

# The transformation of iodate to iodide in marine phytoplankton cultures

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**ABSTRACT:** Six species of phytoplankton, representing 6 major phylogenetic groups (2 oceanic species: a cyanobacteria, *Synechococcus* sp., and a coccolithophorid, *Emiliania huxleyi*; and 4 coastal species: a prasinophyte, *Tetraselmis* sp., the green algae *Dunaliella tertiolecta*, the diatom *Skeletonema costatum* and a dinoflagellate *Amphidinium carterae*) were tested for their ability to reduce iodate to iodide in batch cultures. They all did so to varying degrees. Thus, the reduction of iodate to iodide by phytoplankton may be a general phenomenon in the marine environment. At ambient concentrations of iodate, the rates of depletion of iodate and appearance of iodide varied between 0.8 and 0.02, and between 0.3 and 0.02 nmol  $\mu\text{g}$  chlorophyll  $\text{a}^{-1} \text{d}^{-1}$ , respectively. *E. huxleyi* was the least efficient while *A. carterae* was the most efficient in the depletion of iodate. However, in the formation of iodide, while *E. huxleyi* was also the least efficient, *Synechococcus* sp. were the most efficient. The rates of appearance of iodide were noticeably slower than the corresponding rates of depletion of iodate, suggesting that part of the iodate might have been converted to forms of iodine other than iodide in these cases. The slight mismatch in the rank order of the rates of depletion of iodate and appearance of iodide between the phytoplankton species was traced to this variable and incomplete conversion of iodate to iodide. These rates were increased by up to over an order of magnitude upon enriching the culture medium with 5 and 10  $\mu\text{M}$  of iodate. The depletion of iodate and appearance of iodide occurred in all growth phases. However, the rates might vary with growth phase and the patterns of these variations might be species-specific. Phytoplankton growth was not impeded even under unnaturally high concentrations of iodate implying that there is little interaction between iodine processing and the metabolic activity of cell growth.

**KEY WORDS:** Iodine · Elemental speciation · Nitrate reductase · Marine phytoplankton · Oxidation-reduction

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## INTRODUCTION

Iodine is the most abundant bio-intermediate minor element in the oceans (Wong 1991). It is believed to originate from the excess volatiles in the formation of seawater (Horn & Adams 1966). While the concentration of total dissolved iodine, at around 0.45  $\mu\text{M}$ , does not vary greatly with geographical location in the open

oceans, the concentration in the surface waters is frequently lower than that in the deep water by a few percentage points (Elderfield & Truesdale 1980). Iodine is found in seawater mostly in inorganic forms. However, dissolved organic iodine can be a sizable contributor in coastal and inshore waters (Truesdale 1975, Wong & Cheng 1998, 2001a,b). Based on the thermodynamics of the inorganic iodine system, iodate should be the stable and only detectable form of inorganic iodine in seawater (Sillen 1961, Wong & Brewer 1977, Wong 1980, 1982). However, significant concentrations of iodide have frequently been observed in the surface waters so that the concentrations of iodide and iodate

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may range from <0.01 to 0.3 and <0.1 to 0.45  $\mu\text{M}$ , respectively, in these waters (Tsunogai & Henmi 1971, Wong & Zhang 1992a, Wong 1995, Campos et al. 1999). Higher concentrations of iodide are found primarily in the surface waters. Thus, in the open oceans, the concentration of iodate increases with depth to an approximately constant level while that of iodide decreases with depth to around the detection limit below the euphotic zone (Elderfield & Truesdale 1980, Wong et al. 1985). Nonetheless, even in deep waters, low but detectable concentrations of iodide have been reported (Tsunogai 1971).

Much of the previous research effort on the marine geochemistry of the iodine system has been focused on documenting and understanding this paradox of the presence of iodide in seawater. Based on field observations on the distributions of iodide and iodate, it has been widely speculated that iodide is formed in the oxygenated ocean surface by the biologically mediated reduction of iodate (Wong & Brewer 1974, Elderfield & Truesdale 1980, Jickells et al. 1988, Wong & Zhang 1992a, Wong 1995). How this reduction is coupled to biological production is still unclear, and different linkages have been invoked by different investigators. Thus, while Campos et al. (1996a) linked the production of iodide to primary production, Tian et al. (1996) linked it to regenerated production. Because of the chemical similarity between iodate and nitrate, Tsunogai & Sase (1969) suggested that this reduction may be mediated by the enzyme nitrate reductase. They also provided qualitative evidence indicating that bacterial nitrate reductase may reduce iodate to iodide. Recent field observations and modelling exercises seem to support the linkage between iodate reduction and nitrate uptake (Campos et al. 1999, Hung et al. 2000, Wong 2001, Wong & Hung 2001).

Since nitrate reductase is more commonly found in phytoplankton than in bacteria, if the reduction of iodate to iodide is mediated by this enzyme, then phytoplankton may play an even more important role than bacteria in facilitating this reaction in the oceans. However, several decades of laboratory studies have left only a somewhat confused picture of the role of phytoplankton in the transformation of iodate to iodide. In one of the earliest studies, Sugawara & Terada (1967) reported that *Navicula* sp., marine diatoms, could assimilate both iodide and iodate, although iodide was preferred. In the process, both iodate and iodide could have been converted to the other form of iodine. Fuse et al. (1989) also suggested that iodide was preferentially taken up over iodate by several species of phytoplankton. Truesdale (1978) and Butler et al. (1981), on the other hand, reported that no appreciable inter-conversion between iodate and iodide was observed in the cultures of several species of diatom.

Several possible factors could have contributed to these apparently conflicting results. First, the intensity of nitrate reductase activity in a culture can be affected by the speciation and relative availability of the different forms of combined nitrogen in the culture medium (Conway 1977). For example, in the presence of reduced combined nitrogen, nitrate reduction is suppressed. Thus, if iodate reduction is linked to the activity of nitrate reductase, it may also be suppressed. Furthermore, if the same enzyme system is involved in both iodate and nitrate reduction, then, if the concentration of nitrate is much higher than the concentration of iodate, iodate may not be able to compete successfully with nitrate for the reaction site. As a result, iodate reduction may be impeded. In the earlier studies, the combined nitrogen condition in the culture was not taken into consideration in the experimental design. The culture media were frequently enriched with up to about 1 mM of nitrate while the corresponding concentrations of iodate used were orders of magnitude lower. This uncontrolled combined nitrogen condition might have affected the behavior of the phytoplankton toward the iodine species. Second, the analytical methods used for following the depletion of iodate and the appearance of iodide were not iodine species-specific and the possibility of the formation of organic iodine in the experiments was not considered. If organic iodine was formed, it could have been included as iodate in some analytical schemes so that there might not have been any evidence of a loss of iodate or a formation of iodide. Third, the possible presence of bacteria in the cultures could have affected the results. Thus, while Butler et al. (1981) observed that iodate was converted to iodide in senescent cultures of the diatom *Skeletonema costatum*, they concluded that the release of iodide was probably due to bacteria in the culture. By taking these factors into consideration, we have studied the reduction of iodate to iodide by 6 species of phylogenetically diverse phytoplankton under controlled nutrient conditions. The changes in the concentration of iodate and iodide in the culture medium were followed by using analytical methods that are specific for each of these 2 species of inorganic iodine (Herring & Liss 1974, Luther et al. 1988). Possible contamination by bacteria was carefully minimized and monitored. The results are reported here.

## MATERIALS AND METHODS

Axenic cultures were obtained from the Provasoli-Guillard Center for Culture of Marine Phytoplankton, Bigelow Laboratory, Boothbay Harbor, Maine, USA. Species representing the 6 major phylogenetic groups

of phytoplankton were used as test organisms. Two were isolated from oceanic environments (a cyanobacteria, *Synechococcus* sp. [CCMP 1334], and a coccolithophorid, *Emiliania huxleyi* [CCMP 373]); and 4 were representative of near-shore species (a prasinophyte, *Tetraselmis* sp. [CCMP 896]; a green algae, *Dunaliella tertiolecta* [CCMP 1320]; a diatom, *Skeletonema costatum* [CCMP 1332]; and a dinoflagellate, *Amphidinium carterae* [CCMP 1314]). Stock cultures were maintained in f/2 medium (Guillard & Ryther 1962) at 20°C under a 12 h light:12 h dark cycle at a photosynthetically active radiation of approximately  $50 \mu\text{E m}^{-2} \text{s}^{-1}$ . In order to minimize bacterial activities in the culture solutions, the stock cultures were treated routinely with Guillard's antibiotic solution (Sigma Chemical), which contained penicillin G sodium, streptomycin sulfate and chloroamphenicol, following the procedure of Droop (1967).

Prior to each experiment, an aliquot of a stock culture was first pre-conditioned for 4 to 5 d in an f/2 medium whose nitrate concentration had been reduced to the f/20 level before about 50 ml of it was inoculated into 2000 ml of the final growth medium. In order to provide better control of the speciation and concentrations of the iodine and combined nitrogen species in the batch culture experiments, the final growth medium used for the experiments was prepared with aged deep Sargasso Sea water collected at 2000 m. (The concentration of iodate and iodide in the aged Sargasso Sea water were 0.36 and 0.01  $\mu\text{M}$ , respectively. The concentration of iodate was similar to and the concentration of iodide was lower than those found in the surface North Atlantic; Elderfield & Truesdale 1980, Wong 1995.) Then, various known volumes of a standard potassium iodate solution were added to the growth medium. Four of the 6 species of phytoplankton tested, *Synechococcus* sp., *Tetraselmis* sp., *Dunaliella tertiolecta* and *Amphidinium carterae*, were exposed to 3 concentrations of iodate: the ambient iodate concentration and nominal concentrations of added iodate of 5 and 10  $\mu\text{M}$ . The cultures of *Emiliania huxleyi* and *Skeletonema costatum* were exposed only to a medium with no added iodate. The initial nitrate level, at f/20 (or about 88  $\mu\text{M}$  of nitrate), was still sufficient to support healthy phytoplankton growth. After the inoculation with phytoplankton cells, the culture was incubated at  $100 \mu\text{E m}^{-2} \text{s}^{-1}$  at 20°C. Filtrate controls were prepared by filtering the cultures that had been pre-conditioned at f/20 level of nitrate through 1  $\mu\text{m}$  pore size Nuclepore membrane filters for *Synechococcus* sp. and through 2  $\mu\text{m}$  pore size Nuclepore membrane filters for the other phytoplankton species. Then, about 50 ml of the filtrates was inoculated into 2000 ml of the final growth medium. This filtrate control was incubated in parallel to a culture with phyto-

plankton cells. At regular time intervals for up to 28 d, aliquots of the culture were removed for the determination of relative *in vivo* fluorescence and cell density in order to monitor phytoplankton growth and to calculate specific growth rates. About 5 ml of the culture was used for the determination of relative *in vivo* fluorescence by using a Turner Model 10 AU fluorometer. These measurements were made at the same hour of the day in order to minimize any diel variations.

After the *in vivo* fluorescence measurement, the same aliquot was preserved in a Lugol's solution for a microscopic determination of the cell density. The growth rate,  $\mu$ , was calculated from changes in cell numbers. Cells were counted by using a Neubauer hemocytometer. Separate aliquots of about 30 ml each were also obtained for the determination of chlorophyll *a* (chl *a*), iodate and iodide. These aliquots were filtered through GF/F glass fiber filters. The cells retained on the filters were used for the determination of chl *a* by the method of Parsons et al. (1984) by using a Turner Model 10 AU fluorometer. The filtrates were stored frozen in polyethylene bottles (Wong 1973, Campos 1997) until they were analyzed for iodate and iodide. Both iodate and iodide were determined by using an EG&G PAR Model 384B-4 polarographic analyzer system with a Model 303A static mercury drop electrode. Iodate was determined by differential pulse polarography according to the method of Herring & Liss (1974) as modified by Wong & Zhang (1992b). At concentrations below 0.5  $\mu\text{M}$ , iodate was determined in the sample directly. At higher concentrations, the sample was first diluted with water to give a final concentration of less than 0.5  $\mu\text{M}$  before it was analyzed. Iodide was determined by cathodic stripping square wave voltammetry by the method of Luther et al. (1988) as modified by Wong & Zhang (1992b,c). Concentrations below 0.1  $\mu\text{M}$  were determined directly. At higher concentrations, the sample was first diluted to the appropriate concentration before it was analyzed. A number of samples were analyzed for iodate and iodide in duplicate. The average precision in these determinations of iodate and iodide were both about  $\pm 10\%$  and no better than  $\pm 0.02$  and  $\pm 0.01 \mu\text{M}$  for iodate and iodide, respectively. These precisions were about a factor of 2 to 3 poorer than those obtained in open ocean waters (Wong & Cheng 1998). The high organic content in the growth medium had probably adversely affected the analytical precision. The primary intent of the experiments was to survey the general behavior of multiple species of commonly found marine phytoplankton. Each culture was sampled only 5 to 6 times over an incubation period of 28 d. The sampling intervals were not spaced closely enough to document the detailed behavior of any given species during the different growth phases.

## RESULTS

Chl *a*, relative *in vivo* fluorescence and cell density

Changes in the concentrations of chl *a*, relative *in vivo* fluorescence and cell density with time in the cultures without any added iodate are shown in Fig. 1. As expected, the exact time when a culture entered into the log, stationary and senescent phases of growth varied somewhat from species to species. The log phase of growth, as indicated by a rapid increase in the concentration of chl *a*, *in vivo* fluorescence and cell density until maximum values were reached occurred in the first 3 d of growth in *Dunaliella tertiolecta* and *Skeletonema costatum* and in the first 7 d in the other 4 species of phytoplankton. The initial concentration of chl *a* varied between 0.19  $\mu\text{g l}^{-1}$  in *Tetraselmis* sp. to 9.6  $\mu\text{g l}^{-1}$  in *D. tertiolecta*. The maximum concentrations varied by about a factor of 4, ranging from 114  $\mu\text{g l}^{-1}$  in *D. tertiolecta* to 31  $\mu\text{g l}^{-1}$  in *Amphidinium carterae* (Fig. 1a, Table 1). The stationary phase lasted between 7 and 21 d in *Emiliana huxleyi* and between 7 and 14 d in *Synechococcus* sp. For the other species, a stationary phase was not observed. The concentration of chl *a* decreased systematically and the cells entered into a senescent phase of growth immediately after a maximum concentration of chl *a* had been reached. The cell density of *Synechococcus* sp. was not determined. For the other 5 species of phytoplankton, the initial cell density and the maximum cell density ranged from  $1 \times 10^3$  cells  $\text{ml}^{-1}$  in *Tetraselmis* sp. to  $3.1 \times 10^4$  cells  $\text{ml}^{-1}$  in *E. huxleyi*, and from  $1.2 \times 10^5$  cells  $\text{ml}^{-1}$  in *A. carterae* to  $8.8 \times 10^5$  cells  $\text{ml}^{-1}$  in *E. huxleyi*, respectively (Fig. 1c, Table 1). The growth rate ranged from 0.37  $\text{d}^{-1}$  in *Synechococcus* sp. to 0.97  $\text{d}^{-1}$  in *D. tertiolecta* (Table 1).

The growth of the phytoplankton species tested was followed at nominal concentrations of added iodate of 0, 5, 10 and 25  $\mu\text{M}$  by monitoring the changes in the concentration of chl *a*, relative *in vivo* fluorescence and cell density with time. Increases in the concentration of added iodate did not change any of these curves significantly, as illustrated by the chl *a*-based growth curves obtained in the culture of *Dunaliella tertiolecta* (Fig. 2), and all the species of phytoplankton tested behaved similarly. The growth rate, maximum concentration of chl *a* and maximum cell density remained the

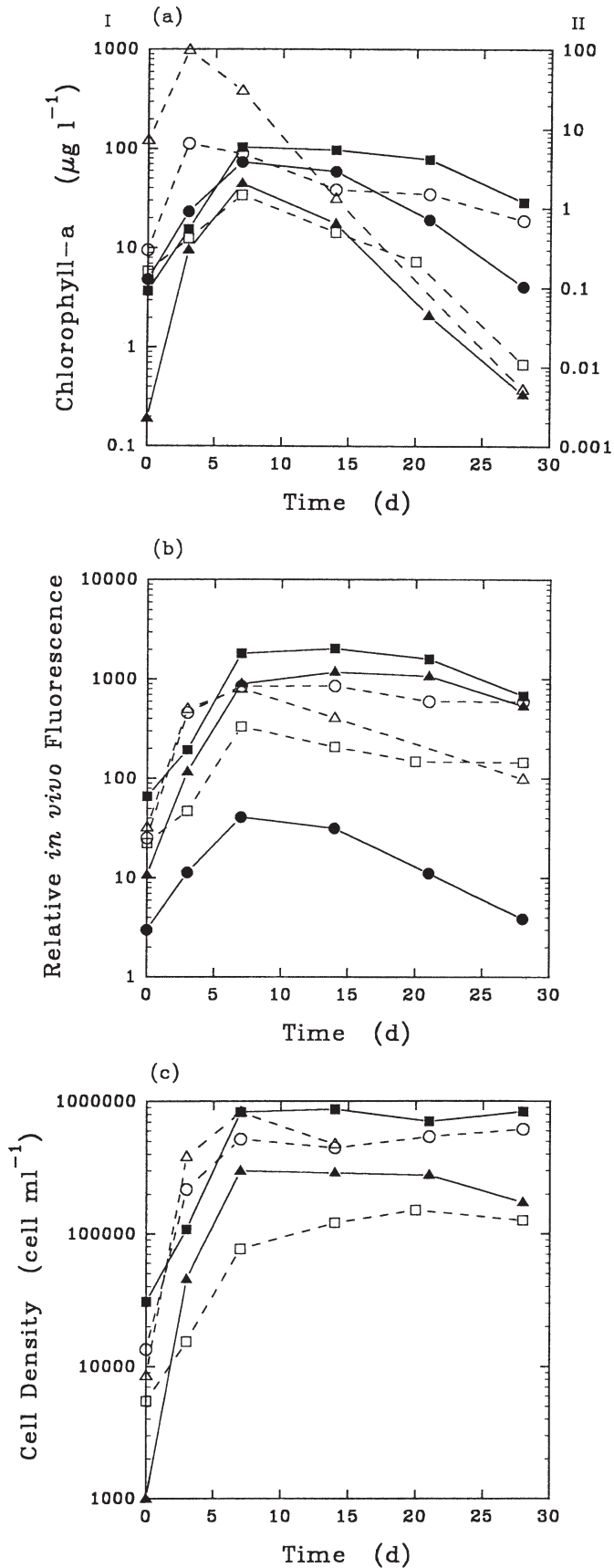


Fig. 1. Time course of change of (a) chlorophyll *a*, (b) relative *in vivo* fluorescence and (c) cell density during the incubation of *Synechococcus* sp. (●), *Tetraselmis* sp. (▲), *Emiliana huxleyi* (■), *Dunaliella tertiolecta* (○), *Skeletonema costatum* (Δ) and *Amphidinium carterae* (□) at the ambient concentration of iodate. In (a), the right scale (II) is for *S. costatum*. No cell density data for *Synechococcus* sp.

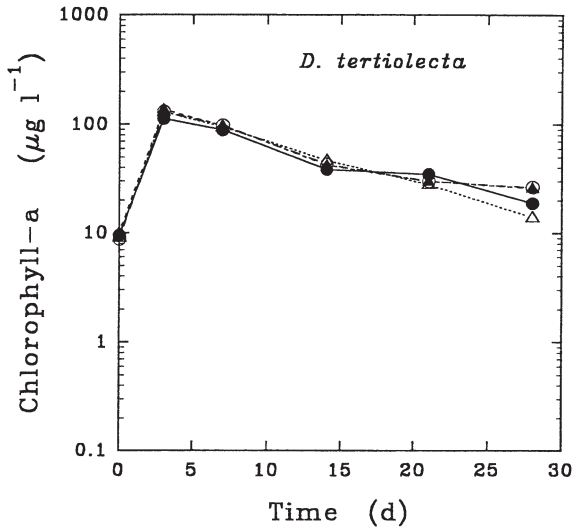


Fig. 2. Time course of change of chl a during the incubation of *Dunaliella tertiolecta* at the ambient concentration of iodate (●) and upon the addition of 5 (○), 10 (▲) or 25 (△) µM of nominal concentration of iodate

same, and they are listed in Table 1. In fact, based on relative *in vivo* fluorescence, the addition of at least up to 100 µM of iodate did not alter the growth curve of any of the species of phytoplankton tested. In the case of *Synechococcus* sp., the growth curve was not altered even at a concentration of added iodate of 2000 µM. Thus, while iodine is toxic to biological systems and is routinely used in solutions, such as Lugol's solution, for preserving phytoplankton samples, at the concentrations of iodate used in the experiments reported here, the behaviors of the phytoplankton species were not affected by the added iodate.

### Iodine speciation

A decrease in the concentration of iodate was observed at the end of the incubation period of 28 d in all the phytoplankton cultures at all the concentrations of added iodate (Figs. 3 to 8). At the ambient concentration of iodate, the concentration decrease in iodate ranged from >0.2 µM for *Dunaliella tertiolecta*, *Amphidinium carterae* and *Synechococcus* sp., to 0.1 to 0.2 µM for *Skeletonema costatum* and *Tetraselmis* sp., to <0.1 µM for *Emiliana huxleyi*. The depletion of iodate in the experiments varied between 70% in *D. tertiolecta* and 10% in *E. huxleyi*. Concomitantly, an increase in the concentration of iodide was observed in all the experiments (Figs. 3 to 8). The

Table 1. Characteristics of growth curves, iodate depletion and iodide production rates in cultures of marine phytoplankton. \* Rates were the slopes of linear regression analyses of concentration vs time. avg: average; Max chl a: maximum chlorophyll a concentration; nd: no data; Norm rate: rates normalized to time averaged concentration of chl a;  $r_d$ ,  $r_p$ : respective correlation coefficients

Phytoplankton species	Iodate added (µM)	Growth rate (d <sup>-1</sup> )	Max cell density (cell ml <sup>-1</sup> )	Max chl a (µg l <sup>-1</sup> )	Time avg chl a (µg l <sup>-1</sup> )	Iodate depletion rate* Rate (nM d <sup>-1</sup> ) Norm rate (nmol µg <sup>-1</sup> d <sup>-1</sup> ) $r_d^2$	Iodide production rate* Rate (nM d <sup>-1</sup> ) Norm rate (nmol µg <sup>-1</sup> d <sup>-1</sup> ) $r_p^2$
<b>Oceanic species</b>							
<i>Synechococcus</i> sp.	0	0.37	nd	73	38	7 ± 2	11 ± 2
	5	0.33	nd	71	33	85 ± 9	46 ± 5
	10	0.32	nd	68	31	110 ± 40	58 ± 6
<i>Emiliana huxleyi</i>	0	0.60	8.77 × 10 <sup>5</sup>	104	70	1 ± 1	1 ± 0.4
<b>Coastal species</b>							
<i>Tetraselmis</i> sp.	0	0.80	3.0 × 10 <sup>5</sup>	44	15	2 ± 2	2 ± 0.6
	5	0.82	2.9 × 10 <sup>5</sup>	38	10	80 ± 30	2 ± 0.7
	10	0.82	3.1 × 10 <sup>5</sup>	19	6	50 ± 10	4 ± 0.7
<i>Dunaliella tertiolecta</i>	0	0.97	5.4 × 10 <sup>5</sup>	114	53	8 ± 1	6 ± 1
	5	1.00	5.4 × 10 <sup>5</sup>	131	58	90 ± 20	60 ± 10
	10	0.99	5.9 × 10 <sup>5</sup>	137	58	90 ± 30	80 ± 10
<i>Skeletonema costatum</i>	0	0.92	8.3 × 10 <sup>5</sup>	98	19	4 ± 1	1 ± 1
<i>Amphidinium carterae</i>	0	0.49	1.2 × 10 <sup>5</sup>	31	13	10 ± 2	0.9 ± 0.2
	5	0.52	1.5 × 10 <sup>5</sup>	27	7	15 ± 9	1.1 ± 0.7
	10	0.51	1.4 × 10 <sup>5</sup>	27	8	24 ± 16	3 ± 1

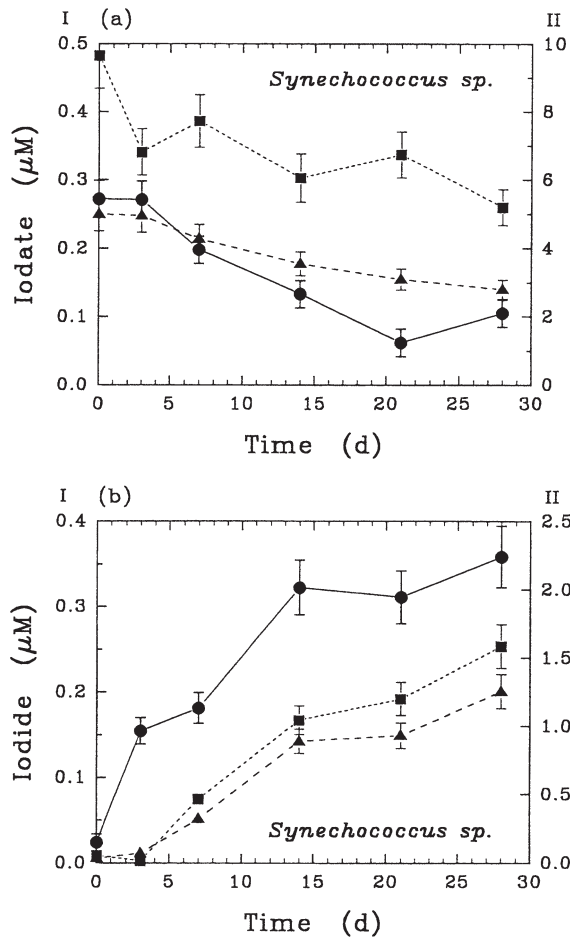


Fig. 3. Time course of change of the concentrations of (a) iodate and (b) iodide in a culture of *Synechococcus sp.* at the ambient concentration of iodate (●) (left concentration scale I) and upon the addition of 5 (▲) or 10 (■)  $\mu\text{M}$  (right concentration scale II) of nominal concentration of iodate

concentration increase in iodide ranged from  $>0.2 \mu\text{M}$  in *Synechococcus sp.* to  $0.1\text{--}0.2 \mu\text{M}$  in *D. tertiolecta* to  $<0.1 \mu\text{M}$  in *S. costatum*, *Tetraselmis sp.*, *E. huxleyi* and *A. carterae*. The concentration of iodate below which its availability may limit its reduction is not known. The concentration of iodate in these experiments did drop below the concentrations of  $0.2$  to  $0.5 \mu\text{M}$  that are usually found at the ocean surface. However, in no case did the concentration drop below  $0.06 \mu\text{M}$ . Upon the addition of nominal concentrations of iodate of  $5$  and  $10 \mu\text{M}$ , the decrease in the concentration of iodate by the end of the incubation period was no more than about  $50\%$  of the initial concentration. Thus, an ample supply of iodate was maintained in these experiments. In the filtrate controls (Figs. 4 & 6 to 8), there were no noticeable systematic changes in the concentrations of iodate or iodide during the incubation. This suggests that the activities of free-living bacteria did not con-

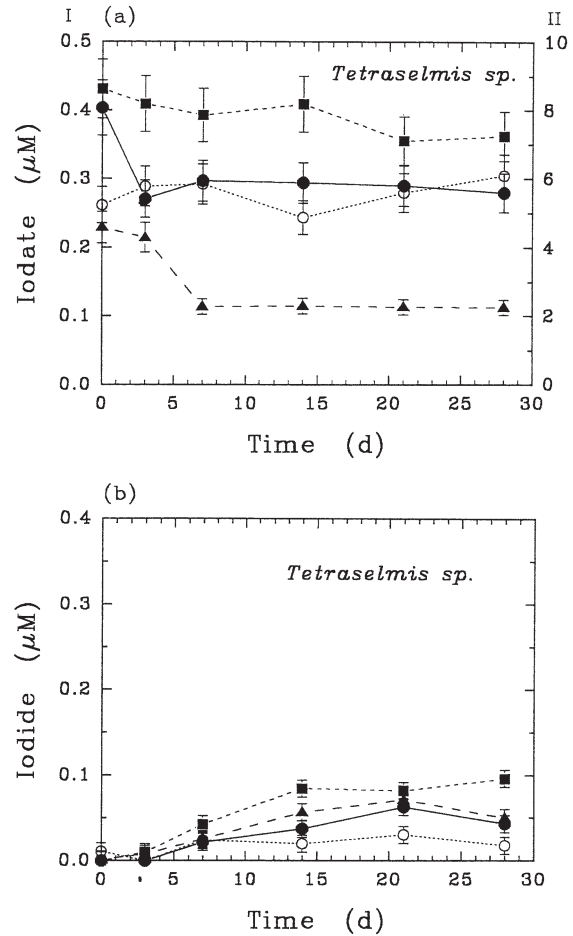


Fig. 4. Time course of change of the concentrations of (a) iodate and (b) iodide in the filtrate control (○) of a culture of *Tetraselmis sp.* and in a culture at the ambient concentration of iodate (●) and upon the addition of  $5$  (▲) or  $10$  (■)  $\mu\text{M}$  of nominal concentration of iodate. In (a), the left concentration scale (I) is for the filtrate control and the culture at the ambient concentration of iodate, while the right concentration scale (II) is for the culture with  $5$  and  $10 \mu\text{M}$  of iodate

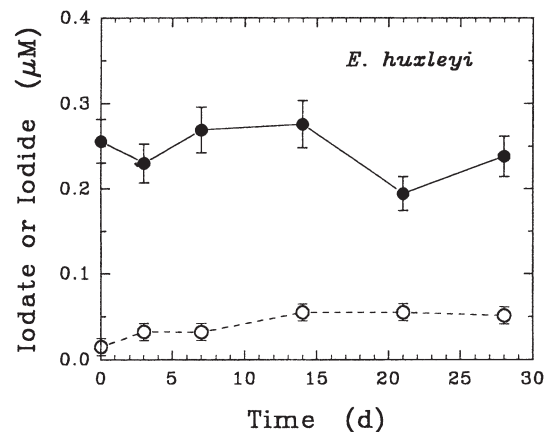


Fig. 5. Time course of change of the concentrations of iodate (●) and iodide (○) in a culture of *Emiliana huxleyi* at the ambient concentration of iodate

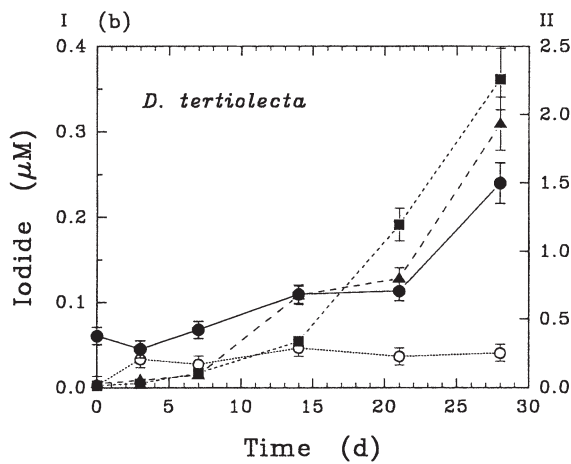
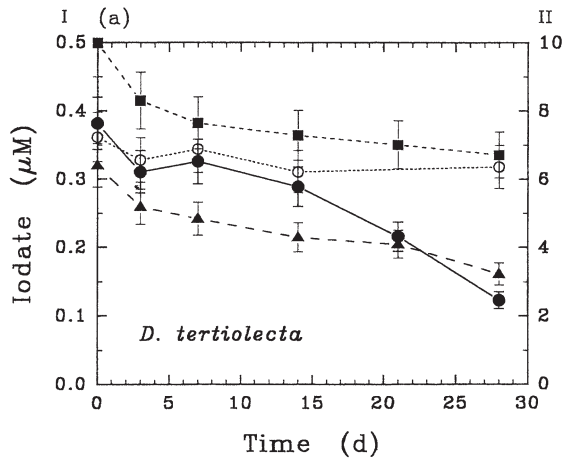


Fig. 6. Time course of change of the concentrations of (a) iodate and (b) iodide in a filtrate control (O) of a culture of *Dunaliella tertiolecta* and in a culture at the ambient concentration of iodate (●) (left concentration scale I) and upon the addition of 5 (▲) or 10 (■)  $\mu\text{M}$  (right concentration scale II) of nominal concentration of iodate

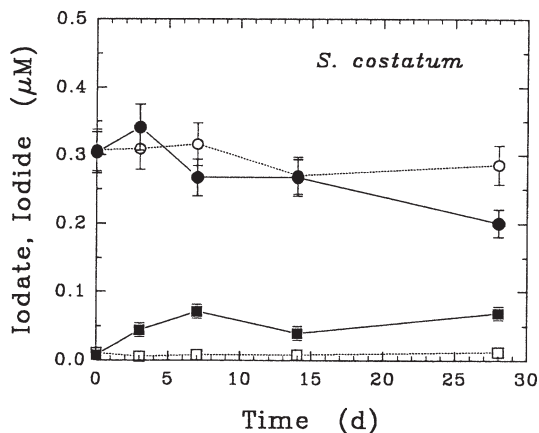


Fig. 7. Time course of change of the concentrations of iodate and iodide in a culture of *Skeletonema costatum* (●: iodate, ■: iodide) and in a filtrate control (O: iodate, □: iodide) at the ambient concentration of iodate

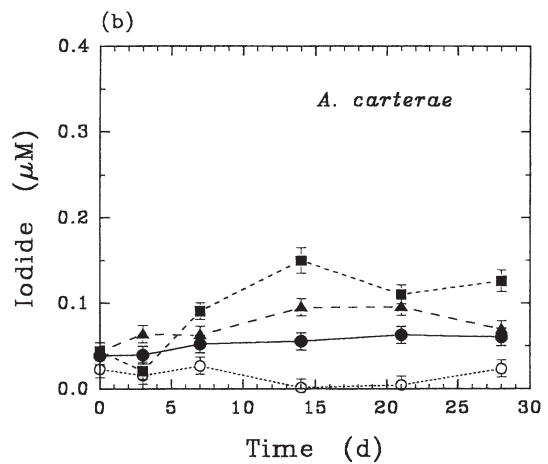
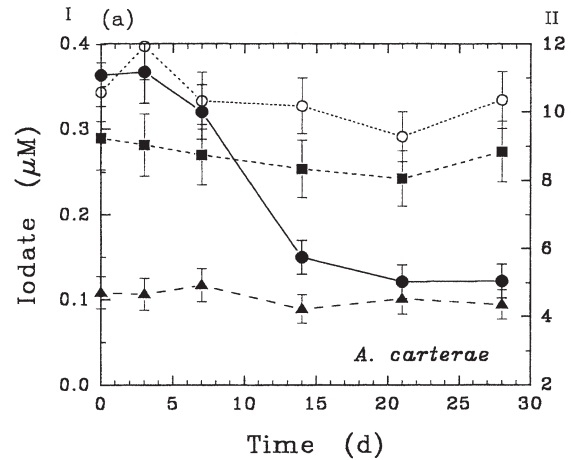


Fig. 8. Same as Fig. 4 in a culture of *Amphidinium carterae*

tribute significantly to the observed changes in the concentrations of iodate on iodide in the phytoplankton cultures.

## DISCUSSION

### Conversion of iodate to iodide by phytoplankton

Unlike the results obtained in previous studies (Sugawara & Terada 1967, Truesdale 1978, Butler et al. 1981), consistent depletion of iodate and concomitant appearance of iodide were found in this study in all the phytoplankton cultures at all concentrations of added iodate. This clearly indicates that all 6 phylogenetically diverse species of phytoplankton tested can induce the conversion of iodate and iodide. Since these 6 species of phytoplankton represent the major groups of phytoplankton found in the oceanic and coastal environments, these results suggest that the reduction of iodate to iodide by marine phytoplankton may be a

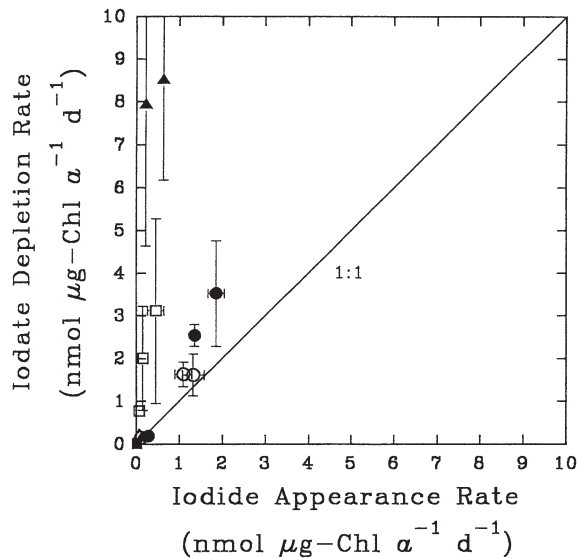


Fig. 9. Relationship between the rate of depletion of iodate and the rate of appearance of iodide at all levels of added iodate. (●) *Synechococcus* sp.; (▲) *Tetraselmis* sp.; (■) *Emiliana huxleyi*; (○) *Dunaliella tertiolecta*; (△) *Skeletonema costatum*; (□) *Amphidinium carterae*. The solid line represents the case where the 2 rates were equal

common phenomenon and may play a major role in controlling the speciation of inorganic iodine in the oceans. The consistent results reported here also support the notion that the previous studies might have been hampered by the suppression of iodate reduction as a result of the high concentrations of nitrate relative to iodate in the culture media, the lack of specificity in the analytical methods used for the determination of the iodine species or the effect of bacterial activities.

#### Rate of depletion of iodate and appearance of iodide

The rates of depletion of iodate and appearance of iodide varied from species to species. Precise quantification of these variations between the species is complicated by the species-dependent temporal variations in biomass (Fig. 1). As a first approximation, the average rates through the 28 d of incubation in each experiment were estimated as the slope of a linear regression analysis, and the results are listed in Table 1. The correlation coefficients  $r^2$  were above 0.6 in most cases. This indicates that the relationship between concentration and time can be described adequately by a linear relationship. The time-averaged chl *a* concentrations in the cultures were estimated by the trapezoidal method for each experiment. The rates of depletion of iodate and the appearance of iodide were then normalized to this time-averaged chl *a* concentration, and the results are also listed in Table 1. Without any added

iodate, the concentration of iodate in the culture medium was similar to those found at the ocean surface. The rates of depletion of iodate varied between 10 and 1 nM d<sup>-1</sup> and decreased in the following rank order: *Amphidinium carterae* ≈ *Dunaliella tertiolecta* ≈ *Synechococcus* sp. > *Skeletonema costatum* > *Tetraselmis* sp. ≈ *Emiliana huxleyi*. The chl *a* normalized rates ranged between 0.77 and 0.02 nmol µg chl a<sup>-1</sup> d<sup>-1</sup> or 0.06 to 0.002 nmol µg chl a<sup>-1</sup> h<sup>-1</sup> for a 12 h day. The rates decreased in the following rank order: *A. carterae* > *S. costatum* ≈ *Synechococcus* sp. ≈ *Tetraselmis* sp. ≈ *D. tertiolecta* >> *E. huxleyi*. Thus, *A. carterae* was the most efficient and *E. huxleyi* was the least efficient species in the utilization of iodate. By using <sup>125</sup>I-labeled iodate to follow the short term (hours) uptake of iodate, Moisan et al. (1994) inferred from the initial uptake rates of iodate into the cells that the iodate depletion rates ranged from 0.003 to 0.24 nmol µg chl a<sup>-1</sup> h<sup>-1</sup> in cultures of *T. oceanica*, *S. costatum*, *E. huxleyi* and *D. tertiolecta*. The rates reported here fell well within this range. Furthermore, unlike the study of Moisan et al. (1994), the rates of appearance of iodide could also be estimated in the present study. They ranged between 11 and 1 nM d<sup>-1</sup>. This range was similar to the corresponding range for the depletion of iodate. However, the rank order of the 6 species of phytoplankton tested was somewhat different. The iodide appearance rate decreased in the following order: *Synechococcus* sp. > *D. tertiolecta* > *Tetraselmis* sp. ≈ *S. costatum* ≈ *E. huxleyi* ≈ *A. carterae*. The chl *a* normalized rates ranged between 0.3 and 0.02 nmol µg chl a<sup>-1</sup> d<sup>-1</sup> and decreased in the following rank order: *Synechococcus* sp. > *Tetraselmis* sp. ≈ *D. tertiolecta* > *S. costatum* ≈ *A. carterae* > *E. huxleyi*. Thus, *Synechococcus* sp. was the most efficient and *E. huxleyi* was the least efficient species in the production of iodide.

The rates of the depletion of iodate and the appearance of iodide increased upon the addition of iodate in all cases (Table 1). The rate of depletion of iodate increased dramatically by more than an order of magnitude in *Tetraselmis* sp. and about an order of magnitude in *Dunaliella tertiolecta* and *Synechococcus* sp. upon the addition of 5 µM of iodate. The increase, about 1.5 times, was much less dramatic in the case of *Amphidinium carterae*. The relationship between the rate of depletion of iodate and the rate of appearance of iodide is shown in Fig. 9. Many of the data points lie above the 1:1 line, indicating that the rate of appearance of iodide was frequently lower than the corresponding rate of depletion of iodate. For a given species of phytoplankton, the discrepancy seemed to increase with increasing rate of depletion of iodate, which corresponded to increasing concentration of added iodate. The discrepancies were the smallest in



the case of *D. tertiolecta* and the most noticeable in the case of *Tetraselmis* sp. Even at ambient concentrations of iodate, where the rates were the lowest, the discrepancies between the rates frequently far exceeded what may be reasonably attributed to analytical uncertainties. In *A. carterae*, the ratio between these 2 rates was about 12. The lower iodide appearance rates relative to the corresponding iodate depletion rates indicate that during the utilization of iodate, iodate is converted not only to iodide but also to other forms of iodine, such as particulate iodine, non-volatile dissolved organic iodine and volatile iodine. Since the magnitude of these discrepancies varied between the phytoplankton species tested, the ability of marine phytoplankton to apportion the iodate utilized between iodide and other forms of iodine may vary from species to species. The increase in the discrepancies with increasing concentration of added iodate indicates that, while the organisms processed iodate at higher rates at elevated concentrations of iodate, more of the iodate processed was converted to forms of iodine other than iodide. The relationships between the rate of depletion of iodate or the rate of appearance of iodide and the initial concentration of iodate in the culture medium are shown in Fig. 10. While the data set was still limited, in general, the rates increased with increasing initial concentrations of iodate.

### Relationship to growth stages

The depletion of iodate and the appearance of iodide occurred during all growth stages. However, there

were indications that these rates may vary with growth stages and the pattern may vary from one species to the next. For example, the concentration of iodide seemed to increase exponentially with time in the culture of *Dunaliella tertiolecta* (Fig. 6b). Little to no iodide was formed during the log phase in the first 3 d of growth. When the average rates in the log and senescent phases were estimated individually by linear regression analyses of the data obtained in each growth phase (Table 2), the rates in the senescent phase were at least several times higher than those in the log phase at all concentrations of added iodate. Since the time-averaged concentration of chl *a* was higher during the log phase than the senescent phase, normalizing the rates to chl *a* would further accentuate the higher rates of appearance of iodide during the senescent phase. On the other hand, a corresponding quasi-exponential drop in the concentration of iodate with time was not observed (Fig. 6a). In fact, the rate of depletion of iodate was probably higher in the log phase than in the senescent phase (Table 2). In the case of *Synechococcus* sp., a reversed trend was observed. The concentration of iodide seemed to increase rapidly in the first 14 d of incubation during the log (0 to 7 d) and the stationary (7 to 14 d) phases before it leveled off (Fig. 3b). Thus, the average rates of appearance of iodide in these 2 phases of growth were several times higher than those in the senescent phase (Table 2). Normalizing the rates to chl *a* did not change this trend under the ambient concentration of iodate. At nominal concentrations of added iodate of 5 and 10  $\mu\text{M}$ , the rates in these 3 phases became similar to each other. The corresponding rates in the depletion of

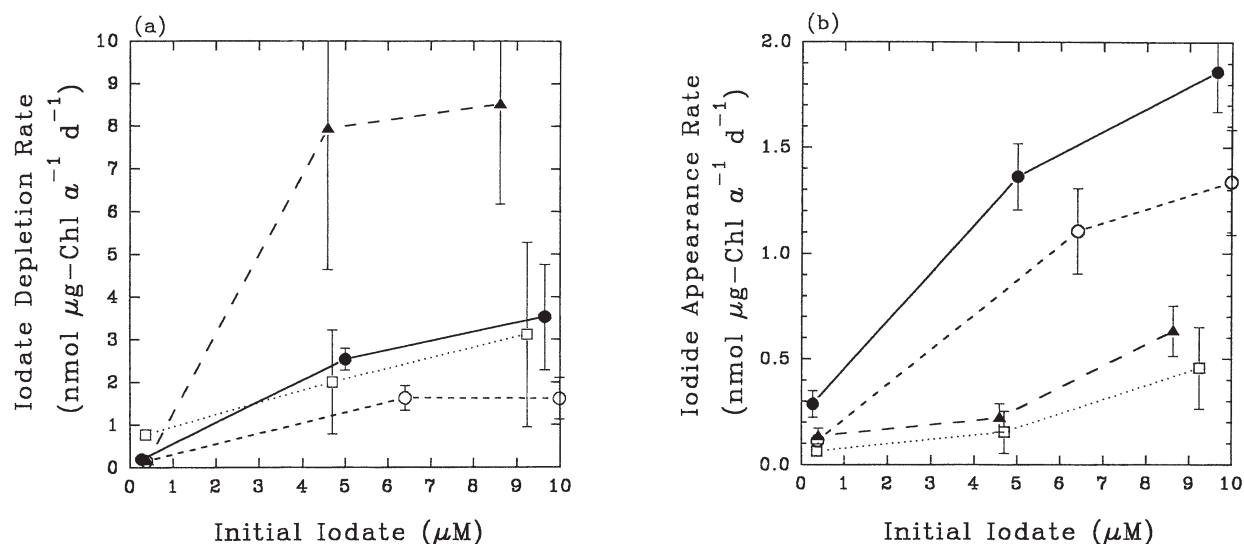


Fig. 10. Relationship between (a) the rate of depletion of iodate and (b) the rate of appearance of iodide and the initial concentration of iodate in the cultures of *Synechococcus* sp. (●), *Tetraselmis* sp. (▲), *Dunaliella tertiolecta* (○), and *Amphidinium carterae* (□)

Table 2. Iodate depletion and iodide production rates at different growth stages in cultures of marine phytoplankton. \*Iodate depletion and iodide production rates are the slopes of linear regression analyses of concentration vs time during each time period. Regression analysis was not used. L: log phase; S: stationary phase; Sc: senescent phase; ud: depletion or production not detected or too uncertain to be estimated

Phytoplankton species	Iodate added ( $\mu\text{M}$ )	Time period (d)	Growth phase	Avg chl <i>a</i> ( $\mu\text{g l}^{-1}$ )	Iodate depletion rate		Iodide production rate	
					Rate* ( $\text{nM d}^{-1}$ )	Norm rate ( $\text{nmol } \mu\text{g d}^{-1}$ ) <sup>a</sup>	Rate ( $\text{nM d}^{-1}$ )	Norm rate ( $\text{nmol } \mu\text{g d}^{-1}$ ) <sup>a</sup>
<i>Synechococcus</i> sp.	0	0–7	L	34	$-11 \pm 5$	-3	$22 \pm 10$	0.6
		7–14 <sup>b</sup>	S	66	-9	-0.1	20	0.3
		14–28	Sc	25	$-2 \pm 5$	-0.08	$3 \pm 0.2$	0.1
	5	0–7	L	33	$-108 \pm 43$	-3	$42 \pm 14$	1
		7–14 <sup>b</sup>	S	59	-104	-2	81	1
		14–28	Sc	21	$-54 \pm 7$	-3	$26 \pm 12$	1
	10	0–7	L	32	$-249 \pm 329$	-8	$62 \pm 35$	2
		7–14 <sup>b</sup>	S	54	-95	-2	82	2
		14–28	Sc	20	$-130 \pm 50$	-7	$39 \pm 9$	2
<i>Dunaliella tertiolecta</i>	0	0–3 <sup>b</sup>	L	62	-24	-0.4	ud	ud
		3–28	Sc	52	$-8 \pm 2$	-0.2	$7 \pm 2$	0.1
	5	0–3 <sup>b</sup>	L	70	-410	-6	9	0.1
		3–28	Sc	56	$-73 \pm 8$	-1	$71 \pm 14$	1
	10	0–3 <sup>b</sup>	L	74	-570	-8	5	0.07
		3–28	Sc	56	$-58 \pm 10$	-1	$88 \pm 16$	2

<sup>a</sup>Depletion or production rate normalized to time averaged chlorophyll *a* concentration

<sup>b</sup>Only 2 data points were available

iodate seemed to follow the same trend in this case (Table 2). The present data set indicates that there may be a species-specific relationship between the growth stages and the transformation of iodate to iodide. However, for a given phytoplankton species tested, there were too few data points in each growth phase to warrant a more rigorous and quantitative analysis of this possible relationship.

### Phytoplankton metabolism and iodine processing, and implications for the marine geochemistry of iodine

Iodate may be transported into the cell either by diffusion or by a carrier-mediated process, reduced to iodide and retained by the phytoplankton cell or excreted from the cell at some time during the life cycle. Since the depletion of iodate was accompanied by an appearance of iodide, although the latter was frequently smaller than the former, at least a fraction of the iodate reduced was excreted as iodide. The remainder would have been retained in the cell as particulate iodine or excreted as volatile or non-volatile organic iodine. A large-scale sequestration of the iodate processed as particulate iodine is unlikely. Macroalgae are known to convert inorganic iodine into organic forms, such as iodotyrosine (Scott 1954, Tong & Chaikoff 1955, Klemperer 1957, Meguro et al. 1967) and lipid halogens (Hewson & Hager 1980), which are stored in their cells. Similar information is not available for phytoplankton. The pattern of the uptake of

<sup>125</sup>I-labeled iodate by marine phytoplankton (Moisan et al. 1994) showed that phytoplankton have a limited capacity for incorporating iodate into the particulate phase. The capacity can be saturated quickly, and any additional iodate taken up is excreted in the dissolved form. Particulate iodine is also a small reservoir of iodine in the oceans as its concentration is 2 to 3 orders of magnitude smaller than the concentration of dissolved iodine (Wong et al. 1976). The data reported here also indicate that iodate reduction is not necessarily linked to the log phase of growth, when photosynthesis, nutrient uptake and cell division are at their maximum. Furthermore, even under conditions of unnaturally high concentrations of iodate, the growth rate, cell numbers and chlorophyll concentrations (Fig. 2) are unaffected. These imply that there is little interaction between iodine processing and the metabolic activity of cell growth. Thus, if iodate enters the cell, phytoplankton must have a detoxification mechanism and excretion of the products formed is a viable possibility.

The production of volatile iodine compounds, such as methyl iodide, by marine phytoplankton has been inferred from their distributions (Klick 1992, Klick & Abrahamsson 1992, Moore & Tokarczyk 1993) and has been observed directly in laboratory studies (Moore & Tokarczyk 1993, Manley & de la Cuesta 1997). Iodate has also been shown to react with the macroalgal metabolites dimethyl- $\beta$ -propiothetin (DMPT) to form methyl iodide (White 1982, Brinckman et al. 1985, Manley & Dastoor 1988). Ultimately, these volatile

organic iodine compounds may make their way to the atmosphere and play a significant role in the chemistry of the troposphere (Chameides & Davis 1980, Chatfield & Crutzen 1990, Solomon et al. 1994). Nonetheless, globally, a large-scale conversion of iodate to volatile iodine, which escapes to the atmosphere, is also unlikely. A typical emission rate of methyl iodide to the atmosphere from the oceans is about  $10^{-6}$  to  $10^{-5}$  mol  $m^{-2}$   $yr^{-1}$  (Campos et al. 1996b). Based on these emission rates, the methyl iodide formed from iodate in the surface 100 m of the oceans is equivalent to a depletion of iodate of  $10^{-5}$  to  $10^{-4}$  nM  $d^{-1}$ . These rates are orders of magnitude smaller than those ( $10^{-3}$  to  $10^0$  nM  $d^{-1}$ ) observed in the cultures at ambient concentrations of iodate (Table 1) after they had been adjusted to the typical concentrations of chl *a* ( $0.1$  to  $1$   $\mu g$   $l^{-1}$ ), in the open oceans. They are not sufficient to account for the depletion of iodate in the ocean surface relative to the deep ocean. Furthermore, the concentration of total dissolved iodine in the ocean surface stays relatively constant, and its depletion relative to the deep oceans is on the order of only a few percentage points. These distributions do not support a large-scale loss of dissolved iodine to the particulate phase or to the atmosphere as volatile iodine.

Significant concentrations of non-volatile dissolved organic iodine, constituting up to over 50% of the concentration of total dissolved iodine, have been reported in coastal marine waters (Truesdale 1975, Butler & Smith 1985, Luther et al. 1991, Wong & Cheng 1998, 2001a,b). The general patterns of increasing concentrations of non-volatile dissolved organic iodine toward the coast and decreasing concentrations below the euphotic zone in the open oceans (Wong & Cheng 1998, 2001a) are in phase with changes in primary production and are thus consistent with a biological origin. However, if dissolved organic iodine is formed from iodate, then the ultimate fate of this fraction of iodate utilized would still be the same as the transformation of iodate to iodide since dissolved organic iodine can be converted readily to iodide through photochemical reactions with sunlight (Wong & Cheng 2001b). In fact, in the open oceans, where photochemical decomposition of dissolved organic iodine is enhanced by the deeper euphotic zone, dissolved iodine exists almost exclusively as iodate and iodide (Wong & Cheng 1998) so that, while the concentrations of iodate and iodide may vary much more than that of total dissolved iodine, their concentrations are linearly related to each other with a slope of  $-1$  mol  $mol^{-1}$  (Wong & Cheng 2001b, Wong & Hung 2001). This relationship between iodate and iodide is consistent with either a quantitative conversion of iodate to iodide followed by an excretion of iodide or a conversion of iodate to iodide and dissolved organic iodine followed

by an excretion of both products and a ready decomposition of dissolved organic iodine to iodide. The enhanced appearance of iodide during the log phase of growth in *Synechococcus* sp. indicates that the release of iodide is not necessarily a passive leakage from the cells as a result of cell lysis, as observed in other metabolites such as dimethylsulfoniopropionate (DMSP) (Matrai & Keller 1994) and methyl chloride (Tait & Moore 1995). Iodine processing may also be decoupled from the metabolic activities of cell growth if iodate is reduced to iodide at the cell surface by a surface enzyme system so that iodate may never have to enter the cell. At present, there is no evidence to support or refute this possibility.

Attempts to link changes in the speciation of dissolved iodine to temporal changes in biomass have not been particularly successful (Jickells et al. 1988, Tian et al. 1996). This is not unexpected. Wong (2001) pointed out that changes in the concentration of iodate and iodide represent a longer-term time-integrated signal in the dissolved phase, while changes in biomass is a much shorter-term phenomenon in the particulate phase. Based on the rates of iodate depletion and iodide appearance found in this study, at the typical concentrations of chl *a* of  $0.1$  to  $1$   $\mu g$   $l^{-1}$  found in the open oceans, several months to decades will be needed before a readily detectable change in the concentrations of iodate and iodide, on the order of  $0.1$   $\mu M$ , can be reached. On the other hand, the turnover time of the biomass in the surface oceans is several weeks. Aside from this mismatch in timescales, the longer timescale involved in the changes in the concentrations of the iodine species also allows physical mixing to modify the signal produced by this biological production of iodide. Furthermore, the ability of a species of phytoplankton to process iodine and its contribution to biomass are not directly related to each other. For example, among the oceanic species, the cyanobacteria can reduce iodate to iodide most effectively. However, in terms of their contribution to biomass, coccolithophores and prasinophytes are major contributors to the chlorophyll maximum, while the cyanobacteria are more evenly distributed with depth (Glover et al. 1988). These divergent behaviors will further complicate any attempt to link changes in iodine speciation to temporal and spatial changes in biomass.

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