Oxygen isotope signature during phosphite oxidation by UV radiation: Prebiotic phosphate reservoir on early Earth

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Recent discoveries have shown that phosphorus (P), not as phosphate (PO_4 with P^{5+}) but as phosphite (PO_3 with P^{3+}), could have been a major source of P for pre-biotic synthesis and major nutrient in early pre-oxygenated oceans [1]. These findings demand an evaluation of initial prebiotic oxygen isotope signatures of phosphate derived from phosphite as well as co-evolution of these prebiotic oxygen isotope signatures and life. However, oxygen isotope systematics of P redox chemistry remain poorly understood. In this study, we determined the $^{18}O/^{16}O$ ratio of dissolved phosphate ($\delta^{18}O_{PO4}$) derived from oxidation of phosphite catalyzed by ultraviolet (UV) radiation, which was known to be relatively strong on early Earth due to lack of an ozone layer [2].

The UV-catalyzed oxidation of phosphite was conducted using ^{18}O-labled phosphite and waters at pH 7 under air and under oxygen-free (Ar-filled atmosphere) conditions. Under UV (with a 1,200W mercury lamp) exposure, aqueous phosphite was (93-100%) oxidized to phosphate after 12 hours. The $\delta^{18}O$ values of product phosphates varied with the $\delta^{18}O$ values of ambient waters. Slopes of linear regressions of $\delta^{18}O_{PO4}$ vs. $\delta^{18}O_{H2O}$ data were ~0.20, which indicated that ~20% of oxygen in product phosphate was derived from ambient water. No difference was observed in the $\delta^{18}O$ values of phosphate between air and Ar-filled conditions, which suggests that atmospheric oxygen (O_2, CO_2 etc.) was not directly incorporated into the product phosphate. These results suggest that the alternative phosphate sources derived from abiotic UV-catalyzed oxidation of phosphite would have oxygen isotope signatures that are distinct from that of igneous apatite. Furthermore, these results would help to interpret phosphate $\delta^{18}O$ biosignatures preserved in ancient terrestrial and extra-terrestrial samples, such as from Mars where surface UV radiation is high.

[1] Herschy et al. (2018) *Nature Communications* 9, 1346.
[2] Miller (1953) *Science* 117, 528.