[AMERICAN JOURNAL OF SCIENCE, VOL. 271, DECEMBER, 1971, P. 481-489]

MAGNESIUM ION CONCENTRATIONS IN THE PRESENCE OF MAGNESIUM CHLORITE, CALCITE, CARBON DIOXIDE, QUARTZ

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ABSTRACT. Concentrations of magnesium were measured in solutions in contact with magnesium chlorite, calcite, and quartz, under carbon dioxide pressures of 5 and 65 atm, and at temperatures from 190° to 300°C. Magnesium concentrations were of the order of 0.5 to 1 ppm at 200°C and 0.02 to 0.05 ppm at 300°C. Comparison is made between values of a_{Mg}/a_H^2 from the experimental solutions and natural high-temperature waters.

INTRODUCTION

A feature of high-temperature dilute natural hydrothermal solutions, as found for example at deep levels in volcanic zones of New Zealand, Japan, and Iceland, is the extremely low concentrations of the common rock-forming element magnesium. In many waters at temperatures of 250 to 300°C the concentrations are often in the range of only 10 to 100 ppb (Mahon, 1965; Ellis, 1970) and are of similar magnitude to those of "trace metals" such as lead, zinc, and copper.

Within hydrothermal areas, observations of waters of similar compositions but of differing temperature have shown that the concentrations of magnesium in solution are temperature dependent. This fact has been used in a semi-quantitative way to suggest deep temperatures within hydrothermal areas from magnesium concentration measurements in waters from springs of good flow (Ellis, 1970).

For the Salton Sea hydrothermal system, the equilibrium between common magnesium-containing hydrothermal alteration minerals and associated sodium, potassium, and calcium phases was related quantitatively by Helgeson (1967) in terms of ion activity ratios a_{Mg}/a_H^2, a_{Ca}/a_H^2, a_{Na}/a_H, and a_K/a_H in the hot solutions. Brown and Ellis (1970) made a similar correlation for the different mineralogy and hot water compositions in the Broadlands, New Zealand, hydrothermal system, and figure 1 is a magnesium, calcium mineral stability diagram for 260° adapted from that paper.

Chlorite is the most common secondary iron-magnesium silicate produced within hydrothermal areas at 250 to 350°C by alteration of the ferro-magnesium minerals in volcanic rock. In the present experiments, the solution compositions in equilibrium with chlorite, calcite, and quartz in the presence of controlled carbon dioxide pressures were determined to obtain experimental calibration of the temperature dependence of magnesium concentrations.

EXPERIMENTAL

The experiments consisted of reacting a granulated mixture of quartz, calcite, and chlorite with water under a controlled pressure of carbon dioxide in a 100 ml pressure vessel. Small (2 ml) samples were

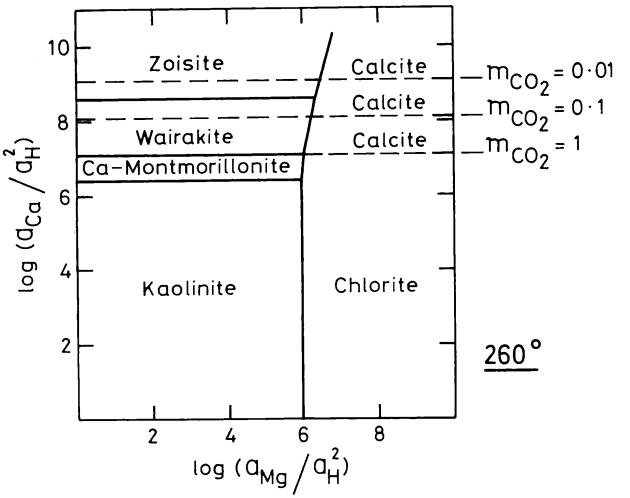

Fig. 1. Stability diagram for calcium and magnesium minerals at 260°. For particular m_{CO_2} values at equilibrium the logarithm of the ratio a_{Ca}/a_H^2 cannot exceed that of the dashed line for calcite solubility.

withdrawn through capillary pressure tubing after several days of reaction (test for attainment of equilibrium by sampling at intervals). Atomic absorption analysis gave calcium, magnesium, and silica concentrations. The composition of the original chlorite as percentage oxides was as follows: SiO_2, 31.3; Al_2O_3, 15.6; total iron as Fe_2O_3, 7.6; TiO_2, 0.22; MgO, 31.1; Na_2O, 0.12; K_2O, 0.09; CaO, 0.23; MnO, 0.04. The clinochlore mineral was clean macro-crystalline material, originating from Kaukapakaha, North Auckland (New Zealand Geol. Survey cat. 9419).

RESULTS

Table 1 summarizes the results and includes analyzed m_{Mg} and m_{Ca} concentrations and calculated m_{CO_2}, m_{HCO_3}, pH, and log (a_{Mg}/a_H^2) values at the reaction temperature. Figure 2 gives the magnesium concentrations in ppm found in solution at carbon dioxide pressures of 5 and 65 atm, together with the atomic ratios Ca/Mg. Silica concentrations were found to be generally within ± 10 percent of the saturation values reported for quartz (Kennedy, 1950).

BACKGROUND TO INTERPRETATION

In the experimental reaction system, in the presence of carbon dioxide and quartz, at equilibrium, chlorite, calcite, and a calcium alumino-silicate could be expected as stable minerals. The relative stability of dolomite is discussed below. The calcium alumino-silicate may be zoisite, wairakite, or calcium montmorillonite, depending in part on the partial pressure of carbon dioxide (Brown and Ellis, 1970). In the solution a particular combination of values of a_{Ca}/a_H^2 and a_{Mg}/a_H^2

TABLE 1
Data from reaction experiments

P_{CO_2} = 5 atm							
t°	Reaction time (days)	Conc Mg (10^{-5}m)	Conc Ca (10^{-4}m)	Conc CO_2 (m)	Conc HCO_3 (10^{-3}m)	pH at t°	$\log(a_{Mg}/a_H^2)$
195	19	2.2	5.2	0.042	1.9	5.7	6.7
195	26	1.6	5.2	0.042	1.9	5.7	6.6
224	5	0.71	2.15	0.047	1.3	5.75	6.4
224	10	0.69	2.20	0.047	1.3	5.75	6.4
224	22	1.0	2.20	0.047	1.3	5.75	6.5
250	33	0.38	0.62	0.052	1.2	6.0	6.6
268	38	0.31	0.54	0.058	0.76	6.1	6.7
283	26	0.23	0.60	0.060	0.48	6.25	6.9
282	46	0.09	0.28	0.060	0.71	6.25	6.5
P_{CO_2} = 65 atm							
t°	Reaction time (days)	Conc Mg (10^{-5}m)	Conc Ca (10^{-3}m)	Conc CO_2 (m)	Conc HCO_3 (10^{-3}m)	pH at t°	$\log(a_{Mg}/a_H^2)$
187	14	4.6	2.13	0.54	4.1	4.85	5.0
187	23	4.8	2.05	0.54	4.2	4.85	5.0
214	13	3.3	1.07	0.59	2.5	4.85	5.2
240	14	0.66	0.40	0.65	1.8	4.95	4.7
240	15	1.1	0.40	0.65	1.8	4.95	4.9
261	17	0.54	0.165	0.72	1.5	5.15	5.0
285	20	0.32	0.064	0.80	1.1	5.55	5.6
298	21	0.23	0.029	0.88	0.5	5.55	5.5

occurs at each controlled partial pressure of CO_2, as the point for equilibrium changes its position along the chlorite plus calcium-mineral boundaries on stability diagrams of the type of figure 1.

At constant temperature and pressure, along a chlorite, calcium alumino-silicate boundary, and for equilibrium also with calcite and quartz, the following equations apply

$$k_1 = a_{Mg}/a_H^{2-2x} \cdot a_{Ca}^{x} \tag{1}$$

where x is the number of calcium ions required to liberate one magnesium ion in an equilibrium of the type below and a_i is the molal activity of an ion.

$$x\text{Ca}^{2+} + \text{Mg-silicate} + (2-2x)\text{H}^+ = \text{Mg}^{2+} + \text{Ca-silicate} + y\cdot\text{SiO}_2 \tag{2}$$

Also, for calcite saturation, if the solution species are essentially Ca^{2+} and HCO_3^-, and for $a_{H_2O} = 1$,

$$k_2 = p_{CO_2} \cdot a_{Ca}/a_H^2 \tag{3}$$

and

$$a_H = k_3^{-1} \cdot p_{CO_2}^{2/3} \cdot \gamma_{Ca}^{1/3}/\gamma_{HCO_3}^{1/3} \tag{4}$$

where γ is an ion activity coefficient.
From these equations,

$$a_{Mg}/a_H^2 = k_1 \cdot k_2^{x}/p_{CO_2}^{x} \tag{5}$$

and

$$a_{Mg} = k_1 \cdot k_2^{x} \cdot k_3^{-2} \cdot p_{CO_2}^{(4/3 - x)} \cdot \gamma_{Ca}^{2/3}/\gamma_{HCO_3}^{2/3} \tag{6}$$

Under the conditions of the preceding paragraph, as x would be much less than 1 for a reaction involving the transformation of chlorite to a mineral such as zoisite, wairakite, or calcium-montmorillonite, magnesium concentrations would be strongly dependent on P_{CO_2}, but the ratio a_{Mg}/a_H^2 would not. In contrast, for a simple replacement reaction of calcium for magnesium, x = 1, and approximate proportionalities between a_{Mg}/a_H^2 and $p_{CO_2}^{-1}$ and between a_{Mg} and $p_{CO_2}^{1/3}$ would be expected. In the case of a replacement reaction the ratio Ca/Mg would be independent of a_H and P_{CO_2}; in the former case, a graph of log (Ca/Mg) versus log p_{CO_2} could have a negative slope of up to nearly 1.3.

Equations 4 and 6 assume a simple calcium and magnesium alumino-silicate and carbonate system, but the chlorite used contained minor concentrations of other cations such as sodium and potassium

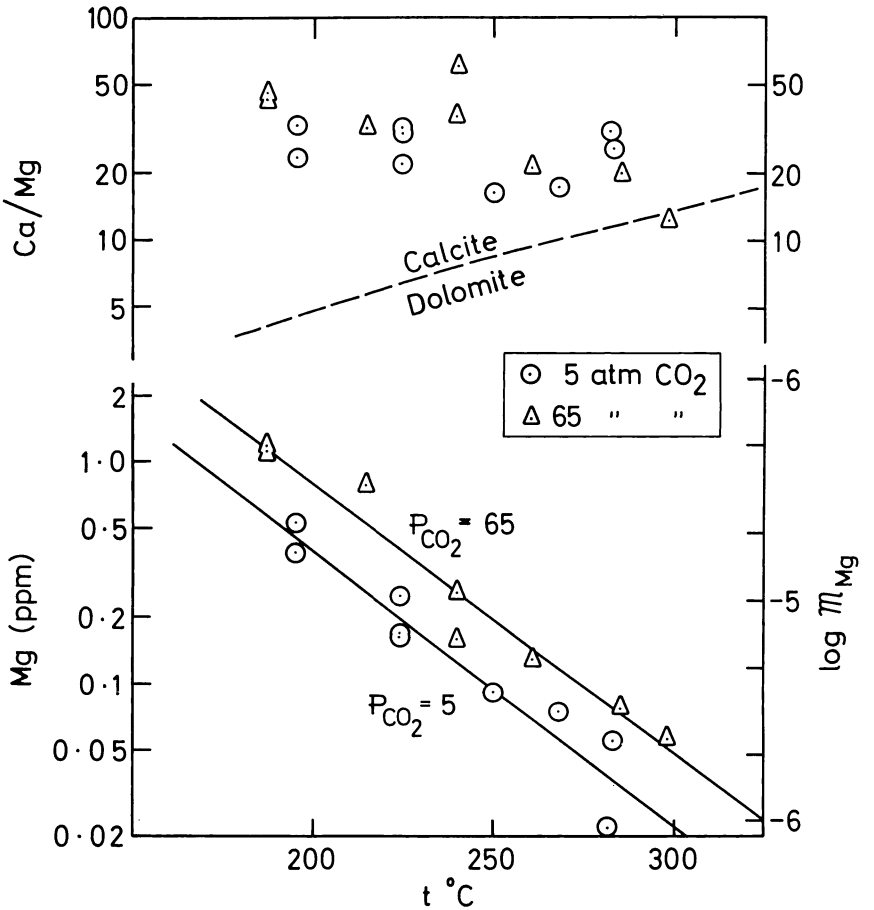

Fig. 2. Concentrations of magnesium and the atomic ratio Ca/Mg in reaction solutions.

which were partly extracted by the carbon dioxide solutions. However, the total concentration of sodium and potassium was usually <0.001 m.

As values of the ratio $m_{Ca} \cdot m_{HCO_3}^2/p_{CO_2}$ for calcite solution in water were known from previous work (Ellis, 1959), approximate values of m_{HCO_3} in the present experiments (table 1) were calculated from m_{Ca} and p_{CO_2}. Knowledge of the molal concentrations m_{HCO_3} and m_{CO_2} and of values for pK_{a_1} for "carbonic acid" (Helgeson, 1969) enabled the pH of the reaction solutions to be calculated. (Solubility information for carbon dioxide was taken from Ellis and Golding, 1963). This enabled the experimental results to be reported in terms of a_{Mg}/a_H^2 and a_{Ca}/a_H^2. Activity coefficient corrections are ignored (a = m), as experimental accuracy in measuring Mg concentrations is not high, and ionic strengths do not exceed 0.01 m.

DISCUSSION

In contrast to expectations from published phase diagrams from field information, the experimental magnesium concentrations at a temperature were not strongly dependent on the carbon dioxide pressure. Between p_{CO_2} values of 5 and 65 atm, magnesium concentrations increased by a factor of about 2, this being of the magnitude expected for x = 1 in equation 6. For x = 1 the Ca/Mg ratio would not vary. Values of Ca/Mg for p_{CO_2} = 65 atm were slightly higher than at 5 atm only at lower temperatures.

The mineralogical implications are that in the experiments magnesium and calcium are exchanged in a simple reaction not involving hydrogen ions.

The approximate values of Ca/Mg ratios for the calcite, dolomite equilibrium (Lovering, 1969) are given for comparison on figure 1. It can be seen that below 300° the solution magnesium concentrations are too low for dolomite to be involved in the interpretation of the experiments. Dolomite is not found in alteration mineral assemblages in volcanic area hydrothermal systems, and calcite obtained from drillcores at deep levels is an almost pure calcium mineral (Browne and Ellis, 1970).

Helgeson, Brown, and Leeper (1969) suggested in several phase diagrams that in the presence of quartz, magnesium chlorite was unstable with respect to dolomite, talc, and magnesite formation, at the temperatures of the present experiments. The chlorite (not a pure magnesium mineral) used in the experiments was examined after reaction, but the crystal plates were bright and unetched. Even the finest fraction of chlorite from the reaction mixture gave a strong X-ray pattern identical to the original mineral.

A comparison of experimental and field results is best made by use of the ratios a_{Mg}/a_H^2, a_{Ca}/a_H^2, and Ca/Mg. In natural hydrothermal systems at equilibrium the deep water pH is usually controlled by an alumino-silicate buffer (Ellis, 1970), rather than by a HCO_3^-/CO_2 solu-

tion buffer as in the experiments. The relationship between m_{Ca}, m_{CO_2}, pH, and salinity in natural systems was described by Ellis (1970).

Table 2 gives calcium and magnesium concentration data from some drilled hydrothermal areas in New Zealand, together with the deep water temperatures, pH, chloride, and p_{CO_2} values. The concentrations of magnesium found in the experiments for particular temperatures and pH conditions are of similar magnitude to those found at deep levels in hydrothermal areas. Figure 3 summarizes the experimental magnesium results in terms of ratio, a_{Mg}/a_H^2, also giving points for the New Zealand hydrothermal areas with their associated p_{CO_2} values in brackets.

For a particular temperature the field values of a_{Mg}/a_H^2 vary less with p_{CO_2} than in the experiments, and there is a wide variation in Ca/Mg ratios for the natural waters, some being close to the experimental values but others at comparable temperatures being higher by as much as ten times. For the natural systems, in equations 1 and 2, x is small, corresponding to a steep phase boundary between chlorite and calcium alumino-silicate phases, as in figure 1.

The reaction equilibrium that controls the magnesium concentrations in the experiments is open to question, but two possibilities are that in chlorite a simple minor replacement of magnesium by calcium occurs, or alternatively, that minor formation of a Ca–Mg–montmorillonite phase occurs, and this is the exchange medium. The amount of magnesium taken into solution was so small that identification of an exchanged or alteration mineral would be extremely difficult (an attempt to identify montmorillonite in the reaction products by usual X-ray techniques for this mineral was not successful).

The experimental results are tentatively explained on the second model. The coexistence of magnesium chlorite, magnesium montmorillonite, and calcium montmorillonite would overall be a metastable situation, but the experimental solution ratios a_{Mg}/a_H^2 are in reasonable agreement with values calculated by Helgeson, Brown, and Leeper (1969) for the Ca-montmorillonite, Mg-montmorillonite boundary at calcite saturation.

On this explanation, at low carbon dioxide pressures, and failing the formation of other calcium alumino-silicate minerals, the experiment values of a_{Mg}/a_H^2 would approach those for a triple point for coexistence of calcium and magnesium montmorillonites plus magnesium chlorite, whereas at high carbon dioxide pressures the ratios a_{Mg}/a_H^2 and a_{Ca}/a_H^2 could be depressed down a 45° slope line on the phase boundary of calcium-montmorillonite and magnesium-montmorillonite away from the equilibrium solution conditions for coexistence with chlorite. The field values should be closer to the ratios for the experiments at $p_{CO_2} = 5$ atm than those at 65 atm, due to the steepness of the chlorite phase boundaries (see fig. 1) for the equilibrium mineral assemblages found in natural systems (x small). Figure 3 shows this to be the situation.

TABLE 2

Deep water conditions in hydrothermal areas

Area and Drillhole	Drillhole Depth (m)	Water t°	P_{CO_2} (atm)	Approx Cl (ppm)	Mg (ppm)	Ca (ppm)	pH at t°	Ca/Mg (atomic)	$\log(a_{Mg}/a_H^2)$
Wairakei (average Western holes)	700	250	1.0	1550	0.03	10	6.4	200	6.6
Broadlands—10	1090	245	30	890	0.035	0.78	6.2	13	6.2
Broadlands—13	1080	255	12	750	0.015	1.7	6.2	70	5.9
Kawerau—8	915	245	7	930	0.032	0.71	6.2	13	6.5
Waiotapu—6	915	235	2	1000	0.04	8.5	6.1	125	6.1

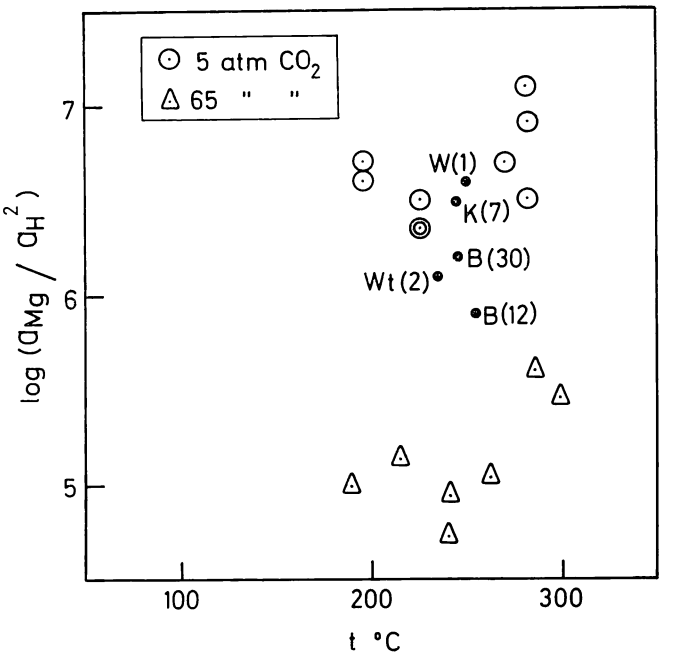

Fig. 3. Calculated values of log (a_{Mg}/a_{H^2}) for the reaction solutions and for waters in some hydrothermal areas (with their associated carbon dioxide pressure shown in brackets). W, B, K, and Wt refer to Wairakei, Broadlands, Kawerau, and Waiotapu.

Under equilibrium field conditions the Ca/Mg ratio can be expected to vary with the value of p_{CO_2} in the system. This results largely from the inverse relationship between calcium concentrations and p_{CO_2} at a temperature (Ellis, 1970). Table 2 shows this trend. This fact is useful when making preliminary surveys of geothermal areas for estimating underground carbon dioxide pressures from the analysis of spring waters.

ACKNOWLEDGMENTS

My thanks to Dr. R. L. Goguel for the mineral analysis and atomic absorption measurements, and to Dr. G. A. Challis, New Zealand Geological Survey, for providing the chlorite mineral.

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