Acid Character of Archean Ocean Waters Revealed by 3.3 Ga-old Ferruginous Chert Compositions, Western Australia

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Abstract : Comparative inspection of Archean ferruginous cherts with Phanerozoic cherts shows that the former precipitated from acid-water hydrothermally supplied during intensive early Precambrian volcanism. The pH of the water is inferred to have been around 4 where Al dissolves, and Ti and Zr do not. The peculiar geochemical environment seems to have been widespread in Archean to early Proterozoic greenstone basins when tremendous volume of banded iron formation (BIF) formed. This suggests that the acid seas were neutralized after the BIF deposition probably during the middle to late Proterozoic; this change of pH in sea water may have promoted the deposition of carbonate rocks.

Key words : Precambrian; banded iron formation; Archean acid sea; chert; Al2O3/TiO2 ratio in sediments.

Introduction. Evolution of ocean and atmosphere on the Earth has been extensively discussed. In particular, banded iron formation (BIF) regarded as chemical precipitates must be an important clue to the environment of atmosphere-ocean system in the Precambrian. Major studies of BIF in this field have been related to the evolution of atmospheric oxygen. We expect, however, that chemical features of the ancient ocean water are confined to chemical precipitates such as BIF, and we scrutinized Precambrian siliceous sediments on the basis of reliable data obtained by analyses of enhanced accuracy.

Samples. The Pilbara Block, Western Australia, is one of the most well-exposed Archean terrains on the Earth and contains non- to weakly-metamorphosed early Archean greenstone sequences. One hundred and sixteen samples were collected from two ferruginous chert outcrops (AB and AI in Fig. 1) near Point Samson and Goldsworthy, northwestern Pilbara Block. The chert beds exposed at outcrop AB are generally gray and some 150 m thick. The bed is an alternation of silica lamina and Fe-Si mixture one. They belong to the Cleaverville Formation (estimated to be 3.3 Ga old) of the Gorge Creek Group.1)

Chemical features of samples. X-ray fluorescence analyses show that the banded ferruginous chert is a nearly pure mixture of silica and iron oxides like common BIF. Their total iron content as Fe2O3 (expressed as Fe2O3*) ranges from 0.1 to 50%. A peculiar feature of the Precambrian cherts has emerged from the comparison with hydrothermal cherts and biogenic ones as their Phanerozoic counterpart, as described below. Geochemically, Al, Ti, and Zr represent the detrital component of sediments. Since these elements are hardly insoluble in natural water, their mutual ratios tend to remain unchanged during weathering and sedimentary processes. As exemplified by the Pacific argillaceous sediments (Fig. 2A), most sediments well mixed within ocean basins show a uniform ratio of Zr/TiO2 around 200 that is similar to the average for continental rocks. Phanerozoic cherts are composed of essentially biogenic (or chemically precipitated) silica and detrital minerals. Triassic bedded radiolarian cherts and their shale partings at Kamiaso, Japan, display a conspicuous Zr-Ti correlation (Fig. 2C). The same is true of other Phanerozoic radiolarian cherts from Costa Rica, Italy, and New Zealand, and hydrothermal cherts form the northwestern Pacific (Fig. 2E). Plots of TiO2 vs. Zr for the Archean Pilbara samples also show a fairly positive correlation (Fig. 2G). These lines of evidence show...
that detritus of uniform composition is involved in the Archean cherts as well as in the Phanerozoic rocks.

In contrast, geochemical aspect of $\text{Al}_2\text{O}_3$ in the Pilbara cherts is essentially different from that of Phanerozoic rocks. We have emphasized the geochemical and sedimentological significance of the universally common $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios in Phanerozoic sediments\textsuperscript{2,3}. Several authors have recently noticed it and discussed origins of several rocks on the basis of this ratio.\textsuperscript{4} Argillaceous and siliceous sediments in the Phanerozoic commonly show an invariant ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2$ around 22 (Figs. 2B, D, and F), which is close to the average for continental rocks.\textsuperscript{3} The Pilbara samples, however, do not show a systematic relationship between Al and Ti; their $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios scatter widely from 0.1 to 200 (Fig. 2H). The conflicting aspect in Precambrian samples—the wide variation of $\text{Al}_2\text{O}_3/\text{TiO}_2$ vs. the fairly close relation of $\text{Zr}/\text{TiO}_2$—suggests a unique environment of greenstone basins.

Discussion. A possible mechanism responsible for the wide fluctuation of $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios is incomplete mixing of detritus in the Archean shallow sea; the higher ratio originating from acidic source rocks and the lower one from basic rocks. However, relation of $\text{SiO}_2/\text{TiO}_2$ vs. $\text{Al}_2\text{O}_3/\text{TiO}_2$ of the present samples does not show the common trend inherent to acidic rocks (Fig. 3A); basic and ultrabasic rocks have commonly the ratio above 5. Thus, source rocks for detritus showing such peculiar $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios are not found in any terrestrial igneous rocks. In addition, the incomplete mixing of detritus interferes with the $\text{TiO}_2$-$\text{Zr}$ correlation detected in the present samples.

Fig. 1. Generalized geologic map of the Pilbara Block, Western Australia\textsuperscript{1} showing two outcrops AB and AI for sample collection.

Fig. 2. (A), (B) Chemical plots for Pacific sediments. Closed circles: Japan Trench sediments.\textsuperscript{2} Open circles: deep-ocean sediments around 3°N, 169°W.\textsuperscript{18} (C), (D) Chemical plots for cherts (0.2% < $\text{TiO}_2$) and associated shale partings from Kamiaso, Triassic cherts.\textsuperscript{19} (E), (F) Chemical plots for Phanerozoic cherts [closed circles: Costa Rica, Cretaceous and Paleogene\textsuperscript{18}; open circles: Italy, Jurassic\textsuperscript{20}; open triangles: New Zealand, Permain\textsuperscript{21}]; helms: Northwest Pacific, Cretaceous\textsuperscript{17}]. (G), (H) Chemical plots for Pilbara ferruginous cherts (open circles). Open circles with a vertical bar represent cherty rocks collected from an upper part, 10 m thick, at outcrop AB; their appearance is different from other ferruginous cherts, particularly in color, and they contain much rutile-like minerals. Stars represent siliceous sinters from Tamagawa hot spring, Japan.\textsuperscript{22}
Therefore, the peculiar feature of the present samples suggests that the elements under consideration were not necessarily conservative during the Precambrian sedimentation process.

A convincing reason for the heterogeneous ratios is dissolution and coprecipitation of Al at low pH during chert deposition. For pH of 2 to 4, Al hydroxide is soluble but Ti and Zr hydroxides are not (Fig. 3B). Although hydroxides of these elements are not always present as detrital minerals, these elements must relate to pH in a manner similar to those of Fig. 3B. Zirconium and Ti are dissolved in strongly acid water of pH < 1.5, and hence the Zr/TiO₂ ratio in detritus does not change much even in the lower pH region where Al dissolves. Thus, the anomalously low Al₂O₃/TiO₂ ratio and the uniform Zr/TiO₂ ratio are produced in lower pH environments.

Ferruginous cherts of comparatively high Al content (and higher Al₂O₃/TiO₂ ratio) may have been formed by Al-Fe coprecipitation from water enriched in Si, Fe, and Al. In silica-rich water, Al coprecipitates with Fe at lower pH, and it is effectively adsorbed on iron hydroxide. Several reports show high concentration of Al in acid hydrothermal waters, acid lakes, and acid groundwater. Accordingly, acid waters involved in ferruginous chert deposition must have been enriched in Al as well as Fe. A part of Al in the present samples may have chemically precipitated in association with Fe, giving rise to the enhanced Al₂O₃/TiO₂ ratio. Electron microprobe analyses disclosed that iron minerals in some Pilbara samples contain as much as 1% Al, and the Al-Fe association is approximately displayed in bulk rocks (Fig. 3C). A rough correlation between Fe₂O₃/Al₂O₃ and Al₂O₃/TiO₂ in the Pilbara samples (Fig. 3D) suggests that Fe tends to be dissolved rather than deposited, and instead Si is the main precipitate in a lower pH region indicated by the lower Al₂O₃/TiO₂. These processes
Molybdenum in the Archean cherts is positively correlated with Fe (Fig. 3E), whereas in the Triassic Kamiasso cherts it is correlated with Si (Fig. 3F). Molybdenum tends to coprecipitate with iron hydroxide in acid waters; it has been shown experimentally that proportion of coprecipitation of Mo with Fe (OH)₃ amounts to 100% at pH<4,¹⁰ whereas, at pH>6, it tends to be adsorbed on silica gel.¹¹ This opposing correlations reinforce therefore the proposition that the Archean cherts originated from acid solutions and the Phanerozoic ones from neutral ones.

The published data for BIFs from Isua (3.8 Ga old), Greenland, Sandur (3.0 to 2.8 Ga old), India, Yilgarn (2.8 Ga old), Australia, Brockman (2.5 Ga old), Australia, Väyrälnänkylä (2.1 Ga old), Finland, and Cuyuna (2.0 Ga old), Minnesota, show the same features as Pilbara (Fig 4), although trace component data are less reliable. This coherence may have important implications for the nature of the Precambrian ocean and biosphere. It suggests that acid marine environments had been widespread in the Precambrian greenstone basins where major BIF had been formed.

BIF formed most abundantly in the late Archean to early Proterozoic, and after that period, it rapidly waned. It seems that this secular change correlates with a rapid increase of stromatolite and dolomite occurrences in the late Proterozoic,¹² and CO₂ in ocean and atmosphere had been fixed as carbonate rocks.¹³ Sedimentary sequences older than 2.0 Ga contain only trivial proportions of carbonate rocks.¹⁴ The sporadic occurrence of Archean carbonates suggests local neutralization of acid seas.

**Concluding remarks.** The extensive greenstone sequences in the Archean indicate intensive volcanism on the early Earth. By analogy with modern hydrothermal waters and volcanic gases, acids such as HCl are inferred to have emanated through the volcanism along with tremendous volume of water and vapor. The emanation contained much Si and Fe. Furthermore, it has been assumed that a major part of terrestrial CO₂ was in the Precambrian ocean and atmosphere,¹⁴ and the carbonic acid also lowered pH. It has generally been believed that the acid water reacted immediately and violently with rocks and was rapidly neutralized. Thus, the occurrence of acid seas on the early Earth has been excluded, without reliable evidence.

In modern geothermal areas, many acid-water ponds persist without neutralization by ambient rocks. Siliceous sinters from an acid hot spring (98°C and pH 1.2) at Tamagawa, Japan, are characterized by lower Al₂O₃/TiO₂ values (stars in Fig. 2H). At Tamagawa, acid thermal water has issued at the rate of 10 tons per minute at least for the past 200 years. In order to dilute acidity, a portion of this thermal water has been introduced since 1940 into Lake Tazawa, which is 425 m deep and has 9.4×10⁹ m³ water in volume. As a result, the pH of the lake water in these 50 years dropped from 6 to 4, and no fish inhabit the lake.¹⁵ During the past several decades many lakes in southern Scandinavia, southern Canada and the northeastern United States have become acid (pH<5) owing to acid rain (pH 4.0–4.6) from pollution. It should be noted that Al concentration in acid lakes is much higher than similar nonacid lakes.¹⁵ The presence of these acid lakes suggests that the acidity of natural waters stored in a basin is not easily neutralized.

Phanerozoic cherts and modern ocean sediments are characterized by a steady Al₂O₃/TiO₂ ratio similar to the average of continental rocks (Figs. 2B, D, F). Hydrothermal cherts resting on basalts in Phanerozoic sequences have Al₂O₃/TiO₂ ratios identical to basalts, confirming that their detrital components were not chemically altered.¹⁶,¹⁷ In this Phanerozoic marine environment, the large reservoir of weakly alkaline ocean water swamps any local supply of acid hydrothermal waters with pH 3 that issue from the spreading ocean ridges.¹⁷ In contrast, ubiquitous volcanism in the Precambrian greenstone basins must have supplied continually an enormous quantity of acid waters enriched in Si and Fe,¹⁸ which may not be readily neutralized and thus they persisted for long periods. As the hydrothermal water cooled, Si and Fe may have precipitated as the ferruginous cherts akin to BIF through the process described above.

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