

## Oxygen isotope fractionation in formation of CO<sub>2</sub>

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The discovery of mass independent isotope fractionation (MIF) of oxygen isotopes [1] opened a new dimension in environmental research. Much subsequent research has focused on isotope effects in ozone formation [2,3]. Despite the apparent similarity to formation of ozone, relatively little attention has been given to the possibility of MIF in the formation of CO<sub>2</sub> through the reaction CO + O(<sup>3</sup>P) + M → CO<sub>2</sub> + M [4]. A better understanding of the isotope fractionation in CO<sub>2</sub> may give insights into mechanisms of MIF.

The photochemical reactor at the Copenhagen Centre of Atmospheric Research [5] was used to study the reaction CO + O(<sup>3</sup>P) + M → CO<sub>2</sub> + M experimentally. O(<sup>3</sup>P) radicals were obtained from photolysis of O<sub>3</sub> in the visible region. The use of ordinary commercial LED lamps ensured that no O(<sup>1</sup>D) and subsequently no OH was formed. An enriched sample of CO (90% <sup>13</sup>C<sup>16</sup>O, 10% <sup>13</sup>C<sup>18</sup>O, trace amounts of <sup>13</sup>C<sup>17</sup>O) was used to distinguish the reaction of interest from possible fluctuations in the background concentrations of <sup>12</sup>CO and <sup>12</sup>CO<sub>2</sub> in the reactor. Infrared spectra were recorded with a Bruker IFS 66v/s Fourier Transform Infrared spectrometer. The spectra were analysed using the non-linear least squares algorithm MALT [6]. Experiments were conducted at pressures ranging from 200 to 980 mbar and the isotope chemical kinetics has been modelled using the chemical kinetics software package KPP [7]. Isotope effects were calculated as:

$\alpha_n = \frac{\ln([C^nO]_{t=0}/[C^nO](t))}{\ln([C^{16}O]_{t=0}/[C^{16}O](t))}$ . We present first results, which show unusual ratios of ( $\alpha_{17}-1$ )/( $\alpha_{18}-1$ ). However, as in earlier experiments [4], unambiguous assignment of this MIF is complicated by the presence of side reactions.

[1] Clayton *et al.* (1973), *Science*, 182, 485-488. [2] Brenninkmeijer *et al.*, *Chem. Rev.*, 103(12). [3] Thiemens (2006), *Annu. Rev. Earth Planet. Sci.* **34** 217-62. [4] Pandey and Bhattacharya (2006), *J. Chem. Phys.* 124 234301. [5] Nilsson *et al.* (2009), *Atmos. Environ.* 43 3029-3033. [6] Griffith (1996), *Appl. Spectrosc.* 50 59-70. [7] V. Damian *et al.*: *Comp. Chem. Eng.*, 26, 1567-79, 2002

## Estimating uncertainties in base cation weathering rates according to mass balance

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Because forestry is often allocated to soils with low weathering capacity, intensive harvesting practices may deteriorate plant nutrition. Reliable estimates of weathering rates are therefore crucial in analyses of sustainability of, e.g., whole-tree and stump harvesting. By the mass balance approach present base cation cycling may be estimated from data on leaching, deposition, and accumulation in biomass and soil. Insight in the uncertainties in the weathering estimates is crucial for the interpretation of the data.

Weathering rate of:	Ca	Mg	K	Na
	(kg ha <sup>-1</sup> yr <sup>-1</sup> )			
Average	4.0	1.4	3.3	-3.3
Conf. int.	±3.8	±1.6	±4.4	±15

**Table 1:** Average weathering rates and approximate confidence intervals (ca 95% level) based on spatial variability and uncertainties in allometric functions etc.

Term in balance	Ca	Mg	K	Na
Deposition	8%	43%	2%	26%
$\Delta K_{\text{exch}}$	3%	5%	1%	0%
Leaching	4%	28%	0.4%	74%
Biomass accumul	86%	25%	97%	0%

**Table 2:** Contributions to overall uncertainty in weathering rates according to soil balance.

The present study was carried out in a Norway spruce (*Picea abies* Karst. (L.)) stand on a podzolic soil in SW Sweden. The results pinpoint the difficulty in assessing low weathering rates in general (Table 1), and demonstrates that the influence of the different terms of the balance varies considerably among the different base cations (Table 2). Details of the uncertainty contributions in the different terms of the balance is shown on a poster with the same title.