repository will be dominantly transported by advection along fractures. However, it has been suggested that, even in systems where the advective flow is dominant in distinct fractures, there may be the penetration of radionuclides due to diffusion toward surrounding rocks in a connected system of pores or microfractures.

The effects of diffusion for the transport of radionuclides are generally negligible compared to those of advection, because of extremely slow diffusion rate. However, in porous rocks under the condition of low pressure gradient, the diffusion can be predominant process. Furthermore, considering the time scale of thousands of years, the diffusion can be significant process for the migration of dissolved species. The matrix of crystalline rocks can be porous because of intergranular pores and microfissures generally developed adjacent to fractures zones or veins. Unfractured fresh plutonic rocks and metamorphic rocks are generally thought to have a very low porosity. However, in a deep granite test hole in northern Illinois, porosity was measured at 1.42% at a depth of 1,600 m, where there was few fractures in the rock (Daniels *et al.*, 1983). Fracturing increases the porosity of crystalline rocks by about 2 to 5% (Davis, 1969; Brace *et al.*, 1966).

The matrix diffusion provides a mechanism for enlarging the rock surface in contact with the advecting solute from fracture surfaces including infill materials to a portion of the bulk rock and it also acts as a retarding mechanism for sorbing and especially non-sorbing radionuclides (Alexander *et al.*, 1990). Accordingly, the diffusivity of rock matrix plays an important role in the prediction of the behavior of radionuclides.

The matrix diffusion process could be modeled and the model is now accepted in safety assessment. But the matrix diffusion process has to be verified not only by theoretical and experimental data but also from natural phenomena, before the process is incorporated into transport models. Two key parameters are required for studies on the matrix diffusion: the depth to which interconnected pores can be shown to extend into the bulk rock from the fracture zone; the diffusion rate of any given radionuclides depending on rock types. Because of very low diffusion coefficients equivalent to around 10^{-10} to 10^{-15} m^2/s, the matrix diffusion is not very amenable to spatial and temporal scales of laboratory. Accurate laboratory measurements of the matrix diffusion and, subsequently, the validation of transport models on the basis of these measurements are presently impossible (Alexander and McKinley, 1991).

Accordingly, natural analogue studies, such as the concentration variation of radionuclides in profiles perpendicular to water-conducting fractures and to intrusive contact zones, can be in use as a indirect method for solving the problems.

NATURAL RECORD OF ROCK MATRIX DIFFUSION

Matrix diffusion by fluid flow

Most of matrix diffusion models to date (Neretnieks, 1980; Hadermann and Roessel, 1985; Kang *et al.*, 1993) visualize the water-conducting fractures as simple and parallel sided-channels, with the diffusion into adjacent porous rock. For a simple verification of the concept of the matrix diffusion, Alexander *et al.* (1990) tried to characterize a profile, in a microscopic scale, perpendicular to a distinct water-carrying fracture showing that the transport of radionuclides into a comparatively sheared rock matrix might be described by the matrix diffusion. In their study, the concentration profile of Ra-226 in the rock matrix is suggested as a result of the diffusion of leached Ra-226 at some distance from main fracture zone through microfractures. In the study of Alexander *et al.* (1990), the time scale of the diffusion process could not be easily defined because of various problems associated with accurately dating events in the complex rock-water system. The reasonable time scale, referring the half-life of Ra-226 and the maximum time of detectable disequilibria in the Ra-226/Th-230 pair was considered as around from 1,600 to 8,000 years.

The analogue study could also validate several of the important assumptions included in the RANCHMD code (Hadermann and Roessel, 1985), in which the diffusion coef ficient of $1.5\times10^{-10} m^2/s$ is considered as the migration rate of most radionuclides in the zone of limited matrix diffusion. This is in good agreement with the range of 1.4 to 6.9×10^{-10} m^2/s derived from the analogue study of Alexander *et al.* (1990). Other natural analogue studies also indicate that the zone of matrix diffusion is limited only 0.01 to 0.05 m away from the fracture, while in the RANCHMD code the zone of matrix diffusion is assumed as only 0.001 m.

In fact, the similar studies such as natural decay series disequilibria in the vicinity of water-bearing fractures of crystalline rocks suggest that the concept of limited matrix diffusion may be inappropriate. Matrix diffusion operated to distances up to 0.5 m from fractures have been reported (Smellie *et al.*, 1986), supporting the KBS-3 assumption on a network with connected pores throughout the whole rock.

Matrix diffusion by thermal effects

As analogues to near-field conditions of high-level radioactive waste repositories, intrusive contact zones are often studied on thermal effects of the waste's heat for the behavior of radioactive elements in surrounding rock matrix. The conditions of intrusive contact zones, of which the initial temperature is conspicuously higher than that in the near-field of repositories, will be similar to those of surrounding rocks close to the high-level waste canisters during cooling over a geologic time scale of 10^4 to 10^6 years. Accordingly, the migration or redistribution of radionuclides in rock matrix, induced by the heat generated from high-level waste, can be examined across the contact zones.

The analogues to near-field conditions have been examined at Eldora Stock, Colorado (Brookins, 1981; Brookins *et al.*, 1982), Notch Peak Monzonite, Utah (Laul and Papike, 1981), Alamosa River Stock, Colorado (Brookins *et al.*, 1983; Wollenberg and Flexer, 1986), Santa Rosa Range, Nevada (Wodzicki, 1971), and Stripa, Sweden (Wollenberg and Flexer, 1986). The results from these different sites and types can be briefly summarized as follows. At the contact zones with conductive thermal system without convective hydrothermal fluid, there has been no apparent migration of elements from intrusive rock more enriched in trace elements into surrounding rock matrix (Brookins, 1981; Brookins *et al.*, 1982; Wollenberg and Flexer, 1986). The migration of elements was observed only in the immediate contact zones of 3 to 4 cm in width. However, at contact zones with convective hydrothermal system around intrusive rock, elemental migration was often observed in rock matrix at the distances varying between a few centimeters and meters from intrusion. The chemical composition of rock matrix was affected in close proximity to the intrusion (Brookins *et al.*, 1983; Laul and Papike, 1981; Wodzicki, 1971).

As an example of elemental migration in conductive thermal system, a pegmatite intrusive into Naeduckri granite, Sangdong-eup, Kangwon-do, is taken from Chang and Lee (1991). The pegmatite intruding the Precambrian Naeduckri granite is about 30 cm in width with the form of vein. These two rocks are a suite of co-genetic. The granite mainly consists of coarse-grained minerals, such as quartz, potassic feldspar, plagioclase, muscovite, tourmaline, and/or biotite and accessory minerals, such as apatite, sphene, and opaque minerals. The pegmatite is mainly composed of very coarse-grained minerals slightly less than 1 cm in size, such as quartz, potassic feldspar, plagioclase, muscovite, and tourmaline.

The thermal alteration zone of the granite in contact with the pegmatite is clearly marked off from the fresh granite by the change of color. The zone of about 3 cm in width is characterized by tourmalinization. Most minerals in the zone are larger in size than those of the fresh granite but smaller than those of the pegmatite. Euhedral tourmaline occurs as prismatic or acicular crystals and grew perpendicular to contact surface. This indicates that strongly mobile boron was migrated toward the surrounding granite and concentrated there. Muscovite and potassic feldspar were partly altered to sericite and plagioclase and they were corroded by quartz and perthitised potassic feldspar.

Granite samples N1, N2, and N3 in Figure 1 were taken at the distance of 0 - 2 cm, 2 - 4 cm, and 6 - 9 cm along a traverse from the contact between the pegmatite and the granite, respectively. Sample N1 was collected from intensively thermal-altered zone which contacts immediately with the pegmatite. The sample N3 belongs to the fresh granite.

From the chemical analyses of these three samples, actual gains and losses of elements in altered zones were calculated from the constancy of the amounts of perfectly immobile elements such as Al_2O_3, TiO_2, and P_2O_5 before and after alteration, using Gresen's equation (1967). The gains and losses of mobile elements which were normalized to the concentrations of the fresh granite are plotted against thermally altered zones from the pegmatite to the fresh granite (Figure 1).

Figure 1 shows that the large alkali and alkaline earth elements such as K, Rb, Sr, and Ba were moderately depleted in and migrated from sample N1. Li, V, and Nb were also migrated during thermal alteration. Both SiO_2 and Na_2O were significantly gained in the alteration zone. The exceptional enrichment of Na_2O in Sample N1 may be due to the fractionation from the hydrothemal fluid enriched in this element. Chondrite-normalized REE pattern of sample N1 is very similar to that of the fresh granite (Chang and Lee, 1991). Rare earth elements were also immobile.

In figure 2, Eu/Eu* ratios are correlated positively with Rb and Sr. The La/Yb ratios increase with decreasing Rb and Sr. The Eu/Eu* ratios slightly decrease with breakdown of plagioclase and potassic feldspar. Sr and Rb forming no mineral of their own are always incorporated in plagioclase and potassic minerals (e.g. biotite, muscovite, and potassic feldspars), respectively. Furthermore, Li and Ba which are generally retained by biotite, muscovite, and potassic feldspar were removed throughout all alteration zones. Therefore, the decrease of Sr and Rb seems to be due to the migration of these elements released from the breakdown of the above-mentioned minerals. Accordingly, the gain and loss of elements in thermally altered zone are assumed to be due to not the fractionation from or partition to the aqueous fluid of the pegmatite but the limited migration of elementsresulting from re-equilibration among minerals, which was caused by thermal effect of the pegmatite. The presence of tourmaline in the thermally altered zone indicates that perfectlymobile B diffused from the pegmatite had reacted with components such as SiO_2, Na_2O, CaO and other trace elements released from the breakdown of feldspars.

However, the migration rate of the elements in the thermally altered zone could not be assumed because of the absence of appropriate minerals for age data.

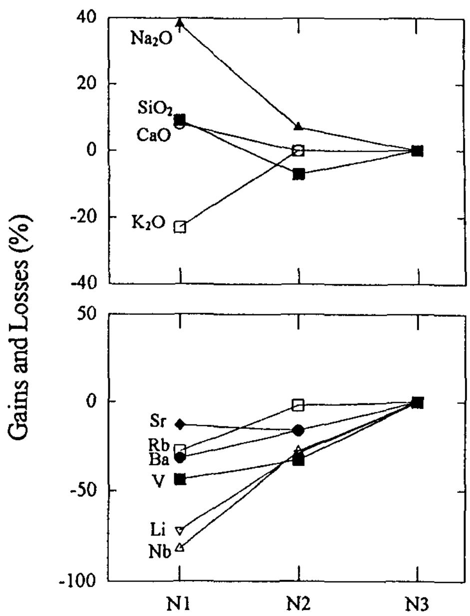

Figure 1. Gains and losses(%) of elements in the thermally altered Naeduckri granites, normalized to the concentrations in fresh equivalent versus alteration zone. Granite sample N1, N2, and N3 were at the distance of 0 - 2 cm, 2 - 4 cm and 6 - 9 cm along a traverse from the contact between the granite and pegmatite, respectively. The figure was taken from Chang and Lee (1991).

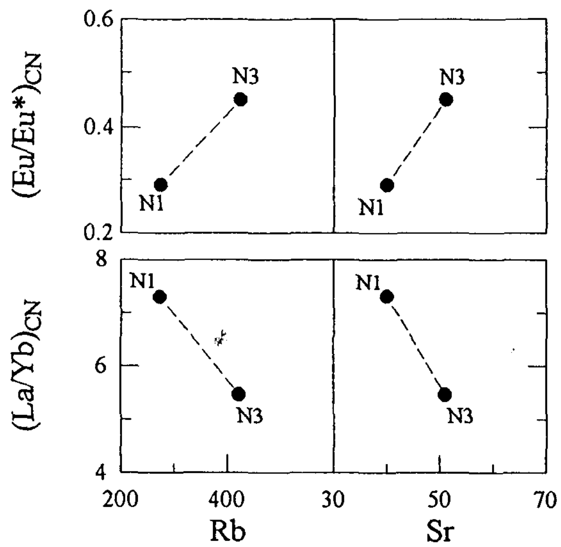

Figure 2. $(Eu/Eu^*)_{CN}$ and $(La/Yb)_{CN}$ variations against Rb and Sr concentrations (ppm). Samples N1 and N3 are the same as those of Figure 1. The figure was taken from Chang and Lee (1991).

CONCLUSION

The above-mentioned natural analogue studies clearly show the concentration variation of radionuclides adjacent to fractures and fissures or across intrusive contacts. In the case of thermally altered zone of Naeduckri granite, the concentration variation of major and trace elements is closely observed across the contact. This seems to be resulted from the local migration of the elements released from the breakdown of primary minerals for re-equilibration due to thermal effect.

For predictive transport models of radionuclides in the safety assessment of repositories, natural analogue studies have to include not only the concentration variation of radionuclides, but also the differentiation of sorbed amount of radionuclides from diffused amount of those, the diffusion time, and other important data for interpreting the behavior of radionuclides. However, most of natural analogue studies simply show only the concentration variation of radionuclides in matrix without concrete data on kinetic processes of the matrix diffusion, because of the absence of appropriate samples.

Nevertheless, there is no doubt that the capability of matrix diffusion in host rocks and engineered barriers to retain radionuclides released from radioactive waste repository has to be confirmed and that the natural analogue study will provide the necessary tool.

ACKNOWLEDGEMENTS

The authors would like to their appreciation to Nuclear Environment Management Center and Center for Mineral Resource Research for supports and to D. C. Ko, K. S. Ko, and J. H. Park for their help in drafting figures and typing manuscripts.

REFERENCES

Alexander, W.R., McKinley, I.G., McKenzie, A.B. and Scott, R. D., 1990, Verification of matrix diffusion by means of natural decay series disequilibria in a profile across a water-conducting fracture in granitic rock, Mat. Res. Soc. Symp. Proc., v.176, p. 567-576.

Alexander, W.R. and McKinley, I.G., 1991, Natural analogues in performance assessment: Improving models of radionuclide transport in groundwaters by studying the natural environment, CEC Report EUR 13014, p.119-151.

Brace, W.F., Paulding, Jr., B.W. and Scholtz, C., 1966, Dilatancy in the fracture of crystalline rock, J. Geophy. Res., v.71, p.3939-3953.

Brookins, D.G., 1981, Geochemical study of a lamprophyre dike near the WIPP site: in Sci. Basis Nuc. Wste. Mngt., v.111 (J.G. Moore, Ed.), p.307-314.

Brookins, D.G., Abashian, M.S., Cohen, L.H., Williams, A.E., Wollenberg, H.A. and Flexser, S., 1983, Natural analogues: Alamosa River Stock monzonite intrusive into tuffaceous and andesitic rocks: Sci. Basis Nuc. Wste. Mngt. VI (D.G. Brookins, Ed.), p.299-306.

Brookins, D.G., Abashian, M.S., Cohen, L.H. and Wollenberg, H. A., 1982, A natural analogue for storage of radwaste in crystalline rocks: Sci. Basis Nuc. Wste. Mngt., IV(S.V. Topp, Ed.), p.231-238.

Chang, H.W. and Lee, K.S., 1991, Behavior of elements in hydrothermal alteration zones of granitic rocks: Examples from the Mugeug granodiorite and the Naeduckri granite, South Korea, J. Geol. Soc. Korea, v.27, p.156-170.

Daniels, J.J., Olhoeft, G.R. and Scott, J.H., 1983, Interpretation of core and well log physical property data from drill hole UDH-3, Stephenson County, Illinois., J. Geophy. Res., v.88(B 9), p.7346-7354.

Davis, S.N., 1969, "Porosity and permeability in natural materials." in Flow through porous media, ed. R.J.M. DeWiest, New York : Academic Press. p.53-89.

Gresens, R.L., 1967, Composition-volume relationships of metasomatism, Chem. Geol., v.2, p.47-55.

Hadermann, J. and Roessel, F., 1985, Radionuclide chain transport in inhomogeneous crystalline rocks: Limited matrix diffusion and effective surface sorption, NAGRA Technical Report p. 85-40.

Kang, C.H., Lee, Y.M. and Han, P.S., 1993, The development of a safety assessment code for the radwaste disposal, KAERI-NEMAC/RR-73/93.

KBS, 1983, Final storage of spent nuclear fuel, SKB(Nuclear Fuel and Waste Management Company), Report KBS-3.

Laul, J.C. and Papike J.J., 1981, Chemical migration by contact metamorphism between granite and silt/carbonate systems: Int. Atomic Energy Agency, Sym. 257, p.603-614.

McCombie, C., 1991, Critical uncertainties in safety assessments and how to address them, CEC Report EUR 13014, p.19-28.

Neretnieks, I., 1980, Diffusion in the rock matrix: an important factor in radionuclide retardation?, J. Geophys. Res., v.85, p. 4379-4397.

Skagius, K. and Neretnieks, I., 1986, Porosities and diffusivities of some nonsorbing species in crystalline rocks, Water Resour. Res., v.22, p.389-398.

Smellie, J.A.T., MacKenzie, A.B. and Scott, R.D., 1986, An analogue validation study of natural radionuclide migration in crystalline rocks using U-series disequilibrium studies, Chem. Geol., v.55, p.233-254.

Wodzicki, A., 1971, Migration of trace elements during contact metamorphism in the Santa Rosa Range, Nevada, and its bearing on the origin of ore deposits associated with granitic intrusion, Miner. Deposita, v.6, p.49-64.

Wollenberg, H.A. and Flexer, S., 1986, Contact zones and hydrothermal systems as analogues to repository conditions, Chem. Geol., v.55, p.345-359.