

Evidence in trace elements and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of Archaean and early Proterozoic shales for the early development of oxic atmosphere

H. Ohmoto

Department of Geosciences, The Pennsylvania State University,
University Park, PA, 16802, USA

Two models for the evolution of atmospheric oxygen

A currently popular model for the evolution of atmospheric oxygen, termed the Cloud-Walker-Kasting-Holland (C-W-K-H) model, postulates essential absence of free O_2 in the atmosphere prior to 2.2 Ga, then a dramatic rise of p_{O_2} from $\leq 10^{-13}$ to $>1\%$ PAL (present atmospheric level) during the period between 2.2 and 1.9 Ga. Another major rise in p_{O_2} to nearly the present level at ~ 600 Ma has been suggested by some researchers. An implication of this theory is that episodic rises in O_2 were major causes for the evolution of organisms, such as the appearance of eukaryotes at ~ 2.0 Ga and of metazoa and H_2S -oxidizing bacteria at ~ 600 Ma.

An alternative model for atmospheric evolution, termed the Dimroth-Ohmoto (D-O) model, postulates an essentially constant atmospheric p_{O_2} level (within $\pm 50\%$ of PAL) since ~ 4 Ga. According to this model, the O_2 requirement for all aerobic organisms ($>10\%$ PAL?) has been satisfied since the early stage of Earth's history, and the evolution of aerobic organisms was not caused by changes in the atmospheric p_{O_2} level. Ohmoto (1997) has recently summarized some geochemical data and concepts that support the D-O model. They include: (1) isotopic (Pb , Sr , Nd , and Hf) and trace element (REE , Nb/U) data on igneous and metamorphic rocks of Archaean ages that support the Armstrong's (1981) crustal growth model postulating an essentially constant volume for the continental crust since ~ 4.0 Ga; (2) isotopic (O , Nd and Sr) and elemental data on Banded Iron Formations (BIFs), suggesting that major BIFs were formed by submarine hydrothermal fluids locally discharged within anoxic basins surrounded by oxic oceans; (3) micro-scale variations in the sulphur isotopic compositions of pyrite crystals in 3.4–2.2 Ga shales, suggesting that they were formed by sulphate-reducing bacteria in sulphate-rich oceans;

(4) textural and paragenetic data on "detrital" grains of uraninite and pyrite in quartz-pebble conglomerates of >2.2 Ga age, suggesting that these minerals were mostly diagenetic or hydrothermal, rather than detrital, in origin; (5) Fe^{3+}/Ti and Fe^{2+}/Ti ratios of pre-2.2 Ga palaeosols, suggesting soil formation under an oxic atmosphere; (6) carbon isotopic compositions of organic matter in 3.8–2.0 Ga sedimentary rocks, suggesting that temporal and spatial fluctuations in redox state of sedimentary basins, much like those occurring in modern Earth, were common during this period; and (7) $\delta^{13}\text{C}$ data on marine carbonates and TOC data on shales of various geologic ages, suggesting essentially constant rates of production and consumption of atmospheric oxygen since at least 3.5 Ga.

Here I present other lines of supportive evidence for the D-O model, which come from our own chemical analyses of more than 300 samples of shales of 3.8–0.5 Ga in age.

S/C, U/C, and Mo/C ratios

Concentrations of S, U and Mo in river and ocean waters are expected to increase with increasing p_{O_2} of the atmosphere. This is because the solubilities of common S-, U-, and Mo-bearing minerals, in which these elements occur mostly as reduced states (S^{2-} , U^{4+} , and Mo^{4+} , respectively), increase when the dominant aqueous species are in oxidized forms (S^{6+} , U^{6+} , and Mo^{6+} species, respectively). S, U and Mo in ocean water are, in turn, removed as reduced forms in sediments, thus producing positive correlations among the contents of sulphide-S, U, Mo, and organic-C in many (but not all) shales of Phanerozoic age (e.g. Holland, 1984).

Among a group of shale samples from a specific geologic formation, the correlations (either positive or negative) are generally poor among the S, C, U and Mo contents. This is true for the ~ 1.9 Ga sediments in Labrador, Canada, and for the ~ 0.54 Ga

sediments in Newfoundland, Canada that were most likely deposited under an oxic atmosphere. The poor correlations among these elements are probably due to the varying degrees of losses of the elements during diagenesis and metamorphism, as most Precambrian sediments were metamorphosed to greenschist facies or higher grades. However, distinctly positive correlations are recognized among the S, C, and Mo contents of the 2.55 Ga Mt. McRae shales in the Hamersley Basin, Australia: the maximum contents are 8 wt.% for S, 10 wt.% for C, and 15 ppm for Mo. These positive correlations suggest that the atmosphere was oxic and the modern-style cycles of S, C, and Mo were already developed in surface environments of the 2.55 Ga Earth. The Mo/C ratios for the McRae shales are about 1/8 of those for the Devonian shales of Holland (1984), probably because the Archaean crust was generally less felsic (i.e. less Mo) than the Phanerozoic one.

Fe³⁺/Fe²⁺ ratios

The Fe³⁺/Fe²⁺ ratios of shales are generally similar to or slightly lower than the average Fe³⁺/Fe²⁺ ratios of soils formed in the source regions, because diagenetic, hydrothermal, or metamorphic modification of shales may decrease, but not increase, the Fe³⁺/Fe²⁺ ratios. Therefore, a comparison of the Fe³⁺/Fe²⁺ ratios of shales with those of igneous rocks in the source regions may put constraints on the atmospheric pO_2 value during the shale formation.

We have found that many (>100 samples) of shales of 3.4–2.4 Ga from South Africa and Australia have retained the ΣFe/Ti ratios of their source igneous rocks, but that the shales have higher Fe³⁺/Fe²⁺ ratios (typically within a range of 0.75 ± 0.25) compared to normal igneous rocks in the source regions

(Fe^{3+}/Fe²⁺ = 0.2 ± 0.1). These data suggest that the parental soils for these shales formed by weathering under an oxic atmosphere. The amount of O₂ consumed in the formation of an average Archaean shale from an average Archaean igneous rock (ΣFe = 6.5 wt.%) can be calculated to be ~7.5 x 10⁻² moles O₂/kg rock. This value is identical to the O₂ consumption during the formation of an average Phanerozoic shale (Fe^{3+}/Fe²⁺ = ~2) from an average Phanerozoic igneous rock (ΣFe = 5.0 wt.% and Fe^{3+}/Fe²⁺ = 0.5). This also suggests that the atmospheric pO_2 level has been essentially the same as the present level since at least ~3.4 Ga ago.}}}

Acknowledgements

Most of the data presented in this paper were obtained by my colleagues and students: K. Hayashi, H. Naraoka, T. Kakegawa, Y. Watanabe, M. Nedachi, Y. Nedachi, M. Ohtake, Y. Lie, H. Kawai, N. Kassai, T. Hanamuro, H. Fujisawa, M. Manaka, K. Hiramatsu, K. Iwakiri, R. Mock, K. Yamaguchi, S. Ono and D. Walizer. This research has been supported by grants (Nos. 03102002 and 07041081) from the Japanese Ministry of Education and by grants (EAR-9003554 and EAR-9706279) from the National Science Foundation.

References

- Armstrong, R.L. (1991) *Austr. J. Earth Sci.*, **38**, 613–30.
- Holland, H.D. (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton Univ. Press.
- Ohmoto, H. (1997) *The Geochemical News*, **93**, 12–13 and 26–7.