

Hydrothermal alteration chemistry of Archean submarine volcanic rocks: evidence for a fully oxygenated atmosphere-ocean system since ~3.5 Ga. Hiroshi Ohmoto¹, David C. Bevacqua¹ and Yumiko Watanabe¹. ¹ Penn State Astrobiology Research Center & Department of Geosciences, The Pennsylvania State University, University Park, PA 16803, hqo@psu.edu.

Most submarine volcanic rocks, including basalts in diverging plate boundaries (e.g., MORB) and andesites/dacites in converging plate boundaries, have been altered by low-temperature seawater and/or hydrothermal fluids (up to ~400°C) under deep oceans. The hydrothermal fluids evolved from shallow/deep circulations of seawater through the underlying hot igneous rocks. Mixing of submarine hydrothermal fluids with local seawater formed volcanogenic massive sulfide deposits (VMSDs) and banded iron formations (BIFs). Therefore, the behaviors of various elements, especially of redox-sensitive elements, in VMSDs, BIFs, and altered submarine volcanic rocks can be used to decipher the chemical evolution of the oceans and atmosphere.

We have investigated the mineralogy and geochemistry of >100 samples of basalts from a 260m-long drill core section of Hole #1 of the Archean Biosphere Drilling Project (ABDP #1) in the Pilbara Craton, Western Australia. The core section is comprised of ~160 m thick Marble Bar Chert/Jasper Unit (3.46 Ga) and underlying, inter-bedded, and overlying submarine basalts. Losses/gains of 65 elements were quantitatively evaluated on the basis of their concentration ratios against the least mobile elements (Ti, Zr and Nb). We have recognized that mineralogical and geochemical characteristics of many of these samples are essentially the same as those of hydrothermally-altered modern submarine basalts and also those of altered volcanic rocks that underlie Phanerozoic VMSDs. The similarities include, but are not restricted to: (1) the alteration mineralogy (chlorite ± sericite ± pyrophyllite ± carbonates ± hematite ± pyrite ± rutile); (2) the depletions/enrichments of S; (3) the characteristics of whole-rock $\delta^{18}\text{O}$ and sulfide $\delta^{34}\text{S}$ values; (4) the ranges of depletions and enrichments of Si, Al, Mg, Ca, K, Na, Fe, Mn, and P; (5) the enrichments of Ba (as sulfate); (6) the increases in $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, depletions of FeO, and enrichments of Fe_2O_3 ; (7) the enrichments of U; (8) the depletions and enrichments of Cr; and (9) the negative Ce anomalies. Literature data on other submarine volcanic rocks in Pilbara, Australia (~3.5 Ga to ~3.2 Ga in age) and the ~2.9 – 2.7 Ga submarine volcanic rocks in Ontario, Canada indicate that many of these rocks exhibit the same characteristics (1) – (9). Characteristics (5) was probably caused by the mixing of Ba-rich hydrothermal fluids and SO_4^{2-} -rich seawater; (6) and the abundance of hematite by reactions between ferrous-rich hydrothermal fluids (and/or minerals) and O_2 -rich seawater and also by reactions be-

tween ferrous-rich minerals and SO_4^{2-} -rich seawater; (7) by reactions between U-rich seawater and goethite/hematite; (8) by leaching of Cr from rocks by O_2 -rich seawater; and (9) by reactions with Ce-depleted oxidized seawater.

These data suggest that the chemistry of ocean water, including the concentrations of major elements and many redox-sensitive elements/compounds (e.g., U, Ce, SO_4^{2-} , and O_2), has been basically the same since at least ~3.5 Ga, except for the higher ΣCO_2 contents in Archean oceans. O_2 contents of deep (>200 m) oceans would become zero when the atmospheric $p\text{O}_2$ decreased to less than ~50% of the present level. Therefore, geochemical data on the Archean submarine volcanic rocks further suggest that the atmospheric $p\text{O}_2$ level, the fluxes of bio-essential elements to the oceans (e.g., K, PO_4^{3-} , NO_3^- , Ba, Mo, W), and the biological productivity in the oceans, have been basically the same since at least ~3.5 Ga.