

powdered TiO₂ in the form of anatase are totally inactive. The catalytic properties of JDF-L1 based materials are now under investigation. We note that JDF-L1, because of its non-centrosymmetric tetragonal structure, may have potential as a pyroelectric material and, either in its natural (hydrated) or intercalated state, as a precursor of polar glass ceramic³². □

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1. Markgraf, S. A., Halliyal, A., Bhalla, A. S., Newnham, R. E. & Prewitt, C. T. *Ferroelectrics* **62**, 17–26 (1985).
2. Jones, R. H. et al. *J. chem. Soc., chem. Comm.* 1170–1172 (1990).
3. Jones, R. H. et al. *J. chem. Soc., chem. Comm.* 1520–1522 (1991).
4. Chippindale, A. M. et al. *J. Solid. St. Chem.* **96**, 199–210 (1992).
5. Chen, J. S. et al. *J. Solid. St. Chem.* **103**, 519–522 (1993).
6. Jones R. H., Chippindale, A. M., Natarajan, S. & Thomas, J. M. *J. chem. Soc., chem. Comm.* 565–566 (1994).
7. Thomas, J. M. et al. *J. chem. Soc., chem. Comm.* 929–931 (1992).
8. Chippindale, A. M., Natarajan, S., Thomas, J. M. & Jones, R. H. *J. Solid. St. Chem.* **111**, 18–25 (1994).
9. Huo, Q. S. et al. *J. chem. Soc., chem. Comm.* 875–876 (1992).
10. Sankar, G. et al. *J. chem. Soc., chem. Comm.* 2279–2280 (1994).
11. Maschmeyer, T., Rey, F., Sankar, G. & Thomas, J. M. *Nature* **378**, 159–162 (1995).
12. Taramasso, M. & Notari, B. US Patent No. 4410501 (1983).
13. Blasco, T., Cambiore, M. A., Corma, A. & Perez-Pariente, J. J. *Am. chem. Soc.* **115**, 11806–11813 (1993).

14. Kim, G. J., Cho, B. R. & Kim, J. H. *Catal. Lett.* **22**, 259–270 (1993).
15. Tanev, P., Chibwe, M. & Pinnavaia, T. *Nature* **368**, 321–323 (1994).
16. Thomas, J. M. *Nature* **368**, 289–290 (1994).
17. Corma, A., Navarro, M. T. & Perez-Pariente, J. *J. chem. Soc., chem. Comm.* 147–148 (1994).
18. Anderson, M. W. et al. *Nature* **367**, 347–351 (1994).
19. Sankar, G., et al. *J. phys. Chem.* **100**, 449–452 (1996).
20. Poojary, D. M., Cahill, R. A. & Clearfield, A. *Chem. Mater.* **6**, 2364–2368 (1994).
21. Harrison, W. T. A., Gier, T. E. & Stucky, G. D. *Zeolites* **15**, 408–412 (1995).
22. Kraushaar-Czarnetski, B., Stork, W. H. J. & Dogerton, R. J. *Inorg. Chem.* **32**, 5029–5033 (1993).
23. Barrett, P. A. & Jones, R. H. *J. chem. Soc., chem. Comm.* 1979–1981 (1995).
24. Waychunas, G. A. *Am. Miner.* **72**, 89–101 (1987).
25. Werner, P. E., Eriksson, L. & Westdahl, M. J. *appl. Crystallogr.* **18**, 367–370 (1985).
26. Murray, A. D., Fitch, A. N. & Jouannaux, A. *MPROFIL program for LeBail Decomposition of powder patterns* (Daresbury Computing Service, 1990).
27. LeBail, A., Duroy, H. & Fourquet, J. L. *Mater. Res. Bull.* **23**, 447–452 (1988).
28. Sheldrick, G. M. *SHELXS86 User Guide* (Univ. Göttingen, 1986).
29. Rietveld, H. M. J. *appl. Crystallogr.* **2**, 65–71 (1969).
30. Wright, P. A., Thomas, J. M., Millward, G. R., Ramadas, S. & Barri, S. A. *J. chem. Soc., Chem. Comm.* 1117–1119 (1985).
31. Meier, W. M. & Olson, D. H. *Atlas of Zeolite Structure Types* (Butterworth-Heinemann, London, 1992).
32. Halliyal, A., Bhalla, A. S., Markgraf, S. A., Cross, L. E. & Newnham, R. E. *Ferroelectrics* **62**, 27–38 (1985).

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Photochemical release of biologically available nitrogen from aquatic dissolved organic matter

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DISSOLVED organic material in marine and freshwater ecosystems constitutes one of the Earth's largest actively cycled reservoirs for organic matter¹. The bacterially mediated turnover of chemically identifiable, low-molecular-mass components of this pool has been studied in detail for nearly three decades, but these compounds constitute less than 20% of the total reservoir². In contrast, little is known about the fate of the larger, biologically more refractory molecules—including humic substances—which make up the bulk of dissolved organic matter. Here we report results from bacterial bioassays and photochemical studies indicating that exposure to sunlight causes dissolved organic matter to release nitrogen-rich compounds that are biologically available, thus enhancing the bacterial degradation of humic substances. We demonstrate that ammonium is among

the nitrogenous compounds released and is produced most efficiently by ultraviolet wavelengths. Photochemical release of ammonium from dissolved organic matter has important implications for nitrogen availability in many aquatic ecosystems, including nitrogen-limited high-latitude environments and coastal oceans, where inputs of terrestrial humic substances are high.

Aquatic humic substances are organic acids (of molecular masses between 500 and 10,000), operationally defined on the basis of their retention on hydrophobic resins and further categorized as humic acids or fulvic acids based on their solubility at low pH². Humic substances make up the largest single class of dissolved organic matter (DOM), accounting for 30 to 60% of the DOM in most natural waters³. Although abundant, they are considered to be the component of DOM from which all easily available energy has already been extracted, and therefore have received little attention from a microbiological perspective. The accessibility of carbon in humic substances to bacteria may, however, be considerably greater than previously assumed^{3,4}. Exposure to sunlight enhances the breakdown of humic carbon to lower-molecular-mass compounds, some of which are assimilated rapidly by natural bacteria^{5–10}.

Despite recent advances in our understanding of the biogeochemistry of humic carbon, the fate of the nitrogen bound in aquatic humic substances and its susceptibility to photochemical degradation have yet to be addressed. Humic substances have been considered as unlikely sources of nitrogen for microbial food webs because the biological availability of humic-bound nitrogen is low for both marine and freshwater environments^{11,12}. Furthermore, C:N ratios of humic substances are high (averaging 50:1; ref. 2), making it unlikely that they can supply nitrogen to bacterial degraders in the required proportions to carbon for growth, and less likely that bacteria can regenerate ammonium from humic substances for use by autotrophs¹³. This current view of the ecological and biogeochemical roles of humic substances would need to be modified, however, should some significant fraction of humic-bound nitrogen prove to be readily assimilable by planktonic microorganisms.

In a study designed to examine the effects of solar radiation on the biological availability of humic substances, the fulvic acid fraction of DOM isolated by hydrophobic resin¹⁴ from a boreal pond was reconstituted in deionized water at its original concentration (891 µM C) and exposed in quartz flasks to natural sunlight

for four hours. Twelve bioassay treatments were established by additions of inorganic nutrients (N only, P only, or N plus P) and/or a labile carbon source (glucose) to irradiated or non-irradiated fulvic acid solutions. The growth of natural bacterioplankton was followed over the next 92 h as an assay for biological availability. Bacterial growth was low in all fulvic acid solutions without added inorganic P (Fig. 1a, c, e). In the presence of sufficient P, however, growth was significantly enhanced in treatments exposed to sunlight and in those with labile carbon additions (Fig. 1b, d, f). The striking lack of an inorganic nitrogen effect on biological availability suggests that the fulvic acids themselves provided sufficient

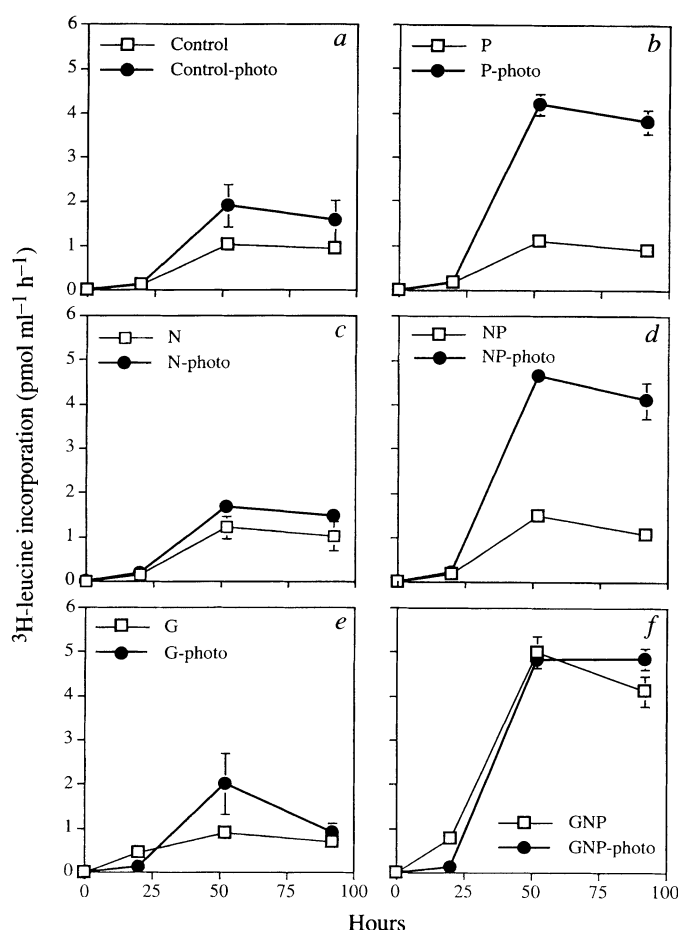


FIG. 1 Bacterial bioassay to determine biological availability of boreal pond fulvic acids. A fulvic acid concentrate was isolated by XAD-8 resin without cation exchange¹⁴ from Tower pond (BOREAS project site, northern Manitoba, Canada) in June 1994 and redissolved at its natural concentration in low organic content deionized water. Bacterioplankton were concentrated from the site by differential filtration³ and inoculated into irradiated or non-irradiated fulvic acid solutions with no amendments (control), or with amendments of 4.5 μM P as PO_4 (P treatment); 40 μM N as NH_4NO_3 (N treatment); both N and P (NP treatment); 116 μM labile C as glucose (G treatment); or glucose, N and P (GNP treatment). Initial bacterial concentrations averaged 2.2×10^5 bacteria ml^{-1} . Bacterial growth on fulvic acids was measured as rates of incorporation of ^3H -leucine into bacterial protein³³ at 0, 20, 52 and 92 h after inoculation; $n = 3$, ± 1 s.d. Rates of growth were significantly higher in the irradiated treatment in both 52 and 92 h samples in a, b and d ($P < 0.05$, Mann-Whitney U-test). Rates of growth were significantly higher in the irradiated treatment in 52 h samples in c and e. There were no significant differences between irradiated and non-irradiated treatments in f.

TABLE 1 Estimated photochemical production of ammonium from aquatic dissolved organic matter

Sample	Production rate ($\mu\text{M h}^{-1}$)	Normalized production rate ($\mu\text{M m h}^{-1} \times 10^3$)	DOC (μM)	DON (μM)	Fractional conversion ($\text{h}^{-1} \times 10^3$)	pH	Exposure time (h)	Exposure region	Exposure type
Boreal pond, whole (July)	0.15 ± 0.010	3.5	3,000	55	2.7	7.6	18	Full	Artificial
Boreal pond, whole (July)	0.11		3,000	55		7.6	18	>320 nm	Artificial
Boreal pond, whole (July)	0.080		3,000	55		7.6	18	>360 nm	Artificial
Boreal pond inlet, fulvic acid (June)	0.37 ± 0.010	ND	895	ND		6.6	4.8	Full	Natural
Boreal pond, fulvic acid (August)	0.065 ± 0.010	2.5	1,133	24	2.7	6.5	6.6	Full	Artificial
Okefenokee swamp, whole	0.34 ± 0.030	3.2	3,840	86	3.4	3.9	18	Full	Artificial
Okefenokee swamp, whole	0.22		3,840	86		3.9	18	>320 nm	Artificial
Okefenokee swamp, whole	0.059		3,840	86		3.9	18	>360 nm	Artificial
Okefenokee swamp, whole	0.040		3,840	86		3.9	18	>425 nm	Artificial
Satilla River estuary, fulvic acid	0.050 ± 0.015	4.2	787	20	2.5	5.6	8	Full	Natural
Suwannee River, whole	0.36		ND	74		ND	36	>320 nm	Artificial
Oyster River, fulvic acid	0.32	3.2	2,840	36	9.2	ND	18	Full	Artificial
Fluka, humic acid	0.23	1.8	1,942	51	4.7	ND	18	Full	Artificial

Whole water samples or humic substance fractions were filtered through 0.22 μm membrane filters and stored at 4 $^{\circ}\text{C}$. Samples were exposed to natural sunlight (33 $^{\circ}$ N, 83 $^{\circ}$ W, Athens, Georgia, USA) or artificial sunlight (DSET Heraeus solar simulator). For some samples, the irradiance was attenuated in the ultraviolet using filters; wavelengths indicated correspond to 50% transmittance. Exposure time is expressed as approximate hours of midday natural sunlight at 33 $^{\circ}$ N latitude in January (860 W m^{-2} for the 200–3,000 nm wavelength range). Ammonium concentrations were measured by ion chromatography using conductivity detection (Alltech Cation/R column; 3 mM HNO_3 eluent)²⁸ or by the Koroleff method²⁹. Normalized production rates for samples exposed to full spectrum sunlight were calculated by dividing hourly production rates by each sample's absorption coefficient at 350 nm (ref. 7). DOC, dissolved organic carbon. DON, dissolved organic nitrogen. Fractional conversion rates for samples exposed to full spectrum sunlight were calculated by dividing the hourly production rates of ammonium by the concentration of DON in the sample. DON concentration for the Satilla River estuary sample was estimated assuming a 40:1 C:N ratio for Satilla River fulvic acids²⁰. Where standard deviations are indicated, $n = 2$ or 3 ± 1 s.d. ND, not determined. The boreal pond site is located in northern Manitoba, Canada; the Okefenokee swamp, Satilla River estuary, and Suwannee River sites are in southern Georgia, USA; and the Oyster River site is in New Hampshire, USA. Fluka humic acid is a commercial preparation.

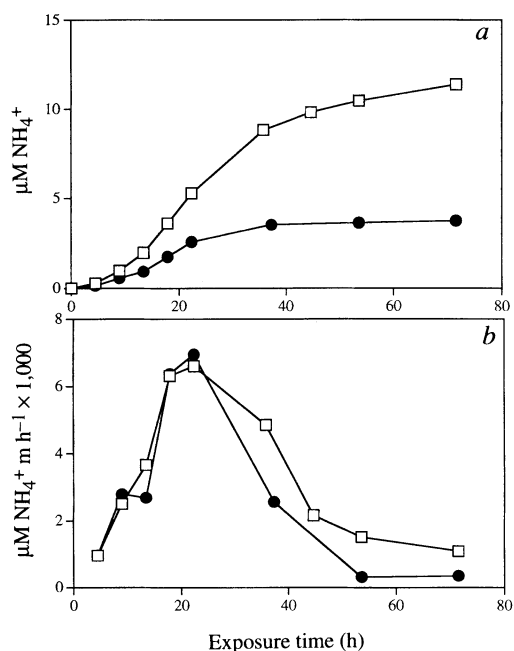


FIG. 2 Concentrations of ammonium (a) and absorptivity normalized rates of ammonium formation (b) in irradiated natural waters from a boreal pond (northern Manitoba, Canada) (●) and from the Okefenokee swamp (Georgia, USA) (□). Water samples were sealed in quartz tubes with no headspace and were irradiated in a DSET Heraeus solar simulator at 860 W m^{-2} (200–3,000 nm wavelength range) for 72 h. Concentrations of ammonium were determined at intervals during continuous irradiation by ion chromatography using conductivity detection²⁶. Absorptivity-normalized rates were calculated by dividing average hourly production rates by the average absorptivity of the sample at 350 nm (ref. 7).

BOX 1 Coastal photo-ammonification

PHOTOCHEMICAL ammonification from DOM on the southeastern United States continental shelf was calculated using near-surface daily fractional conversion rates of riverine DON to ammonium for Satilla River estuary water in July (this work), modified based on relative action spectra that have previously been determined for DOM photodegradation⁶ and average seasonal solar spectral irradiance at 32°N latitude (assuming a 15% reduction in ultraviolet irradiance from average daily cloud cover)⁶. Seasonal estimates of $23.8 \times 10^{-3} \text{ d}^{-1}$ (spring), $26.7 \times 10^{-3} \text{ d}^{-1}$ (summer), $16.8 \times 10^{-3} \text{ d}^{-1}$ (autumn), and $12.2 \times 10^{-3} \text{ d}^{-1}$ (winter)⁶ were then averaged across seasons and corrected for light attenuation with depth^{30,31} to give corrected daily fractional conversion rates of $0.40 \times 10^{-3} \text{ d}^{-1}$ for the inner shelf (0–20 m depth, 1 m photic zone), $8.5 \times 10^{-3} \text{ d}^{-1}$ for the mid-shelf (20–40 m depth, 50 m photic zone), and $5.1 \times 10^{-3} \text{ d}^{-1}$ for the outer shelf (40–60 m depth, 50 m photic zone). The DON available for photochemical conversion in each litre of exported river water was estimated to be 0.21 mg N, calculated from the weighted average of DON in river water in the southeastern United States^{20–22} and assuming half the DON pool to be photochemically active. The average residence time of riverine DON on the southeastern United States shelf was taken to be 75 d: 25 d on the inner shelf, 43 d on the mid-shelf and 7 d on the outer shelf^{22,31,32}.

From these calculations, 6.0 μmol ammonium are estimated to be produced photochemically from each litre of water exported from rivers to the southeastern United States continental shelf. On an annual basis, 0.44×10^4 tons N (as ammonium) are formed on the shelf from exported DON, with 0.30×10^4 tons N formed on the mid-shelf alone. Relative to dissolved inorganic nitrogen export, photochemical ammonification increases calculations of available terrestrially derived N in this coastal ecosystem by 20%. □

assimilable nitrogen for bacterial degraders, a finding in conflict with the reported recalcitrance of humic nitrogen. However, nitrogen sufficiency was only observed after exposure to sunlight, indicating that photochemical processes made the humic nitrogen available to natural bacterial populations.

To confirm that assimilable nitrogen was indeed being released photochemically from humic substances, natural DOM and/or humic substances from five environments and a commercial humic acid were exposed to sunlight in quartz vessels. Chemical analysis indicated that ammonium was formed in all samples during exposure to solar radiation (Table 1), regardless of the matrix (that is, unmanipulated DOM or humic substances reconstituted in deionized water); alteration of the solar spectrum by filters demonstrated that ultraviolet wavelengths (295 to 360 nm) were primarily responsible. In long-term irradiations of DOM from two sites with simulated sunlight (equivalent to nine sunny days⁷), kinetics of ammonium formation were found to be complex, with a lag of 22 h before peak formation rate (Fig. 2); these data suggest the possibility of a multistep mechanism for photochemical ammonification. Initial rates of ammonium formation in these two samples were dependent on exposure time but were nearly identical when normalized to the absorbance at 350 nm, a wavelength at which absorbance is approximately proportional to humic substance concentration. During longer exposures, photo-production rates of ammonium were more variable (Fig. 2), as were overall conversions of dissolved organic nitrogen (DON) to ammonium (16% conversion for the Okefenokee swamp, 7% for the boreal pond). The high rate of ammonium production measured for the June boreal pond sample (Table 1) suggests that photochemical ammonification may be greatest for DOM with little prior exposure to sunlight, in this case immediately after the spring thaw.

Element analysis of typical aquatic humic substances indicates that nitrogen accounts for 0.5 to 2% of humic substances by weight². About 25 to 50% of this N appears to be an integral and unreactive component, although relatively little is known about its exact chemical structure¹⁵. The remainder includes a mixture of amino sugars and other nitrogen-rich compounds that, under acidic conditions, hydrolyse to ammonia and amino acids^{2,16}. We propose that this latter class of compounds, although clearly not biologically available when associated with humic substances (Fig. 1), can be converted to ammonium and other assimilable forms of nitrogen by photochemical processes and subsequent hydrolysis reactions. For example, ketones and aldehydes, known constituents of humic substances, photoreact with organic amines to produce imines that hydrolyse to ammonium¹⁷. Radiolabelled amino acids complexed to soil humic substances have likewise been found to be biologically unavailable until irradiated with ultraviolet light¹⁸.

The bacterial bioassays indicate that conversion of DON to a readily assimilable form resulted in an increase in the rate of degradation of humic substances. Based on increases in bacterial biomass and assuming a 30% carbon conversion efficiency³, we calculate that bacteria used 1.3% of photodegraded boreal pond humic carbon in 52 h when inorganic nitrogen and phosphorus were both limiting, but 2.6% when inorganic nitrogen was the only nutrient in limited supply. Assuming first-order degradation kinetics, the release of assimilable nitrogen results in a decrease in the half-life of photodegraded humic substances from 124 to 57 d under inorganic nitrogen limitation. Nitrogen is generally limiting to production in boreal ecosystems¹⁹, suggesting that the photochemical release of ammonium and possibly other biologically available nitrogenous compounds from humic substances may be a key process regulating microbial turnover of DOM in these systems.

This discovery of photochemical ammonification of DOM will alter current views of the sources of nitrogen available to fuel autotrophic and heterotrophic processes in planktonic environments. For example, organic nitrogen is a dominant form of terrestrial N exported to the coastal waters of the southeastern

United States (2.2×10^4 tons year⁻¹; 48% of total N export^{20–22}). Although terrestrially derived organic N has previously been considered unavailable to coastal plankton^{23,24}, our calculations indicate that $\sim 0.44 \times 10^4$ tons of ammonium can be produced photochemically from DOM on the southeastern United States shelf annually (see Box 1). This value increases calculations of the terrestrial N available to microorganisms on the shelf by 20%, and suggests the importance of this and other coastal regions as sites of DON decomposition in the ocean. The minimal light penetration on the inner shelf of the southeastern United States greatly reduces photoreaction rates, and thus most of the photochemical ammonification ($\sim 70\%$) occurs on the mid-shelf, a region not expected to receive significant terrestrial inorganic N through riverine export²⁴.

The general importance of photochemical N release from DOM is also suggested by previous studies in Swedish coastal waters²⁵, in which additions of riverine humic substances were found to increase nitrogen availability and stimulate rates of primary and secondary production. Worldwide, DON is estimated to account for almost 70% of the N that enters coastal oceans in rivers (10×10^{12} g N yr⁻¹; ref. 26), and future changes in global climate and precipitation patterns are expected to increase the movement of riverine DON to the sea²⁷. Ultimately, the participation of DON in autotrophic and heterotrophic biomass production, N₂O production, denitrification, eutrophication and other fundamental biogeochemical processes requires conversion to biologically available forms. This previously unrecognized mechanism for DON conversion to assimilable N by photochemistry significantly alters current understanding of the sources of biologically active nitrogen in aquatic ecosystems. □

Determination of olivine cooling rates from metal-cation ordering

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THE mineral olivine—(Fe,Mg,Mn)₂SiO₄—is the dominant phase in the Earth's upper mantle, and is also present in a wide range of igneous rocks. Metal cations in olivine crystals are partitioned between two structurally distinct octahedral sites, a property which could in principle be used to obtain important information regarding the thermal history of the host rock. But attempts to establish the temperature and pressure dependence of cation ordering, mainly from the room-temperature structures of samples that have been annealed and quenched^{1–3}, have yielded contradictory information. In fact, recent studies have shown that considerable re-ordering occurs during the quenching process^{4,5}, and thus cation ordering is unlikely to be representative of high-temperature equilibration. Here we present a new model of the thermodynamics and kinetics of metal partitioning in olivine, derived from *in situ* neutron-diffraction measurements of cation ordering in the synthetic olivine (Fe_{0.5}Mn_{0.5})₂SiO₄. Our results suggest that the room-temperature structure of a quenched olivine reflects the rate at which the mineral cooled. The extension of this approach to common rock-forming olivines should provide a valuable 'geospeedometer' for determining the cooling rates of rocks that have cooled relatively rapidly.

It has been recognized for some time that non-equilibrium cation ordering in minerals might provide a means to measure rock cooling rates, from early work on Mg/Fe ordering in amphiboles⁶ and extensive studies of pyroxenes^{7,8} to more recent analysis of Al/Si ordering in alkali feldspars⁹. Displacive phase transitions and exsolution phenomena can obscure the behaviour of these rather complex phases, however, and cation ordering in structurally simple olivine might provide a more robust method of determining thermal histories. The ability to determine cooling rates of olivine phenocrysts from partitioning of the cations over the structurally distinct M1 and M2 octahedral sites would be invaluable in a number of geological scenarios. For example, ancient strombolian-type eruptions could be distinguished from eruptions involving less-rapid quenches on the basis of expected differences in M-site partitioning of olivines contained within them. Such a geospeedometer could also be applied to understanding the cooling processes of high-level alkali olivine basaltic sills, which contain picritic units formed by emplacement of magmas carrying suspended olivine (such as observed in the Scottish Tertiary province). Cooling rates measured from an olivine geospeedometer would resolve the serious disagreement over whether such sills cooled rapidly by a process involving convection¹⁰ or more slowly, mainly by conduction^{11,12}. The ability to determine olivine cooling rates would transform our appreciation of a host of such problems in igneous petrology, so far unaddressed because of the lack of a reliable method.

Geospeedometry from intracrystalline cation partitioning demands precise and accurate knowledge of site occupancies. To test the viability of olivine geospeedometry we therefore chose first to focus on Fe–Mn intracrystalline exchange, exploiting the very large contrast between the neutron scattering lengths of Fe

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- Hedges, J. I. *Mar. Chem.* **39**, 67–93 (1992).
- Thurman, E. M. *Organic Geochemistry of Natural Waters* (Junk, Boston, 1985).
- Moran, M. A. & Hodson, R. E. *Limnol. Oceanogr.* **35**, 1744–1756 (1990).
- Tranvik, L. J. *Appl. envir. Microbiol.* **56**, 1572–1677 (1990).
- Kieber, D. J., McDaniel, J. & Mopper, K. *Nature* **341**, 637–639 (1989).
- Valentine, R. & Zepp, R. G. *Envir. Sci. Technol.* **27**, 409–412 (1993).
- Miller, W. L. & Zepp, R. G. *Geophys. Res. Lett.* **22**, 417–420 (1995).
- Lindell, M. J., Granéli, W. & Tranvik, L. J. *Limnol. Oceanogr.* **40**, 195–199 (1995).
- Wetzel, R. G., Hatcher, P. G. & Bianchi, T. S. *Limnol. Oceanogr.* **40**, 1369–1380 (1995).
- Miller, W. L., Zepp, R. G., Moran, M. A., Sheppard, E. S. & Hodson, R. E. *Eos* **75**, 327 (1994).
- Rice, D. L. *Mar. Ecol. Prog. Ser.* **9**, 153–162 (1982).
- Valiela, I. & Teal, J. M. *Nature* **280**, 652–656 (1979).
- Caron, D. A., Goldman, J. C. & Dennett, M. R. *Hydrobiologia* **159**, 27–40 (1988).
- Bourbonnière, R. A. *Org. Geochem.* **14**, 97–107 (1989).
- Schnitzer, M. in *Humic Substances in Soil, Sediment, and Water* (eds Aiken, G. R., McKnight, D. M., Wershaw, R. L. & MacCarthy, P.) 303–325 (Wiley, New York, 1985).
- Stevenson, F. J. *Humus Chemistry* (Wiley, New York, 1994).
- Cohen, S. G. & Ojanpera, S. J. *Am. chem. Soc.* **97**, 5633–5634 (1975).
- Amador, J. A., Alexander, M. & Zika, R. G. *Appl. Envir. Microbiol.* **55**, 2843–2849 (1989).
- Pastor, J. & Mladenov, D. J. in *A Systems Analysis of the Global Boreal Forest* (eds Shugart, H. H., Leemans, R., Boman, G. B.) 216–240 (Cambridge Univ. Press, Cambridge, 1992).
- Alberts, J. J. & Filip, Z. *Trends Chem. Geol.* **1**, 143–162 (1994).
- Stokes, W. R., Hale, T. W., Pearman, J. L. & Buell, G. G. *Water Resources Data Georgia US Geological Survey Water-Data Reports GA-85-1* (1986); *GA-87-1* (1988); *GA-90-1* (1991); *GA-92-1* (1992).
- Moran, M. A. & Hodson, R. E. *Limnol. Oceanogr.* **39**, 762–771 (1994).
- Verity, P. G., Emmanuele, K. A. & Yoder, J. A. *Estuaries* **7**, 506–512 (1984).
- Verity, P. G. et al. *Cont. Shelf Res.* **13**, 741–776 (1993).
- Carlsson, P., Segatto, A. Z. & Granéli, E. *Mar. Ecol. Prog. Ser.* **97**, 105–116 (1993).
- Meybeck, M. *Am. J. Sci.* **282**, 401–450 (1982).
- Galloway, J. N., Schlesinger, W. H., Levy, H., Michaels, A. & Schnoor, J. L. *Global biogeochem. Cycles* **9**, 235–252 (1995).
- Krol, J., Alden, P. G., Morawski, J. & Jackson, P. E. *J. Chromat.* **626**, 165–170 (1992).
- Grasshoff, K., Ehrhardt, E. & Kremling, K. *Methods of Seawater Analysis* (Verlag Chemie, Weinheim, 1983).
- Zepp, R. G. & Cline, D. M. *Environ. Sci. Technol.* **11**, 359–366 (1977).
- Yoder, J. A. in *Oceanography of the Southeastern US Continental Shelf* (eds Atkinson, L. P., Menzel, D. W. & Bush, K. A.) 93–103 (Am. Geophys. Union, Washington DC, 1985).
- Atkinson, L. P., Blanton, J. O. & Haines, E. B. *Estuar. Coastal Mar. Sci.* **7**, 464–472 (1978).
- Smith, D. C. & Azam, F. *Mar. Microb. Food Webs* **6**, 107–114 (1992).

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