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agreement with that (about fivefold) hypothesized by Shirahata and colleagues. (25); it is lower than the increase (about tenfold) speculated by Patterson earlier (26). During the Greco-Roman times, most Pb emitted to the atmosphere would have been due to lead-silver mining and smelting in Spain (which represented \sim 40% of the worldwide Pb production during the Roman Empire), Central Europe, Britain, the Balkans, Greece, and Asia Minor (5, 6). The Pb was produced in open-air furnaces with no control on emission rates. Small Pb aerosol particles emitted during these activities could easily be transported from these regions to the Arctic through well-known pathways (27, 28). However, differences in transport efficiencies between the different source regions and central Greenland cannot be ruled out. Such differences could, for instance, help to explain why Pb levels in the ice during the Greek and Roman periods are similar, although Pb production was severalfold lower during Greek times. An alternative explanation could be the differences in Pb emission rates for mining and smelting activities between the Greek and Roman times or uncertainties in the historical data shown in Fig. 1A.

The cumulative anthropogenic Pb fallout over Greenland from ~ 2500 to 1700 years ago, estimated by combining a Pb excess value of $\sim 1 \text{ pg/g}$ over the value during the pre-Pb time with a mean ice accumulation rate of 23 g of H_2O cm⁻² year⁻¹, is 23 × 10⁻¹² g of Pb cm⁻² year⁻¹. Over 800 years, this rate represents 1.84 imes 10^{-8} g of Pb cm⁻². For the whole Greenland ice cap (surface of $1.4 \times 10^6 \text{ km}^{2}$, mean annual accumulation rate of 34 g of $H_2O~cm^{-2}~year^{-1}$), the net deposition is about 400 tons during these 800 years. This estimate is as much as $\sim 15\%$ of the cumulative fallout of Pb to Greenland during the past 60 years that is linked to the massive use of Pb alkyl additives in gasoline, calculated from a mean concentration of 100 pg of Pb per gram in 1930 to 1990 Greenland snow (29). Further evidence of this hemispheric-scale pollution by Greco-Roman civilization might be found in other archives, such as sea sediments in the North Atlantic Ocean and in the Mediterranean Sea. Analyses of lead isotopes could fingerprint the relative contributions of the different ancient mining districts to this pollution.

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$$\begin{split} & EF_{crust}(Pb) = (Pb_{ice}/Al_{ice})/(Pb/Al)_{mean\ crust} \\ & \text{where Pb}_{ice} \text{ and } Al_{ice} \text{ are the measured concentrations of Pb and Al in the ice, respectively, and (Pb/Al)_{mean\ crust} is the Pb/Al ratio in mean\ crustal material given by Taylor and McLennan (22). Such crustal reference material is appropriate to characterize the$$

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Nitrogen Uptake, Dissolved Organic Nitrogen Release, and New Production

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In oceanic, coastal, and estuarine environments, an average of 25 to 41 percent of the dissolved inorganic nitrogen (NH₄⁺ and NO₃⁻) taken up by phytoplankton is released as dissolved organic nitrogen (DON). Release rates for DON in oceanic systems range from 4 to 26 nanogram-atoms of nitrogen per liter per hour. Failure to account for the production of DON during nitrogen-15 uptake experiments results in an underestimate of gross nitrogen uptake rates and thus an underestimate of new and regenerated production. In these studies, traditional nitrogen-15 techniques were found to underestimate new and regenerated production by up to 74 and 50 percent, respectively. Total DON turnover times, estimated from DON release resulting from both NH₄⁺ and NO₃⁻ uptake, were 10 \pm 1, 18 \pm 14, and 4 days for oceanic, coastal, and estuarine sites, respectively.

A paradigm of modern oceanography is that the production of biomass within the surface ocean is nitrogen-limited and that primary production is supported in part by nitrogen supplied from outside the system (new production) and in part by nitrogen supplied within the system [regenerated production (1)]. Researchers have assumed that new and regenerated production could be traced independently by using ¹⁵N tracer

measuring NO_3^- uptake, and regenerated production is estimated by measuring NH_4^+ uptake (1). Furthermore, uptake of new nitrogen (that is, NO_3^-) by phytoplankton is thought to be equal to the upward flux of NO_3^- into surface waters, and this flux is approximately balanced by the flux of particulate nitrogen (PN) out of surface waters over appropriate space and time scales (2) (Fig. 1A).

techniques; new production is estimated by

This paradigm for new production has been used to guide our thinking about the interaction between inorganic nitrogen $(NH_4^+ \text{ and } NO_3^-)$, primary production, and particle flux for the past two decades.

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One nitrogen pool conspicuously absent from this discussion, however, is DON. Although DON can constitute nearly 100% of the available nitrogen in oligotrophic systems (3), relatively little is known about it, in part because of the perception that DON is a largely refractory pool and in part because of the considerable methodological problems involved in measuring DON fluxes. Although researchers have hypothesized various roles for DON over the past 15 years (2), there were no quantitative data on flux rates of the DON pool as a whole; however, the tiny fraction of the DON pool composed of dissolved and combined amino acids and urea has been extensively studied (4). Recently, methods have been developed to isolate DON so that its release and uptake rates could be quantified (5, 6). It now appears that DON release is a ubiquitous process that can be measured in every environment that has been studied, from eutrophic rivers to oligotrophic oceans.

Traditionally, nitrogen uptake rates are measured with the stable isotope ¹⁵N, resulting in estimates of the accumulation of ¹⁵N-labeled nitrogen in phytoplankton cells, designated by ρ ; we refer to this rate as the net uptake rate. Our data indicate that the total amount of nitrogen taken up by phytoplankton, regardless of its ultimate fate, is up to 74% greater than the net uptake rate; we refer to this rate as the gross uptake rate, ρ_G (7). The discrepancy between gross and net uptake rates results from the release of ^{15}N label to the DON pool during ¹⁵N tracer experiments (5) (Fig. 1B). When ¹⁵N-labeled DON is released into the extracellular DON pool, it is lost from PN and is no longer measured as uptake in the traditional calculation of ρ .

We performed ¹⁵N uptake and DON release experiments in oligotrophic ocean waters of the Caribbean Sea, in offshore and coastal waters of the Southern California Bight, and in the Chesapeake Bay estuary (8). The ratio of $\rho:\rho_G$ was 0.59 ± 0.21 in the oligotrophic and offshore oceanic regions, 0.73 ± 0.11 in the coastal system, and 0.75 ± 0.12 in the estuary (Table 1). Thus, an average of 25 to 41% of the nitrogen taken up by phytoplankton as NH₄⁺ or NO₃⁻ was released as DON. Rates of DON release from these studies ranged from 3.4 to 66.2 ng-atoms of nitrogen per liter per hour.

To address the general lability of DON, we calculated turnover times by dividing the ambient DON concentration by the rate of DON release; turnover times ranged from 6 to 91 days (Table 1). If we assume that both $\rm NH_4^+$ and $\rm NO_3^-$ are used as nitrogen substrates by plankton and thus contribute to DON release, a total DON turnover time can be calculated if we use the sum of release rates from both $\rm NH_4^+$ and $\rm NO_3^-$ incubations at

Fig. 1. (A) The traditional view of new production where (a) the upward vertical flux of NO_3^- is equal to (b) the rate of net NO_3^- uptake (measured with traditional ¹⁵N techniques, ρ) and also equal to (c) the downward flux of PN to the deep ocean. (B) Revised view of nitrogen flow where (a) upward vertical flux of NO_3^- plus (f) nitrification plus (g) atmospheric deposition is equal to (b) the net NO_3^- uptake rate plus (d) the rate of DON release. The sum of (b) and (d) equals the gross NO_3^- uptake rate, ρ_G . Over appropriate time and space scales, (b) the net uptake rate plus (h) the N_2 fixation



rate plus (e) the incorporation of DON into bacterial or autotrophic biomass is equal to (c) the downward flux of PN plus (i) the downward advection of DON.

those sites where they were measured simultaneously. Total DON turnover times were 10 ± 1 , 18 ± 14 , and 4 days for oceanic, coastal, and estuarine sites, respectively. Although it is likely that a fraction of the DON pool is refractory, these relatively short turnover times suggest that another fraction appears to be turning over rapidly with flux rates of the same order of magnitude as the inorganic nitrogen fluxes traditionally considered (5, 6).

The measurement of ¹⁵N in the DON pool and subsequent revision of nitrogen uptake rates provides insight into a number of questions in biological oceanography. First, if we are to correctly estimate rates of new and regenerated production with ¹⁵N, the release of ¹⁵N label to the DON pool must be taken into account. Our gross uptake data from the coastal and oceanic sites suggest that new and regenerated production were underestimated by up to 74 and 50%, respectively, with traditional ¹⁵N techniques (Table 1). The degree of underestimation will depend on natural DON release processes as well as any potential artifactual DON release. Environments in which cells are exposed to nutrient limitation, light inhibition, viral infection, or heterotrophic grazing are areas where traditional ¹⁵N techniques will likely underestimate rates of nitrogen uptake (9). Furthermore, any condition that imparts a stress to cells, such as changes in temperature, light, or salinity, can result in artifactual release of DON; in these studies, extreme care was taken during incubation and filtration to minimize artifactual release (10).

It may be particularly important to consider the release of DON and its effect on new production estimates during periods in which biomass levels are not in near steady state, such as during the development and dissipation of a bloom. Blooms are especially interesting because a large fraction of the annual nitrogen flux out of surface waters in particles can occur at these times. Blooms can decline because of intense grazing by heterotrophs or nutrient or light limitation; these are the same conditions that have been shown to increase the release of organics (11). Release of DON, measured during a spring bloom in Chesapeake Bay, increased severalfold when the bloom began to decline (12). The larger the rate of DON release, the larger the underestimation of uptake rates and new production that will occur.

Second, a common observation in ¹⁵N tracer experiments is that the amount of ¹⁵N label added at the beginning of an experiment cannot be accounted for in the measured nitrogen pools, the ¹⁵N-labeled inorganic substrate and PN, at the end of the experiment (9, 13). This lack of mass balance prompted researchers to speculate that the missing ¹⁵N passed into another unmeasured pool (14, 15). Two common fates of unrecovered label are release as DON or incorporation of ¹⁵N-labeled inorganic substrate or recently released ¹⁵Nlabeled DON by organisms too small to be collected on the glass fiber filters (0.7 μ m) used in uptake experiments (9). The widespread observation of missing ¹⁵N in mass balances, which can be as high as 100% in some studies (13), underscores the importance of quantifying the loss of ¹⁵N to the DON pool and the widespread underestimation of uptake rates that is likely occurring.

Third, release of DON affects the calculation of a commonly determined parameter, the *f*-ratio, that is, the ratio of new production (usually NO_3^- uptake) to the sum of new production and regenerated production [usually NH_4^+ and sometimes urea uptake (1, 2)]. The *f*-ratio links new production to particle flux through the assumption that, over appropriate time and space scales, the total flux of NO_3^- into surface waters from the deep water reservoir must balance the total flux of PN out of

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Table 1. Gross (ρ_G) and net (ρ) nitrogen uptake rates, dissolved organic nitrogen (DON) release rates, and DON turnover times for studies in the Caribbean Sea (CS), oceanic and coastal Southern California Bight (SCB), and upper (north) and lower (south) Chesapeake Bay (UCB and LCB, respectively).

Loca- tion	Date	Sub- strate	Rates (ng-atoms of N per liter per hour)			ρ/	DON
			Gross uptake	Net uptake	DON release	ρ _G *	(days)
	<u> </u>		Oc	eanic			
CS CS CS SCB SCB	11-9-88 11-9-88 11-15-88 10-14-92 10-14-92	NH4 ⁺ NH4 ⁺ NH4 ⁺ NH4 ⁻ NO3 ⁻	27.9 39.4 38.9 53.2 ± 6.1 5.7 ± 1.9	20.1 30.7 25.9 26.8 ± 4.5 1.5 ± 0.4	7.8 8.7 13.0 26.4 ± 2.1 4.2 ± 1.5	0.72 0.78 0.67 0.50 0.26	49 44 29 11 ± 1 62 ± 12
Coastạl							
SCB SCB	10-15-92 10-15-92	NH4 ⁺ NO3 ⁻	60.8 ± 5.0 9.7 ± 0.7	48.4 ± 4.8 6.3 ± 0.8	12.4 ± 3.2 3.4 ± 0.2	0.80 0.65	24 ± 8 85 ± 4
Estuarine							
LCB LCB LCB UCB UCB	5-9-89 5-9-89 5-20-89 5-20-89 5-22-90 5-22-90 5-22-90	$\begin{array}{c} {\sf NH_4}^+ \\ {\sf NO_3}^- \end{array}$	36.0 44.9 303.8 154.8 151.8 539.0	32.0 30.4 237.6 92.4 100.0 478.4	4.0 14.5 66.2 62.4 51.8 60.6	0.89 0.68 0.78 0.60 0.66 0.89	91 25 6 9 8

*Averages for oceanic, coastal, and estuarine areas are 0.59 ± 0.21 , 0.73 ± 0.11 , and 0.75 ± 0.12 , respectively.

surface waters if biomass is to stay constant (Fig. 1A). If gross uptake rates, rather than traditional net uptake rates, are used, the *f*-ratios increase from 0.05 to 0.10 in the oceanic samples and from 0.12 to 0.14 in the coastal Southern California Bight. Additional research is needed to determine whether such increases in *f*-ratios are representative of other oceanic regions.

Fourth, f-ratio estimates made with traditional net uptake rates are often at odds with other independent f-ratio measures. During experiments in the equatorial Pacific, f-ratio estimates made with traditional net uptake rates were 8 to 78% lower than those calculated from $^{14}CO_2$ uptake data for all areas studied and were 63 to 89% lower than f-ratios calculated with NO₃⁻ concentration data in four out of five areas studied (16). The discrepancy between the ¹⁵Nbased f-ratios and those based on $^{14}CO_2$ uptake or on NO3⁻ concentration data could be attributable in whole or in part to the underestimate of nitrogen uptake rates due to DON release. Furthermore, estimates of NO_3^- vertical flux in the equatorial Pacific were much higher than the net NO_3^- uptake rates (16). According to our data, the vertical NO_3^- flux estimates and NO_3^- uptake rates would have been more in line if DON release had been measured and gross NO_3^- uptake rates had been used in the comparison.

Finally, how do our findings affect the new production paradigm? The paradigm states that the upward vertical flux of NO_3^- , the rate of NO_3^- uptake, and the downward flux of PN should all be in balance (Fig. 1A). According to this reason-

ing, the gross nitrogen uptake rate should be the rate compared to the upward vertical flux of NO_3^- , as it represents the total flux of NO_3^- into phytoplankton cells. However, the impact of DON release on measures of new production ultimately depends on the time scales of interest and the process by which the released DON is reassimilated by organisms. Incubation studies, in which ¹⁵N tracer techniques are used, have time scales from minutes to hours, and these short-term rates are most affected by release of DON.

On short time scales, the impact of released DON on production estimates will depend on whether the bulk of the DON is consumed by bacteria, which do not have appreciable sinking rates, or by phytoplankton, which can sink more rapidly. If most of the DON is incorporated by bacteria, the net uptake rate traditionally measured is the appropriate rate to use when comparing uptake to particle flux because the net uptake rate represents the nitrogen that has been incorporated into primarily autotrophic biomass and thus should be more directly related to the amount of nitrogen in larger particles, which are likely to sink into the deep ocean. The DON consumed by bacteria remains in the euphotic zone. If, however, a significant fraction of the released DON is used by autotrophs, whose nitrogen is more easily incorporated into sinking particles, then the gross uptake rate may more accurately predict the amount of nitrogen leaving the euphotic zone in particles because all of the nitrogen, either assimilated as inorganic nitrogen or reincorporated DON, will be in particles that would potentially sink. Although bacteria are considered the primary users of DON, recent work has shown that some phytoplankton have cell-surface enzymes that could allow them to utilize DON in larger proportions than previously thought (17). On longer time scales (months to years), the gross uptake rate should be used in particle flux comparisons because the release of DON is a temporary loss for autotrophs, and, through recycling or grazing, the nitrogen will ultimately be consumed by autotrophs again or by larger heterotrophs that will eventually sink from the euphotic zone (Fig. 1B).

The measurement of DON release rates and the recognition that traditional uptake rates have been underestimated are the latest in a series of important findings that require that the assumptions of the new production paradigm be reevaluated (Fig. 1B). The paradigm assumes that traditional ¹⁵N methods measure the total flux of NO_3^- into cells. We have shown that ρ is usually an underestimate of the total flux of nitrogen into cells because of significant release of DON. The theory assumes that all NO_3^- in the surface ocean is "new" nitrogen. Nitrification, however, has been documented at the base of the photic zone that results in the production of "regenerated" NO₃⁻ (13, 18). The practical application of the theory usually results in NO3uptake being determined as the sole measure of new production and NH4+ (and occasionally urea) uptake as the sole measure of regenerated production. New production, however, can also result from N_2 fixation; rates of N_2 fixation are increasingly recognized as higher than previously thought (19). Furthermore, the recent discovery that some phytoplankton have cell-surface enzymes (17) opens the possibility for a significant use of DON (in addition to the commonly measured urea) by autotrophs, thus affecting estimates of regenerated production. The theory has the simplifying assumption that the NO_3^- in surface waters results solely from diffusive flux from the deep ocean. Recent findings have shown that atmospheric deposition of NO_3^- is an important source of NO3⁻ to marine systems (20). Finally, the theory assumes that organic matter is transported to the deep ocean in particulate form. It has been suggested, however, that downward advection and diffusion of DON is another important transport mechanism (21); these mechanisms would be especially important for highly refractory DON components that likely have long residence times in oceanic surface waters.

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7. We measured the ¹⁵N present in the DON pool at the end of ¹⁵NH₄⁺ and ¹⁵NO₃⁻ uptake experiments by isolating DON with ion retardation resin that removes inorganic nitrogen ions [including NH₄⁺ and NO₃⁻ (5)]. Gross PN enrichments, in atom percent, which include ¹⁵N measured in the PN and extracellular DON pools, were calculated as follows:

$$N_{\rm G} = \frac{({}^{15}N_{\rm PN} + {}^{15}N_{\rm DON})}{([{\rm PN}] + [{\rm DON}]_{\rm rel})} \times 100$$
(1)

where PN_G is the gross atom percent enrichment of the PN pool corrected for loss of ^{15}N label to the DON pool; $^{15}N_{PN}$ and $^{15}N_{DON}$ are the mass of ^{15}N in the PN and extracellular DON pools, respectively; [PN] and [DON]_{rel} are the concentrations of PN_r at the end of the incubation, and nitrogen lost to the extracellular DON pool, during the incubation, respectively. Gross uptake rates (ρ_{G}) were calculated with the equation

$$P_{G} = \frac{PN_{G}}{DIN \times time} \times ([PN]+[DON]_{rel})$$
 (2)

where DIN is the atom percent enrichment of the DIN substrate pool, time is the period of incubation, and other terms are as defined in Eq. 1. Release rates of DON were calculated as

ease rate =
$$\rho_{\rm G} - \rho$$
 (3)

- 8. All experiments were performed with the basic experimental protocols described in (5). In the Caribbean Sea, 1-hour incubations were performed at 0800, 2400, and 0300 (in the order in which the data appear in Table 1) with surface water and trace additions (0.03 µg-atoms of nitrogen per liter) of 15Nlabeled NH_4^+ . In the Southern California Bight, we performed 3-hour incubations in the midafternoon, using 20-liter samples of surface water and near trace additions (0.10 µg-atoms of nitrogen per liter) of ¹⁵N-labeled NH₄⁺ or NO₃⁻. We recovered 101 \pm 11 and 99 \pm 26% of the added ¹⁵N label for the experiments in the Caribbean Sea and the Southern California Bight, respectively. All Chesapeake Bay experiments were performed with surface water and 0.5-hour incubations. In experiments performed on 9 May 1989 we used 1-liter samples and trace additions (0.03 µg-atoms of nitrogen per liter per hour) with the first performed during the day and the second performed at night (in the order in which the data appear in Table 1). Experiments on 20 May 1989 were performed at night with 1-liter samples and 5 μ g-atoms of nitrogen per liter per hour NH₄⁺ additions (final addition was 30% of the ambient NH, concentration). Experiments on 22 May 1990 were done during midday with 20-liter samples incubated with 1.8 µg-atoms of nitrogen per liter per hour additions of NH_4^+ (21% of ambient NH_4^+) and 3.7 µg-atoms of nitrogen per liter per hour additions of NO_3^- (5% of ambient NO_3^-). We recovered 94 ± 10% of the added ¹⁵N label for the experiments performed in the Chesapeake Bay
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Origin and Metamorphic Redistribution of Silicon, Chromium, and Phosphorus in the Metal of Chondrites

Brigitte Zanda, Michèle Bourot-Denise, Claude Perron, Roger H. Hewins

Chromium, silicon, and phosphorus concentrations of 0.1 to 1 percent by weight are common in metal grains in the least metamorphosed ordinary and carbonaceous chondrites. These concentrations are fairly uniform within single chondrules (but different from chondrule to chondrule) and are inversely correlated with the fayalite concentrations of the chondrule olivines. This relation shows that these chromium, silicon, and phosphorus concentrations could not have been established by condensation or equilibration in the solar nebula but are the result of metal-silicate equilibration within chondrules. Two generations of inclusions made by the exsolution of those elements have been identified: One formed during chondrule cooling and the other formed during metamorphism. The distribution and composition of the latter in type 3 to type 5 chondrites are consistent with increasing metamorphism relative to type 2 and type 3.0 material.

In primitive carbonaceous and ordinary chondrites, Fe-Ni grains contain measurable quantities of Cr, P, or Si (1-7). The presence of these elements has commonly been interpreted as resulting from equilibrium condensation in the nebula (1-3, 5, 5)7). On the basis of this hypothesis, thermodynamic calculations have been used to derive the temperature and pressure in the nebula at the time of metal condensation (1-3). However, Weisberg *et al.* (8) reported that Renazzo-like carbonaceous chondrite metal exhibits much wider ranges of Cr, P, Co, and Ni than calculated condensation curves would predict, and Scott and Taylor (9) have suggested that metal compositions could have been established during chondrule formation. Depending on these two hypotheses, two different patterns could be observed. If the latter is true, some compositional links should exist between the different components (metal and silicates) of each chondrule. In the first case, on the contrary, no relation is in principle expected between the composition of a metal grain

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and that of its close environment in the chondritic material because this composition is supposed to have been established as the grain was freely floating in the nebula.

We have carried out a systematic study of Fe-Ni metal grains in chondrites from different chemical (redox) groups and metamorphic types (10), including primitive ones whose metal was known to contain Cr, P, or Si (1–7). Metal composition was determined with an electron microprobe (minor elements were either dissolved or were in the form of small inclusions), inclusion composition with a scanning electron microscope (SEM), and inclusion structure with a Raman microprobe. Associated silicates in chondrules were also analyzed.

In all the chondrites examined, Si, P, and Cr, when present in opaque minerals (Fe-Ni and FeS), were found to be partially or totally contained in inclusions of various compositions and sizes. Solid solutions were identified only in Murchison, Renazzo, Acfer 186, and Semarkona by a clear Si, P, or Cr signal from the metal in the energy-dispersive x-ray spectrometer of the SEM, in the absence of visible inclusions or far enough from these to reject them as the source of the signal. Although occasionally mentioned (5, 11), inclusions in metal have generally been

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