Discovery of Ni-Fe phosphides in 3.46 Ga-old Apex basalt from Western Australia

*塚本 雄也[1]、掛川 武[1]、グラハム ウーシー[2]、リュウ ジークイ[3]、大本 洋[4]
*Yuya Tsukamoto[1], Takeshi Kakegawa[1], Uschi Graham[2], Zi-Kui Liu[3], Hiroshi Ohmoto[4]

1. 東北大学理学研究科地学専攻、2. ケンタッキー大学、3. ペンシルヴァニア州立大学 材料工学科、4. ペンシルヴァニア州立大学地球科学科
1. Department of Earth Science,Tohoku University, 2. Department of Pharmaccutical Sciences, University of Kentucky, 3. Department of Material Science and Engineering, The Pennsylvania State University, 4. Department of Geosciences, The Pennsylvania State University

Phosphate ($P^{5+}O_4^{3-}$) is an essential constituent of nucleic acids. Today, phosphate for terrestrial and marine organisms has been supplied primarily by weathering of apatite in rocks. An important question for astrobiologists has been the source of phosphate in the Archean oceans. Pasek and Lauretta (2005) suggested that schreibersite ($(Fe, Ni)_3P$) in meteorite was the primary source of phosphate on the early Earth. However, no direct evidence of meteoritic schreibersite has been reported from any Archean-aged geologic formations.

We have discovered Ni-Fe phosphides in the 3.46 billion-year-old Apex Basalt at depth 214.4 m in the ABDP #1 drill core from the East Pilbara Craton, Western Australia. Spot analyses by FE-SEM/EDS indicate their compositions as Ni = 75.8 ±4.4, P = 10.8 ±1.0, and Fe = 2.4 ±0.9 wt%, or $Ni_{3.74\pm0.37}Fe_{0.13\pm0.05}P_{1.0}$. The (Ni+Fe)/P atomic ratio varies from 2.9 (±0.4) to 4.5 (± 0.4), indicating mixtures of nickel-rich schreibersite ($(Ni, Fe)_3P$) and nickel-rich melliniite ($(Ni, Fe)_4P$). They have much higher Ni/Fe atomic ratios (31±9.9) compared to typical meteoric schreibersite and melliniite (Ni/Fe = 0.17±0.01). The only other known occurrence of Fe-Ni phosphides in basalt is from the Tertiary basalt on Disko Island, Denmark. Whether they originated from meteorites or are products of assimilation of carbon-rich sediments by basalt magma has been debated. However, we can conclude that the Ni-Fe phosphides in the Apex Basalt most likely represent pieces of an asteroid body (>20 km in diameter) that impacted the Marble Bar area at 3.45 Ga for the following reasons: (1) the association with various meteoritic minerals, such as metallic iron, various alloys (Fe-Ni, Fe-Ni-Co-Cr, Fe-Ir, Cu-Al-Si, Au-Si, and C-Ca-Al-Fe-Si), coesite (high-pressure polymorph of SiO_2), and titanite and rutile with Ti^{3+} and Ti^{4+}; (2) the highly distorted lattice structures of the titanite crystals, which were most likely produced by a planetary collision; and (3) the association with impact spherules, shock metamorphic features in the underlying rocks, and tsunami deposits. Thermodynamic analyses of the meteoritic minerals suggest that the parental planetesimals of the Apex meteorite condensed from the Solar Nebula at fO_2 conditions more than 10 log units below the Fe/FeO buffer, compared to the parental planesimals of ordinary and carbonaceous chondrites, which condensed near or above the Fe/FeO buffer.

Our study suggests that the phosphorus delivery by asteroids/meteorites was important in the phosphorous cycle on the early Earth. However, this does not necessarily support the currently popular model for the origin of phosphates and life in the early oceans (e.g., Pasek, 2005), which speculates that meteoritic Fe-Ni phosphides (P^{3+}) were directly dissolved in the early oceans and subsequently oxidized to phosphates (P^{5+}) by H_2 loss. This is because the results of their experiments, which were performed under highly oxidizing conditions, may not be applicable to the pre-biotic world, which was supposedly highly reducing. Our finding of schreibersite in the basalts, which were highly altered by submarine hydrothermal fluids, suggests that schreibersite is not highly soluble in aqueous solutions.

Phosphorization to form macromolecules like RNA and DNA by reactions with Fe-Ni phosphides has not been demonstrated by researchers. Furthermore, H_2 loss from the oceans to the atmosphere would not have occurred under the presumed H_2-rich pre-biotic atmosphere.
Therefore, we must search for (an) alternative mechanism(s) to explain the transformation of the meteoric P^{3+} to phosphates (P^{5+}) via igneous processes, and the transfer of those igneous phosphates to the oceans.

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