

Geochemical Constraints on the Rise of Atmospheric O₂

JAMES F. KASTING

Department of Geosciences, Penn State University, University Park, PA 16802 (kasting@essc.psu.edu)

The rise of atmospheric oxygen was perhaps the most biologically significant environmental change in Earth history, as it allowed multicellular, eukaryotic organisms to evolve and proliferate. The rise of O₂ is thought to have occurred around 2.0-2.4 Ga, based on a variety of geochemical evidence [1]. More recently, Farquhar et al. [2] showed that Archean and early Proterozoic rocks contain mass-independently fractionated S isotopes, whereas rocks of younger age do not. According to current understanding, such anomalous fractionation patterns could only have been produced by photochemical reactions (e.g., SO₂ photolysis) in a low-O₂ atmosphere. A recent photochemical model study [3] places a firm upper limit of 10⁻⁵ PAL (times the Present Atmospheric Level) on the O₂ concentration at the time when these rocks were formed.

Seemingly at odds with this conclusion is organic biomarker evidence for the existence of cyanobacteria and isotopic evidence for rapid organic carbon burial as early as 2.7 Ga [4,5]. What then prevented atmospheric O₂ from accumulating? Kasting et al. [6] had suggested that volcanic gases became more oxidized with time as a consequence of H escape to space and the subduction of oxidized materials down into the mantle. This idea appears to be ruled out, however, by data on the Cr and V contents of ancient basalts and komatiites [7,8]. Catling et al. [9] suggested that the oxygen went into the continents, resulting in an increase in the oxidation state of low-temperature, metamorphic gases. However, the mechanism by which the oxidation took place was not specified. More likely, the important O₂ sink was H₂ and CH₄ produced by serpentinization of ultramafic seafloor. In any case, the reduced gas sink for oxygen must have been larger in the past; else, either O₂ or sulfate would have accumulated in the Archean atmosphere and ocean.

References

- Holland, H. D. (1994), in *Early Life on Earth*, Bengtson, S. ed., p. 237-244 (Columbia Univ. Press, New York).
- Farquhar, J., Savarino, J., Jackson, T. L. & Thiemans, M. H. (2000), *Nature* 404, 50-52.
- Pavlov, A. A. & Kasting, J. F. (2002), *Astrobiol.* 2, 27-41.
- Brocks, J. J., Logan, G. A., Buick, R. & Summons, R. E. (1999), *Science* 285, 1033-1036.
- Kump, L. R., Kasting, J. F. & Barley, M. E. (2001), *Geol. Geophys. (on Line)* 2, (2001).
- Kasting, J. F., Egglar, D. H. & Raeburn, S. P. (1993), *J. Geol.* 101, 245-257.
- Delano, J. W. (2001), *Origins of Life and Evol. of the Biosphere* 31, 311-341.
- Canil, D. (2002), *Earth Planet. Sci. Lett.* 195, 75-90.
- Catling, D. C., Zahnle, K. J. & McKay, C. P. (2001), *Science* 293, 839-843.

Oxygen isotope variations in Cycladic eclogites: assessing the significance of zircon ages

Y. KATZIR¹, M. BRÖCKER², J. W. VALLEY¹ AND M. J. SPICUZZA¹

¹ Department of Geology and Geophysics, University of Wisconsin, 1215 W. Dayton St., Madison WI 53705, USA (ykatzir@bgumail.bgu.ac.il)

² Institute für Mineralogie, Universität Münster, Corrensstr, 24, D-48149, Münster, Germany (brocker@nwz.uni-muenster.de)

Upper Cretaceous U-Pb zircon ages, recently obtained for eclogites from the Alpine orogen in the Cyclades (Aegean Sea, Greece), were interpreted as related to a high-pressure event. Thus the time-scale for orogenesis in the Cyclades, previously constrained to the Tertiary by white mica dating, is doubled. The origin of zircon is debated: it could either be inherited from the igneous protoliths or formed by metamorphic process prior or during the crystallization of the high-pressure phases. Since closure temperatures for oxygen diffusion in zircon, garnet and omphacite are higher than peak metamorphic temperatures in the Cyclades (500°C), an oxygen isotope study might shed light on their crystallization history. Oxygen isotope ratios of the dated rocks are given in the table below.

δ ¹⁸ O ‰ SMOW	1081	1049
	Syros omphacitite	Tinos jadeitite
whole rock	5.64 ± 0.23 (3)	5.74 ± 0.14 (2)
omphacite	5.15 ± 0.02 (3)	5.07 ± 0.03 (2)
garnet		5.03 ± 0.09 (3)
zircon	5.09 ± 0.03 (4)	5.01 ± 0.06 (6)
titanite	1.23 ± 0.06 (2)	1.81 ± 0.04 (2)

() number of repeat analyses

Both whole rock values are similar to the average δ¹⁸O of the oceanic crust, and thus indicate that the eclogites behaved as closed systems with respect to oxygen since their magmatic formation. The measured equilibrium fractionations between zircon and garnet (Δ¹⁸O Zrc-Grt = 0‰) and the indistinguishable values of three size fractions of zircon do not necessarily indicate coeval crystallization. Zircons, growing either from magma or during metamorphism, would equilibrate with the same whole rock composition and would thus have the same values. Omphacite-garnet isotopic temperatures (Δ¹⁸O Omp-Grt = 0‰) are >100°C higher than petrologic estimates in 'common' Cycladic eclogite and might suggest that the zircon-bearing eclogites preserve an earlier, hotter HP-metamorphism. Titanite δ¹⁸O values are out of equilibrium with those of zircon by 1.2-1.7 ‰. These values agree with late, fluid-related crystallization of titanite at blueschist to greenschist facies conditions. Further oxygen isotope analyses of zircon-bearing eclogites are needed to decipher their evolution.