

**Mobility of authigenic rhenium, silver and selenium
during post-depositional oxidation in marine sediments.**

John Crusius, Oceanography Group, Dept. of Earth and Ocean Sciences, University of
British Columbia, Vancouver, B.C. Canada V6T 1Z4. crusius@eos.ubc.ca
John Thomson, Southampton Oceanography Centre, Empress Dock, Southampton SO14
3ZH, U.K. John.Thomson@soc.soton.ac.uk

Revised version submitted to Geochimica et Cosmochimica Acta- 4July 2002

Abstract

Sedimentary records of redox-sensitive trace elements hold significant potential as indicators of paleoceanographic environmental conditions. Records of Re can reveal the intensity of past reducing conditions in sediments at the time of deposition (Crusius et al., 1996), while records of Ag may record the magnitude of past diatom fluxes to the seafloor. Confidence in paleoenvironmental reconstruction from records of either metal, however, requires it to have experienced negligible redistribution since deposition. This study examines diagenetic re-arrangements of Re and Ag that occur in response to exposure to bottom-water O₂ in environments of low sedimentation rate, including Madeira Abyssal Plain turbidites and eastern Mediterranean basin sapropels. Authigenic Re was remobilized quantitatively by oxidation, but poorly retained by the underlying sediments. All records are consistent with previous work demonstrating that only a limited re-immobilization of Re occurs preferentially in C_{org}-rich, reducing sediments (Crusius and Thomson, 2000). Silver was also mobilized quantitatively by oxidation, but was subsequently immobilized more efficiently in all cases as sharp peaks immediately into anoxic conditions below active oxidation fronts, and these peaks remain immobile in anoxic conditions during long-term burial. Comparison of Ag, S and Se records from various cores suggests that Ag is likely to have been immobilized as a selenide, a mechanism previously proposed for Hg in similar situations (Mercone et al., 1999). Co-existing narrow peaks of Ag and Hg with Se offer a means of assessing whether oxidative burndown has ever occurred at the top of C_{org}- and sulfide-rich sedimentary units. While these results suggest that caution must be used when inferring paleoenvironmental information from records of Ag and Re in cores with low sediment accumulation rates (<5 cm ka⁻¹), they should not affect the promise that authigenic Ag and Re records hold for paleoenvironmental reconstruction in sediments with higher accumulation rates and where anoxic conditions have been maintained continuously.

1. INTRODUCTION

Redox-sensitive trace elements have great potential as paleoenvironmental indicators in marine sediments, due to the different mechanisms and different redox conditions that are necessary to form their authigenic enrichments. For example, whereas the oxyanions of U, Re and Mo all behave conservatively in seawater (Colodner, 1991; Anbar et al., 1992), Re is enriched in mildly-reducing (*i.e.* sub-oxic or post-oxic *sensu* Berner (1982)) sediments by diffusion from seawater. This occurs at a redox potential close to or slightly more reducing than that necessary for U, and well before reduction of Mo in strongly-reducing (sulfidic) sediments (Crusius et al., 1996; Nameroff et al., 2002). Rhenium also shows a greater degree of enrichment in reducing sediments than any other element, because its detrital flux in crustal materials is often very low relative to its authigenic flux from seawater (Colodner et al., 1993; Crusius et al., 1996). As a consequence of the large potential authigenic contents and the different reduction potentials of Re and Mo, sedimentary concentrations of these metals have been suggested as useful indicators of the intensity of past reducing environments (Calvert and Pedersen, 1993; Crusius et al., 1996).

The mechanism of Ag delivery to marine sediments is quite different from that of Re. Silver is removed from surface waters by biogeochemical processes and is regenerated by remineralisation processes at depth, which results in a nutrient-like Ag distribution in the water column (Martin et al., 1983). A close correlation noted between water column profiles of dissolved Ag and Si implies that Ag is associated with the hard parts of diatoms (Flegal et al., 1995). This inference is supported by culture experiments that reveal that diatoms take up Ag much more readily than do coccolithophoridae (Fisher and Went, 1993), perhaps indicating uptake of Ag into the siliceous diatom shell. There is also preliminary evidence to suggest that scavenging of Ag onto settling particulate material may deliver Ag to the sediment surface (McKay et al., 2000). The

mechanism by which Ag is ultimately sequestered in sediments is not well established either. One possibility is that Ag is immobilized by trace concentrations of sulfide to form Ag_2S , the same immobilization mechanism as proposed for Cd uptake in sediments (Rosenthal et al. 1995). Yet another possibility, that Ag is sequestered as a silver selenide species, will be discussed in this work.

A confident interpretation of either Re or Ag data as paleoenvironmental indicators in sedimentary records crucially requires an understanding of their geochemical behavior during diagenesis and long-term burial. The primary focus of this paper is on the redistribution of Re and Ag during diagenesis and burial in three different sedimentary environments, each with low sedimentation rates, which maintain authigenic enrichments of the metals prior to diagenesis: turbidites of the Madeira Abyssal Plain, the most recent sapropel (S1) in the eastern Mediterranean basin, and glacial/ interglacial transition sediments of the NE Atlantic. The retention and elemental associations of the re-immobilized Ag and Re during the post-depositional oxidation are then compared, and finally the paleoenvironmental implications are discussed.

2. METHODS

Sediment samples for analyses of Re and Ag were subjected to total dissolution by microwave digestion in Teflon bombs in a mixture of HCl, HNO_3 and HF, after adding isotope dilution spikes of ^{185}Re and ^{109}Ag . After drying under a heat lamp in a laminar flow hood/fume hood, samples were wetted with 0.1 N HCl and briefly reheated. Silver and rhenium were isolated by adsorption to Dowex anion exchange resin in 0.1 N HCl and eluted with 8 N HNO_3 using a procedure similar to that described elsewhere for Re (Colodner, 1991; Crusius et al., 1996). Analyses were carried out by isotope-dilution ICP-MS on a VG Plasmaquad II+ at the University of British Columbia in Vancouver (MD69 MC7, MC7S and MC12) or at the IAEA Marine Environment Lab in Monaco (CD63#9K, 950A-15H, 11135). Analysis of reference material BCSS-1 yielded an Ag concentration of $119 \pm 11 \text{ ng g}^{-1}$ (certified value = $110 \pm 30 \text{ ng g}^{-1}$), while analysis of

RGM-1 yielded a value of $109 \pm 14 \text{ ng g}^{-1}$ (certified value = 108 ng g^{-1}) (Govindaraju, 1989). The precision and accuracy of the Re determination is on the order of $\pm 2\%$, as discussed in Crusius et al., 1996.

The CaCO_3 and organic carbon contents of core 11135 were determined by the LECO method of Thomson et al. (1984), while those of cores 950-15H, MC7, MC7S and MC12 and CD63#9K were determined by coulometry as described in Thomson et al. (1997). Barium and Mn were determined by ICP-AES analysis following dissolution by HF and HClO_4 , and final solution in 1N HNO_3 . Selenium was determined by hydride generation ICP-AES or atomic fluorescence spectrometry in solutions prepared from aqua-regia extraction; this extraction method is believed to reduce or oxidise all Se forms present to Se(IV) for analysis (Kuldvere, 1989). Total sulfur was determined by ICP-AES in 950A-15H on aqua regia leachates and by XRF on powder briquettes for cores MC7, 7S and 12.

3. RESULTS AND DISCUSSION

3.1. Turbidites of the Madeira Abyssal Plain

The Madeira Abyssal Plain (MAP) is in the north-east Atlantic Ocean and lies at a mean water depth of 5440 m. The presence of C_{org} -rich turbidites on this plain provides a natural laboratory in which to assess the behavior of different elements in response to oxidation by bottom water O_2 , and during subsequent long-term burial (Middelburg, 1993). This class of MAP turbidites tends to be homogeneous in the vertical in terms of grain size and detrital element composition (Jarvis and Higgs, 1987; Thomson et al., 1987) and in addition they contain authigenic redox-sensitive element enrichments and pyrite developed at their initial site of deposition. Between turbidite deposition events, pelagic sediment deposition on the MAP is slow ($0.5\text{-}1 \text{ cm ky}^{-1}$; Weaver and Kuijpers, 1983), and as a consequence the upper surface of each turbidite unit is exposed to diffusive contact with bottom-water O_2 for tens of thousands of years until the next turbidite emplacement event occurs. Because of their initial compositional homogeneity,

the effects of this post-depositional oxidation can be readily discerned from the geochemical signals of redox-sensitive elements above and below the O₂ penetration depth in the turbidite sediments (Thomson et al. 1993).

Rhenium and Ag data have been generated for sediments from three MAP turbidites: the most recent turbidite *a* which comprises all 50+ cm of box core 11135 (Thomson et al 1987); turbidite *t* which is present from 23.60-25.00 m in giant piston core MD24 (Colley and Thomson, 1985); and a turbidite present at 134.19-134.73 metres below sea floor in ODP core 950A-15H (Thomson et al. 1998). The depth of O₂ penetration in all three turbidites has been established in the cited references, and is indicated by the shadings in Figure 1. The oxidation redistribution process was active in turbidite *a* between its deposition 0.9 ky ago (Thomson and Weaver, 1994) and the time of core collection, but the oxidation fronts in both turbidite *t* and in the core 950A-15H turbidite are relict, having persisted for the period between turbidite deposition (700 ky and 3.4 My ago, respectively) and some tens of thousands of years subsequent to turbidite deposition.

In all three turbidites, the authigenic Re and Ag that were initially present in the turbiditic sediments have been mobilized out of the oxidized zone, as indicated by the much lower concentrations above the O₂ penetration front compared to the values below the front (Figure 1). Indeed, the Re and Ag values above the O₂ penetration front, expressed on a carbonate-free basis, are ~0.5 and ~20-60 ng g⁻¹, respectively. These values are similar to the typical crustal values of 0.5 ng g⁻¹ for Re (Colodner et al., 1993) and 50 ng g⁻¹ for Ag (Taylor and McClennan, 1985). Rhenium has been convincingly re-immobilized in a peak ~50 cm wide in only the C_{org}-rich turbidite *t* from core MD24 (Figure 1; see Crusius and Thomson, 2000), but there is no clear evidence of any Re re-immobilization in the other two turbidites in cores 11135 and 950A-15H. In contrast to Re, a sharp Ag peak exists immediately below the O₂ penetration front in all three turbidites. This indicates that an efficient re-immobilization of Ag has occurred

immediately once the oxidized Ag species in pore water solution encountered reducing conditions in the underlying turbiditic sediments. Such peaks must move downwards by oxidation on the top face of the peak with reductive immobilization on the bottom of the peak, and must also increase in size over time as more Ag is remobilised from the turbidite sediments. The sharpness of the relict peaks in turbidite *t* and in the core 950A-15H attests to the long-term stability of the Ag peaks after the oxidation process ceases. It is worth noting that in core 11135 roughly 30% of the oxidized authigenic Ag is retained in the thin Ag peak below the oxidation front (assuming the lithogenic Ag concentration is equal to the Ag concentration above the front).

3.2. S1, the Most Recent Eastern Mediterranean Sapropel

Eastern Mediterranean sapropels are discrete sedimentary units that contain high levels of C_{org} and pyrite and enrichments of a range of authigenic redox-sensitive trace elements (e.g. Calvert and Fontugne, 2001). Oxidized sediments are normally deposited in the eastern Mediterranean basin, but sapropel units have been regularly deposited, each for only a few thousand years, at astronomically predictable times (Hilgen et al. 1995). The mechanism of sapropel deposition is controversial (e.g. Rohling, 1994; Calvert and Fontugne, 2001), but is generally thought to involve periods initiated by increased monsoon intensity (Rossignol-Strick, 1985) of either high productivity or reduced deep-water O_2 content (e.g. Rohling, 1994), or both. The sapropels are evident in cores as sharply-defined, dark units that contrast with the surrounding sediments laid down under lower productivity and/or higher oxic bottom water conditions. In contrast to the MAP turbidites, the eastern Mediterranean sapropels are continuously-accumulated sediments in which changes in productivity or bottom water O_2 conditions have altered the nature of the sediment laid down. Nevertheless, the same suite of redox-sensitive elements found enriched in sediments of high C_{org} and sulfide content have been found to be redistributed in similar ways at the upper faces of

the turbidites and sapropels (Thomson et al. 1995). Interpretation of sapropel data is more complicated than for the MAP turbidites, however, because sapropels cannot be assumed to have been vertically homogeneous initially. Sapropels also have much greater enrichments of authigenic trace elements, including Re and Ag, than the MAP turbidites (Warning and Brumsack, 2000). In the case of the most recent sapropel, S1, diffusion of O₂ from bottom waters after sapropel formation between 6 and 9.5 ky ago (Mercone et al. 2000) has been shown to have diagenetically modified by post-depositional oxidation a substantial fraction of the S1 unit originally laid down (Thomson et al., 1995, 1999; van Sandtvoort et al. 1996). However, Ba records in sediments can yield a record of past periods of elevated productivity (Dymond et al., 1992) and fortunately an excess of Ba originally deposited with the sapropel appears to have remained unaffected when sapropel C_{org} and sulfides were oxidized by bottom water O₂. The original thickness of the S1 unit can therefore be estimated accurately as those core sections where the Ba/Al data exceed the “background” average value of ~0.0035 (Thomson et al. 1999). Oxygen is inferred to have penetrated to the depth within this high Ba interval at which Mn/Al values decrease to constant low detrital values and the C_{org} contents increase to the high values characteristic of the sapropel. The post-depositionally oxidized sections and the unoxidised sections of the S1 units in three cores studied are indicated by shading differences (Figure 2). The initial S1 thicknesses were ~11, ~8 and ~6 cm in cores MC12, MC7S and MC7, respectively, but post-depositional oxidation has thinned the visual sapropel thickness (the unoxidised section with high residual C_{org} values) to ~6, ~2 and 0 cm. Cores MC7S and MC7 are from the same multicorer deployment and therefore were collected within 0.5 m of each other on the sea floor. The S1 unit must therefore pinch out laterally on this distance scale at this coring location (Thomson et al. 1995).

In each multicore, a sharp maximum in Ag concentration occurs immediately below the inferred depth of O₂ penetration (Figure 2). The original Ag signals that were contained in the original sapropel units at the time of deposition have been mobilized by

oxidation and a fraction re-immobilized below the depth of O₂ penetration. The consistent location of the Ag peaks immediately below the decrease in Mn concentrations, despite the varying sapropel thicknesses, clearly indicates that the Ag peaks must have moved downwards in the sediment over time as the upper reaches of the sapropel were oxidized.

Rhenium has been shown by Warning and Brumsack (2000) to be the element with the most pronounced enrichment over crustal values in the eastern Mediterranean sapropels, with concentrations up to 1 µg g⁻¹ Re. Like Ag, authigenic Re has been quantitatively mobilised by oxidation. Unlike Ag in core MC12, Re displays a peak concentration at the base of the original sapropel unit, ~3 cm deeper than the Ag peak (Figure 2). The dissimilarity between the shapes of the Ba and Re profiles in the sediments of MC12, as well as the location of the Re peak towards the base of the residual sapropel unit, suggests that this Re peak may be at least in part a result of re-immobilization of Re which was originally present higher in the core within the original sapropel unit. In core MC7S, Re is also present at significant levels only within (and arguably at the base of) the residual sapropel unit.

3.3. Sediments at the Last Glacial/Interglacial Transition

North Atlantic sediments deposited during the last glacial maximum show elevated concentrations of uranium that may reflect a decrease in bottom water oxygen concentration (Mangini et al., 2001) in response to an increase in productivity in the Atlantic Subantarctic Zone (Chase et al., 2001). As a consequence, the surficial oxic layer during glacial times was thinner than at present (Thomson et al., 1996). The shallower mean oxic depth that was typical of glacial sediments has increased since the last glacial period towards a deeper oxic depth. In fact the appropriate mean interglacial oxic depth has not yet been achieved in core CD63#9K, and as a result the oxic/suboxic (post-oxic) boundary in this core has moved very little during the change, but has

penetrated slightly downwards into previously anoxic glacial sediments. From the Fe/Al profile, it is estimated that only 7 cm of the glacial sediments have been re-oxidised (59-66 cm in Figure 3). A series of redox sensitive elements have formed concentration peaks around the locus of this active, slow-moving front (Thomson et al. 1996). This suite of elements turns out to be similar to those observed to redistribute to form peaks in the MAP turbidites and eastern Mediterranean sapropels. They include Fe and Mn that have diffused upwards into oxic conditions from reducing conditions at depth to form oxyhydroxides, and Se, V, Cd and U that have diffused downwards and been reduced on the reducing side of the oxic/suboxic boundary. This latter group of elements may have been sourced from the glacial sediments on re-oxidation, or alternatively they may have diffused down from bottom waters or the sediment/water interface.

By comparison with the other cores studied, Re levels are consistently low at around 0.3 ng g^{-1} in core CD63#9K, which are so similar to detrital Re levels that there is no evidence of any authigenic Re uptake in this core. A pronounced Ag peak does however occur immediately below the inferred limit of oxidation (indicated by the base of the local increase in the Fe/Al ratio; Figure 3). Unlike the MAP turbidites and sapropels, there is no evidence that sulfides have ever been present in the core CD63#9K sediments, which suggests that Ag sequestration as Ag_2S is unlikely, although the possibility of the presence of S at trace levels in the sediments, perhaps created in microenvironments, cannot be entirely discounted. This was the mechanism invoked for Cd immobilisation by Rosenthal et al. (1995). It is interesting to note, however, that the Cd profile in core CD63#9K bears little resemblance to the Se or Ag profile, further suggesting that Se and Ag are not sequestered as sulfides.

3.4. The Relationship of Ag with Se

The consistent formation of narrow Ag peaks immediately below the penetration depth of O_2 in all the cases investigated above (turbidites, sapropel and glacial/interglacial

transition sediments) suggests a common sequestration mechanism. As discussed earlier, all the elements could be immobilized by trace amounts of sulfide, as has been suggested for Cd (Rosenthal et al., 1995). However, the absence of a Cd peak at the depth of the Ag and Se peaks in core CD63#9K (Figure 3) argues against this possibility. Another possibility is that Ag, Se and Hg are all reduced to immobile elemental forms at mildly-reducing conditions. Indeed thermodynamics predict stability fields for the zero-valent forms of all three elements at an Eh from ~-0.2 to ~0 at pH between 7-8 (Brookins, 1988), and there is some overlap in Eh/pH space although the Se(0), Hg(0), and Ag(0) fields are not identical. This possibility cannot be ruled out. Yet there is another mechanism that must also be considered. All the Ag peaks inferred to have formed by immobilisation in anoxic conditions below the active oxidation fronts, and preserved below the relict fronts of turbidite *t* and the core 950A-15H turbidite, are coincident with a corresponding peak in Se (where data for both elements are available). This coincidence of peaks suggests that Ag may be sequestered by precipitation of a silver selenide species, AgSe or Ag₂Se (naumannite). Note that because Se is a much more abundant element than Ag, only a small fraction of the total Se is required to react with all the mobilized Ag. The Se:Ag ratio (mass) within the peaks varies from ~10 in cores CD63#9K and MC12 to ~50 in cores MC7S and MC7, suggesting that Ag does not react in constant proportion with total Se but rather will be sequestered as long as excess Se is present. Mercone et al. (1999) noted a very similar behavior of Hg and Se in a study of MAP turbidite and S1 sapropel examples (including some of the same cores investigated here) and concluded that formation of HgSe (tiemannite) was the most likely explanation. Mercone et al (1999) further speculated, by analogy with selenium ore occurrences (Simon and Essene, 1996; Simon et al. 1997), that other elements including Ag and Pt might also be expected to be involved in selenide formation. The co-occurrence of a more abundant element such as Hg with Se peaks suggests that much, if not all, the Se may be involved at oxidation fronts as selenides.

There are some indications from the literature regarding redox conditions leading to immobilization of Se as observed in this work. In the thermodynamic Eh-pH diagrams for Se (*e.g.* Seby et al. 2001), a large field where Se(0) is the dominant form appears to extend into the space where sulfide formation occurs. As a result, the authigenic uptake of Se into sediments, which can occur independently of sulfate reduction and under less reducing conditions (Oremland et al. 1989), is often discussed in terms of reduction of the dominant selenate form SeO_4^{2-} [Se(VI)] in oxic waters to the selenite form SeO_3^- [Se(IV)] or the elemental form [Se(0)] in reducing sediments (*e.g.* Belzile et al. 2000). Selenite uptake on to Fe-Mn oxyhydroxides has been invoked as a mechanism leading to concentration of Se (Balistrieri et al. 1990), but the Se peak in core CD63#9K occurs immediately below the corresponding Fe oxyhydroxide enrichment at 66 cm, and peaks in all other cores occur immediately below the region of elevated Mn, suggesting that this mechanism is not important in these settings. Other indications of the mechanism can be inferred from biological systems, where selenide formation has also been recognized as common. Occurrence of Se and Hg in virtually equimolar concentrations in liver and kidney tissue of marine mammals was first demonstrated by Koeman et al. (1973). Becker et al. (1995) have also demonstrated in whale liver nearly equimolar concentrations of Se and Hg along with proportional but smaller concentrations of Ag. Similarities in the behavior of Ag, Hg and Cd with Se are well documented in the medical literature as well, where formation of Ag, Cd and Hg selenides in the body has been invoked as the mechanism by which selenium supplied as Se(IV) counteracts the toxicity of these elements in the body (Nuttall, 1987). This author has proposed that Se sequestration applies to elements which induce disproportionation of elemental selenium because of the high insolubility of their selenides. The selenides of Pt, Pd, Ag and Hg are particularly insoluble, with $-\log$ (solubility product) values of >50 (Nuttall, 1987). Subsequently it has been demonstrated that selenides of Ag, Hg and Cd first form in the in the blood stream before the resultant selenides bond through Se to a plasma protein

(Sasakura and Suzuki, 1998). The very similar nature of the Se and Ag profiles in the cores examined here, therefore, suggest that Ag sequestration in sediments may be occurring via a similar silver selenide formation mechanism.

The fact that coincident Se and Ag peaks are observed in core CD63#9K, where sulfide formation is not expected, opens up the possibility that selenide formation via the uptake of Se in mildly-reducing sediments may be a common occurrence. If selenide [Se(-II)] formation is common, the 8-electron reduction from Se(VI) in seawater to Se(-II) in sediments has an even greater potential to develop Se isotope fractionation than currently anticipated (*e.g.* Johnson et al. 1999; Herbel et al. 2000).

3.5. The Behavior of Re

The behavior of Re in these cores will only be discussed briefly because a more thorough discussion of Re behavior in the turbidites has been presented elsewhere (Crusius and Thomson, 2000). Although authigenic Re contents are enhanced in the original turbidite sediments (to tens of ng g^{-1}) and dramatically enhanced in the original sapropel sediments (to hundreds of ng g^{-1}), there appears to be convincing evidence only of Re re-immobilisation spread over 50 cm in the C_{org} -rich turbidite *t* (Figure 1; see Crusius and Thomson, 2000), and possibly at the base of the sapropel in multicore MC12 where the Re concentration exceeds $1 \mu\text{g g}^{-1}$ (Figure 2). No significant Re retention is seen in the sediments under the sapropels in cores MC12 and 7S, and only a few ng g^{-1} Re are retained under the oxidation front in the sediments of core MC07 that is now located well below the depth of the original, fully oxidised sapropel (Figure 2). A pattern of Re retention only in organic-rich sediments is consistent with the Re immobilization observed in a wider set of MAP turbidites (Crusius and Thomson, 2000), and implies that oxidised authigenic Re must remain in pore water solution and be lost to bottom waters or diffuse to even greater depths in the sediment. Cores MC12 and MC07 contain

distinct grey “protosapropel” features under the sapropel unit itself (Figure 2). These are syndepositional diagenetic features caused by the formation of pyrite where sulfide diffusing downwards from the sapropel meets Fe^{2+} diffusing upwards from below (Passier et al. 1996). The turbidite in core 950A-15H also contains a large enrichment of diagenetic pyrite at 134.63 m that is believed to have developed after emplacement (Figure 1; Thomson et al 1998). It is noteworthy that neither Re nor Ag is incorporated into any of these diagenetic pyrites, while As is significantly enriched and Mo slightly enriched (Thomson et al, 1998). Given the propensity of Ag to form sulfides, a lack of significant Ag enrichment is at first glance surprising. However, this absence of Re and Ag enrichment may be due to an absence of significant quantities of either metal in the porewater for incorporation into the pyrite at the depth where the pyrites are forming. Thus, this observation does not necessarily contradict the suggestion of Koide et al. (1986) and Colodner et al (1993) that Re is incorporated into sulfides.

The inventories (mass/cm^2) of Ba, Ag, Re and C_{org} in the sapropel sediments shed light on the effectiveness of the mobilization of the metals by oxygen. Because conditions in the water column and sediments were certainly variable during the period of deposition of S1, it is not possible to determine the original inventory of any metal in the sapropel units. However, the ratio of each metal inventory to that determined for MC12 (with the broadest original sapropel) yields insight into the relative mobilities of each metal. The inventory of Ba in the sapropel of core MC7S (with remaining sapropel) is 82% as large as that in MC12 (Table 1). By contrast, the inventory of Ba in MC7 is 63% as large as that in MC12. This relatively small difference in Ba inventories reflects the differences in thickness of the original sapropel, rather than any post-depositional mobility. Silver shows a different pattern. The inventory of Ag in core MC7S (with residual sapropel) is 103% as large as that in MC12, while the Ag inventory in the sapropel of MC7 (fully oxidised sapropel) is only 35% as large as that in MC12. The much smaller inventory in MC7 probably reflects loss of Ag from the original sapropel unit. Proceeding with a

similar analysis of Re, the Re inventory in core MC7S (with remaining sapropel) is 35% as large as that in MC12 (Table 1), while the Re inventory in the sapropel of MC7 (no sapropel) is only 2% as large as that in MC12. The large differences between the MC12 Re inventory and those in cores MC7S and MC7 indicates that most of the Re has been mobilized from the sapropel units in both MC7S and MC7. Clearly the Re has not been retained, to any significant extent, in the C_{org} -poor sediments underlying the S1 sapropel (Figure 2). A similar assessment was also carried out for C_{org} , which should not be re-immobilized once oxidized. The C_{org} inventory in MC7s was 47% as large as that in MC12, while the inventory in MC7 was 15% as large. It is interesting to note that the relative loss during burndown was greater for Re than for C_{org} , indicating that the fraction of C_{org} that is refractory is larger than the fraction of Re that is lithogenic.

Bear in mind, of course, that Ba is incorporated into settling particulate material, while Re (and perhaps to some extent Ag) are probably incorporated below the sediment-water interface by diffusion. Therefore, comparison of inventories within the original sapropel unit could be misleading. However, such comparisons factor in all of the significant quantities of Ag and Re within AND below the sapropels, and thus provide a useful qualitative indication of the relative mobilities of the three metals. It must be kept in mind as well that lateral diffusion in cores MC7S and MC7 could be as important as vertical diffusion in redistributing metals.

3.6. Implications for Paleoenvironmental Records of Ag and Re

It is clear from this work that exposure to bottom-water O_2 oxidizes and fully remobilizes the Re, Ag and Se that were originally present in the sediments deposited in reducing conditions. The extreme redistribution of these elements in the Mediterranean cores with sedimentation rates of $\sim 2 \text{ cm ka}^{-1}$ suggests that paleoenvironmental interpretations of sedimentary Ag and Re will be compromised in low-sedimentation-rate ($< 5 \text{ cm ka}^{-1}$?) environments where bottom waters and surficial sediments are well

oxygenated. In a similar vein, others have suggested complete loss of authigenic U (Mangini et al., 2001) and non-refractory C_{org} (Jung et al., 1997) when sedimentation rates are below $1-2 \text{ cm ka}^{-1}$.

Given the evidence of diffusion of mobilized Re over depths of 0.5-3 m before re-sequestration (Crusius and Thomson, 2000), any Re signal from eastern Mediterranean sapropels deeper than S1 (~20 cm depth) may reflect a mixture of original signal and Re from a later sapropel that has undergone mobilization and downward diffusion during a period of O_2 penetration subsequent to its deposition. Therefore, sedimentary records of Re from Eastern Mediterranean sapropels may not provide any straightforward paleoenvironmental information. Interpretation of Re/Mo ratios in sapropels (e.g. Warning and Brumsack 2000) is also not straightforward, both because of the behavior of Re discussed above and because authigenic Mo has been shown to be enriched above, within and below the sapropel units (Thomson et al., 1995). This behavior suggests Mo may also be mobilized from within the sapropel unit upon exposure to bottom-water O_2 , and re-immobilized outside of the original sapropel boundaries. Therefore, because of the prolonged sediment exposure to bottom-water O_2 following cessation of conditions that led to sapropel formation, the Re/Mo ratio within a buried sapropel unit may have changed dramatically from the value at the time of sapropel deposition. In environments where sedimentation rates are much higher, however, the period of surficial sediment exposure to O_2 is much reduced because the sediments are more rapidly buried. The steep gradients in Re and Ag still present in sedimentary records that have been buried for up to 3.4 Myr (Figure 1), suggest negligible subsequent mobility of these metals for periods of millions of years after the sediments are buried without exposure to O_2 . Thus, high sedimentation-rate and anoxic environments still offer promise for high-quality paleoenvironmental reconstructions from records of authigenic Ag and Re.

4. CONCLUSIONS

Cores from a variety of environments have been investigated in which sediments that were initially anoxic, with a clear authigenic component of Ag and Re, have been exposed subsequently to bottom water O₂. In all cases, the authigenic Ag and Re were quantitatively mobilized by exposure to O₂, as previously documented for Re (Colodner et al., 1992; Crusius and Thomson, 2000). The mobilized Ag was efficiently, although not quantitatively, re-immobilized in thin (~1 cm) layers immediately below the front of O₂ penetration. This Ag immobilization is likely to be caused by formation of a silver selenide species, as has been suggested for Hg (Mercone et al., 1999). Selenium peaks coincident with Ag, Hg and Cd at the tops of C_{org}- or sulfide-enriched units may be permissible evidence that some post-depositional exposure occurred after their formation. In contrast to Ag, Re appears to be inefficiently re-immobilized only in underlying C_{org}-rich sediments, consistent with the results of Crusius and Thomson (2000). Paleoenvironmental interpretations of sedimentary Ag and Re will be compromised in low-sedimentation-rate, (< 5 cm ka⁻¹?) oxic environments due to O₂ exposure, but sedimentary records of Ag and Re from high sedimentation-rate and consistently anoxic environments still hold promise for paleoenvironmental reconstructions.

Acknowledgements.

The authors acknowledge financial support from the Japan Science and Technology Fund (JSTF), the Natural Sciences and Engineering Research Council of Canada (NSERC), the International Atomic Energy Agency (IEEA) and the EU Marine Science and Technology Programme (project MAS3-CT97-0137 "Sapropels and Palaeoproductivity"). We thank Tom Pedersen for his encouragement of this project, David Sage for his careful laboratory work, three journal referees for their constructive reviews of the original version and David Burdige for his editorial comments.

References:

- Anbar A. D., Creaser R. A., Papanastassiou D. A., and Wasserburg G. J. (1992) Rhenium in seawater: Confirmation of generally conservative behavior. *Geochimica et Cosmochimica Acta* **56**, 4099-4103.
- Balistreri, L.S. and Chao, T.T. (1990) Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* **54**, 739-751.
- Balsam W. L. and McCoy Jr. F. W. (1987) Atlantic sediments: Glacial/interglacial comparisons. *Paleoceanography* **2**, 531-542.
- Becker, P.R., Mackey, E.A., Demiralp, R., Suydam, R., Early, G., Koster, B.J. and Wise, S.A. (1995) Relationship of silver with selenium and mercury in the liver of two species of toothed whales (Odontocetes). *Mar. Poll. Bull.* **30**, 262-271.
- Belzile, N., Chen, Y.-W. and Xu, R. (2000) Early diagenetic behavior of selenium in freshwater sediments. *Appl. Geochem.* **15**, 1439-1454.
- Berner, R.A. (1982) A new geochemical classification of sedimentary environments. *J. Sed. Petrol.* **51**, 359-365.
- Brookins D. G. (1988) *Eh-pH Diagrams for Geochemistry*. Springer Verlag.
- Calvert S. E. and Pedersen T. F. (1993) Geochemistry of Recent oxic and anoxic sediments: Implications for the geological record. *Mar. Geol.* **113**, 67-88.
- Calvert S. E. and Fontugne, M.R. (2001) On the late Pleistocene-Holocene sapropel record of climatic and oceanographic variability in the eastern Mediterranean. *Paleoceanography*. **16**, 78-94.

- Chase Z., Anderson R. F., and Fleischer M. Q. (2001) Evidence from authigenic uranium for increased productivity of the glacial Subantarctic ocean. *Paleocean.* **16**, 468-478.
- Colley S. and Thomson J. (1985) Recurrent uranium relocations in distal turbidites emplaced in pelagic conditions. *Geochim. Cosmochim Acta* **49**, 2339-2348.
- Colodner D. (1991) The Marine Geochemistry of Rhenium, Iridium and Platinum. Ph.D., MIT/WHOI Joint Program in Oceanography.
- Colodner D. C., Boyle E. A., Edmond J. M., and Thomson J. (1992) Post-depositional mobility of platinum, iridium and rhenium in marine sediments. *Nature* **358**, 402-404.
- Colodner D., Sachs J., Ravizza G., Turekian K., Edmond J., and Boyle E. (1993) The geochemical cycle of rhenium: a reconnaissance. *Earth Planet. Sci. Lett.* **117**, 205-221.
- Crusius J., Calvert S. E., Pedersen T. F., and Sage D. (1996) Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and anoxic conditions of deposition. *Earth Planet. Sci. Lett.* **145**, 65-78.
- Crusius J. and Thomson J. (2000) Comparative behavior of authigenic Re, U and Mo during reoxidation and subsequent long-term burial in marine sediments. *Geochim. Cosmochim. Acta* **64**, 2233-2242.
- Dymond J., Suess E., and Lyle M. (1992) Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. *Paleoceanography* **7**, 163-181.
- Fisher N. S. and Wentz M. (1993) The release of trace elements by dying marine phytoplankton. *Deep-Sea Research I* **40**, 671-694.

- Flegal A. R., Sanudo-Wilhelmy S. A., and Scelfo G. M. (1995) Silver in the eastern Atlantic Ocean. *Mar. Chem.* **49**, 315-320.
- Govindaraju K. (1989) 1989 compilation of working values and sample description for 272 geostandards. *Geostandards Newsletter* **13**(Special Issue), 1-113.
- Herbel, M.J., Johnson, T.M., Oremland, R.S. and Bullen, T.D. (2000) Fractionation of selenium isotopes during bacterial respiratory reduction of selenium oxyanions. *Geochim. Cosmochim Acta* **64**, 3701-3709.
- Hilgen, F.G., Krijksman, W., Langereis, C.G., Lourens, L.J., Santarelli, A. and Zachariasse, W.J. (1995) Extending the astronomical (polarity) time scale into the Miocene. *Earth. Planet. Sci. Lett.* **136** 495-510.
- Jarvis I. and Higgs N. C. (1987) Trace-element mobility during early diagenesis in distal turbidites: late Quaternary of the Madeira Abyssal Plain, N. Atlantic. In *Geology and geochemistry of abyssal plains*, Geol. Soc. (Lond.) Spec. Vol. No. 31 (eds. P. P. E. Weaver and J. Thomson), pp. 179-213.
- Johnson, T.M., Herbel, M.J., Bullen, T.D. and Zawislanski, P.T (1999) Selenium isotope ratios as indicators of selenium sources and oxyanion reduction. *Geochim. Cosmochim. Acta* **63**, 2775-2783.
- Jung M., Ilmberger J., Mangini A., and Emeis K.-C. (1997) Why some Mediterranean sapropels survived burn-down (and others did not). *Mar. Geol.* **14**, 51-60.
- Koeman, J.H., Peeters, W., Koudsaal-Hol, C., Tijoe, P.S. and van Haften, J.L. (1975) Mercury-selenium correlations in marine mammals. *Nature* **245**, 285-286.
- Koide M., Hodge V. F., Yang J. S., Stallard M., and Goldberg E. G. (1986) Some comparative marine chemistries of rhenium, gold, silver and molybdenum. *Applied Geochemistry* **1**, 705-714.

- Kuldvere A. (1989) Extraction of geological materials with mineral acids for the determination of arsenic, antimony, bismuth and selenium by hydride generation atomic absorption spectrometry. *Analyst* **114**, 125-131.
- McKay J. L. and Pedersen T. F. (2000) Geochemical Behavior of Redox-sensitive Trace Metals in Iron-Sulfide Layers. *EOS* **81**, F613.
- Mangini A., Jung M., and Laukenmann S. (2001) What do we learn from peaks of uranium and of manganese in deep-sea sediments? *Mar. Geol.* **177**, 63-78.
- Martin J. H., Knauer G. A., and Gordon R. M. (1983) Silver distributions and fluxes in northeast Pacific waters. *Nature* **305**, 306-309.
- Mercone, D., Thomson, J., Croudace, I.W. and Troelstra, S.R. (1999) A coupled natural immobilisation mechanism for mercury and selenium in deep-sea sediments. *Geochim. Cosmochim. Acta* **63** 1481-1488.
- Mercone, D., Thomson, J., Croudace, I.W., Siani, G., Paterne, M. and Troelstra, S.R. (2000) Duration of S1, the most recent sapropel in the eastern Mediterranean Sea, as indicated by AMS radiocarbon and geochemical evidence. *Paleoceanography* **15** 336-347.
- Middelburg, J.J. (1993) Turbidites provide a unique opportunity to study diagenetic processes. *Geologie en Mijnbouw* **72**, 15-21.
- Nameroff T. J., Balistrieri L. S., and Murray J. W. (2002) Suboxic Trace Metal Geochemistry in the Eastern Tropical North Pacific. *Geochim. Cosmochim. Acta* **66**, 1139-1158.
- Nuttall K. L. (1987) A model for metal selenide formation under biological conditions. *Med. Hypotheses* **24**, 217-221.

- Oremland, R.S., Hollibaugh, J.T., Maest, A.S., Presser, T.S., Miller, L.G. and Culbertson, C.W. (1989) Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture: Biogeochemical significance of a novel, sulfate-independent respiration. *Applied Environ. Microbiol.* **55**, 2333-2343.
- Passier, H.F., Middelburg, J.J., van Os, B.J.H. and de Lange, G.J. (1996) Diagenetic pyritisation under eastern Mediterranean sapropels caused by downward sulfide diffusion. *Geochim. Cosmochim. Acta* **60**, 751-763.
- Rohling, E.J. (1994). Review and new aspects concerning the formation of Mediterranean sapropels. *Mar. Geol.* **122**, 1-28.
- Rosenthal Y., Lam P., Boyle E. A., and Thomson J. (1995) Authigenic cadmium enrichments in suboxic sediments: Precipitation and post-depositional remobilization. *Earth Planet. Sci. Lett.* **132**, 99-111.
- Rossignol-Strick, M. (1985) African monsoon, an immediate climate response to orbital insolation. *Nature* **304**, 46-49.
- Sasakura, C. and Suzuki, K.T. (1998) Biological interaction between transition metals (Ag, Cd and Hg), selenide/sulfide and selenoprotein P. *J. Inorg. Biochem.* **71**, 159-162.
- Seby, F., Potin-Gautier, M., Giffaut, E., Borge, G. and Donard, O.F.X. (2001) A critical review of thermodynamic data for selenium species at 25°C. *Chem Geol.* **171**, 173-194.
- Simon, G. and Essene, E.J. (1996) Phase relations among selenides, sulfides, tellurides and oxides: I. Thermodynamic properties and calculated equilibria. *Econ. Geol.* **91**, 1183-1208.

- Simon, G. and Essene, E.J. (1997) Phase relations among selenides, sulfides, tellurides and oxides: II. Applications to selenide-bearing ore deposits. *Econ. Geol.* **92**, 468-484.
- Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: its Composition and Evolution*. Blackwell Scientific.
- Thomson J., Wilson T. R. S., Culkin F., and Hydes D. J. (1984) Non-steady state diagenetic record in eastern equatorial Atlantic sediments. *Earth Planet. Sci. Lett.* **71**, 23-30.
- Thomson J., Colley S., Higgs N. C., Hydes D. J., Wilson T. R. S., and Sørensen J. (1987) Geochemical oxidation fronts in the NE Atlantic distal turbidites and their effects in the sedimentary record. In *Geology and Geochemistry of Abyssal Plains*, Geol. Soc. (Lond.) Spec. Vol. No. 31 (eds. P. P. E. Weaver and J. Thomson) pp. 167-177.
- Thomson J., Higgs N. C., Croudace I. W., Colley S., and Hydes D. J. (1993) Redox zonation of elements at an oxic/post-oxic boundary in deep-sea sediments. *Geochim. Cosmochim. Acta* **57**, 579-595.
- Thomson, J. and Weaver, P.P.E. (1994) An AMS radiocarbon method to determine the emplacement time of recent deep-sea turbidites. *Sed. Geol.* **89**, 1-7.
- Thomson, J., Higgs, N.C. and Clayton, T. (1995) A geochemical criterion for the recognition of Heinrich events and estimation of their deposition fluxes by the ($^{230}\text{Th}_{\text{excess}}\text{)}_0$ profiling method. *Earth Planet. Sci. Lett.* **135** 41-56.
- Thomson, J., Higgs N.C. and Colley, S. (1996) Diagenetic redistributions of redox-sensitive elements in NE Atlantic glacial/interglacial sediments. *Earth Planet. Sci. Lett.* **139** 365-377.
- Thomson J., Jarvis I., Green D. R. H., and Green D. (1997) Oxidation fronts in Madeira Abyssal Plain turbidites: persistence of early diagenetic trace-element

- enrichments during burial, ODP Site 950. In *Proceedings of the Ocean Drilling Program, Scientific Results*, Vol. 157 (ed. H.-U. S. P.P.E. Weaver, J. V. Firth, W. A. Duffield).
- Thomson, J., Jarvis, I., Green, D.R.H., Green, D.A. and Clayton, T. (1998). Mobility and immobility of redox-sensitive elements in deep-sea turbidites during shallow burial. *Geochim. Cosmochim. Acta* **62** 643-656.
- Thomson, J., Mercone, D., de Lange, G.J and van Santvoort, P.J.M. (1999) Review of recent advances in the interpretation of Eastern Mediterranean sapropel S1 from geochemical evidence. *Mar. Geol.* **153**, 77-89.
- van Santvoort, P.J.M., de Lange, G.J., Thomson, J., Cussen, H., Wilson, T.R.S., Krom, M.D. and Strohle, K. (1996) Active post-depositional oxidation of the most recent sapropel (S1) in the eastern Mediterranean. *Geochim. Cosmochim. Acta* **60**, 4007-4024.
- Warning, B. and Brumsack, H.-J. (2000) Trace metal signatures of eastern Mediterranean sapropels. *Palaeogeog. Palaeoclimat. Palaeoecol.* **158** 293-309.
- Weaver P. P. E. and Kuijpers A. (1983) Climatic control of turbidite deposition on the Madeira Abyssal Plain. *Nature* **306**, 360-363.

Table 1: Ratios of biogenic Ba, Ag and Re inventories¹ (mass cm⁻²) in the sapropel portion of MC7s (with sapropel) and MC7 (no sapropel) to those in MC12, the core with the broadest original sapropel unit.

	MC7S/MC12	MC7(no sapropel) /MC12
biogenic Ba	0.82	0.63
Ag	1.03	0.35
Re	0.35	0.02
C _{org}	0.47	0.15

¹ Inventories were determined assuming a porosity of 0.75 within the sapropel units and a dry density of 2.5 g cm⁻³. Inventories presented for Ba are calculated for the biogenic barium fraction by subtracting the lithogenic Ba content from the total Ba content after normalizing each to the Al content. The lithogenic Ba content was assumed to be 140 µg g⁻¹, determined from the region of constant Ba below the sapropel units. Inventories of Ag and Re are total inventories, which are virtually identical to the authigenic inventories, given the small lithogenic content of each element. The inventory of C_{org} is calculated for the portion of each core that contains elevated biogenic Ba.

Figure Captions

Figure 1: Sedimentary profiles of C_{org} , S, Se, Ag and Re in turbidites from the Madeira Abyssal Plain (30° - $32^{\circ}30'N$, $23^{\circ}30'$ - $25^{\circ}30'W$; 5440 m), including the most recent turbidite (*a*) in box core 11135 (upper panels), turbidite *t* from Madeira Abyssal Plain giant piston core MD24 (middle panels) and a turbidite from ODP core 950A-15H (lower panels). Light stippling represents the region of the turbidite above the oxidation front (active in core 11135 and relict in cores MD24 and 950A-15H), while closely-spaced diagonal lines shade the unoxidized portion. Note that the dashed horizontal line at 134.63 m in 950A-15H aligns features with the region of highly elevated S (diagenetic pyrite). Note that for most elements the concentration axes change between panels. The Re data have been previously presented in Crusius and Thomson, 2000.

Figure 2: Sedimentary profiles of Ba, Mn/Al, C_{org} , S, Se, Ag and Re in multicores MC12, MC7S and MC7, all containing the S1 sapropel of the eastern Mediterranean Sea. Cores MC7s and MC7 were from $34^{\circ}19.2'N$, $20^{\circ}02.7'E$, 2703 m, while core MC12 was from 470 km to the east south east ($33^{\circ}23.7'N$, $25^{\circ}01.3'E$, 2211 m). The light stippling represents the oxidized portion of the original sapropel, while closely-spaced diagonal lines shade the unoxidized portion of the original sapropel. The boundary between these two shadings represents the position of the active oxidation front in cores MC12 and MC7S. The more broadly spaced diagonal shading (in MC12 and MC7S) represents the “protosapropel” region that contains elevated S but not C_{org} (see text). The horizontal line in MC7 denotes the position of the active oxygen penetration front in that core where the sapropel has been completely oxidised. Note that for most elements the concentration axes change between panels.

Figure 3: Sedimentary profiles of Fe/Al, Se, Ag, Re and Cd in north-east Atlantic core CD63#9K (46°23.8'N, 12°32.8'W; 3849 m). The dashed line marks the position of the active oxidation front.





