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Estimate of secular change in seawater salinity through Earth history

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THESIS OUTLINE

Chapter 1: General introduction and overview

The birth of ocean and its history of chemical evolution must have been one of the most critical factors to unravel the origin and evolution of life on the Earth. However, this topic has not fully understood yet, because of methodological problems including samples to be analyzed. Here, the author tried to reveal secular change in oceanic chemical evolution by introducing the systematic analysis of fluid inclusions of hydrothermal quartz veins originated at mid-oceanic ridges which cover the Earth history from 3.5 Ga to 600Ma. The result showed there were 2 big changes in salinity through the time. Comparing to the modern value of 565 CI mmol/kg in the Phanerozoic time, the salinity in the Archean was more than 1500 mml/kg, which was ca. 3 times higher than the modern value. This result is consistent with previous works by Foriel et al. (2004) for 3.5Ga North Pole region in the Western Australia.

Salinity of the Hadean ocean remains still unknown because there is no Hadean rocks on the Earth except for zircon fragments. To estimate the salinity in Hadean ocean, the author calculated the salinity from the meteorites of enstatite chondrite and carbonaceous chondrite. Although it is highly depending on the model, the salinity of Hadean primordial ocean seems to be ca 30 times more saline, compared to that in the modern ocean.

Also, the primordial ocean must be too toxic to bear and evolve life. To remove salinity, salts in seawater have to be fixed as evaporite. During the Hadean time, huge landmass was inevitably effecting the surface environment. On the other hand, surface records of the Archean Earth clearly show the absence of huge landmass. Instead, numbers of intra-oceanic island arcs were scattered, and their summits were above the sea-level. The appearance of embryonal continents began since 2.6Ga, and the first supercontinent called Nuna emerged at 1.8-1.9Ga, but the surface area of Nuna was still ca. 40% of present landmass. Extensive formation of evaporites have began since the onset of Phanerozoic time at ca. 600Ma. This suggests the rapid drop of salinity must have occurred during the Neoproterozoic, ca. 0.8-0.6Ga because of the appearance of supercontinent called Rodinia and its breakup. Minor evaporite ore has also been reported in the 1.9-1.8Ga in supercontinent Nuna (Evans, 2006), which may suggest considerable decrease of salinity since then, although no direct measurement yet.

To summarize the data on salinity, three-step model of salinity is proposed in this thesis. In Hadean Earth, high salinity is expected, however, first rapid decrease happened in the end of Hadean. Salinity level seems to have some fluctuation between the end of Hadean until the onset of Phanerozoic, but in proposed three-step model, this period is thought to maintain a certain level of salinity. And second rapid decrease was in Late Proterozoic. Evaporites is trapped and enclosed by sediments on the surface of continents like the case of the modern Western Mediterranean Sea which would finally subduct into deep mantle together with continents and/or by tectonic erosion at consuming plate boundary. Through such process, salinity settle down to current level.

CHAPTER 2: Accreted Kula plate fragment at 94 Ma in the Yokonami-Melange, Shimanto-Belt, Shikoku, Japan

To estimate the secular change in the whole seawater composition, it is necessary to collect mid-oceanic ridge basalt (MORB) with quartz veins containing hydrothermal fluid inclusions, because part of past seawater remains as such fluid inclusions in it which indicate previous salinity as the average of whole ocean of the Earth. To establish the use of a technique of accretionary complex geology, the Cretaceous Shimanto belt in Japan was chosen.

The Cretaceous Shimanto belt that is distributed along the Pacific side of southwest Japan contains one of the best records of accretionary processes and history of oceanic plate subduction in the circum-Pacific region. Yokonami melange, Shimanto belt, Shikoku, SW Japan is composed of pillowed basalt that erupted in the equatorial region, about 200m-thick bedded radiolarian chert sequence that contains radiolarians with age determinations spanning c.a. 135 Ma (Upper Valanginian) to 93.9 Ma (Cenomanian), younging southward with repetition, and alternated sandstone and mudstone. Although the chronology of the bedded chert sequence is well studied using the radiolarian, the chronology of the clastic units was not reported sufficiently. We performed a detailed geologic mapping investigation of rock outcrops along the Goshiki-no-Hama Coast, the Yokonami melange. We have determined U-Pb ages of zircon grains extracted from tuffs and sandstones to determine the depositional age of the turbidite and hemipelagic units. The youngest depositional age of these clastic sediments is interpreted to be the arrival time at the trench. We reconstructed the ocean plate stratigraphy with our new chronological data, which includes mid-oceanic basalt, bedded chert, hemipelagic sediments, and trench-turbidite deposits. We recognize the turbidite sequence has been repeated by layer-parallel thrust in the study area. We have delineated the travel trajectory of the oceanic lithosphere based on (1) the relative plate motion model of the Paleo-Pacific Ocean, (2) the arrival time of the subducted lithosphere at the trench (94.32 Ma), and (3) paleomagnetic measurement of the basalt and turbidite. The trajectory suggests that the MORB in the Goshiki-no-Hama Coast, Yokonami melange, erupted at the Kula-Pacific Ridge in the Paleo-Pacific Ocean, traveled northward, and eventually arrived at the continental margin of East Asia at 94.32 Ma.

CHAPTER 3: Geochemistry of accreted metavolcanic rocks from the Monian Supergroup of Anglesey-Llyne, NE Wales, U.K.

Accretionary complex geology is powerful tool to identify MORB and its formation age which is written in the Chapter 2. In some cases accretionary complex contains mixture of fragments of oceanic crusts, so that it keep ocean island basalt (OIB) as well as mid-oceanic ridge basalt (MORB). OIB should be eliminated when analysis of salinity is conducted. This study is to establish theory to eliminate samples derived from OIB from accretionary complex.

The Gwna Group in the Anglesey-Lleyn region, NW Wales, UK, includes a typical accretionary complex that consists of tectonically mixed oceanic materials; metabasalt, bedded cherts, red claystone, and trench turbidites. In order to distinguish the types of basalt, we identified mineral assemblage of the basalts under microscope. The microscopic observations demonstrate that some basalts preserve original igneous minerals such as olivine and clinopyroxene, but the other suffered from hydrothermal alteration at seafloor and regional metamorphism up to greenschist facies and later oxidation at the surface. Therefore, immobile elements such as Al_2O_3 and TiO_2, REE and HSFE are appropriate for the discussion of origin of basalts in the Gwna Group. We determined major and trace elemental compositions using fused glass and pellet samples prepared from the basalts. Chemical compositions of some basalts are plotted on MORB domain in discrimination diagrams, which is consistent with previous works. However, other basalts are plotted on WPB domain and show light REE-enriched pattern. Taking their occurrences into consideration, we interpret that these basalts erupted at ancient oceanic island. OIB is usually included in the Phanerozoic accretionary complex, and this study is the first report providing the evidence of OIB in Neoproterozoic accretionary complex. Fluid inclusions are trapped in hydrothermal minerals within OIB, however it does not reflect original salinity of seawater when fluid is trapped. Therefore, such samples are not appropriate for analysis of salinity.

Chapter 4:Fluid inclusion geochemistry of the 2.2 Ga Ongeluk Formation, South Africa

To establish a method to estimate ancient seawater compositions from fluid inclusions preserved in subseafloor hydrothermal quartz deposits, we investigated the fluid inclusions in hydrothermal quartz preserved in the 2.2 Ga Ongeluk Formation, Kaapvaal Craton, South Africa, as a case study. The Ongeluk Formation consists mainly of submarine volcanics (pillow lavas and sheet flows) of basaltic andesites, which is wedged between the underlying and overlying glaciogenic deposits (Makganyene diamictite and a dropstone layer at the base of the Hotazel Formation, respectively). This geological occurrence of the Ongeluk Formation indicates that the Ongeluk volcanism took place in the period of the global glaciation. Such Ongeluk volcanic rocks retain subseafloor hydrothermal quartz deposits in their drainage cavities and interpillow voids. The hydrothermal quartz contains many primary and secondary liquid-vapor fluid inclusions as well as inclusions that are not diagnosed as primary nor secondary inclusions, which were petrographically classified and analyzed individually with microthermometry and PIXE methods. The results show that the primary fluid inclusions were highly saline while the secondary fluid inclusions have relatively lower salinity. The fluid inclusions that were not petrologically categorized into primary nor secondary inclusions have a wide range of salinity enclosing the salinities of the primary and secondary fluid inclusions. Among such various salinities of fluid inclusions, a negative correlation between NaCl and $CaCl_2$ concentrations was identified for the high-salinity fluid inclusions. Considering that the primary fluid inclusions have only high salinity whereas such high salinity was not observed in the secondary fluid inclusions, the high-salinity fluid inclusions with the $NaCl/CaCl_2$ negative correlation are considered as subseafloor fluids at the time of the Ongeluk hydrothermal circulation. The $NaCl/CaCl_2$ negative correlation can be explained by a mixing between Na-rich seawater and Ca-rich hydrothermal fluid derived from albitization of the host basaltic andesites, in which Na is removed from the fluids into host rocks while Ca is released from the host rocks into the fluids. Accordingly, the high-salinity Na-rich endmember is considered as the 2.2 Ga seawater composition. This estimated seawater composition has approximately six times higher salinity than the modern entity. The estimated salinity is higher than a previous estimate for the early seawater based on total amounts of the extant continental salt deposits and saline ground water, which is deemed as the minimum salinity of seawater before the formation of a certain volume of continents. Furthermore, the 2.2 Ga seawater salinity estimated in this study is three times the previous salinity estimate from the fluid inclusions in the quartz samples collected from the same locality. This discrepancy is obviously derived from the misclassification that all fluid inclusions not fulfilling a clear petrographic criterion of "primary" were classified in to primary fluid inclusions in the previous work. Therefore, this study revealed that a combination of detailed petrographic classification and analysis of individual fluid inclusion is necessary to find out ancient subseafloor seawater/hydrothermal fluids from fluid inclusions in hydrothermal quartz.

Chapter 5: Ar-Ar dating by fluid inclusions in hydrothermally precipitated quartz

Fluid inclusions separated from quartz veins were dated by Ar-Ar methods. In this study, four samples were prepared. Two samples, GU103a and GU103b, gave the values of 1952 ± 279Ma and 1967.32 ± 63.73 Ma Ar-Ar isochron ages, respectively. Ar-Ar plateau ages were 2063.86±34.56Ma and 1967.11±25.82Ma, respectively. The other two samples were also dated in the same manner as well, but failed to obtain a tight line of isochron with diffused age because of a large error bars.

The result indicated Ar-Ar age is ca.100-200 m.y. younger than the expected result from Pb-Pb age, 2222±12Ma (whole rock sochron age) derived from well-established stratigraphy of the Transvaal Supergroup, South Africa, where the Ongeluk Formation is a member of the Postmasburg Group that belongs to the middle horizon of the Transvaal Supergroup. This is because fluid inclusions analyzed in this work is thought to be re-equilibrated at 1.97Ga by granite intrusion at called Olifantshook event. In other words, the age of generation of fluid inclusions were reset at that time.

Although secondary effect must be carefully examined to determine the age of samples, however it can be concluded that the method is useful and being excellent tool as dating method.

CHAPTER 6: Salinity of Seawater from Archean to Present

Mid oceanic-ridge metamorphism produces abundant hydrothermal quartz veins where a series of fluid inclusions are trapped. Salinity was obtained from measurement of those vein inclusions from different host rocks, pillowed basalts, sheeted dikes and gabbros in descending order of oceanic crust with ascending order of mid-oceanic ridge metamorphism which changes systematically. The salinity depends on volatilization of circulating fluids. Higher saline fluids tend to be trapped in the higher grade quartz in gabbro layers, after it was boiled, while lower saline fluids are trapped in basalt at shallower crust. Hence the most appropriate fluid inclusions to unravel past seawater salinity are from topmost pillow lava flows, and fluid temperature must be below 200℃.

Based on this method, the author collected a series of pillow lava flow resting on the accreted oceanic crusts of 3.5Ga, 3.3-3.0Ga, 2.6-2.5Ga, 2.3-2.2Ga, 0.65Ga, and 0.5Ga to measure salinity of ocean. In addition, methods to separate available fluid inclusion in previous works and their results were also reviewed to delineate the evolutional curve of salinity through time.

The obtained curve to show the secular change in salinity indicates that it was ca.5 times more salty since the onset of Archean. Although the details are not well-known, rapid drop of salinity could have occurred in Neoproterozoic, because of the sudden emergence of huge landmass by return-flow of seawater into mantle.

Chapter 7: Estimation of Secular Change in Seawater Salinity through Earth’s History from Hadean to Present

Cl-abundance in the Hadean primordial ocean was estimated. If the Earth-Moon system was made from enstatite chondrites at 4.56Ga, a 35km thick anorthosite-KREEP basalt complex must be covered by Cl-bearing minerals such as lawrencite, sodalite, chlorapatite, and sylvite as solid phases in the crust. When the heavy bombardment occurred at 4.4Ga which delivered components for primordial atmosphere and ocean, those Cl-bearing minerals were moved into ocean to make its salinity extremely high, ca. 15 times more than today (565 mmol/kg). At the same time, extremely low pH was affected by primordial sulfur compounds which was formed during the consolidation of magma ocean by 4.53Ga.

Evolution of seawater salinity is summarized as follows; salinity of primary ocean was ca. 15 times more than today, decreased down to 3 times at the onset of Archean, then gradually decreased down to three times at around 3.0Ga followed by rising up again 5 times through Proterozoic, and finally dropped to the present level in the Phanerozoic. The mechanism to drop salinity during the Neoproterozoic was the buried evaporite ores on continents, but the similar decrease during the Hadean time could be extensive tectonic erosion of enclosed evaporite masses within Primordial continents of anorthosite, suggesting the distribution of localized masses in the present mantle.

Cl contents in CI chondrites delivered by second bombardments (dominated by CI chondrites) was only 180 mmol/kg, and did not cause any considerable change in Cl contents of primordial ocean.

It should be mentioned that considerable amount of Cl entered into metallic core when the Earth was formed through collision-accretion of planetesimals up to the final Giant Impact stage.

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