Geochemistry of high molecular weight dissolved organic matter in the sea as implied by amino acids and organic nitrogen

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INTRODUCTION

Oceanic dissolved organic matter (DOM), represents one of the largest dynamic reservoirs of reduced carbon on Earth, however the biological and geochemical mechanisms controlling the DOM pool remain poorly understood. Tangential flow ultrafiltration (UF) has recently emerged as a promising method in the study of oceanic DOM. In addition to providing a more chemically representative sample of DOM (Benner et al., 1992), the higher molecular weight material isolated as ultrafiltered DOM (UDOM) may have unique roles in the ocean carbon cycle. It has been suggested that the colloidal-size organic matter collected by UF may undergo important biological and chemical processes distinct from either "truly" dissolved compounds or sinking particulates (Kepkay, 1994; Johnson and Kepkay, 1991). In particular it may provide a conduit between dissolved and particulate carbon pools: coagulation of smaller organics into the colloidal size range and then into sinking particles has been proposed as an important process of colloidal size material, especially in the cycling of trace metals and radionucleides (Honeyman and Santschi, 1989).

We present here the first molecular-level amino acid analyses of oceanic UDOM, isolated from surface, oxygen minima, and deep waters in three oligotrophic ocean basins: the central Gulf of Mexico, North Pacific and Sargasso Sea. These samples provide the first opportunity for a multi-depth comparison of UDOM from 3 different sites in the world ocean, allowing investigation of both potential reactivity, and geographic and depth - related compositional patterns. Amino acids are among the most quantitatively important biochemicals in living organisms, and also among the most labile compound classes in detrital organic matter. Thus, their abundance and distributions can provide an important indictor of the role played by UDOM at the interface between the dissolved and particulate organic matter in the sea.

RESULTS AND DISCUSSION

Amino acid concentrations in UDOM size fraction - Total dissolved amino acid concentrations (TDAA) in the UDOM size fraction (UDOM-AA) are not dramatically different from TDAA measured previously in whole seawater. Surface water UDOM-AA ranged from 178 nM in the Sargasso Sea to 278 nM in the N. pacific (Table 1). In both the Atlantic and Pacific, deep ocean values were almost identical, near 100 nM. On the whole these values are somewhat lower than those previously measured in bulk surface seawater (about 300 - 1000 nM; *e.g.* Lee and Bada, 1976, 1977; Ittekkot, 1982; Henrichs and Williams, 1985; Hubberten et. al., 1994) or deep water (about 150 - 200 nM. eg: Lee and Bada, 1975, 1976; Hubberten et al., 1994). Considering that UDOM represents about 20 - 30% of total DOM, UDOM-AA and literature values seem comparable. This suggests that amino acids are neither greatly enriched nor depleted in the UDOM size fraction.

Table 1: UDOM Recoveries and Bulk Characterization

	N. Pacific			Sargasso Sea			Gulf of Mexico	
	10	**750**	**4000**	**2**	**900**	**2400**	**10**	**750**
DOC(uM)	82	38	41	71	50	50	95	48
UDOM(uM)	27	10	9	16	9	nd	29	12
UDOM-AA(nM)	278	51	109	178	122	89	262	150
THAA (mg/100mg OC)	10.2	5.2	12.1	14.7	14.0	6.5	8.7	13.1
%AA-N	17.4	14.2	28.3	28.7	21.9	11.5	16.6	24.3
ßAla+γAba (Mol %)	1.4	4.6	2.6	2.8	1.4	1.2	3.6	1.4

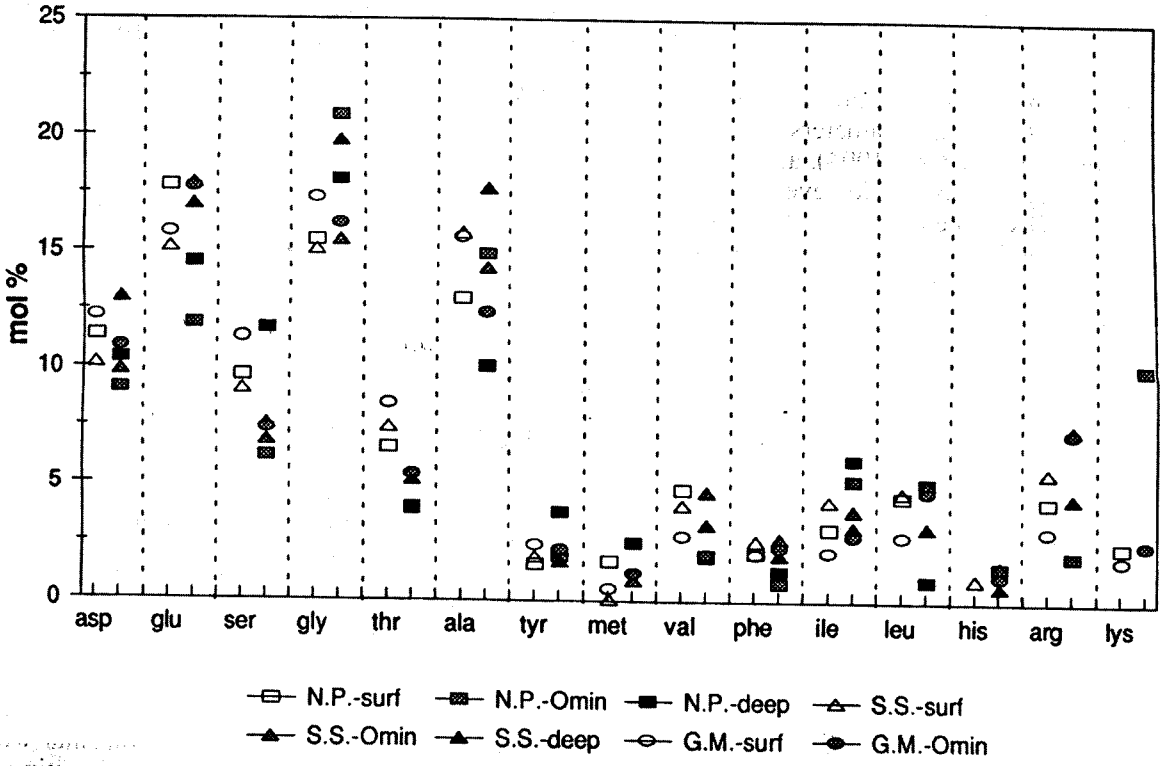

Fig. 1. UDOM Amino Acids

While the clear drop in UDOM-AA with depth indicates reactivity, the decrease corresponds well to the overall drop in DOC concentration. As a result, UDOM-AA makes up a small but relatively constant ~1 % of total DOC and about 4% of UDOM organic carbon at all depths. Thus there is no suggestion from UDOM amino acid gradients that UDOM cycling is distinct from cycling of overall DOC in the upper ocean.

Molecular-level distributions- Molecular-level distributions can often provide more sensitive tracers for origin and alteration. If the amino-acid containing components of deep UDOM underwent significantly different processes than the bulk DOM pool, these differences might be reflected in the different amino acid signatures. Studies from a number of different environments have indicated that the molar compositions of DCAA in whole sea water are largely similar, dominated by aspartic acid, glutamic acid, glycine, alanine, and serine (*e.g.* Coffin, 1989; Henrichs and Williams, 1985, Lee and Bada, 1975; Hubberten, 1994). UDOM-AA distributions are dominated by the same amino acids, and in addition are marked by the lack of any consistent compositional differences between surface and deep waters(Fig. 1). Molecular-level amino acid distributions thus suggest that proteinaceous components of UDOM are very similar to unfractionated DOM, and that little molecular-level alteration occurs in deep ocean isolates.

Non-protein amino acids- Four non-protein amino acids, β-alanine (β-ala), ornithine (orn), γ-aminobutyric acid (γ-aba), and α-amino butyric acid (α-aba), were measured in UDOM-AA. Non-protein amino acids (NPAA) are produced from the breakdown of specific protein amino acids, and their increasing concentration has generally been interpreted as a strong indicator of organic matter aging or diagenesis (*e.g.* Cole and Lee, 1986; Cowie and Hedges, 1994). Dissolved NPAA have only rarely been measured in bulk seawater, and never in ultrafiltered isolates. β-ala and γ-aba made up a small but relatively constant 1-3 mol% of UDOM-AA from both surface and deep waters (Table 1), while α-aba and orn were not detected in most samples. There is thus no evidence of increasing NPAA in deeper UDOM, as might be expected with increasing degradation of coherent particles or colloids.

Total AA and percent amino acid-nitrogen in UDOM- Another way to examine UDOM components are not as concentrations in seawater, but normalized within UDOM itself. This approach allows comparison of UDOM composition to other forms of marine organic matter. Both the total hydrolyzable amino acid yield (THAA- normalized to UDOM carbon) and percent of nitrogen composed of amino acids (%AA-N- normalized to UDOM nitrogen) are very low relative to marine biomass or most detrital material. THAA ranged from 5-14 mg per 100mg OC, while %AA-N ranges from 11.5 - 28.7 (Table 1). In

marine biomass and most detrital material THAA yields typically fall within the range of 50 to 100 mg/100 mg OC, and amino acids make up 40 -80% of total organic nitrogen (Cowie and Hedges, 1992; 1994).

Although there is variation in both THAA and %AA-N, there are no consistent trends with increasing water depth. These parameters have been found to be consistent indicators for organic matter degradation (Cowie and Hedges, 1994), and if applied directly they suggest that both surface and deep UDOM are significantly degraded. However, it is uncertain whether such parameters can be extended to the dissolved phase. Given the reactivity of surface UDOM, it is more likely that the low values and lack of consistent depth trends in %AA-N indicate 1) that the majority of nitrogen in UDOM is in a form other than amino acids, and 2) that the amino acids and other nitrogen forms in the UDOM are utilized to similar degrees in surface waters.

CONCLUSIONS

1) While amino acids do account for an appreciable fraction of organic nitrogen in UDOM, the majority of nitrogen is composed of non-amino acid forms. Carbohydrates appear to be the dominant single biochemical class in UDOM (Benner et al., 1992; McCarthy et al., 1993), and pyrolysis results have suggested that amino sugars may be important contributors to UDOM nitrogen (Van Heemst et al., 1993).

2) The low %AA-N and amino acid content of UDOM clearly differentiate it from either living or detrital particulate material, and suggest it is not produced from a direct breakup of either. The lack of consistent change in these parameters with depth suggests that there is little overall selectivity in utilization of organic nitrogen forms during UDOM remineralization.

3) Amino acid data are generally not supportive of the idea that UDOM represents a physically separate colloidal material which is compositionally or functionally distinct from the lower molecular weight DOM pool. UDOM isolates appear to well represent unfractionated DOM with respect to both amino acid concentrations and molecular distributions, and reactivity.

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