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# Estimation of Redox Reactions of Deep Groundwaters in Japan

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## I. INTRODUCTION

Geochemical characteristics of deep groundwater are essential information for safety assessments for the geological disposal of radioactive wastes (Nuclear Waste Management Organization of Japan (NUMO), 2004), and the sequestration of carbon dioxide (Xue and Matsuoka, 2008), one of the known green house gases, because groundwater chemistry could affect migration of the species included in disposal wastes. In order to facilitate the smooth advance of the above disposal projects, it is necessary to investigate the geochemical characteristics economically across a wide area extending over several kilometres.

Existing investigations of groundwater chemistry so far have involved drilling a borehole, purging the drilling mud, pumping up the groundwater, sampling it at the surface and conducting analyses in the laboratory. At potential disposal locations (hereinafter referred to as in-situ), the groundwater is generally under high pressure to dissolve gases i.e. carbon dioxide, and is in a reduced condition. When pumped up to the surface, it could be degassed with depressurization to increase its pH and it could be oxidised by contact with the atmosphere to increase its oxidation redox potential (ORP) (Gascoyne, 1997, 2004; Grenthe *et al.*, 1992; Iwatsuki *et al.*, 2009).

In order to procure quality data on the pH and ORP of the deep groundwater, it is recommended to measure them in-situ (Furue *et al.*, 2005; Li *et al.*, 1997), and some apparatus has been developed for in-situ groundwater measurement and sampling. One problem

is that since in-situ measurement takes longer and is more expensive, it is difficult to set up a network of measurements consisting of many test intervals in boreholes. A realistic solution is considered as follows: (1) perform not only in-situ measurements, but also the existing ones; (2) develop a method for estimating the in-situ pH and ORP using existing data in comparison with in-situ data; (3) estimate the in-situ values of test intervals where in-situ measurements are not conducted; (4) economically obtain data on the in-situ pH and ORP across a wide area. Hokari *et al.* (2014) presented a means of estimating the in-situ pH and ORP on the basis of existing groundwater data and chemical equilibrium analysis, which was applied to a geochemical pumping test measuring the in-situ pH and ORP for validation. It was performed by the Japan Atomic Energy Agency (JAEA) in the deepest borehole drilled in the course of the Horonobe Underground Research Laboratory Project (Horonobe URL project). Figure 1 illustrates a location and geology of the Horonobe site.

Existing pumping tests were also conducted in several boreholes at the Horonobe site (Kunimaru *et al.*, 2007). Hokari and Kunimaru (2008) applied this estimation method to those pumping tests in order to estimate distributions of the in-situ pH and ORP at the site (Figure 2). Figure 2 includes pH and ORP values measured in-situ in the geochemical pumping test, values measured with flow-through cell sensors at the surface in the existing pumping tests, and values estimated from the groundwater analysis data. ORP\_SHE represents an ORP relative to the standard hydrogen electrode.

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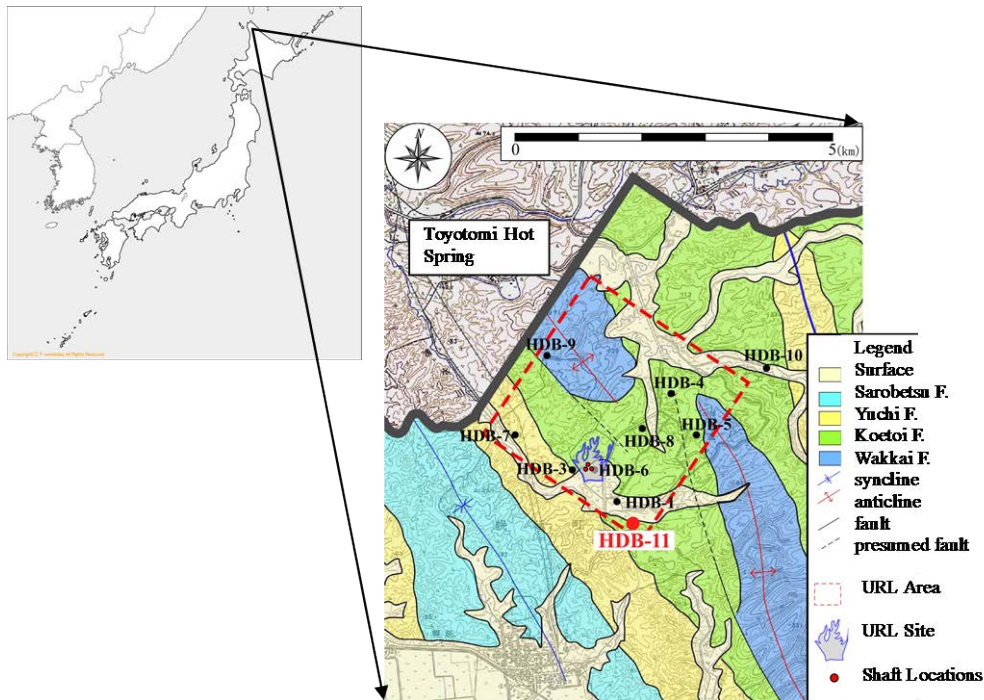


Figure 1 : Location and geology of the Horonobe Underground Rock Laboratory (URL) Project site

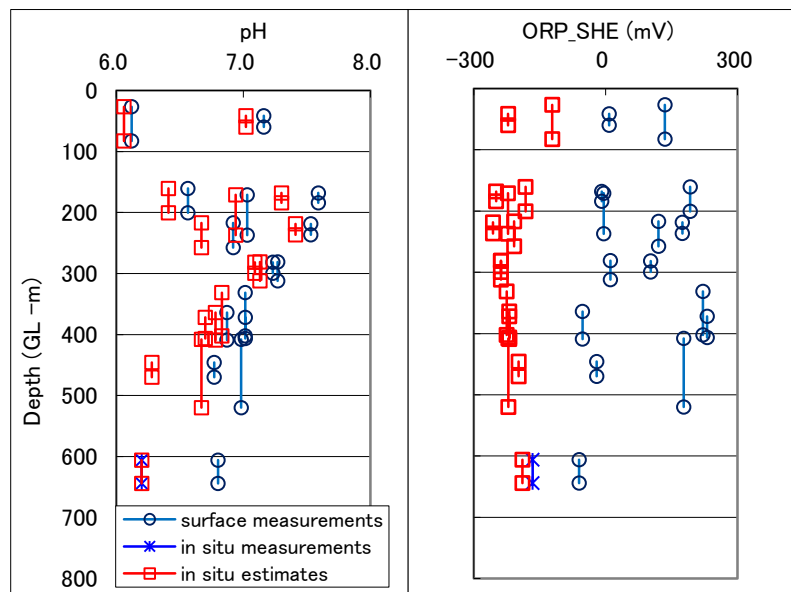


Figure 2 : Depth distributions of the in-situ pH and ORP estimates at the Horonobe site

It is confirmed that the in-situ pH and ORP estimates are in good agreement with the in-situ measurements at depths of approximately 600 m, which shows that the estimation method is valid. The in-situ pH estimates are more acidic than the surface measurements and have a tendency towards acidity to approximately 6.2 with depth. It is coincident with the pumping test results that more CO<sub>2</sub> gas was released from the deeper groundwater pumped up to the surface. The in-situ ORP estimates represent a greatly more reduced condition than the surface measurements, and

show stable reduction of approximately -200 mV at depths of below some 200 m. It is estimated that the underground environment is reductive and stable.

Figure 3 is a pH-ORP diagram for the system Sulphur-Oxygen-Hydrogen, showing the pH and ORP measurements in the pumping tests and the in-situ pH and ORP estimates. Since the in-situ estimates are on the equilibrium curves of sulphate and sulphide ions, the in-situ groundwaters at the Horonobe site could be governed by a redox couple of sulphate and sulphide ions.

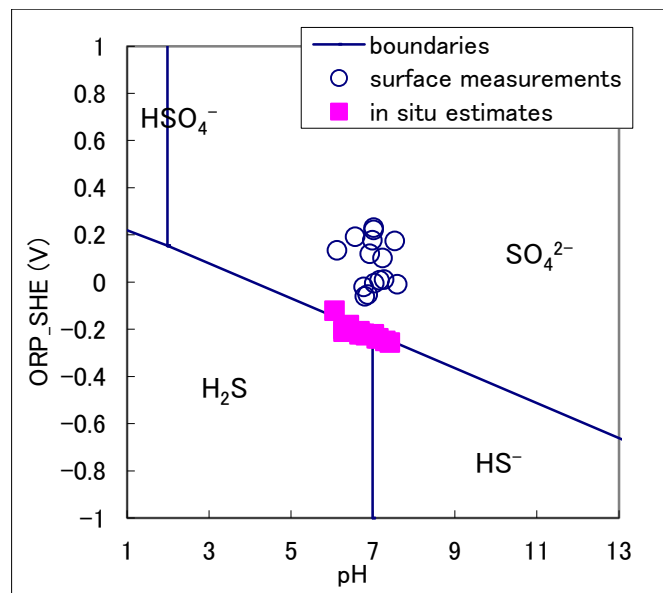


Figure 3 : pH-ORP diagram for the system S-O-H with the pumping test measurements and the in-situ estimates at the Horonobe site

Seki *et al.* (2004), after conducting measurement and analysis of deep hot spring waters at the eastern Kanto District in Japan, addressed that ORP measurements for the waters with very low content of dissolved oxygen (DO) were in good agreement with values calculated from a redox couple of sulphide and solid sulphur ( $S^0$  rhombic) as shown in Figure 4. It gives the pH and ORP measurements for the water samples with approximately zero DO at the eastern Kanto District, which are found to be on equilibrium curves for solid sulphur and aqueous hydrogen sulphide at different

total sulphur content. Solid and broken curves are for 25°C and 50°C, respectively. Plots with h are for more than 40°C. Eh in Figure 4 represents an ORP relative to the standard Hydrogen electrode, which is used especially when it is calculated thermodynamically. Seki *et al.* (2004) argued that ORP for deep groundwaters could be actually buffered with sulphide ions and solid sulphur in the assumption that the pH and ORP values, which were measured at the surface, should be the same as those in-situ.

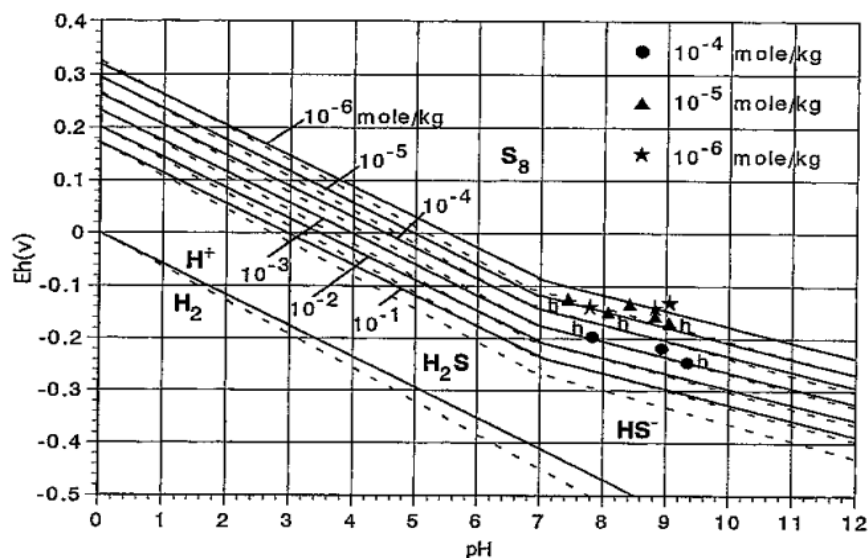


Figure 4 : pH-ORP diagram for the system S-H, showing the pH and ORP measurements for the water samples with approximately zero dissolved oxygen at the eastern Kanto District

All of the groundwaters at the Horonobe site were sampled in mud stone formations of the Neogene Period. An approximately half of the water samples at the eastern Kanto District came from sedimentary rocks

(sand stone, mud stone, and tuff) of the Neogene Period, and the rest of them came from granite and gneiss of the Cretaceous Period and sedimentary rocks (sand stone and shale) of the Jurassic Period.

The groundwaters in the different two regions are found to be governed with redox couples of sulphur. This characteristic could generally prevail in some geological environment which is common in the two regions, for example, groundwaters in sedimentary rocks of the Neogene Period. In order to assess the safety for radioactive waste disposal or CO<sub>2</sub> sequestration, the characteristic could be very useful information on underground geochemical properties in a stage of preliminary investigations such as literature researches, which precedes site investigations.

This paper, using a groundwater database, estimated the in-situ pH and ORP of the following groundwaters: the Dohoku area including the Horonobe site, the Kanto District and the other hot springs, and studied whether those groundwaters should be governed with redox couples of sulphur or not, and whether there should be common redox reactions governing the groundwaters or not.

## II. ESTIMATION OF pH AND ORP FOR IN-SITU GROUNDWATERS

### a) Groundwaters

In order to study possibility that groundwaters in some region of Japan should be governed with redox couples of sulphur, in-situ groundwater pH and ORP were estimated in use of groundwater analysis data of the region compiled up in the groundwater database (Asamori *et al.*, 2003) on the basis of a method proposed by Hokari *et al.* (2014). Of redox reactions, which were assumed to be possible to occur under the ground, the most predominant reaction was identified thermodynamically. A relationship between the predominant reaction and the in-situ pH and ORP estimates was studied graphically with a pH-ORP diagram. This groundwater database has collected and sorted out chemical analysis data on groundwaters and hot springs in Japan, and studied and added sampling location data (latitudes, longitudes and elevations) as possible.

Figure 3 shows that the groundwater samples in the pumping tests conducted at the Horonobe URL Project could be governed with the redox couple of sulphide and sulphate ions in-situ. In order to investigate if this tendency should be contributed to limited local characteristics at the Horonobe site, in-situ predominant reactions surrounding the Horonobe site were studied by collecting existing groundwater condition data of existing boreholes surrounding the site and estimating the in-situ pH and ORP values.

Figure 4 shows that the groundwater samples of Seki *et al.* (2004) at the eastern Kanto District could be governed with the redox couple of sulphide and solid sulphur. Since the data of Seki *et al.* (2004) were measured at the surface, whatever low contents of DO for the groundwaters were, in-situ predominant reactions

were studied by estimating the in-situ pH and ORP. And in order to investigate if the above tendency should be contributed to limited local characteristics at the eastern Kanto District, in-situ predominant reactions surrounding the eastern Kanto District were studied by collecting existing groundwater condition data of existing boreholes surrounding the District and estimating the in-situ pH and ORP values.

As the other groundwaters than those in the above site, District and surroundings, another groundwaters were studied which fall in the following four types of hot springs in Japan, which Matsubaya *et al.* (1973) classified on the basis of their hydrogen and oxygen isotopic ratios and major element chemistry in terms of their origins: green tuff type (3 samples), ocean coastal type (4 samples), volcanic type (4 samples) and Arima type (2 samples). The green tuff type waters are in the green tuff formation of the Tertiary Period, and are of neutral sodium chloride sulphate type chemistry with a chloride content of less than 3 g/L.  $\delta D$  and  $\delta^{18}O$  values of the groundwaters are in agreement with those of local meteoric waters, and  $\delta^{34}S$  and  $\delta^{18}O$  values of the sulphate in the groundwaters are similar to those of the sulphate in the sea water. It is deduced that the green tuff type waters are simply recycled meteoric waters. The ocean coastal type waters show intermediate  $\delta D$  and  $\delta^{18}O$  values between the standard mean ocean water (SMOW) and local meteoric waters as a result of mixing of sea water and the meteoric waters. Na-Ca-Cl type waters of low Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations are typically produced by chemical reactions between fresh or diluted sea water and wall-rock minerals.  $\delta^{34}S$  values of SO<sub>4</sub><sup>2-</sup> are similar to those of the fresh sea water sulphate, because SO<sub>4</sub><sup>2-</sup> is removed by anhydrate precipitation. The volcanic type waters are found in close affiliation with Quaternary volcanism. Although the waters essentially occur as a mixing of sea water and local meteoric waters, they indicate varying degrees of isotopic shifts that  $\delta D$  and  $\delta^{18}O$  values of the waters are shifted towards heavier values from the meteoric water line on a  $\delta D$  and  $\delta^{18}O$  diagram. Those isotopic shifts are assumed to be attributed to an isotope effect in evaporation near the surface and an O-isotopic exchange between the meteoric waters and geothermal rocks in Japan. The Arima type waters are found in the Cretaceous granitic rocks and metamorphic rocks around Arima region. The waters show highly salinity and isotopic shifts towards heavier values than the meteoric waters. Those waters are not mixtures of the meteoric waters and sea water, but occur by mixing of the meteoric waters and the possible fossil magmatic, metamorphic or geothermal fluids.

*The groundwaters and hot springs studied here are as follows:*

1. Pumping test samples at the Horonobe URL site (Kunimaru *et al.*, 2007): 11 samples

2. Petroleum well and hot spring samples surrounding the Horonobe site (Asamori *et al.*, 2003): 14 samples
3. Deep hot spring samples at the eastern Kanto District (Seki *et al.*, 2004): 16 samples
4. Naturak gas well, hot spring, observation well and coal mine samples surrounding the District (Asamori *et al.*, 2003): 13 samples
5. Samples supposed to fall in typical hot springs in Japan (Asamori *et al.*, 2003): 13 samples

The studied groundwaters should include the following analysis data:

- cation contents:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and anion contents:  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  or / and  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ;
- pH and temperatures when the waters were sampled;
- sampling depths for boreholes;

- released gas

Figure 5 illustrates locations of the groundwaters studied here in Japan. The above groundwater data (1) and (2) correspond to Dohoku in Figure 5, the data (3) corresponds to Seki *et al.* (2004), and the data (4) and (5) correspond to Others, respectively.

Although the above groundwater data are not necessarily enough to represent all groundwaters in Japan, rock types in which the groundwaters were sampled widely vary as follows:

Sedimentary rocks: mudstone, shale, siltstone, sandstone, green tuff, tuffaceous conglomerate, welded tuff  
Igneous rocks: granite, granodiorite, rhyolite, andesite  
Metamorphic rocks: gneiss  
Rock types of more than half of the pumping intervals in boreholes are unknown and there are no records on geology.

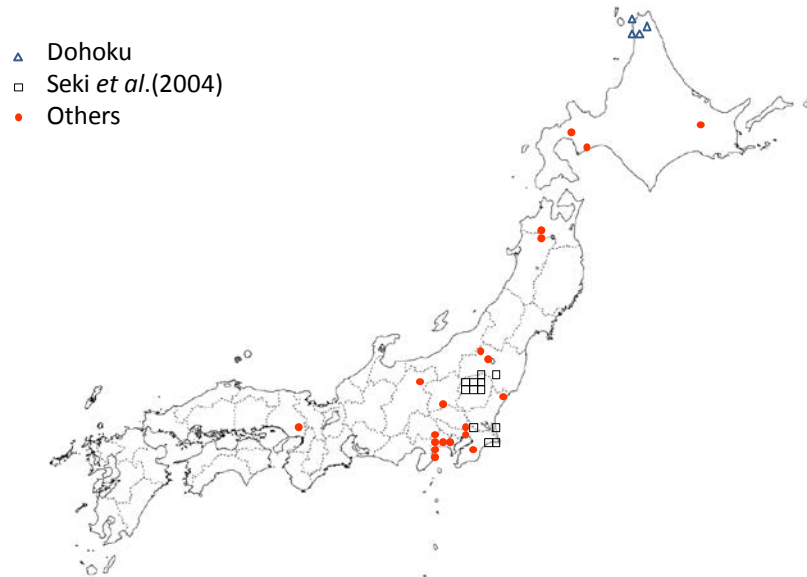


Figure 5 : Map showing localities of the 67 groundwaters studied here in Japan

#### b) Estimation method of the in-situ pH and ORP

At this section, the estimation method of the in-situ pH and ORP proposed by Hokari *et al.* (2014) is briefly presented. It estimates the in-situ pH and ORP of groundwaters by using data of existing pumping tests, as are seen in the groundwater database, on the basis of geochemical equilibrium simulations and the in-situ mineral-water interactions.

In order to understand the evolution mechanism of groundwater chemistry, it is convenient to calculate speciation of elements in some environments with a thermodynamic code for geochemical modelling. The geochemical code enables calculations of species activities, concentrations and saturation indices in water on the basis of the mass balance law and the mass action law with a thermodynamic database that includes mass action constants. This paper employs one of the

open codes, called PHREEQC (Parkhurst and Appelo, 1999), developed by the U.S. Geological Survey to estimate the in-situ pH and ORP. There are several codes for geochemical modelling other than PHREEQC, which are detailed in the following websites (Geotechnical & geoenvironmental software directory, 2008).

Since the details of PHREEQC were presented by Parkhurst and Appelo (1999), only a summary of PHREEQC is given here. It is designed to perform a wide variety of low-temperature aqueous geochemical calculations on the basis of an ion-association aqueous model. In order to estimate the in-situ water conditions on the basis of the existing surface data, of the many geochemical calculation capabilities of PHREEQC, speciation and batch reactions with gas at equilibrium are focused on here. It uses the mole balance Equation

(1), the mass action Equations (2), (3), and the activity coefficient expression including the Davies Equation (4) or the extended Debye-Huckel Equation (5) (Truesdell and Jones, 1974) to calculate the activities,

$$\sum_i^{N_{aq}} b_{m,i} n_i + \sum_g^{N_g} b_{m,g} n_g = const. \quad (1)$$

where  $N_{aq}$  is the number of aqueous species,  $N_g$  is the number of gas-phase components. The moles of each entity in the system are represented by  $n_i$  for aqueous species and  $n_g$  for gas components. The moles of element  $m$  per mole of each entity are represented by  $b_{m,i}$  for aqueous species and  $b_{m,g}$  for gas components.

The mass action equations can lead to the total moles of an aqueous species  $i$  and a gas component  $g$ :

$$n_i = \frac{K_i W_{aq}}{\gamma_i} \prod_m^{M_{aq}} a_m^{c_{m,i}} \quad (2)$$

$$n_g = \frac{N_{gas}}{P_{total} K_g} \prod_m^{M_{aq}} a_m^{c_{m,g}} \quad (3)$$

where  $n$  is the moles,  $K$  is the mass action constant,  $a_m$  is the activity of master species  $m$ ,  $M_{aq}$  is the total number of aqueous master species,  $c_m$  is the stoichiometric coefficient of master species  $m$ ,  $W_{aq}$  is the mass of solvent water in an aqueous solution,  $\gamma$  is the activity coefficient,  $N_{gas}$  is the total moles of gas,  $P_{total}$  is the total pressure, subscript  $i, g$  represents a solutions species and a gas component, respectively.

Activity coefficient  $\gamma$  of aqueous species  $i$  is defined with the Davies Equation (4) or the extended Debye-Huckel Equation (5):

$$\log \gamma_i = -A z_i^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3 \mu \right) \quad (4)$$

concentrations and saturation indices of the species in solution.

The mole balance equation of an element  $m$  is expressed:

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i^0 \sqrt{\mu}} + b_i \mu \quad (5)$$

where  $z_i$  is the ionic charge of aqueous species  $i$ ,  $\mu$  is the ionic strength of solution,  $A$  and  $B$  are constants dependent only on temperature,  $a_i^0$  and  $b_i$  are ion-specific parameters fitted from mean-salt activity-coefficient data.

The initial input to PHREEQC was the following analysis data on the groundwater pumped up to the surface: the temperature, pressure (1 atm), pH, ORP, main species concentrations, if there were found free gases, the gas / water ratio, and content of each gas. The groundwater conditions under the in-situ pressure and temperature were computed with PHREEQC on the basis of the initial solution. With increasing pressure, the free gases in the solution were expected to be all solved. The equations below the bubble point were expected to differ from those above it according to the presence or dissolution of the gases. In order to estimate the bubble point, a stepwise computation was applied from the surface pressure and temperature conditions to the in-situ ones. If the in-situ mineral information was available, effects of the mineral on pH or ORP were to be considered and added to the simulation result with PHREEQC.

### III. RESULT AND DISCUSSION

The in-situ groundwater pH and ORP, estimated in use of PHREEQC, are shown in Figure 6.

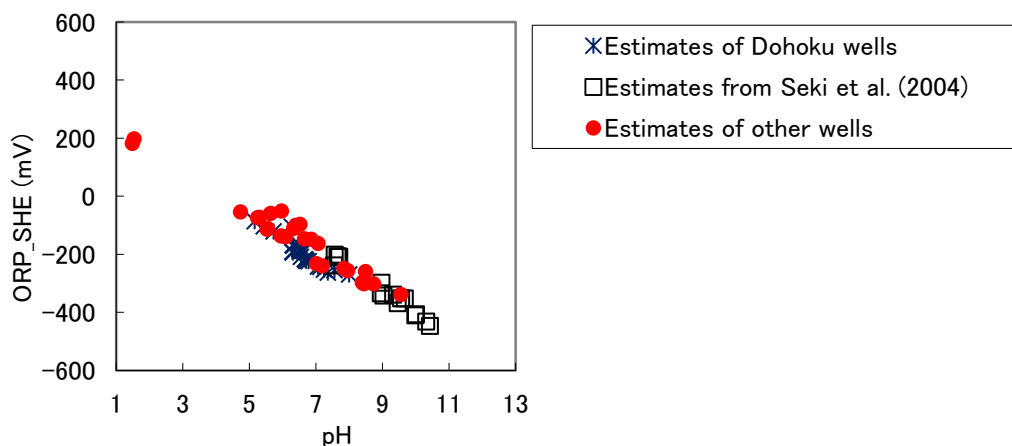


Figure 6 : The in-situ pH and ORP estimates for the 67 groundwaters

Elements involved in redox reactions are contained in the in-situ rocks and the groundwaters, which could vary in valence states depending upon the redox condition. At first, the elements of Fe, Mn, S and C

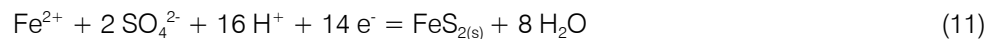
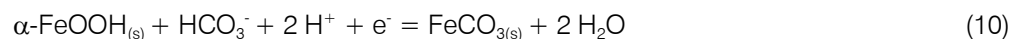
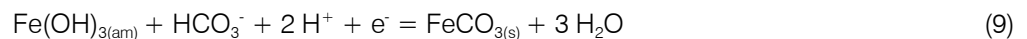
are selected as redox relevant ones in the rocks, because they exist in greater content in the various rocks (Hem, 1970). The contents of the elements in the crust are summarised in Table 1.

Table 1 : Average composition of main elements concerning redox conditions in the crust (Hem, 1970)

Element (ppm)	Igneous rock		Sedimentary rock	
		Sandstone	Shale	Carbonate
Fe	42200	18600	38800	8190
Mn	937	392	575	842
S	410	945	1850	4550
C	320	13800	15300	113500

The following redox reactions including those elements in the underground could possibly be assumed according to Stumm and Morgan (1996) and

Langmuir (1997). Since the existing groundwater data seldom include Mn, the redox reactions concerning Mn are not considered here.



where subscripts (am) and (s) represent amorphous and solid states, respectively.

The predominant reaction of all the above could be revealed with thermodynamic analysis using changes in Gibbs free energy of the reactions. The energy change was calculated for each reaction for each groundwater data under the in-situ temperature and pressure conditions. At first, the change in Gibbs free energy of the reaction  $\Delta G_r^0$ , was calculated at a specified standard state (25°C and 1 atm) with Equation (13) (Stumm and Morgan, 1996).

$$\Delta G_r^0 = \sum_i \mu_i \Delta G_{f,i}^0 \quad (13)$$

Where  $\mu_i$  is stoichiometric coefficient of the species  $i$  and  $\Delta G_{f,i}^0$  is the Gibbs free energy of formation of the species  $i$  at the standard state. Equation (14) produces the Gibbs reaction energy at a temperature of  $T$  Kelvin  $\Delta G_r^T$ , (Appelo and Postma, 2005). The species activities calculated by PHREEQC were used as ones essential for the Gibbs reaction energies.

$$\Delta G_r^T = \Delta G_r^0 + RT \prod_i \ln [i]^{\mu_i} \quad (14)$$

where  $R$  is the gas constant and  $[i]$  is the activity of the species  $i$ . Pressure compensation was conducted using Equation (15) – (18) (Millero, 1982; Tanger and Helgeson, 1988).

$$\ln \frac{K^P}{K^0} = \frac{1}{RT} \left( -\Delta V^0 P + \frac{1}{2} \Delta \kappa^0 P^2 \right) \quad (15)$$

$$\Delta V^0 = \sum_i \mu_i V_i^0 \quad (16)$$

$$\Delta \kappa^0 = \sum_i \mu_i \kappa_i^0 \quad (17)$$

$$\Delta G_r^P = \Delta G_r^0 + RT \ln \frac{K^P}{K^0} \quad (18)$$

where  $K^P$  and  $K^0$  are the equilibrium constants at a pressure of  $P$  and at the reference pressure, which is atmospheric pressure here;  $\Delta V^0$  is the standard molar volume change of the reaction, and  $V_i^0$  is the standard partial molar volume of the species  $i$ ;  $\Delta \kappa^0$  is the standard molar compressibility change of the reaction, and  $\kappa_i^0$  is the standard partial molar compressibility of the species  $\kappa_{r,i}^P \rightarrow \Delta G_r^P$  is the Gibbs reaction energy at a pressure of  $P$ .

For example, the Gibbs reaction energies of the deepest groundwater sample for Reaction (6) are shown, which is 1510m deep and at 61.5 °C. The standard Gibbs reaction energy, the Gibbs reaction energy at 61.5 °C, and the Gibbs reaction energy in-situ are -192.07 KJ/mol, -7.10, and -193.19, respectively. It is found that an effect of temperature on the Gibbs reaction energy is by far greater than those of pressure,



and the pressure compensation for the Gibbs reaction energy is not considered in this analysis.

The probability of each reaction is shown in Table 2.

Table 2 : Analysis result of the predominant in-situ redox reactions

Reaction No	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Probability (%)	0	0	34	1	12	36	17

The above probability means, for example, that Reaction (11) is the most likely to occur in 36 % of all the data. As a result, the pyrite / the sulphate ion reaction is estimated to be predominant in 36 % of all the data, the ferrous ion / ferric oxihydroxide reaction predominates in 34 % of the data, the ferrous sulphide mineral / the sulphate ion reaction prevails in 17 %, and the siderite / the ferric oxihydroxide reaction prevails in 12 %. In other words, the sulphate ions / the iron sulphide, which includes the pyrite and the ferrous sulphide mineral, are estimated to be predominant in more than half, that is, 53 % of all the data. The redox reactions of the ferrous sulphide minerals could govern the in-situ groundwater conditions. The in-situ pH and ORP estimates are analysed on the basis of Reaction (11), as shown in Figure 7. Most of the estimates are plotted on an

equilibrium curve between pyrite and sulphate. Analysed data here are located mainly at the northern Hokkaido region and the Kanto District. The groundwaters in the northern Hokkaido region evolve in the sedimentary rocks of the Tertiary period, and the groundwaters in and around the Kanto District evolve in the sedimentary rocks of the Tertiary period, igneous and metamorphic rocks of the Cretaceous period, sedimentary rocks of Jurassic period and sedimentary rocks of the Quaternary period and others. Many data of these two areas are related to the groundwaters in the Tertiary sedimentary rocks. It is deduced from the result that the redox state of the in-situ groundwater could be governed by the pyrite-sulphate reaction in the Tertiary formations of Japan.

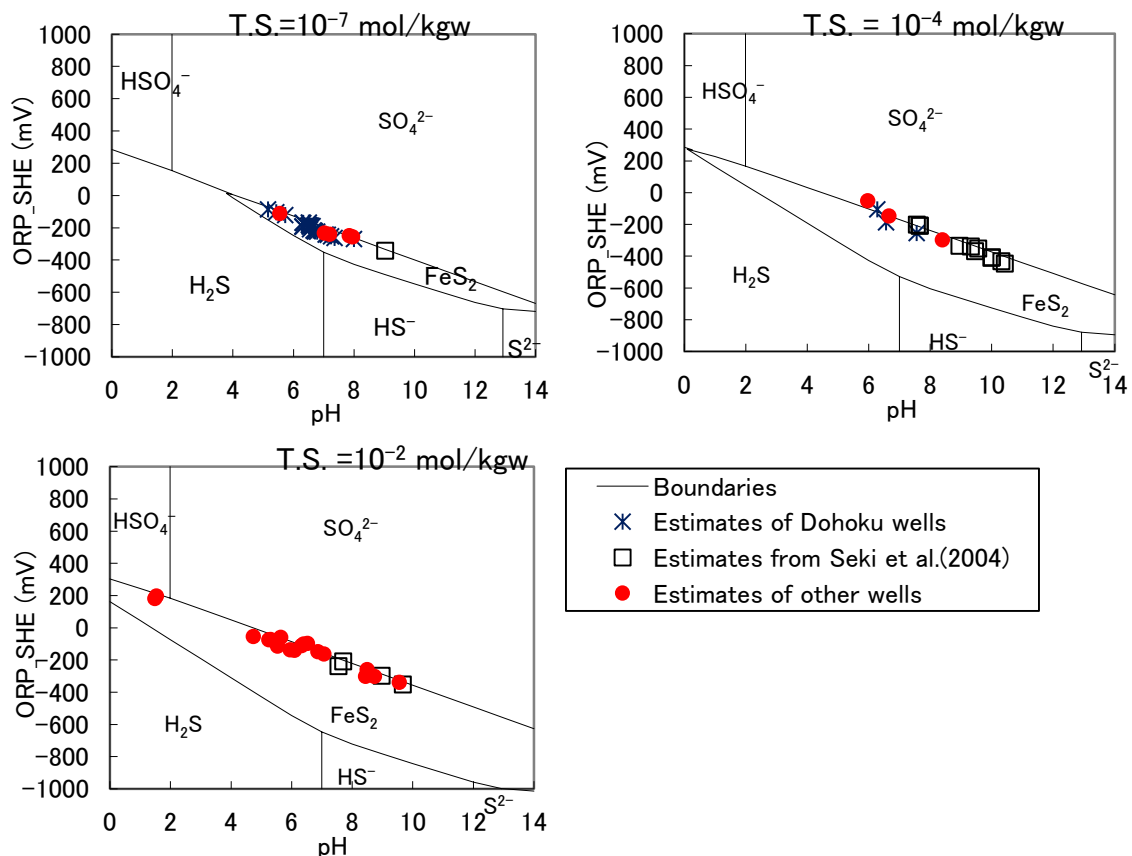


Figure 7 : pH-ORP diagram for the system S-O-H and the pyrite, showing the in-situ pH and ORP estimates for the 67 groundwaters

#### IV. CONCLUSION

This study, using the groundwater database in Japan, estimated the in-situ pH and ORP of the groundwaters and hot springs in northern Hokkaido

region, in and around the Kanto District and in the other areas. It also thermodynamically investigated possibility that those groundwaters should be governed by redox couples of sulphur and possibility that there should be a

redox reaction governing the in-situ redox condition of those groundwaters.

As a result, the in-situ predominant redox reaction for the data analysed here was revealed to be the ferrous sulphide mineral / the sulphate ion reaction. It is also confirmed that the in-situ pH and ORP estimates of those groundwaters were plotted on an equilibrium curve between the pyrite and the sulphate ion. The data analysed here are mainly situated in the northern Hokkaido region and the Kanto District, and many of them are related to the groundwaters in the Tertiary sedimentary rocks. It is deduced that the ferrous sulphide mineral / the sulphate ion reaction should govern the in-situ redox condition in the Tertiary sedimentary formations in Japan.

This study revealed that it was possible to estimate the predominant redox reaction by estimating the in-situ groundwater pH and ORP on the basis of the existing groundwater database. When this estimation method is applied to the safety assessment for radioactive waste disposal, it is expected to be very effective at the preliminary investigation, which corresponds to documents investigation and is followed by borehole investigations at the surface.

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