

# Fundamentals of Mineralogical and Chemical Analysis for Lacustrine Sediments and Water

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# Fundamentals of Mineralogical and Chemical Analysis for Lacustrine Sediments and Water

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## I. Introduction

Terrestrial sediments, especially, lacustrine sediments have some advantages that include high-resolution environmental records; physical, chemical and biological records, compared with deep-sea sediment records and ice core records. They may provide more detailed and different stories from ones written through ocean sediment and/or ice information (Kashiwaya, 2003).

The sediments consist of minerals such as quartz, feldspar, calcite, kaolinite, smectite, illite and chlorite, organic materials as the organic remains and excrements, biogenic silica such as diatoms, chitinous material from planktons and pollens. Except for minerals and pollen, the constituent materials have been produced in the lake. The variation in their quality and quantity therefore indicate the environmental changes at the lake itself. On the other hand, minerals and pollens have been used as proxy indicators of long term history of environment around the lake due to their stability. On geologic time scale, several proxy indicators have been proposed to reflect variations of monsoon climate through quasi-independent pathways in the continental and atmospheric systems. For example, grain-size variations of the coarse quartz fraction in loess indicate the relative wind strength of the dust-bearing winter monsoon (Xiao et al., 1995). Magnetic susceptibility of loess-paleosol sequences responds to the intensity of pedogenesis and records the circulation change of the summer monsoon. However, each of these monsoon proxies needs to be verified by other indices that are independent and vary synchronously. Some geochemical parameters, such as the Ge/Si ratio of opaline silica (Filippelli, 1997) and the strontium isotopic ratio of marine carbonates (Edmond, 1992; Yang et al., 2000), have proved to be important in reconstructing the history of continental weathering. The Rb/Sr ratio may also be used as an indicator of chemical weathering in relict profiles (Chen et al., 1999). Although such geochemical parameters are useful for the estimation of monsoon strength, in order to estimate loess flux from the sedimentary record, it is necessary to distinguish subcomponents within detrital component, specify origin, and estimate their content.

As mentioned above, the geochemical, geophysical and mineralogical investigations of loess can provide useful information about climatic history. On the contrary, from the viewpoint of the material cycle, the role of loess as a media of reaction and material transportation in troposphere is also important due to their high chemical affinity. It was well documented that mineral aerosol particles are mixed with aerosols from pollution sources in Eastern Asia (Gao et al., 1999), and the originally alkaline aerosol is neutralized by acidic sulfates (Winchester and Wang, 1989). If the loess records the atmospheric transport and input of anthropogenic pollutants into lacustrine sediments, their vertical distributions of the pollutant would be used as an excellent proxy of human activities. For picking out the above information from the sedimentary records, it is necessary to carry out the qualitative and quantitative analyses of the constituent minerals in lacustrine sediments.

Geochemistry of lake water and pore water in the sediments is an interdisciplinary science

concerned with the chemistry of water in the surface environment. Although stream and lake water is only 0.01 % of the water at the earth's surface, water in the lake significantly relate to human life as drinking water and agricultural use. Pore water in lacustrine sediments is also key material for material cycle and biogenic productivity in lake. Chemical analysis of lake water is therefore important skill for environmental scientists to assess the environmental impacts at the lake. Apart from natural processes as controlling factors on lake water quality, in recent years the effect of pollution, such as nitrate from fertilizer and acid rain, also influences the lake water chemistry. The interest of society in lake water geochemistry is mainly to endure good quality drinking water. Preservation of lake water as good water resources therefore has a high priority for environmental authorities.

In the above context, this chapter gives fundamentals of mineralogical and geochemical analyses for lacustrine sediments and water, especially identification and analysis of clay minerals, and routine analytical items and conservation of water samples, and the evaluation of the quality of chemical analysis deserve some special attention.

## II. Mineralogical Analysis of Lacustrine Sediments

Lacustrine sediments consist of particles with different sizes. If the sediments come from surrounding catchment area without size fluctuation, the mineralogical composition of sediments is completely same as rocks or soils at the catchment area. However, the fluctuation necessarily occurred during transportation through river flow and sedimentation. The size distribution of particles and mineral composition in each fraction are therefore key parameter to understand the environmental changes around the lake for long-term. Especially, clay minerals mainly consisting in small fraction are useful as indicators for environmental changes. However, it is very difficult to separate from sediments and make identification because of their extremely small sizes, and it is necessary for the complicated sample preparation. If you get a skill to identify the small amount of minerals from the atmosphere, you can estimate the flux of inputs from air. If you can separate the particular mineral from the sediment mixture, you can get chemical and isotopic data from particular minerals.

In this section, the method of particle-size separation, quantitative analysis of clay minerals by using XRD and sequential extraction method are briefly explained.

### 2.1 Particle-size separation

At this point we have a suspension in which, ideally, the particles are single crystals. One of the important reasons for washing the suspension free salt is that if there is enough dissolved salt in the suspension, it will cause flocculation. Suspensions must be washed free of salt by centrifuge cups and spin them for a few minutes at 2000 rpm. If the suspension has flocculated, the supernatant liquid after centrifugation will be crystal clear. Decant the water and discard it. Redisperse the suspension in another 200 mL of distilled water by means of ultrasound and repeat the centrifugation. After three or four of these washing, the supernatant will show some turbidity that may be extreme or only a faint opalescence. This condition indicates full or incipient dispersion, and that process should be completed by the addition of a suitable dispersing agent.

Dispersing agents all have one feature in common—they produce a buffered pH from neutral to high. The most effective ones also have phosphate ions that promote dispersion, presumably by the adsorption of the phosphate ions on clay edges where they reverse normally positive edge charge and thus help prohibit flocculation. Sodium pyrophosphate is our choice, although you may want to try other sodium phosphates if you encounter

particularly recalcitrant sample. You do not want to add too much dispersing agent, or you can actually promote flocculation because of an increase in ionic strength. About  $10^{-3}$  to  $10^{-4}$  M is suitable, and for 200 mL of suspension, that is about equal to 20 to 30 mg of the reagent. Take about half a “pinch” of the powder, and you will see that this is just about right. Such an approximate measure is good enough, and you need not go to the trouble of weighing the powder that is added to each suspension. Add the reagent and disperse by ultrasound. Let it stand a few minutes and gently stir the surface with a rod or spatula. Notice that the streamlines stand out, just as they do when you stir aluminum paint. This effect is caused by the orientation of the clay mineral crystals in the stream lines with reflection of light from their cleavage faces, and signifies that dispersion is good and that the suspension is suitable for particle-size separation. Seldom will dispersions be good enough to see this effect, but it is a goal.

Here gives a few comments about difficult samples. Some materials resist dispersion, even after repeated washing by centrifuge and the addition of normal peptizing (dispersing) agents. If this happens, try adding 20 to 30 mg (per 200 mL) of sodium carbonate.

The next step is the separation of the clay-size fraction, which we take here to be the  $< 2$   $\mu\text{m}$  equivalent spherical diameter. Particle-size separations are based on Stokes's law, and it applies strictly to spherical particles, which platy clay minerals are not. Below a particle size of about 20  $\mu\text{m}$ , particles settling in a fluid approximately obey Stokes's law, which is a numerical expression that describes a particle being pulled by gravity but whose fall is resisted by a viscous fluid.

Table 1 and 2 give solutions of Stokes's law for normal gravity and for centrifuge sedimentation. Table 1 gives the settling times for a standing cylinder, and Table 2 gives times for one centrifuge.

The data in Table 1 are easily modified for other conditions. Just remember that if you double the settling distance you must double the time. Notice that a lower specific gravity is used for 0.2  $\mu\text{m}$  clay particles. This reduction specific gravity is necessary to take into account the bound water at the mineral surface because very fine particles have very high specific surface areas and their absorbed water is no longer a negligible portion of their volume. Particle-size separations should be made as soon as dispersion is achieved, because some clay minerals flocculate slowly even though they were once well dispersed.

Normal gravity settling in tubes is not recommended because it takes too long. Centrifugation is the best method. If you have a 15-cm machine, spin for 3.3 min at 750 rpm (Table 2) and decant the supernatant liquid into a separate container. The supernatant is the yield of the process. All the particles in it are  $< 2$   $\mu\text{m}$ , but the material in the bottom of the centrifuge cup is not entirely  $> 2$   $\mu\text{m}$ . It contains a good deal of the  $< 2$   $\mu\text{m}$  suspension, so if sample size is limited and there is not yet enough clay in the yield or if you wish to measure the amount of the  $< 2$   $\mu\text{m}$  fraction, redisperse the sediment from the cup by ultrasound, centrifuge again, and add the supernatant to the yield from the first separation. Three separations are about all that are practical because that constitutes almost all the  $< 2$   $\mu\text{m}$  material in the suspension.

## 2.2 Quantitative analysis of minerals

### *XRD (X-ray diffraction)*

The intensity of a diffraction peak from a particular mineral seems to be simply related to the abundance of that mineral in a mixture. Unfortunately, that simplicity is deceptive. You will see that quantitative analysis by XRD is a complicated works requiring attention to many details. You will encounter samples that produce inaccurate results even if you work hard to

deal with all the possible variables.

How good can quantitative analysis of minerals based on XRD be? If precision is the criterion the answer is very good indeed. A set of replicate analyses should provide a standard deviation of perhaps  $\pm 5\%$  (or less) of the amounts present if the constituent minerals are all present in reasonably large quantities more than 20%. Accuracy is another matter. Quantitative analysis should be considered good if errors amount to  $\pm 10\%$  of the amounts present for major constituents, and  $\pm 20\%$  for minerals whose concentrations are less than 20%.

A most important problem, over which little control can be exercised, is choosing a standard mineral whose diffraction characteristics are identical to those of that same mineral in the unknowns. A sample of mineral powder must possess certain characteristics if it is to produce the most accurate results. The following outline summarizes the key points we will document.

1. The sample must be longer than the spread of the incident beam at the lowest diffraction angles used. Therefore, two quantities need attention: (1) the sample length, and (2) the angular divergence of the beam or size of the divergence slit.
2. The sample must be infinitely thick at the highest diffraction angles used.
3. The sample must be mounted in the diffractometer so that, for all diffraction angles, the angle between the sample surface and the incident beam is equal to the angle between the sample surface and the diffracted beam
4. There must be no particle-size gradient between the top and bottom of the sample.

These factors can be difficult to control, but their effects on the accuracy and precision of analyses are minimized if you adhere to two important principles.

1. Avoid the use of low-angle reflections for quantitative analysis.
2. Select analytical peaks that are as close together as possible.

#### *Sequential extraction method*

A sequential extraction method was used to obtain information on the amount of particular mineral fraction and on the distribution of the interested metals such as Pb and Cd among the operationally defined mineral components. The sediment residues are dried, and samples of approximately 0.75 g were retained for sequential extraction analysis. The samples are first washed with distilled water and centrifuged, and the wash water is discarded. The sediment is then subjected to the following sequential extraction procedures:

1. *Exchangeable*. The sample is extracted for 1 hr at room temperature with 8 ml of magnesium chloride solution (1 mol/L  $\text{MgCl}_2$ , pH 7) with continuous agitation.
2. *Carbonate Bound*. The residue from step 1 is leached at room temperature for a contact period of 5hr with 30 ml of 1 mol/L sodium acetate (NaOAc) adjusted to pH 5 with acetic acid (HOAc) under continuous agitation
3. *Oxide Bound*. The residue from step 2 is leached at room temperature using 30 ml of 0.1 mol/L oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ), buffered to pH 3 by ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ), and continuously agitated in the dark for 5 hr.
4. *Bound by Natural Organic Matter*. The residue from step 3 is leached in a boiling water bath for 30 min with 8 ml of 5% sodium hypochlorite (NaOCl) adjusted to pH 9 with hydrochloric acid (HCl).
5. *Residual*. The residue from step 4 is subjected to an acid digestion procedure. The sediment is subjected to nitrogen acid ( $\text{HNO}_3$ ) addition and heated to  $95^\circ\text{C}$ , followed by the addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with slight warning. The final step requires the addition of hydrochloric acid (HCl) heated to the point of reflux without

boiling.

### III. Chemical Analysis of Lake Water

#### 3.1 Field analysis and sample conservation

When a groundwater sample is brought to the surface, it is exposed to physico-chemical conditions which are different from those in the aquifer. For example, atmospheric oxygen may readily oxidize components like  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{S}$ , etc. which are commonly present in anoxic groundwater. Furthermore, degassing of  $\text{CO}_2$  may occur, causing changes in pH, alkalinity and total inorganic carbon, which may also induce carbonate precipitation. Thus, measures are needed to prevent changes in the chemical composition of the sample before analysis. Such measures are of two kinds: conservation and field measurements. An overview of the required treatment is presented in Table 3.

Conservation is in most cases done by adding acid to the sample until the pH is  $< 2$ . (0.7 ml of 65%  $\text{HNO}_3$  is usually enough to neutralize alkalinity and to acidity 100 ml sample). Acidification stops most bacterial growth, blocks oxidation reactions and prevents adsorption or precipitation of cations. Prior to acidification, the water sample has to be filtered to remove suspended material which could dissolve when acid is added.

Pressure filtration, using an inert gas is preferred since vacuum application may seriously degas the sample. The normal procedure is to filtrate through  $0.45 \mu\text{m}$  membrane filters. However, finely dispersed Fe- and Al-oxyhydroxides may pass through  $0.45 \mu\text{m}$  filters and  $0.1 \mu\text{m}$  is a better choice. The effect of improper sample handling on the analytical results is illustrated in Example 1.2.

Field analyses are usually carried out for parameters like pH, EC, Eh,  $\text{O}_2$ , which are measured by electrode, and sometimes also for alkalinity and  $\text{Fe}^{2+}$ . Electrode measurements should preferably be carried out in a flow cell in order to prevent air admission. EC measurements are particularly useful as a control on analysis and conservation of samples. Eh measurements are only qualitative indicators for redox conditions and should be made as sloppy as possible, so that you will not be tempted to relate them to anything quantitative afterwards. The necessity of measuring labile parameters in the field is illustrated in Figure 1.

The Figure 1 shows that substantial differences between field and laboratory measurements are observed which become even more significant when it is remembered that pH is a logarithmic concentration unit ( $\text{pH} = -\log[\text{H}^+]$ ). pH is a crucial parameter, which has major importance in quantitative calculations of saturation states with respect to minerals and great care should be taken to obtain reliable measurements.

The problems involved in pH measurements of lake water are manifold. Some are related to the removal of lake water from its in situ position during sampling. These include degassing of  $\text{CO}_2$ , which will increase the pH and also may cause precipitation of  $\text{CaCO}_3$ . Others concern the oxidation of  $\text{Fe}^{2+}$  and precipitation as  $\text{FeOOH}$  and are analogous for other oxidizable species like  $\text{H}_2\text{S}$ , which may seriously affect pH values. Most of this type of problems can be overcome by careful sampling and field measurement procedures. In particular the use of flow cell for pH measurement, directly coupled to the sampling system, helps to minimize these problems. Other sources of error particularly in low ionic strength lake water, concern the liquid junction between the calomel electrode and the solution to be measured. The fundamental problem is that the liquid junction potential across the porous ceramic plug of the calomel electrode will vary with the composition of the solution to be measured.

### 3.2 Accuracy of chemical analysis

In general, two types of errors are discerned in chemical analyses:

*Precision* or statistical errors which reflect random fluctuations in the analytical procedure.

*Accuracy* or systematic errors displaying systematic deviations due to faulty procedures or interference during analysis.

The precision can be calculated by repeated analysis of the same sample. It is always a good idea to collect a number of duplicate samples in the field as a check on the overall procedure. Systematic errors can be tested only by analyzing reference samples and by interlaboratory comparison of the results. At low concentrations duplicate analyses may show large variations when the sensitivity of the method is insufficient. The accuracy of the analysis for major ions can be estimated from the Electro Neutrality (EN) condition since the sum of positive and negative charges in the water must balance:

$$EN(\%) = (\text{Sum cations} + \text{Sum anions}) / (\text{Sum cations} - \text{Sum anions}) \times 100$$

where cations and anions are expressed as meq/l. The sums are taken over the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , and anions  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . Sometimes other elements contribute significantly, like for example  $\text{Fe}^{2+}$  or  $\text{NH}_4^+$  in reduced water, or  $\text{H}^+$  and  $\text{Al}^{3+}$  in acid water. The presence of the last two substances in significant amounts requires more accurate calculations of EN balances using special computer programs. Differences in EN of up to 2% are inevitable in almost all laboratories. Sometimes an even larger error must be accepted, but at deviations of more than 5% the sampling and analytical procedures should be examined.

Another useful technique is to compare calculated conductivities with measured electrical conductivity. The electrical conductivity (EC) is related to the ions which are present in solution and relation between EC and concentrations of different salts is shown in Figure 2. Therefore, at 25°C, the EC divided by 100 yields a very good estimate of the sum of anions or cations (both in meq/l):

$$\text{Sum anions} = \text{Sum cations (meq/l)} = EC / 100(\mu\text{S/cm})$$

This relation is varied for EC values up to around 2000  $\mu\text{S/cm}$ .

Calculation of EN or EC as a check on the chemical analyses is only applicable for major elements. The accuracy of the results for minor elements is much more difficult to estimate. Sometimes the incompatibility of different elements found together in one sample can be a warning that something went wrong. Thus, it is unlikely that  $\text{O}_2$  or  $\text{NO}_3^-$ , which indicate oxidizing conditions, are found together with appreciable concentrations of  $\text{Fe}^{2+}$  in natural water. Ferrous iron ( $\text{Fe}^{2+}$ ) only occurs in appreciable concentrations (more than 1  $\mu\text{mol/l}$ ) in reduced environments or at low pH, or when organic material is present which acts as a complexing agent. Ferric iron ( $\text{Fe}^{3+}$ ) has very low solubility in water with pH between 3 and 11, and precipitates very rapidly as  $\text{Fe}(\text{OH})_3$ . Total iron concentrations should therefore be low in water where  $\text{O}_2$  or  $\text{NO}_3^-$  is present. Aluminum has also a low solubility at a pH between 5 and 8, and it is unlikely to find concentrations of more than 1  $\mu\text{mol/l}$  in water having a near neutral pH.

### 3.3 Major inorganic components and their significance for lacustrine sciences

In lacustrine water, there are dissolved and colloidal matters. Although it is very difficult for distinguish between them, in general, the matters pass thorough 1  $\mu\text{m}$  filter are defined as dissolved.

Natural water mainly consists of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SiO}_2$ . The main components except for bicarbonate and silica are ionic species. The bicarbonate and silica are changeable between ionic and neutral due to pH of solution. In this section, the source of several main components in lacustrine water and their significance are discussed individually

below.

#### *Ca and Mg*

In western lake, the water has calcium and magnesium with comparatively high concentrations. Chemical species of calcium is dominantly  $\text{Ca}(\text{HCO}_3)_2$  in the western lake. Therefore,  $\text{Ca}(\text{HCO}_3)_2$  should be transformed as follows after consumption of  $\text{CO}_2$  by active photosynthesis by aquatic plant,



Due to low solubility of  $\text{CaCO}_3$ , calcium carbonate precipitations are frequently found on leaf of aquatic plant or lake floor. However, there are not frequent in Japanese lake. In freshwater of Japanese lake, the productivity of shellfishery is minimized due to low calcium contents.

#### *Na and K*

Sodium in lacustrine water has root in sea water and anthropogenic origin. Sodium from sea water is transported to lake as sea salt particle and rain. Potassium is essential material for plant growth and depleted same as nitrogen and phosphorus. However, potassium is not limiting factor for photosynthesis by plant in lake.

#### *Cl*

Measurements of Cl concentration in lake and river are very important for understanding of water source and pollution. Origin of Cl is mainly as follows.

- 1) sea: Cl is included about 19 g/l in sea water. This concentration is thousand times higher than that of freshwater in lake. Therefore we can quantitatively observe the effect of sea water or sea salt particle on chemistry in lake water.
- 2) pollution by human activity: human usually intakes 10-20 g of salt a day. Drainage from factory also contains much of Cl. Therefore we can detect the pollution by Cl.
- 3) hot springs and volcano: If Cl concentration is so high at the lake effected minimally by sea and human activity, it is necessary to consider the effect of hot springs and volcano.

#### *S and $\text{SO}_4$*

Sulfate is from sea salt particle and combustion of fossil fuel. The latter is very closed to acid rain. Because of the constant ratio between sulfate and chlorine in sea water (0.140 in weight and 0.103 in equivalent), you can distinguish the sulfate originated in the human activity from natural origin based on the measured Cl concentration.

In summer season, we can found a reducing condition in lake by consumption of dissolved oxygen. As the results of this condition, hydrogen sulfide and pyrite are preferably produced in the lake. The reducing mud and sludge with black color on lake floor is attributed to the pyrite formation. The chemical species of sulfur and sulfate are usually affected by bacteria such as sulfur bacteria and sulfur reducing bacteria as shown in Figure 3.

#### *Si*

Silica is very important material for shell formation of diatom. Si concentrations in Japanese lake are relatively higher than those in foreign lake (10-50 mg/l). In sea water and western lake, Si concentration is limiting factor for productivity of phytoplankton. In most of Japanese lake except for Lake Biwa, Si concentration is not limiting factor for that.

### *Fe and Mn*

When the dissolved oxygen is sufficiently exist in lake water, Fe(III) and Mn(IV) is dominant species and precipitate as  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$  at  $\text{pH} > 6$ . The concentration of iron in lake water is therefore poor and limiting factor for productivity of phytoplankton in lake. If organic material contain in lake water, iron makes a complex with the organic material. In this case, iron concentration in lake water hold at relatively high.

In summer season, we can found a reducing condition in lake by consumption of dissolved oxygen. In the condition, the Fe and Mn precipitates on lake floor dissolved by the reduction of Fe(III) to Fe(II) and Mn(IV) to Mn(II). However, in autumn season, there are oxidizing condition and Fe and Mn oxidation again. Thus the cycle and migration of the redox elements is considerably attributed to the redox condition in lake.

### 3.4 Chemical factors determining environmental behavior of dissolved elements

The behavior of dissolved elements is determined by several chemical factors. Among the factors, pH, alkalinity, and dissolved carbonate and oxygen are significantly important. In this section, the above major factors are commentated about their principal and significance for lacustrine sciences.

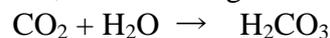
#### *pH*

Because proton in water have a wide range in concentrations (or activity), we normally use pH as index of proton concentrations in its stead.

$$\text{pH} = -\log [\text{H}^+]$$

pH varies as function of temperature. pH is decreasing with increasing of temperature. That is why it is precipitant to conclude that it is alkali when the measured pH is higher than pH 7.

pH of pure water is absolutely 7. However, if we leave the water be in air,  $\text{CO}_2$  from air would dissolve in the water. After that, the following reactions are proceeded:



In these reactions, all of the reactions proceed to right hand side when the dissolved  $\text{CO}_2$  increased. As the result, the proton activity is increased, and pH of the water is decreased.

pH of lake water is governed by geology of the catchment area. Recently, the effect of human activity, however, can not be ignored. The active photosynthesis by phytoplankton lead to consume  $\text{CO}_2$ , and then to alkaline condition of the water. On the other hand, in the deep water in lake, the consumption of  $\text{CO}_2$  by photosynthesis is decreased. In that condition,  $\text{CO}_2$  in the water is increased by the decomposition of mortal remains and aspiration by animal and bacteria, and then pH of the water decrease. As shown in Figure 4, the stratifications of pH in deep lake are frequently observed in summer time.

#### *Alkalinity*

As mentioned above, alkalinity is important factor to understand and assess the buffer capability of natural water. To measure alkalinity, there are many methods. In general, an acid titration to pH 4.8 by strong acid solution has been carried out to measure the amount of acid for the acidification. Recently, acid rain is urgent issue for global environmental assessment, and the measurement of alkalinity is necessary to understand the capacity of buffer to acid rain.

Lake water in Japan has generally high alkalinity due to high bicarbonate contents. Therefore, in that case, the measured alkalinity is nearly equal to the content of carbonate ions.

However, when the lake water includes inorganic weak acid such as silica, phosphate and borate, and humic acid, the amount of bicarbonate ion from the alkalinity should be overestimated. Alkalinity is also closely related to the geology of the catchment area because the weak acids were mainly produced through the water-rock interactions.

#### *Dissolved carbonate and oxygen*

Carbonate is the main raw material from photosynthesis of plant. In lake water, carbonate is consumed by the process of photosynthesis and discharged from aspiration and decomposition of organic materials. Dissolved carbonate and oxygen is significantly important for understanding of organic matter production and decomposition. Carbonate materials consist of  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . The relative abundance of these species in lake water vary depending on pH, temperature and salt concentration of the water. Figure 5 shows the relationship between the relative abundance of carbonate species and pH of solution.

Main processes of material cycle in lake are alteration and transportation of the materials accompanied with production and decomposition of organic matters. When we want to understand the process, it is necessary to observe the dissolved oxygen and carbonate concentrations in the water columns. In summer season, the decreasing of the dissolved oxygen leads to the reducing condition at lake. With the decreasing of redox potential, bacterial metabolism for energy is changed stepwise as shown in Figure 6.

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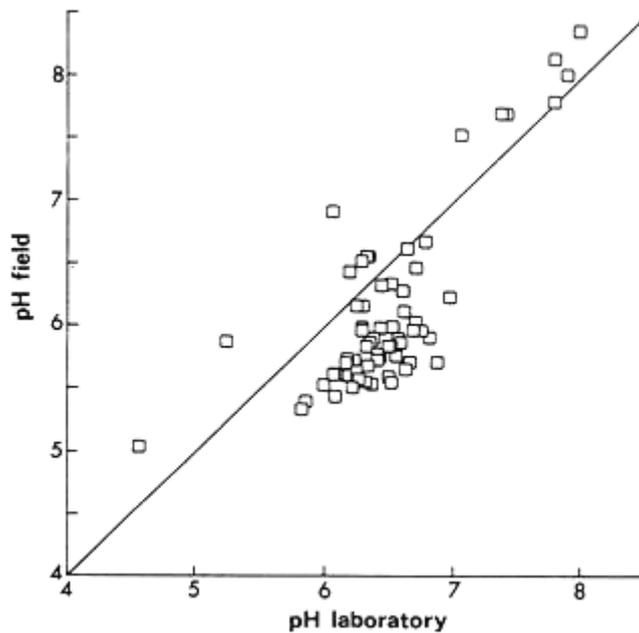


Fig. 1. Comparison of field measurements of pH, in a carbonate-free sandy aquifer, with those performed in the laboratory (Postma, unpublished results)

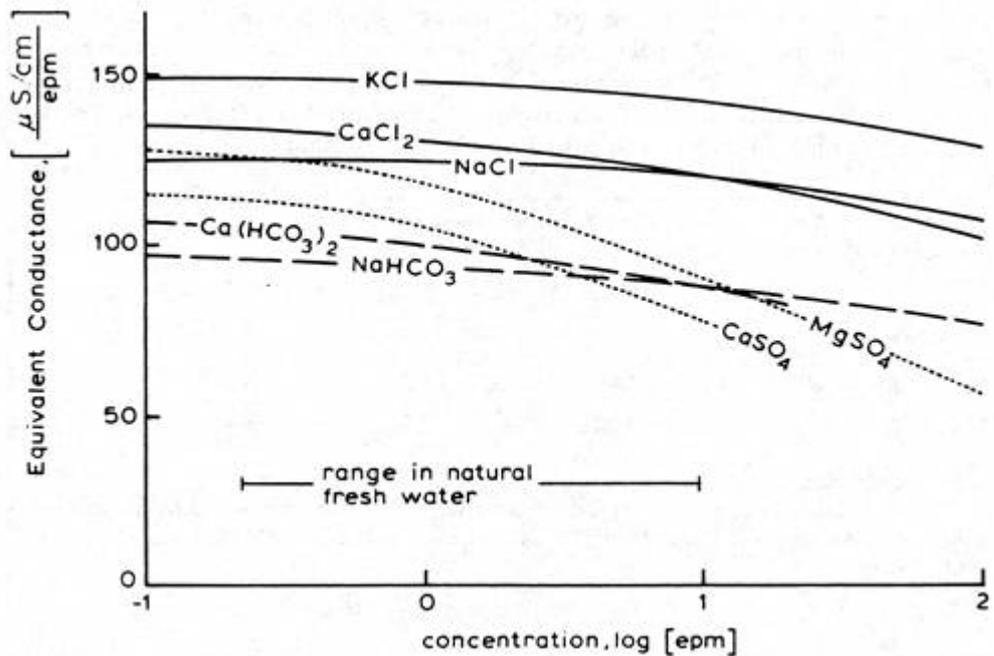


Fig. 2. Relationship between equivalent electrical conductivity and concentration for different salt solution

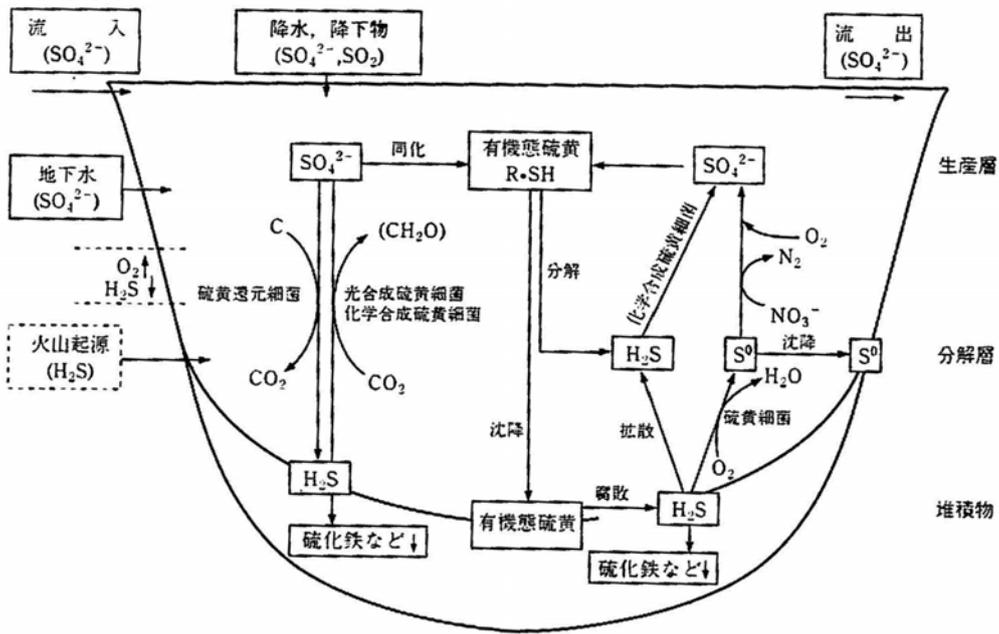


Fig. 3. Sulfur cycle in lake

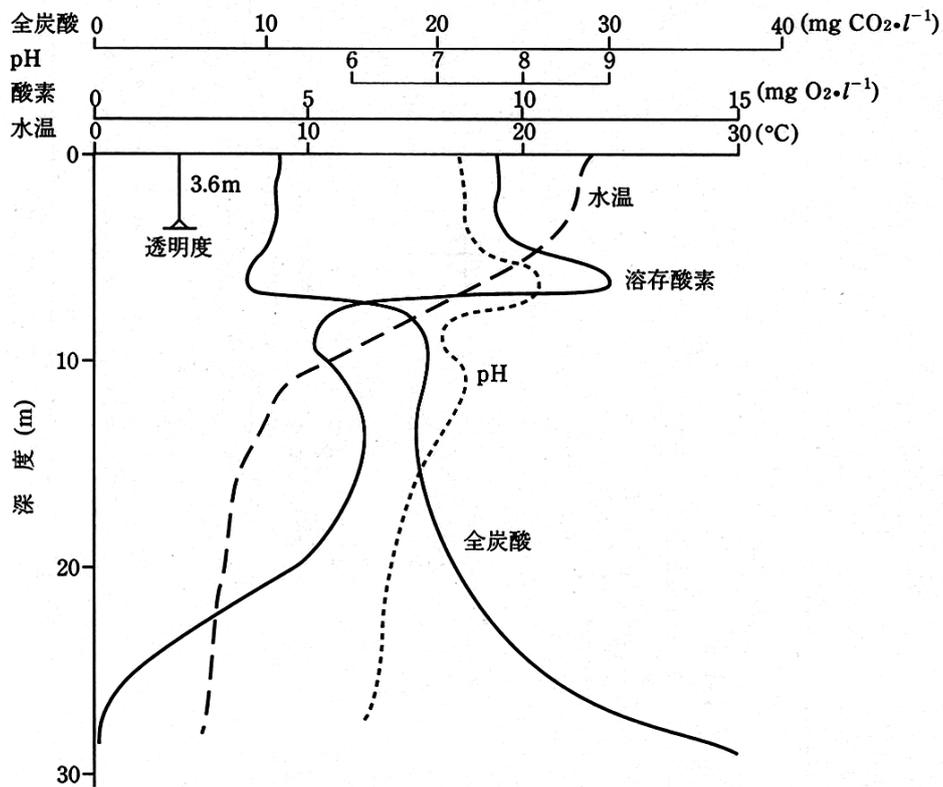


Fig. 4 Depth profile of temperature, pH, dissolved oxygen, and carbonate in Lake Kizaki

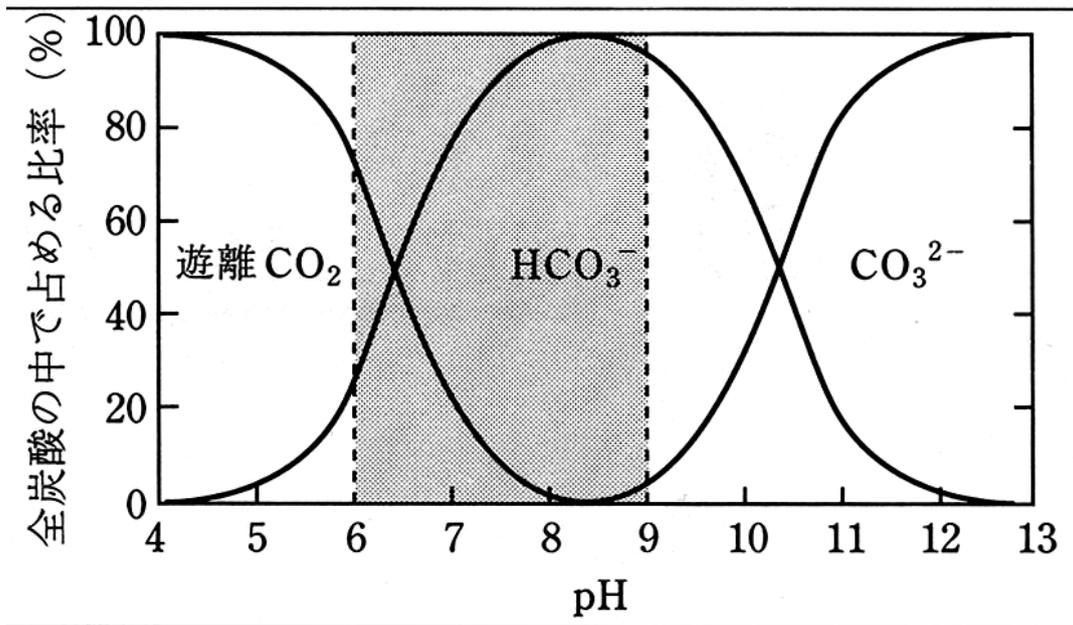


Fig. 5. Abundance ratio of carbonate species as function of pH

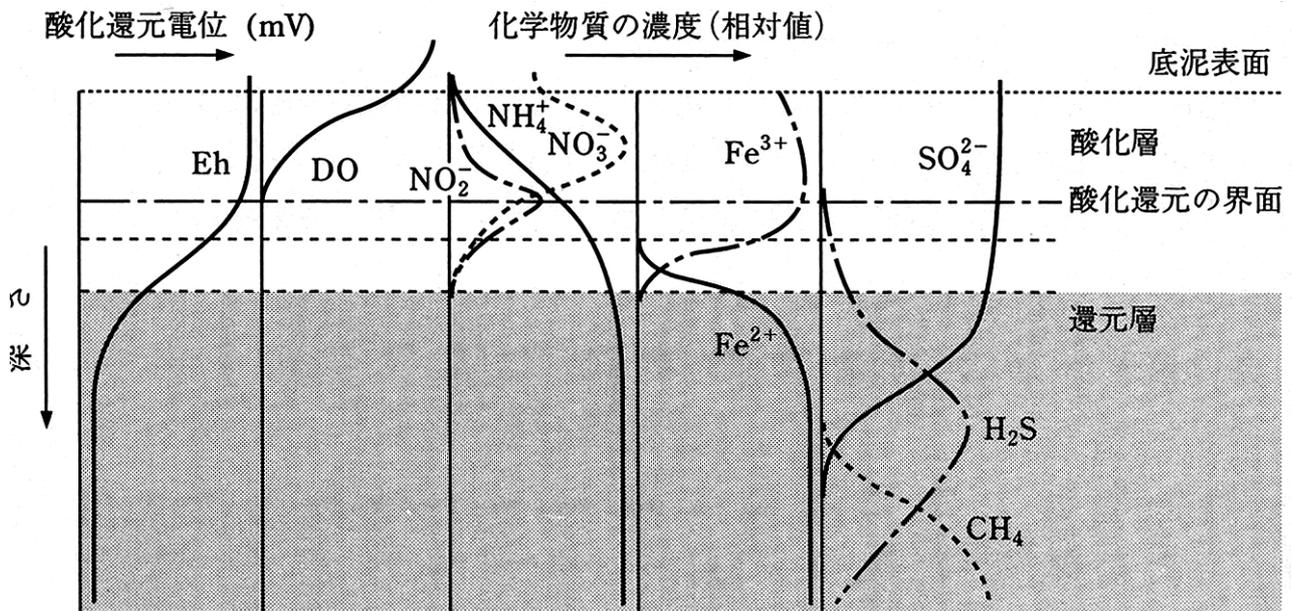


Fig. 6. Depth profiles of redox potential (Eh) and chemical substances derived by bacterial metabolism

Table 1 Settling times for gravity sedimentation of particles in water at 20°C

Particle diameter ( $\mu\text{m}$ )	h	min	sec
50	—	—	22
20	—	2	20
5	—	37	30
2	3	50	

Table 2 Settling times for a specific centrifuge for sedimentation of particles

Particle diameter ( $\mu\text{m}$ )	sp. g. mineral	Centrifuge speed (RPM)	time (min)
5	2.65	300	3.3
2	2.65	750	3.3
0.2	2.50	2400	35.4