



Library Indian Institute of Science Education and Research Mohali



DSpace@IISERMohali (/jspui/)

/ Publications of IISER Mohali (/jspui/handle/123456789/4)

/ Research Articles (/jspui/handle/123456789/9)

Please use this identifier to cite or link to this item: <http://hdl.handle.net/123456789/170>


Title:	Fractionation of sulfur isotopes during heterogeneous oxidation of SO ₂ on sea salt aerosol: A new tool to investigate non-sea salt sulfate production in the marine boundary layer
Authors:	Sinha, B. (/jspui/browse?type=author&value=Sinha%2C+B.)
Keywords:	nonmetal redox kinetics size distribution atlantic-ocean
Issue Date:	2012
Publisher:	Atmospheric Chemistry and Physics
Citation:	Atmospheric Chemistry and Physics, 12, PP. 2707- 2742
Abstract:	<p>The oxidation of SO₂ to sulfate on sea salt aerosols in the marine environment is highly important because of its effect on the size distribution of sulfate and the potential for new particle nucleation from H₂SO₄ (g). However, models of the sulfur cycle are not currently able to account for the complex relationship between particle size, alkalinity, oxidation pathway and rate – which is critical as SO₂ oxidation by O₃ and Cl catalysis are limited by aerosol alkalinity, whereas oxidation by hypohalous acids and transition metal ions can continue at low pH once alkalinity is titrated. We have measured ³⁴S/³²S fractionation factors for SO₂ oxidation in sea salt, pure water and NaOCl aerosol, as well as the pH dependency of fractionation. Oxidation of SO₂ by NaOCl aerosol was extremely efficient, with a reactive uptake coefficient of ~0.5, and produced sulfate that was enriched in ³²S with $\alpha_{\text{OCl}} = 0.9882 \pm 0.0036$ at 19 °C. Oxidation on sea salt aerosol was much less efficient than on NaOCl aerosol, suggesting alkalinity was already exhausted on the short timescale of the experiments. Measurements at pH = 2.1 and 7.2 were used to calculate fractionation factors for each step from SO₂(g) → multiple steps → SO₂-3. Oxidation on sea salt aerosol resulted in a lower fractionation factor than expected for oxidation of SO₂-3 by O₃ ($\alpha_{\text{seasalt}} = 1.0124 \pm 0.0017$ at 19 °C). Comparison of the lower fractionation during oxidation on sea salt aerosol to the fractionation factor for high pH oxidation shows HOCl contributed 29% of S(IV) oxidation on sea salt in the short experimental timescale, highlighting the potential importance of hypohalous acids in the marine environment. The sulfur isotope fractionation factors measured in this study allow differentiation between the alkalinity-limited pathways – oxidation by O₃ and by Cl catalysis ($\alpha_{34} = 1.0163 \pm 0.0018$ at 19 °C in pure water or 1.0199 ± 0.0024 at pH = 7.2) – which favour the heavy isotope, and the alkalinity non-limited pathways – oxidation by transition metal catalysis ($\alpha_{34} = 0.9905 \pm 0.0031$ at 19 °C, Harris et al., 2012a) and by hypohalites ($\alpha_{34} = 0.9882 \pm 0.0036$ at 19 °C) – which favour the light isotope. In combination with field measurements of the oxygen and sulfur isotopic composition of SO₂ and sulfate, the fractionation factors presented in this paper may be capable of constraining the relative importance of different oxidation pathways in the marine boundary layer.</p>
Description:	Only IISERM authors are available in the record.
URI:	http://www.atmos-chem-phys-discuss.net/12/2707/2012/acpd-12-2707-2012.html (http://www.atmos-chem-phys-discuss.net/12/2707/2012/acpd-12-2707-2012.html) doi:10.5194/acpd-12-2707-2012 (doi:10.5194/acpd-12-2707-2012) http://hdl.handle.net/123456789/170 (http://hdl.handle.net/123456789/170)

Appears in Research Articles (/jspui/handle/123456789/9)
Collections:

Files in This Item:

File	Description	Size	Format	
Untitled 1.odt (/jspui/bitstream/123456789/170/1/Untitled%201.odt)		8.44 kB	OpenDocument Text	View/Open (/jspui/bitstream/123456789/170)

[Show full item record \(/jspui/handle/123456789/170?mode=full\)](/jspui/handle/123456789/170?mode=full)

 [\(/jspui/handle/123456789/170/statistics\)](/jspui/handle/123456789/170/statistics)

Items in DSpace are protected by copyright, with all rights reserved, unless otherwise indicated.