Silver as a palaeo proxy for high productivity

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Trace metals Re, Mo, U and Cd have been used in many studies as palaeoindicators for productivity and/or redox conditions of bottom water and sediments, whereas the use of Ag as such a tracer is not yet established. Ag enrichments might result from increased productivity where the metal is delivered to sediments as a trace component of the organic matter (as is the case for Cd) and/or by diffusion into suboxic sediments from bottom waters (as observed for Re and Mo). In this paper we present the first evidence for both of these processes.

Ag enrichment by diffusion in the Arabian Sea

Surface-sediment samples from the oxygen minimum zone in the Arabian Sea show high Ag concentrations (200 ppb) compared to samples from proximal well oxygenated areas (~50 ppb). This distribution is similar to that for Re which is known to be enriched under suboxic conditions (Crusius *et al.*, 1997). The process leading to the enrichment of Ag in the oxygen minimum is postulated to be similar to that for Re, diffusion across the sediment water interface and subsequent precipitation, in this case as Ag_2S. Removal of Ag as Ag_2S requires no redox change in Ag and thus could occur as soon as trace concentration of sulphide are present.

Particulate Ag sedimentation in Saanich Inlet

Particulate authigenic Ag is formed in the surface waters of Saanich Inlet, as evidenced by the high concentrations in particles trapped at 50 m (Table 1). The Ag content of trapped particles as well as the vertical flux of particulate Ag significantly increased with depth. Two processes, chemical scavenging and sediment resuspension could add to the particulate flux. The oxic/anoxic interface was situated between the 135 and 180 m traps. Therefore chemical scavenging of dissolved Ag by particles settling through the oxic and the anoxic zone did add significantly to the particulate flux of Ag. While we cannot rule out the presence of resuspended sediments in the samples, the increase in the Ag content with depth and the absence of a Ag source with high Ag concentrations does indicate that resuspended sediment does not add to the Ag fluxes. It appears that most of the flux of particulate Ag originates in the surface waters, and only part of it is added by scavenging from either oxic or anoxic waters.

The spring bloom in Saanich Inlet typically runs from April to June and is reflected in higher fluxes of particulate Corg and opal (Sancetta and Calvert, 1988). The samples collected in February and March (pre-bloom) and November and December (post-bloom) had notable differences in their composition. Organic carbon was low in the pre-bloom samples. Biogen silica contents were the lowest in the pre and post-bloom samples. Silver contents varied strongly over the months and did not show any systematic differences between summer and winter samples. The correlation between Ag and opal concentrations is poor. However, there exists a negative correlation between Ag contents and particle fluxes. As Ag concentration in surface waters are expected to be very low, large export from the surface water due to particulate Ag flux might result in a depletion of the Ag concentration. At times of high productivity the overall Ag flux would therefore be high whereas the Ag content of the particles would decrease. This is exactly what we observe in the sediment trap samples: tight coupling of the Ag flux with the opal flux but widely varying Ag concentrations (Table 1).

Conclusion

Ag enrichments might result from increased productivity where the metal is delivered to sediments in particles as shown in Saanich Inlet. Diffusion into suboxic sediments from bottom waters leads also to Ag enrichment. For the successful application of Ag as a palaeoindicator it is important to distinguish between the two processes. The Re shows strictly conservative behaviour. It is not delivered to the sediment by particles. The Ag/Re ratio therefore can be used as a parameter of increased particle flux.

This approach was applied on a down core record

TABLE. 1. Concentrations and fluxes in sediment trap samples from Saanich Inlet in three different depths

	1985	Concentrations Corg (%)	opal (%)	Ag [ppb]	Fluxes Total g/m^2/d	Corg g/m^2/d	Opal g/m^2/d	Ag μg/m^2/d
Trap 50 m	Jan	7.51	13.10	710	0.97	0.073	0.13	0.69
	Feb	6.74	17.51	341	0.97	0.066	0.17	0.33
	Mar	7.41	22.11	885	1.03	0.076	0.23	0.91
	Apr	7.36	57.62	367	2.90	0.213	1.67	1.06
	May	10.20	64.62	540	2.92	0.298	1.89	1.58
	Jul	11.02	53.74	585	2.96	0.326	1.59	1.73
	Aug	14.92	46.52	676	1.90	0.283	0.88	1.28
	Sep	11.13	51.06	613	1.58	0.176	0.81	0.97
	Oct	10.65	46.12	439	1.72	0.183	0.79	0.75
	Nov	11.77	26.28	729	0.67	0.079	0.18	0.49
	Dec	11.02	19.44	572	0.72	0.079	0.14	0.41
Trap 135 m	Mar	5.12	17.12	898	2.42	0.124	0.42	2.18
	Apr	5.97	43.24	638	3.56	0.212	1.54	2.27
	May	7.06	55.86	631	4.58	0.323	2.56	2.89
	Jul	8.88	52.05	520	3.64	0.323	1.90	1.89
	Aug	13.02	40.34	961	1.85	0.240	0.74	1.77
	Sep	8.66	42.13	890	1.43	0.124	0.60	1.27
	Oct	11.19	44.62	534	1.38	0.155	0.62	
Trap 180 m	Mar	5.10	17.68	1186	2.25	0.115	0.40	2.67
	Apr	5.78	40.81	1225	3.05	0.176	1.24	3.74
	May	6.68	53.74	796	3.81	0.254	2.05	3.03
	Jul	8.89	51.77	687	2.96	0.263	1.53	2.04
	Sep	9.18	42.41	787	1.69	0.155	0.72	1.33
	Oct	9.47	32.75	473	2.37	0.224	0.78	1.12
	Nov	8.56	10.45	658	2.74	0.235	0.29	1.80

from the Gulf of Alaska, where past episodic increases in primary production were paralleled by rapid accumulation of diatom oozes. In each diatom-rich stratum, Ag, Re and Mo are enriched (Friedl and Pedersen, 1997). The silver contents reach ~400 ppb, seven times higher than the background (~60 ppb). The Ag/Re ratio is high and varies from 15 to 40. In contrast, suboxic sediments which lack the rapid input of diatoms show lower Ag/Re ratios (5–8). Such values are characteristic of modern suboxic sediments on the Pakistan Margin. The data collectively imply that the accumulation of authigenic silver in sediments, unlike rhenium, is greatly facilitated by the delivery of opaline silica to the sea floor.

References

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