

Atmospheric chemistry and dynamics recorded in the isotopic ordering in O₂ and CO₂

LAURENCE Y. YEUNG,^{1*} EDWARD D. YOUNG,¹ EDWIN A. SCHAUBLE,¹ HAGIT P. AFFEK,² KRISTIE A. BOERING,³ JOHN M. EILER⁴ AND MITCHIO OKUMURA⁵

¹Department of Earth and Space Sciences, University of California, Los Angeles, CA, USA
(*correspondence: lyyeung@ucla.edu)

²Department of Geology & Geophysics, Yale University, New Haven, CT, USA

³Departments of Chemistry and Earth & Planetary Science, University of California, Berkeley, CA, USA

⁴Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

⁵Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA

Molecules in Earth's atmosphere undergo photochemical oxidation while being transported through regions where they are mixed and/or stratified. Chemistry, transport, and mixing all alter the distribution of gases in the atmosphere, and tracing these processes over large spatial and temporal scales is therefore challenging. Concentrations of the short-lived free radical oxidants that drive atmospheric chemistry are especially difficult to quantify due to short chemical lifetimes and spatial and temporal variations in source strengths.

Our studies of O₂ and CO₂ molecules containing more than one rare stable isotope (¹⁸O¹⁸O and ¹⁶O¹³C¹⁸O) suggest that these species preserve signatures of isotope-exchange reactions in the stratosphere and troposphere [1,2]. For instance, ¹⁶O¹³C¹⁸O can be used to constrain the isotopic signature of O(¹D) in the midlatitude stratosphere as well as the chemistry and dynamics of the stratospheric polar vortex. In contrast, atmospheric ¹⁸O¹⁸O traces O(³P) chemistry and stratosphere-troposphere exchange.

Our most recent measurements of ¹⁸O¹⁸O in stratospheric air and in air drawn from the firm layer in Antarctica bolster the case for O(³P) + O₂ isotope exchange reactions governing the distribution of ¹⁸O¹⁸O (i.e., Δ₃₆) throughout the atmosphere. Using these observations together with laboratory experiments and modeling, we show that Δ₃₆ in the atmosphere is sensitive to O(³P) concentrations. Because O(³P) is linked directly to NO₂ and O₃ in the troposphere, Δ₃₆ is a proxy for global NO₂ and O₃ concentrations.

[1] Yeung *et al.* (2012) *J. Geophys. Res.* **117**, D18306. [2] Yeung and Affek *et al.* (2009) *Proc. Natl. Acad. Sci. USA* **106**, 11496-11501.

δ⁶⁶Zn values: An isotopic tool for comprehension of metallurgical slags weathering

N.H. YIN^{1,2,3*}, Y. SIVRY¹, P.N.L. LENS² AND E.D VANHULLEBUSCH³

¹Univ. Paris Diderot, Sorbonne Paris Cité, IPGP, UMR 7154, CNRS, F-75205 Paris, France (*correspondence: yin@ipgp.fr, sivry@ipgp.fr)

²UNESCO-IHE, 2601 DA Delft, The Netherlands (p.lens@unesco-ihe.org)

³Univ. Paris-Est, LGE (EA 4508), 77454 Marne-la-Vallée, France (eric.vanhullebusch@univ-paris-est.fr)

The considered slags are originated from Lead Blast Furnace (LBF) and Imperial Smelting Furnace (ISF) Smelters. LBF and ISF slags contain 9.8 wt% and 8 wt% of Zn respectively, embedded in CaO-SiO-FeO matrix. Complete acid digestions showed that these bulk materials are enriched in heavy isotopes, with δ⁶⁶Zn_{JMC} +0.77 ± 0.06‰ and +0.12 ± 0.06‰ in ISF and LBF in agreement with previous studies [1]. Chemical dissolution kinetics were conducted at fixed pH values (4, 5.5, 7, 8.5 and 10), both in open-air and nitrogen atmospheres.

Zn dissolution was shown to be strongly governed by its mineral bearing phases: Spinel Zn(Al_{0.8}Fe_{0.2})O₄ and Wurtzite (ZnS) in ISF, and Franklinite [(Zn,Mn²⁺,Fe²⁺)(Fe³⁺,Mn³⁺)₂O₄] in LBF. Zn from Spinel phases was more resistant to weathering comparing to Zn from sulfide phases and from glassy silicates matrix. Furthermore, Zn dissolution in both slags was enhanced by the collateral dissolution of matrix elements such as Ca, Fe and Si. At all pHs tested, dissolved Zn of ISF reached higher concentration when there was no secondary precipitates formation like Zincite (ZnO) and Zinc carbonate (ZnCO₃), i.e. under N₂ atmosphere.

Such dissolution was related to extremes zinc isotopic signatures in the leachate solutions collected under open-air atmosphere. Both ISF and LBF displayed the same trend: heavier δ⁶⁶Zn values at low pH than at high pH (i.e. +0.91 ± 0.06‰ and -0.19 ± 0.06‰ at pH 4 and 10, respectively for ISF, and +0.10 ± 0.06‰ and -1.25 ± 0.06‰ at pH 4 and 10 respectively for LBF).

In open-air atm., δ⁶⁶Zn values remained constant with time from 48 to 200hrs (e.g. -0.19 ± 0.08‰ and -0.27 ± 0.06‰, respectively, for ISF), whereas they became enriched in heavier isotopes under N₂ atm. (e.g. +0.07 ± 0.06‰ and +0.71 ± 0.06‰ after 48 hrs and 200 hrs, resp.). This may imply that the absence of secondary precipitates allows more congruent slag dissolution and, thus, weathered Zn reaches isotopic signature closer to the bulk slag.

[1] Sivry, Y., *et al.* (2008) *Chem. Geol.* **255**, 295–304.