

GEOCHEMICAL STUDIES ON THE MINERALS OBTAINED BY THE DRY VALLEY DRILLING PROJECT

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Abstract: Preliminary X-ray diffraction mineral analysis was carried out at the Thiel Earth Sciences Laboratory, McMurdo Station, on about three hundred samples from DVDP #6, from Lake Vida and from the McMurdo region. Chemical analyses of some of the minerals were carried out at our laboratory in Tokyo. From mineral species found in the core, it was suggested that there was some hydrothermal effect in the area. The secondary minerals of the Lake Vida core are different from those of the Ross Island core, and this indicates a differences in geological history between these sites. Using the distribution coefficient of alkaline earth elements in calcite, chemical constituents of the mineral-forming solution were calculated. The calcite might have been deposited from Sr- and Mg-poor solution compared to sea water.

From the calculation using Debye-Hückel equation, the ground water at Lake Vanda is almost in equilibrium with calcium sulfate but the lake water is super-saturated with calcium sulfate.

1. Minerals Obtained by the Dry Valley Drilling Project

1.1. Minerals found in the Lake Vida core (core #6)

Minerals in the core were picked up and X-ray diffraction mineral analyses were carried out. Finely powdered samples were irradiated with Ni-filtered Cu K_{α} radiation at 40 kV, 20 mA on a Toshiba X-ray diffractometer at a scan rate of 2°/min.

The minerals found in the core were as follows:
aragonite, calcite, chabazit, chlorite, gypsum, hydrous mica, illite, laumontite, prehnite and sericite.

Most of the minerals existing in the joints or fractures of the DVDP #6 core were powders, thin sheets, or small crystals. Calcite and gypsum are most abundant secondary minerals present in fractures in the core. The occurrence of aragonite is restricted from 88 to 92 m in the vicinity of a fault recognized in the core. Similarly, lamontite and chlorite are most abundant from 77 to 86 m and near 90 m. Another hydrous mica including mica occurs at 49, 63, 79 and 82 m. These secondary minerals in the shallow part of the core adjacent to the fault appear to be hydrothermal origin, not a result of replacement of primary

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minerals. The presence of laumontite and aragonite suggests high water temperature or Mg-rich water which indicates faulting occurred in the pre-glacial time. Most abundant secondary minerals in the deep part of the core #6 are also calcite and gypsum. And some minerals such as aragonite and laumontite or other zeolite are localized in the vicinity of intrusive plutonic rocks. This means that the secondary minerals may have been formed in the hydrothermal processes in this area. For example, minerals found at Onuma, a geothermal area in Japan, are calcite, chlorite, dolomite, kaolinite, laumontite, montmorillonite, pyrophyllite sericite and wairakite.

The distribution of the minerals in the core DVDV #6 is summarized in Fig. 1.

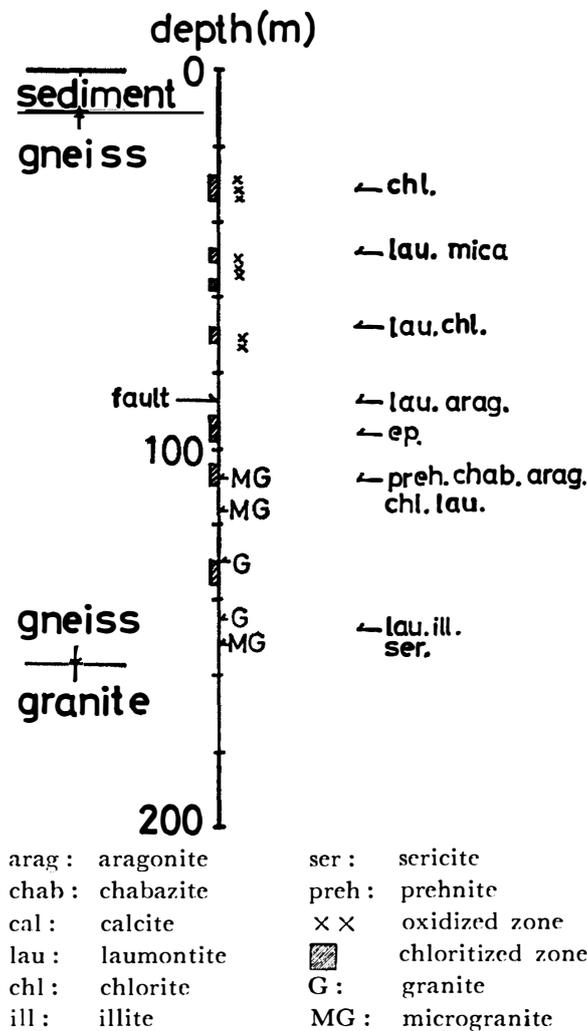


Fig. 1. Distribution of minerals in the core DVDV #6.

1.2. Minerals found in the McMurdo region

Minerals found in the McMurdo region were calcite, Mg-rich chlorite, dolo-

mite, magnesite, mirabilite, halite, laumontite, soda nither and thenardite. Most abundant secondary mineral in the Ross Island core was thenardite. The difference in the secondary minerals of the Lake Vida core and the Ross Island core indicates that geological history was largely different between these two sites.

2. Geochemistry of Calcium Carbonate Found at Lake Vida

2.1. Description of mineral

Calcium carbonate found at the Lake Vida was a thin flat form having zonal bands of alternating brown and white. This sample contained some rounded quartz that might be originated from the Beacon sandstone.

Chemical composition of calcium carbonate is shown in Table 1. This

Table 1. Chemical composition of calcium carbonate from Lake Vida.

Composition	Analytical result (%)
CaO	48.11
MgO	0.29
SrO	0.06
FeO	0.12
Fe ₂ O ₃	0.99
Al ₂ O ₃	1.51
CO ₂	38.75
R*	8.03
-H ₂ O	0.67
	98.53

* Undissolved with 4 M HCl.

Table 2. Results of X-ray analysis of calcite.

Standard calcite ASTM 5-0586		Calcite from Lake Vida	
d	I/I ₀	d	I/I ₀
3.86	12	3.85	9
3.035	100	3.04	100
3.845	3	3.84	3
2.495	14	2.49	13
2.285	18	2.29	18
2.095	18	2.09	17
1.913	17	1.91	21
1.875	17	1.87	17
1.626	4	1.63	4
1.604	8	1.61	8

mineral contained a considerable amount of undissolved matter by treatment with 4 M hydrochloric acid. Main portion of undissolved substance was silicate. The treating solution was yellow, which suggested existence of ferric ions. The analytical results showed that ferric ions were dominant over ferrous ions. It means that calcium carbonate was deposited in an oxidizing environment.

From the data of X-ray diffraction of the mineral, calcium carbonate from the Lake Vida is a typical calcite. The results were shown in Table 2, where d is a lattice distance and I/I_0 is a relative intensities of X-ray diffraction.

2.2. Estimation of the chemical constituents of the mineral-forming solution

Using the distribution coefficient of alkaline earth elements in calcite, the authors estimated the chemical constituents of the mineral-forming solution.

The distribution of the elements between the solution and the crystal is expressed as follows:

$$\left(\frac{A}{B}\right)_{\text{cryst.}} = D \left(\frac{A}{B}\right)_{\text{sol.}} \quad (1)$$

where A and B are mol of the elements A and B , and D is the distribution coefficient. The left hand side is the mol ratio of the elements in the crystal, and the right hand side is a product of D and the mol ratio of the elements in the solution.

The distribution of the elements between the solution and the crystal was a problem of analytical chemistry, that is, the problem of coprecipitation of a minor element with a main component of the precipitate.

KOLTHOFF (1938) examined the precipitation of lead in barium sulfate, and expressed the relation as follows:

$$\left(\frac{M_{\text{Pb}^{2+}}}{M_{\text{Ba}^{2+}}}\right)_{\text{cryst.}} = K \left(\frac{M_{\text{Pb}^{2+}}}{M_{\text{Ba}^{2+}}}\right)_{\text{sol.}} \quad (2)$$

The values of K in equation (2) at the temperatures 26°C, 95°C and 185°C were 0.0255, 0.0266 and 0.038, respectively. Temperature dependence of the distribution coefficient is not so large within a given temperature range.

Determination of distribution coefficient of some metal ions between calcite and solution was attempted by KINSMAN *et al.* (1969) and HOLLAND (1963). LERMAN (1965) estimated the concentration of some elements of sea water in ancient time, using distribution coefficients of calcite.

HOLLAND *et al.* determined the distribution coefficient of strontium in calcite (1960) and in aragonite (1963). In equation (3), N denotes the mol fraction of strontium carbonate in the solid phase, and the right hand side in parentheses is the mol fraction of strontium in the solution. If the content of strontium is low, m_{Sr} may be neglected. The mol fraction of the strontium in the solution may be equal to the mol ratio of strontium to calcium.

$$(N_{\text{SrCO}_3})_{\text{cryst.}} = K \left(\frac{m_{\text{Sr}}}{m_{\text{Ca}} + m_{\text{Sr}}}\right)_{\text{sol.}} \quad (3)$$

Values of the distribution coefficient in equation (3) were as follows (Calc. is calcite and A is aragonite):

$$K_{Sr}^{Calc} = 0.13 \pm 0.02 \text{ (25}^\circ\text{C)}$$

$$K_{Sr}^A = 1.17 \pm 0.04 \text{ (16}^\circ\text{C)}$$

$$K_{Sr}^A = 0.88 \pm 0.33 \text{ (80}^\circ\text{C)}$$

The authors assumed that the distribution coefficient of strontium in the calcite is 0.13, even in the formation of calcite at low temperature such as in Antarctica. As the mol fraction of strontium carbonate in the Vida calcite is 0.0708 mol percent, the mol ratio of strontium to calcium is 0.00543 in the mineral-forming solution, while sea water has a ratio of 0.0089. If the concentration of calcium in the solution is assumed to be the same as that in sea water, the concentration of strontium may be 4.8 mg/kg which is equivalent to 60% of present sea water strontium content.

From the thermodynamical calculations by LERMAN, the logarithmic mol ratio of magnesium to calcium in the solution that formed the calcite at the Lake Vida is $-0.25 \sim 0.8$, while sea water has a value of 0.86. The ground water collected from Lake Vanda drilling hole has a value of -0.4 .

From these data, calcium carbonate at Lake Vida may have been deposited from strontium- and magnesium-poor solution compared to sea water.

3. Estimation of Solubility of Calcium Sulfate in the Saline Water

Gypsum crystals were found in the fractures of the core #4. And in the ice block in the core, thin flat hexagonal sheets of gypsum crystals were also found. These gypsum crystals coexisted with needlelike small crystals of aragonite. This suggests that the minerals were formed from a magnesium-rich solution or from a high-temperature solution.

Table 3. Chemical composition of ground water obtained from drill hole at Lake Vanda (g/kg).*

Locality	A	B	C
Depth from lake ice	67.0 m	72.2 m	75.7-76.7 m
Specific gravity	1.095	1.121	1.143
Na ⁺	6.11	7.82	8.75
K ⁺	6.59	0.98	1.08
Ca ²⁺	24.4	28.9	33.2
Mg ²⁺	7.40	9.03	10.5
Cl ⁻	74.28	94.24	108.7
SO ₄ ²⁻	0.615	0.463	0.248

A: Lake water B, C: Ground water

* after T. TORII.

The lake water and the ground water collected at Lake Vanda were highly saline, as shown in Table 3. The authors estimated the solubility of calcium sulfate using Debye-Hückel equation.

$$\log \gamma_{\pm} = - \frac{A |Z_{+} \cdot Z_{-}| \sqrt{I}}{1 + Ba \sqrt{I}} \quad (4)$$

$$I = \frac{1}{2} \sum Z_i^2 m_i \quad (5)$$

$$A=0.488, B=0.324. \quad a=6 \text{ for } \text{Ca}^{2+}$$

In equation (4), γ_{\pm} denotes mean activity coefficient, and in equation (5), I is ionic strength of the solution. A , B and a are parameters given by HARND, OWEN and KLOTT.

Table 4. Solubility of calcium sulfate in the saline water.

Locality	A	B	C
	(67m)	(72.2m)	(75.5—76.7m)
I	3.03	3.70	4.26
$\log \gamma_{\pm}$	0.168	0.161	0.157
Ionic product $\times 10^{-5}$	4.9	4.4	2.9

From the calculation, ionic product of calcium sulfate is 4.9, 4.4 and 2.9 respectively as shown in Table 4. As the solubility product of calcium sulfate is about 3×10^{-5} , the ground water is almost in equilibrium with calcium sulfate, but the lake water is supersaturated with calcium sulfate.

From these data, the lake water may be part of the origin of gypsum-forming solution.

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