学　位　論　文　要　旨

Dissertation Abstract

Evaluation of Magnesium Carbonate Formation in Freezing Alkaline Saline Lakes

凍結するアルカリ塩湖におけるマグネシウム炭酸塩の生成評価

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Summary

The weathering of silicate rocks is the most important natural process of atmospheric CO_2 removal in natural. It has been suggested that alkaline saline lakes form special carbonates from those carbonate ions and may serve as sink tanks for carbon at the Earth's surface. Furthermore, it is known that in alkaline saline lakes, water chemistry is dominated by a special carbonate, which is an important substance. In this study, long-term field works were conducted in an alkaline saline lake in Mongolia to observe changes in water chemistry with seasonal changes. In addition, the solubility of a special Mg carbonate (amorphous magnesium carbonate: AMC) that is formed in alkaline saline lakes was experimentally measured to determine its temperature dependence. In the discussion, the geochemical modeling was performed using the solubility of AMC obtained from the experiments. The results suggest that in alkaline saline lakes during the winter, CO_2 accumulates in the lake water along with the formation of carbonate. At the same time, it was suggested that CO_2 could be temporarily released into the atmosphere at the same time as the ice melts in early spring.

Dissertation Abstract

Weathering of silicate rocks and formation of carbonate minerals at the Earth's surface is the most important natural process of atmospheric CO_2 removal in nature. The weathering of calcium-bearing silicates is described by the following equation.

$$CaSiO_3 + 2CO_2 + 3H_2O \ = \ Ca^{2+} + 2HCO_3^- + H_4SiO_4$$

Thus, calcium and bicarbonate ions are released in aqueous environments in response to the consuming atmospheric CO_2. The ocean then uses the calcium influx from the land to produce calcium carbonates as follows.

$$Ca^{2+} + 2HCO_3^- \ = \ CaCO_3 + CO_2 + H_2O$$

This carbonate synthesis releases one molecule of CO_2, but the difference between this and the weathering of silicate rocks results in one molecule of CO_2 being fixed as carbonate. Weathering of silicate rocks and precipitation of carbonate minerals are carbon fixation processes in the natural environment. Therefore, they are attracting attention in terms of negative emission technologies for active CO_2 removal.

Inland environments with similar carbon fixation processes are alkaline saline lakes. Alkaline saline lakes are closed lakes and form at the terminus of rivers. Furthermore, they are more common in dry and cold regions and are found in basins and plains in the continental interior. The volume of water is controlled by evaporation, and

carbonate precipitation associated with concentration has been observed. The carbonates precipitated in alkaline saline lakes are thought to be monohydrocalcite (MHC: $CaCO_3{\cdot}H_2O$) and amorphous magnesium carbonate (AMC: $MgCO_3{\cdot}nH_2O$). This means that alkaline saline lakes, unlike oceans, may be able to utilize magnesium as well as calcium for carbon fixation. In oceans, the pH is about 8, and under these conditions, dissolved inorganic carbon exists mainly as bicarbonate ions (HCO_3^-). Alkaline saline lakes, on the other hand, have a pH higher than 9 and a higher proportion of carbonate ions (CO_3^{2-}). Therefore, the following reactions are likely to occur.

$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

It can be assumed that alkaline saline lakes do not release CO_2 through carbonate precipitation and that more efficient carbon fixation takes place. This suggests that alkaline saline lakes may be a better carbon removal unit than the ocean. Therefore, the processes governing the behavior of CO_2 in alkali lakes and their consequences need to be clarified, not only to predict the regional CO_2 budget, but also to make functional use of alkali lakes for negative emission technologies. However, alkaline saline lakes in cold regions have not been studied. In fact, the above-mentioned processes favoring carbon fixation in alkaline lakes were observed only in summer seasons. Almost nothing is known about the changes in water chemistry, authigenic carbonate mineral formation/dissolution, CO_2 budget, and their interrelationships during the freezing of alkaline lakes. The purpose of this study is to characterize the chemical processes in alkaline lakes during the freezing of alkaline lakes combining field observations, laboratory experiments to obtain the missing thermodynamic parameter of an authigenic carbonate mineral (AMC) in low temperature and theoretical consideration by means of geochemical modeling.

In this study, fieldworks were carried out in summer and winter (frozen condition) at the Valley of the Gobi Lakes in Mongolia (Figure 1) The Valley of the Gobi Lakes exists in a latitudinally oriented depression of tectonic origin, located in between the Altai mountains and Khangai mountains (Figure 1). The lake of most interest in this study is Olgoy lake, located south of the Khangai Mountains. Olgoy lake is an alkaline saline lake at about 2100 m elevation in Mongolia, with salinity of 1–2 g/kg and pH of 9-10 (Figure 2). The lake has no permanent outlet, and inflowing streams form temporarily during the rainy season. The average temperature in the region is about 1 ℃ and the lake freezes over during the period October to April. Compared to some of the other lakes in the Valley of the Gobi Lakes, Olgoy lake was selected for the study because it had the highest saturation to AMC and a higher carbonate concentration.

In addition, in this study, the solubility of AMC under low temperature conditions was experimentally estimated, allowing quantitative assessment of AMC precipitation in the low temperature range.

The solubility of AMC was found to be log$K$ = -5.20 ± 0.02 by experimental measurements under low temperature conditions. This indicates that AMC is significantly less likely to precipitate at low temperatures. Water chemistry investigations showed that most of the concentrations of the major components (Na, Cl, Mg, DIC, SO_4) increased due to ice formation (Figure 3). In contrast, Ca concentrations were almost the same as in summer, suggesting the formation of MHC in response to the enrichment process; the conservative behavior of Mg could be explained by the increased solubility of AMC at low temperatures. However, the factors responsible for the accumulation of CO_2(g) in the lake water during freezing, which is accompanied by a decrease in pH, were unclear. A detailed understanding of the relationship between carbonate formation and water chemistry behavior is needed for a quantitative assessment of carbon fixation in alkaline saline lakes.

Using the temperature dependence of AMC solubility, I attempted to reproduce the water quality behavior of a winter alkaline saline lake by means of the geochemical modeling to determine which processes is plausible to explain the observed increase of the CO_2 partial pressure in the lake water. The results show that carbonate formation during ice formation promote an increase in CO_2 partial pressure, leading to a decrease in pH (Figure 4).

In alkaline saline lakes during the winter, CO_2 was accumulated in the lake water. Therefore, the temporal emissions of CO_2 to the atmosphere is possibly occurred in early spring, when the ice melts. This process must affect the CO_2 budget associated with the alkaline lakes. This study provide the importance of freezing process of alkaline lake to quantitatively to determine r the annual carbon budget of the alkaline saline lakes for the first time.

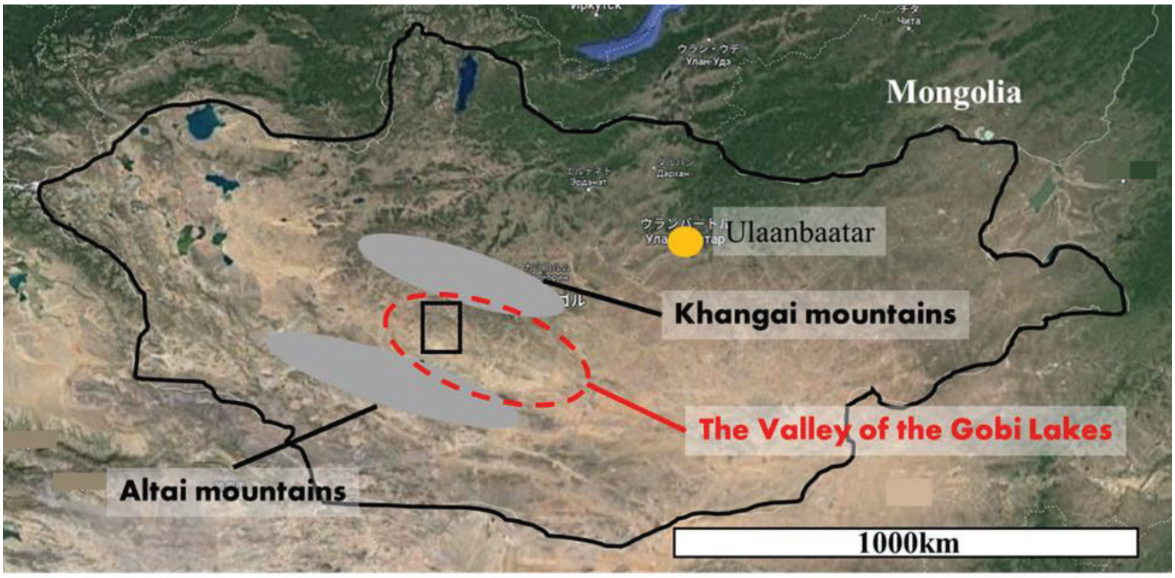

Figure 1

Map of Mongolia and location of the Valley of Gobi Lakes (red oval). The study area of this study is surrounded by a black square. Satellite images of this target lake are shown in Figure 2. The mountain ranges (Khangai and Altai mountains) are represented by grey ovals.

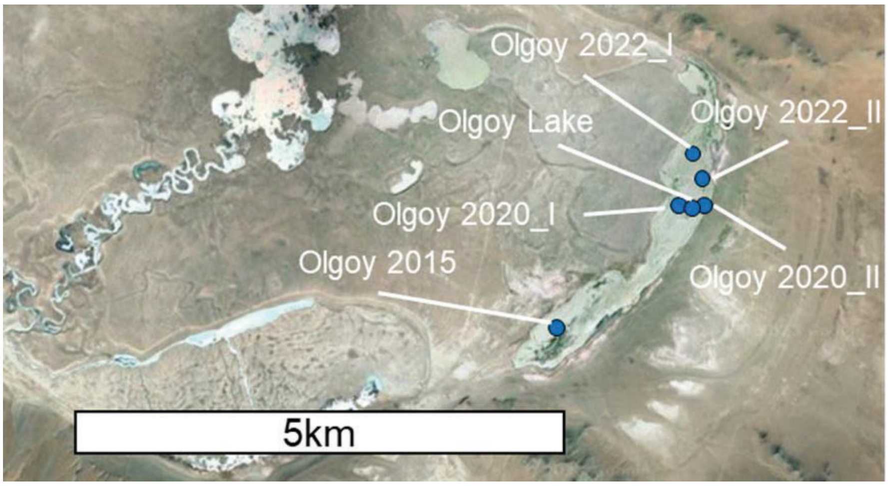

Figure 2

Satellite images of Olgoy lake which was taken from Google Earth. Blue dots represent the sampling locations in the January 2020, February 2019 fieldworks and previous studies.

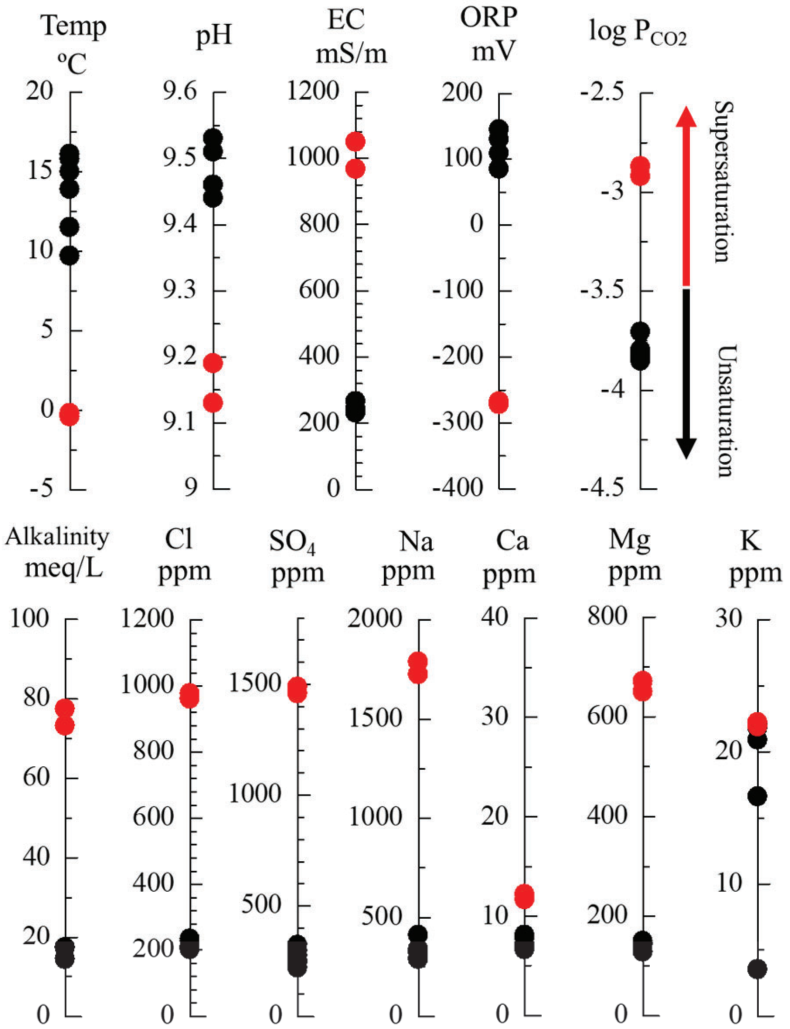

Figure 3

Comparison of the concentration (ppm) of each major dissolved ion species (Cl^-, SO_4^{2-},Ca^{2+},K^+,Mg^{2+} and Na^+), pH, temperature (℃), EC (mS/m), ORP (mV) and pressure of CO_2 for samples during winter (red: two samples) and summer (black: five samples) in Olgoy lake.

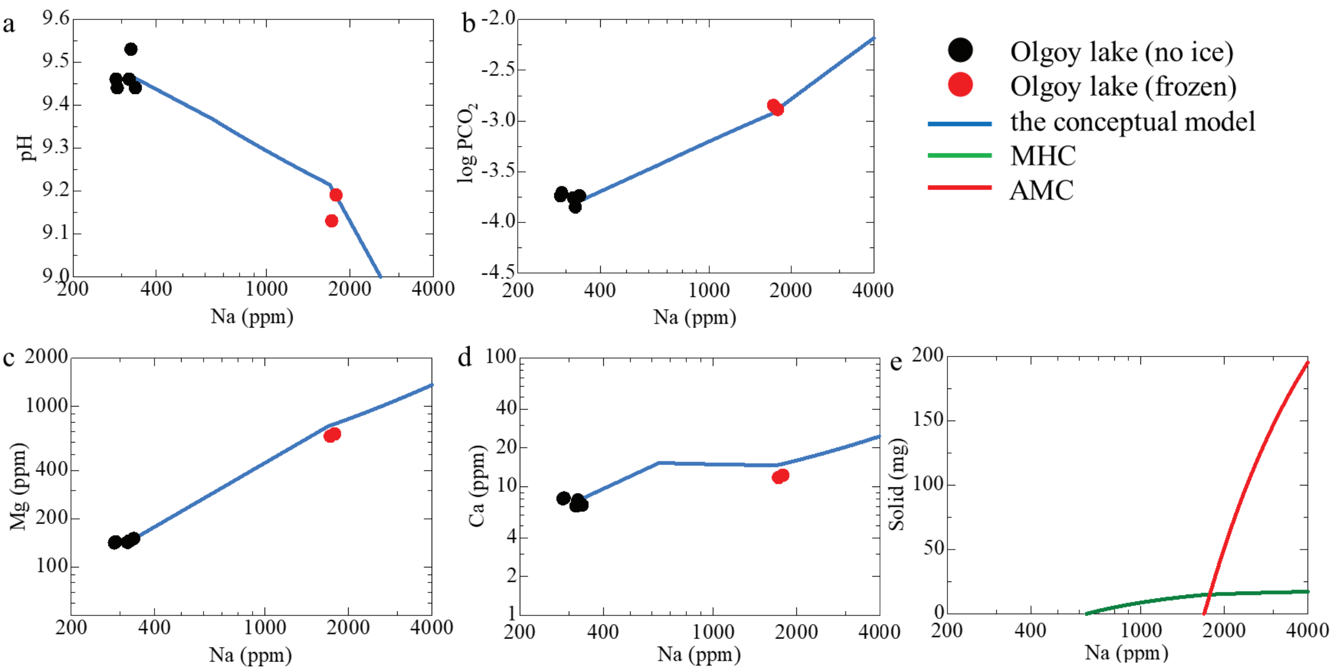

Figure 4

Chemical model of water chemistry changes associated with freezing in Olgoy lake. CO_2 partial pressure increased and pH decreased with lake water enrichment. In addition, MHC precipitates first, followed by AMC. It is harmonic with the measured values for Olgoy lake.

令和　５年　７月２７日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Evaluation of Magnesium Carbonate Formation in Freezing Alkaline Saline Lakes

(和訳) 凍結するアルカリ塩湖におけるマグネシウム炭酸塩の生成評価

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３．審査結果の要旨（600～650 字）

地球温暖化により、大陸内部湖沼の縮退と塩湖化が進行している。近年の観測研究からアルカリ性の塩湖では、大気の CO_2 を吸収する事例が報告された。アルカリ塩湖の多くは大陸内部の寒冷・乾燥地域に分布しており、これらの地域の塩湖は年間のおよそ半分は凍結している。一方、凍結条件が CO_2 の動態に及ぼす影響はよくわかっていなかった。北島氏は塩湖にみられる CO_2 の動態にはアルカリ塩湖に生成する含水炭酸塩鉱物が重要な役割を果たすと考え、低温条件における非晶質マグネシウム炭酸塩(AMC)の生成過程に関する研究を行った。湖水からの鉱物生成を理解するためには、その鉱物の溶解度の理解が必須であるが、これまで AMC の低温条件における溶解度は報告されていなかった。そこで北島氏は、室内実験により低温下における AMC の溶解度の精密測定を行い、AMC の溶解度に及ぼす温度依存性を世界で初めて明らかにした。次に北島氏は夏季および結氷期においてモンゴル・アルカリ塩湖の水質調査を行った。その結果、結氷期の湖水は夏季に比べ pH が減少し、湖水中の CO_2 分圧は大気分圧を大幅に超えるほど増加することを見出した。北島氏は実験的に見積もった AMC の溶解度を用いた地球化学モデリングを行い、冬季において観測される湖水の pH 減少と CO_2 の増加は、結氷に伴う炭酸塩鉱物の生成反応により生じることを明らかにした。この結果は、アルカリ塩湖では生物活動によらず結氷プロセスにおいて湖内に CO_2 が蓄積され、雪融け期にパルス的な放出をもたらす可能性を示唆している。アルカリ塩湖の冬季における CO_2 動態を明らかにした本研究は、地球表層における炭素循環の理解に資することが大であり、博士（理学）に十分値すると判断される。

４．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　博　士（理学）