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Creation of Soils by Humic Substances and CO_2 for Space Agriculture

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Abstract: In the present research, we investigated that soil created from Ca-plagioclase (source from Crystal Bay) by geochemical weathering with non-living natural humic substances (humic acid extracted by Canadian peat moss) and nano-bubble aqueous solution of CO_2 gas. The CO_2 bubble solution was adjusted to pH 3.4 (calculated concentration: 320 mmol-CO_2/L) with nano-size bubble. Production of soils were accomplished by the addition of 0.1 g of Ca-plagioclase, 0.0~0.2 g of humic acid and 20 mL of CO_2 bubble water in the 25 mL of high-pressure Teflon reactor under 293 or 473 K (autogenous pressure 0.02 or 1.62 MPa). After reaction, these metal elements released from Ca-plagioclase were useful in assessment of soil formation. As the result, four metal ions composed in Ca-plagioclase were slightly soluble by the addition of humic acid but freely soluble by the addition of humic acid and CO_2 gas in combination. In addition, the increasing reaction temperature was characterized by a marked difference in this dissolution tendency of Ca-plagioclase. Consequently, terrestrial humic materials including fulvic acid can not only accelerate to dissolute elements and synthesize clay form from Lunar and Martian regolith with chemical weathering but also control to buffer for nutrient, toxic element and CO_2 gas. And the derived water-soluble humic materials with CO_2 and its complex with metals bring the expected results to accelerate for physiological activities of root growth in higher plants and chlorophyll production in phytoplankton for space agriculture.

Key Words: Chemical weathering, CO_2 nano-bubble, Humic substances, Soil, Space agriculture

1. Introduction

Scope for manned space activities is widely discussed among space faring nations as one of the important features in post-International Space Station era. There seems to be a consensus that human presence is necessary to expedite Moon and explore to Mars for purpose of clarifying the birth and origin of life. The goal of space agriculture is to create and maintain optimum living environment on extraterrestrial planet for human and other living organisms, including animal, plant and microorganism to live comfortably. Although new philosophy suggests that the hyperthermophilic aerobic composting bacterial ecology utilize to create soil from human and animal waste and inedible biomass, an exploration of astrobiology may be complicated in case living bacteria administer irresponsibility. But then the global climate change of our living earth is accelerating by human activities involving land-use management. Despite great progress in overall agricultural productivity in recent decades, land degradation has reduced the productive capacity of soils on nearly 40% of the world's agricultural land. On oneself, today's people lost readily soil resource created fortuitously by ancient microbes. Consequently, we may be difficult to sustainedly control the chemical and biochemical reaction in biosphere before creating "good soil" on the Earth and Moon.

We investigated that soil created from Ca-plagioclase by geochemical weathering with non-living natural humic substances and nano-bubble aqueous solution of CO_2 gas. The concept of our research suggested not only an application for space agriculture by terrestrial desert technologies but also a feedback to clarify the origin of desertification on the earth.

2. Experimental Methods

2.1. Soil materials

We employed Ca-plagioclase from Crystal bay, Minnesota, with An76 ($Ca_{0.78}Na_{0.23}Al_{1.73}Si_{2.23}O_8$), which is in between lunar mineral regolithes and Martian ones. After smash, the powdered Ca-plagioclase through a sieve less than 75 μm in diameter, and its relative surface area was 1.75 m^2/g. The used humic acid in this experiment was extracted from Canadian peat moss in accordance with the standard method of International Humic Substance Society. This humic material had average molecular weight of 60,000 g/mol, and $C_{2450}H_{3000}N_{86}O_{1650}$ as chemical formula. The nano-bubble aqueous solution of CO_2 gas was prepared by nano/micro bubble generator with pressure type (Aura Tec Co., Japan). The formed solution was pH 3.4, which is equivalent to 320 mmol-CO_2/L, with void ratio of 0.15% and bubble diameter of 340 nm.

2.2. Hydrothermal reaction and analysis

The 0.1 g of Ca-plagioclase and 20 mL of water with/without CO_2 bubble added into high-pressure gas vessel with 25 mL. The each 0.0, 0.1, and 0.2 g of humic acid

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added to those reaction systems, and reacted at 293 or 473 K for 24 h. Each self-begotten pressures in vessel were comparable to 0.02 or 1.62 MPa.

After predetermined time, these reaction solutions were refreshed immediately to 293 K and separated into solid-liquid by centrifuge. Each supernatant liquids were measured for pH, metal ions (Na, Ca, Al, and Si) by atomic absorption spectrophotometer, and dissolved organic C (DOC) by total organic carbon analyzer.

3. Results and Discussion

3.1. Dissolution reaction of Ca-plagioclase by humic acid and CO_2 bubble

The concentration changes of Si and DOC with reaction time under 293 and 473 K show in **Figure 1** (a) and (b), respectively.

As estimation of process of Si concentration in reaction solution, the carbonated bubble water was accelerated to dissolute Ca-plagioclase under 293 K in comparison with water (reaction route ① in **Fig. 2**). Moreover it was confirmed to dissolute Ca-plagioclase by H^+ ion dissociated from humic acid (route ②). With raise in temperature, dissolution rates of all reaction system were accelerated, the combinational effect of humic acid and carbonated bubble water became prominent (route ④). The process of DOC concentration in Figure 1 (b) leads to a further understanding of this advantageous effect, humic acid was slightly soluble under 293 K but freely soluble to 1/4 ~ 1/3 of DOC in initial added humic acid under 473 K. So, it has a guess that water-solubilization of humic acid was accelerated by hydrothermal decomposition and carboxylation with CO_2 gas and metal cation (M^+) eluviated from Ca-plagioclase (route ③). As mentioned above, the H^+ ion was sequentially generated in reaction system with exchanging between H^+ in acidic functional groups of water-soluble humic acid and M^+, and the chemical weathering made further progress to create soil (organo-clay complex, aggregation, route ⑤).

At a carboxylic concentration of 0.01 mol-COOH/L in acid solution under 293 K, the relative effectiveness of these ligands on promoting dissolution rate of Ca-plagioclase was humic acid (2.0 nmol/m^2/s) with the standard of Si element. This value was only little lower than oxalic (14 nmol/m^2/s), lactic (9.0), garlic (7.8) and fulvic (5.7) acid however dramatically increased to 10.5 by a combination of humic acid and carbonate bubble solution. The strengths of organic acids to promote dissolution is related to the initial p*K*a 2.58 (oxalic), 3.52 (lactic), 4.37 (garlic) and 4.16 (fulvic or water-soluble humic), respectively, but it is related to strength of Ca-ligand complex formed in solution (formation of secondary mineral; clay) or on the mineral surface (development of soil

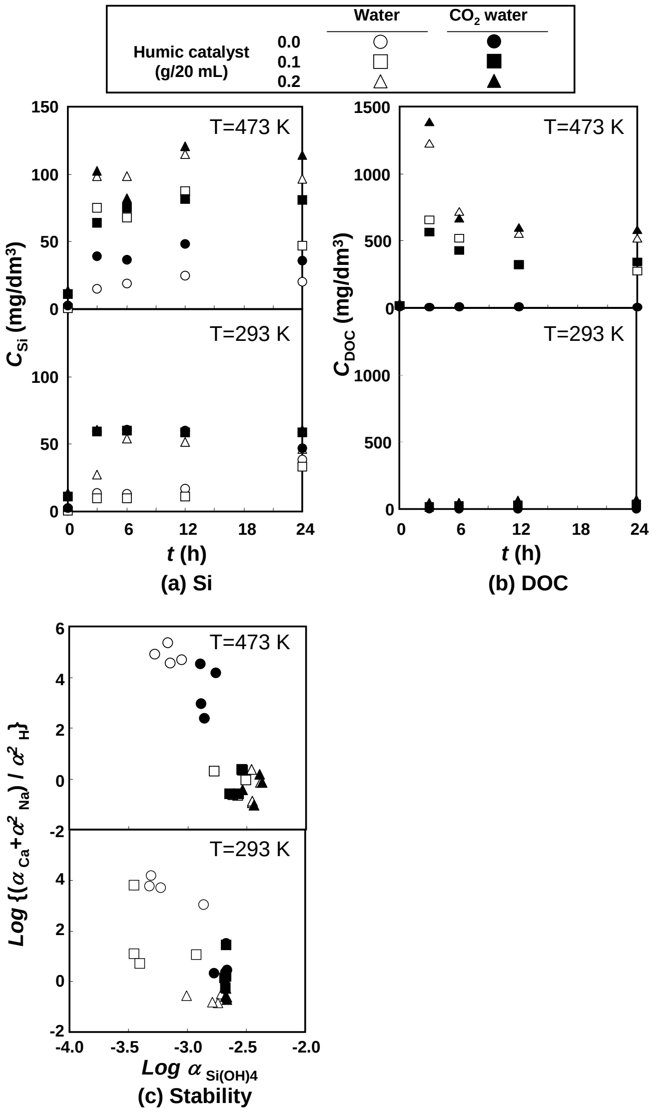

Fig. 1. Time dependence of Si dissolved from Ca-plagioclase and DOC by humic acid and carbonated bubble water under 293 or 473 K. Estimation of stability in mineral solutes on a basis of dissolution equilibrium with acid.

aggregation). Formation of clay minerals is expected after adjusting condition of pH and Al/Si ratios to bring them in the stability field of clay minerals.

As estimation about temperature dependence of dissolution rate of Ca-plagioclase by the Arrhenius equation, the addition of humic acid caused frequency factor and activation energy to increase. In contrast, the carbonate bubble solution was substantially reduced activation energy of reaction between Ca-plagioclase and humic acid, therefore acted as catalyst for this reaction.

3.2 Estimation of stability in mineral solutes on a basis of dissolution equilibrium with acid

The stability of secondary mineral from mineral solutes as the mentioned in 3.1 organized on the Ca-plagioclase, Ca-montmorillonite, kaolinite, and gibbsite of dissolution

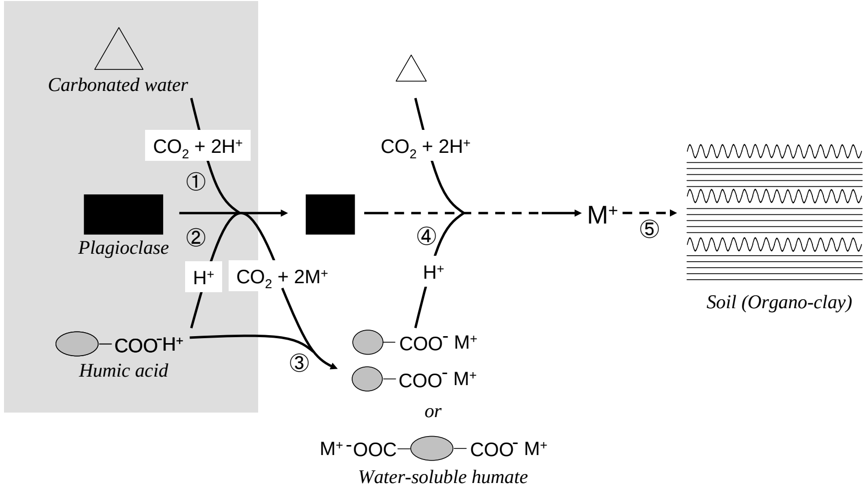

Fig. 2. Reaction mechanism of Ca-plagioclase, humic acid, and carbonate bubble water to soil.

equilibrium with acid. This means the generation of gibbsite has an advantage in the event that *Log* $\alpha_{Si(OH)4}$ value lower, and the generation of clay with layer silicate (i.e. montmorillonite, kaolinite) in the event that both values of *Log* $\alpha_{Si(OH)4}$ and *Log* $\{(\alpha_{Ca}+\alpha^2_{Na})/\alpha^2_H\}$ higher. From the result in Figure 1 (c), the addition of humic acid significantly increased *Log* $\alpha_{Si(OH)4}$ value but decreased *Log* $\{(\alpha_{Ca}+\alpha^2_{Na})/\alpha^2_H\}$ value. In comparison with 293 K, both values were increased by a combination of humic acid and carbonate bubble solution under 473 K, especially the stabilization of clay formation was expected.

4. Point of Soil Creation by Humic Substances for Space Agriculture

Wada *et al*. (2009) examined the possibility of space agriculture, for which air, water and regolith are brought into a pressurized dome at the first stage. At the second stage, they plan to revitalize air and water, in addition to supplying ordinary agricultural products such as foods, fibers and timber. Recycled use of materials is a major function of agriculture on Moon and Mars. Space agriculture is also characterized by limited species in the ecosystem, contained inside a small dome.

Because the main target of lunar and Martian exploration is astrobiology research to search for extraterrestrial life or biotic substances, Wada *et al.* (2008) pointed out that physical isolation barriers or a minimum distance should be secured between the site of scientific exploration and the dwelling site. Since it is important to keep microorganisms within a small space in the dome, we should not use microorganisms to make agricultural soils in the dome. Organic matter contributes to many important functions of the soil, to form and maintain suitable aggregate sizes in the fine regolith, and to store nutrients (bio-elements), especially Wada *et al.* (2009) pointed out that storage of the nutrients in organic matter can be achieved by applying compost and excreta of animals.

The important functions of microorganisms inhabiting the soil on the earth, are decomposition of various organic waste, release of nutrients stored in the organic matter, nitrification, and N-fixation. Wada *et al.* (2009) proposed to use peat moss with the desired microorganisms to endow the soils with these functions, but it is to be avoided to rely upon microorganisms by the above reasons. Desalinization and neutralization are required to grow plants in lunar and Martian soil. These soils usually contain water-soluble salts. Removal of the water-soluble salts can be achieved by leaching the salt-rich soil with non-saline water. Common plants are damaged by soil with too low or too high pH. The pH of the soil should be adjusted for both too acidic and too alkaline soils. Improvement of physical properties of soil is also difficult if we do not know where we are going to live on Moon and Mars.

There seems to be a consensus that human presence is necessary to explore Moon and Mars for the purpose of clarifying the origin of life. Microorganisms should not be used for this goal. The goal of space agriculture is to create and maintain optimum living environment on extraterrestrial planet for human life. Although some scientists promoting an idea to utilize ecological system of the hyperthermophilic aerobic composting bacteria for producing soil from human and animal waste and inedible biomass, astrobiological exploration of Moon and Mars may encounter problems for detecting signs of life on Moon and Mars if living terrestrial bacteria were introduced to Moon and Mars. Yazawa *et al.* (2009) are also trying to introduce vegetables to support our life on Moon and Mars, which have been evolved on soils and atmosphere of the earth for billions of years. We have to produce soils from Martian rocks for terrestrial vegetables keeping microorganisms as small as possible.

This section has been designed to determine if it is possible to grow plants that will provide a significant portion of the

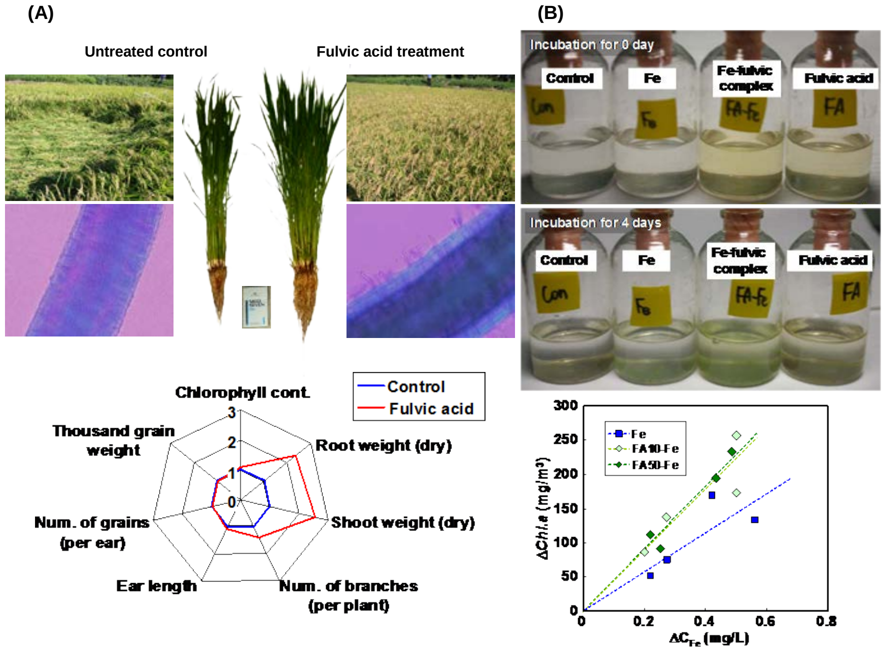

Fig. 3. Influence of fulvic acid or its iron complex on physiological activities of rice plant (A) and sea phytoplankton (B) under solar energy (Yazawa *et al.*, 2009).

NASA-defined human nutritional requirements utilizing lunar and Martian regolith as the growing medium. Photosynthetic plants require N, P, K, Ca, Mg and S in considerable quantities and Fe, Mn, Zn, Cu, B and Mo in trace quantities. The lunar and Martian regolith contains P, Ca, Mg, S, Fe, Zn, Cu and Mo in sufficient quantities.

Other elements provide special concern due to the specific nature of the lunar and Martian regolith. Aluminum is present in a smaller concentration than is common in earth soils, but due to the acidic conditions on Moon and Mars, it may be a toxic level for plants. In soil solution culture experiments, Yazawa *et al*. (2000) found that addition of humified natural organic matter reduced the amount of monomeric Al present in solution and alleviated the toxic effect of Al on root growth of wheat under acidic condition. Consequently, terrestrial humic matters including fulvic acid can not only control to buffer for nutrient and toxic element but also accelerate to dissolute elements and synthesize clay from Martian regolith with chemical weathering.

Fulvic acid and its complex with iron had a strong accelerative for physiological activities of root growth in rice and chlorophyll production in phytoplankton (**Fig. 3**). Confirmation of dissolution of the main rock-forming silicates by fulvic acid will give us better understanding of the basic process of weathering in nature on the earth, as well as of application for lunar and Martian agriculture (Yazawa and Takeda, 2008).

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