Hydrothermal silicification of mafic and ultramafic rocks in the Barberton Greenstone Belt, South Africa: Relationship between bioessential element influxes into the seawater and secular variation of atmospheric CO_2 contents

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The presence and composition of liquid water on the earth’s surface through geologic time are essential to sustain biological system. Therefore, it is important to understand the chemical evolution of elemental cycles of an oceanic environment. Especially, it is necessary to understand ocean floor alteration of oceanic crusts because they supply bioessential elements into the ocean, but the quantitative estimates still lack for the Archean hydrothermal systems.
We analyzed major and trace element contents of the silicified, carbonated and metamorphosed (non-silicified/non-carbonated) volcanic rocks, including sixty-five basalts and seventy-three peridotitic and basaltic komatiites and sixteen overlying cherts in the Komati and Hooggenoeg formations in the Onverwacht Group of the Mesoarchean Barberton Greenstone Belt, South Africa. Some of the basalt and komatiites underwent severe hydrothermal silicification and carbonation as well as hydrothermal metamorphism up to the amphibolite facies condition. The silicified peridotitic komatiites are more enriched in SiO_2, Rb, Ba and U contents and depleted in FeO^{tot}, MgO, CaO, transition elements such as Ni and Co, and Sr contents than the non-silicified/carbonated basalts and peridotitic komatiites. The carbonated basalts and peridotitic komatiites are enriched in CaO, Rb, Ba, U and Sr, and depleted in FeO^{tot}, MgO, and the transition element contents.
The chemical contrast indicates that Co and Ni are significantly released from the peridotitic komatiites due to the silicification and carbonation. We performed petrographic and petrological study of the peridotitic komatiites to understand the petrological cause. The non-silicified/non-carbonated peridotitic komatiites commonly contain olivine and serpentine, but the silicified and carbonate rocks contain quartz, potassium-rich white micas and carbonate minerals, replacing the magmatic minerals. The silicate minerals such as the serpentine and olivine can host the transitional metals such as Co and Ni, but the alteration minerals such as quartz, potassium-rich white micas and carbonate minerals cannot contain the transition elements compared with the serpentine and olivine. The disappearance of the serpentine and olivine due to the silicification and carbonation caused decrease of Co and Ni contents of altered peridotitic komatiites, namely supply of the transition elements into the seawater.
Previous study suggested that the basalts under the sedimentary cherts underwent silicification but avoided carbonation, whereas the basalts under the silicification zone suffered from only the carbonation. However, our geological mapping showed that the upper part of the basalt (komatiite) unit suffered from both silicification and carbonation. In addition, disseminated carbonate minerals are replaced by quartz in some partially silicified rocks. The evidence indicates that the carbonation was followed by the silicification because of change of pH condition of the hydrothermal fluid from alkaline to acidic conditions possibly due to mixing with acidic seawater. The change of pH condition caused that the carbonate minerals were dissolved and replaced by silica minerals.
The carbonation of ocean floor basalts was caused by high atmospheric CO_2 contents and ceased due to its decrease around 2.7 Ga. On the other hand, Ni and Co contents of banded iron formation indicate that Ni and Co contents of seawater also decreased around 2.7 Ga. Previous work suggested that the decrease of Ni contents was due to decrease of komatiitic volcanic activity in the Late Archean. But, it is well known

that the komatiite occurred at least until 1.9 Ga. This study proposes that the decrease of the marine Ni and Co contents was not due to disappearance of peridotitic komatiites but decrease of atmospheric CO_2 contents in the Late Archean because the silicification and/or carbonation are necessary to supply Ni and Co from oceanic crust to seawater.

Keywords: Archean silicification, marine transition element content, bioessential element, komatiite, secular change of seawater composition

