

A Geochemical Basis for Phosphate Stabilization and Containment of Waste Materials

T.T. EIGHMY

Environmental Research Group, University of New Hampshire, 216 Environmental Technology Building, 35 Colovos Road, Durham, NH 03824, USA, taylor.eighmy@unh.edu

The use of orthophosphate (PO_4^{3-}) as a chemical stabilization agent for wastes is widespread. It is used to treat soils, sediments, contaminated groundwaters, industrial wastewaters, smelter dusts and slags, wire chopping wastes, mine tailings, and incineration residues. The technology relies on the fact that PO_4^{3-} forms about 300 naturally-occurring insoluble and stable minerals for about 26 cations and four oxyanions: notably U (IV,VI), Pb(II), Cd (II), Cu (II), Zn (II), Ni (II), and As (V). The ability to readily form solid solutions (e.g., $(\text{Pb, Zn, Ca})_5(\text{PO}_4)_3\text{Cl}$) is also an important feature of the technology. A variety of soluble, mineral, and other sources of phosphate are employed in the stabilization processes. Systems are used in waste processing lines; within *in-situ* treatment systems; and within reactive caps, reactive impermeable barriers, and reactive permeable barriers. The geochemical basis for use of PO_4^{3-} is presented with a focus on the generally wide pH distribution, pH-pE predominance, and redox stability of reaction products within the context of typical cation/anion-Ca-Al-P-S-C-Cl- H_2O geochemical systems. The theoretical and observed stabilization mechanisms in solutions (precipitation, Ostwald ripening, and solid solution formation), as well as on phosphate mineral (typically apatite) surfaces (sorption, surface precipitation, precipitation) are presented.

$^{13}\text{C}^{18}\text{O}^{16}\text{O}$ in air

JOHN M. EILER, EDWIN SCHAUBLE AND NAMI KITCHEN

Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125, eiler@gps.caltech.edu

The atmospheric budget of CO_2 is constrained by its concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. However, these are insufficient to resolve source and sink processes, which vary complexly in flux and/or isotope signature. There are twelve stable isotopologues of CO_2 , each of which has unique thermodynamic and kinetic properties and could offer unique constraints on the budget. However, only three are commonly measured ($^{12}\text{C}^{16}\text{O}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, and $^{12}\text{C}^{18}\text{O}^{16}\text{O}$); most of the rest have not been previously analyzed in natural materials

We measured the stable isotope composition, including $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and mixing proportion of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}^{18}\text{O}$, in samples of CO_2 extracted from air or produced or processed by various experiments. These measurements were made on a Finnigan Matt 253 gas source stable isotope ratio mass spectrometer configured to measure ion beams corresponding to $M/z = 44$ through 49, inclusive. We focus here on data for $^{13}\text{C}^{18}\text{O}^{16}\text{O}$. In discussing these data, we define the new variable, $\Delta 47$ as the difference in per mil between the $^{13}\text{C}^{18}\text{O}^{16}\text{O}/^{12}\text{C}^{16}\text{O}^{16}\text{O}$ ratio of the sample and that expected for random distribution of isotopes among all isotopologues, in that sample.

Tropospheric air samples from southern California in winter of 2003 have $\Delta 47$ values of $+0.72 \pm 0.07$ (1 σ). Sources of CO_2 involving high-temperature reactions, including car exhaust and natural gas combustion in the laboratory, have $\Delta 47$ values of 0.0. CO_2 equilibrated with H_2O at temperatures between 268 and 303 K has $\Delta 47$ values between 1.1 and 0.7 ‰ (respectively), varying with temperature as predicted for thermodynamic equilibrium at these temperatures. Photosynthesis and plant respiration produce small changes of $\Delta 47$ in ambient air for moderate amounts of uptake or production, consistent with isotopic exchange in leaf water being the dominant factor controlling $\Delta 47$.

The $\Delta 47$ value of atmospheric CO_2 depends on: (1) the ratio of CO_2 derived from high-temperature combustion sources to CO_2 produced or isotopically exchanged with water at ambient temperatures; and (2) the weighted average ambient temperature at which these lower-temperature processes take place. $\Delta 47$ of CO_2 in air should vary with season and latitude, and is expected to decrease with time due to growing anthropogenic CO_2 . Finally, measurements of $\Delta 47$ could resolve dependences of the $\delta^{18}\text{O}$ of CO_2 on the $\delta^{18}\text{O}$ of water with which it exchanges (no $\Delta 47$ signal) vs. the temperature of that exchange (significant $\Delta 47$ signal).