

Fluid displacive resin embedding of laminated sediments: preserving trace metals for high-resolution paleoclimate investigations

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Abstract

For the high-resolution study of trace metal profiles in laminated anoxic sediments, a specially adapted method of resin embedding has been developed. Fluid displacement is the preferred means of sediment dehydration, offering optimum structural preservation and facilitating desalination. Exchanges of deionized water, acetone, and low-viscosity resin are performed in an oxygen-deficient atmosphere to maintain anoxia in the sediments. Analysis of the rinsing fluids indicates both efficient removal of brine salts and minimal dissolution of redox-sensitive trace metals. This contrasts with oxic fluid displacement experiments, in which several metals appear to be removed from the solid phase during desalination. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) scanning of the embedded blocks shows that the adapted preparation viably preserves both the redox-sensitive chemistry and physical structure of the sediment.

Laminated sediments provide an important high resolution archive of paleoclimatic data. Downcore variations in trace metals, preserved by the absence of bioturbation, can be used as tracers of changing environmental conditions (Outridge et al. 2005). However, in preparation for geochemical microanalyses, these poorly consolidated sediments must be stabilized.

Resin embedding of core sections into solid, inert blocks is an established preparatory step for micropaleontological analysis (Grimm 1992; Pike and Kemp 1996) and varve-counting (Lotter and Lemcke 1999), and has been adopted more recently by geochemists to facilitate scanning techniques such as XRF spectrometry (Haug et al. 2003) and LA-ICP-MS. However, as most reported protocols were not developed for geochemical studies, there is little known about redox-related alteration to chemical signatures in the sediment during the

stages of resin embedding. With porewater anoxia typical of most laminated sediment sequences (Kemp 1996), a preparation is necessary to fix anoxic sediment archives for geochemical analyses with minimal loss of redox-sensitive components. Meanwhile, the level of structural preservation offered by existing protocols should be maintained.

Here we present an embedding method that satisfies these criteria. To ensure that the method is suitable for sediments from the most extreme anoxic conditions, we have embedded trace metal rich sediments from the hypersaline Urania basin in the Eastern Mediterranean (MEDRIFF 1995), and have tested our protocol against existing procedures.

Materials and procedures

The three primary stages of any embedding method (as summarized by Boës and Fagel 2005), are the initial sampling of sediment from the open core, dehydration to remove porewaters, and the resin embedding itself. The protocol of Pike & Kemp (1996) is considered to cause minimal structural damage to the sediment, employing acetone fluid exchange as the method of dehydration and Spurr Epoxy Resin as the embedding polymer (Spurr 1969). In contrast to protocols which include freeze-drying stages (e.g., Boës and Fagel 2005), the fluid exchange method allows the sediment matrix to be supported continually. It also is essential for brine sediment embedding as it facilitates salt removal, necessary to avoid salt domination of elemental analyses and the possible disruption

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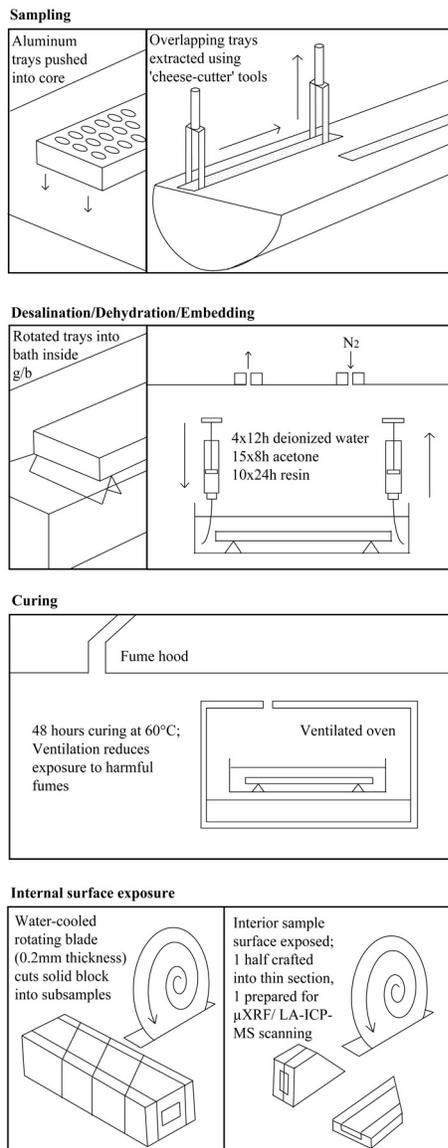


Fig. 1. Stages of the resin embedding procedure. See text for further details.

of lamina by salt crystallization during dehydration. Hence, the Pike and Kemp protocol forms the basis of our own, with a desalination stage (Seeberg-Elverfeldt et al. 2004) included. However, as an improvement of these protocols, we perform all fluid exchange stages in a nitrogen-filled glove box (de Lange 1992) to maintain anoxia in the sediment. A visual summary of each stage is presented in Fig. 1.

Sampling

A variety of implements designed to extract soft sediment from open cores has been described in the literature (e.g., Schimmelman et al. 1990; Francus and Cosby 2001; Boës and Fagel 2005), all crafted with the purpose of minimizing struc-

tural damage during sampling. The required care and elaboration generally is greater for highly unconsolidated and clay-rich sediments. In our case, aluminum foil trays similar to those used by Lamoureux (1994) (foil thickness 0.2 mm, tray dimensions 200 × 20 × 10 mm) pushed into the sediment and recovered using the 'cheese-cutter' style tool of Francus and Cosby (2001) – with foil strip attached but without the use of electro-osmosis – were sufficient to retrieve undisturbed sections. The tray bottoms were pre-punched with a grid of holes, so that around 50% of their area was open to assist fluid flow in later stages of the method (*see also* Rohrig and Scharf 2006). After sampling, filled trays were transferred to a nitrogen-filled glove box for all fluid exchange stages. We recommend the use of a non-Perspex glove box, as this material is sensitive to reaction with acetone, and, possibly, also resin vapors. If Perspex is the only option, we advise readers that the glove box may become unsuitable for other work after prolonged exposure. When embedding highly clay-rich sediments, it may be advisable to remove the sample from the aluminum tray before fluid exchange (Lamoureux 1994) as even a perforated tray may hinder fluid flow. Of course, care must be exercised to prevent structural damage during this process.

Desalination—Inside the glove box, deionized water was purged overnight with nitrogen gas and transferred into 250 × 50 × 40 mm aluminum baths. The filled sample trays were immersed in the baths, and the water was exchanged by syringe four times over 48 h to promote salt diffusion out of the sediment.

Dehydration—Acetone is miscible with both water and embedding resin and thus was used as a dehydrating agent. All acetone was purged overnight with nitrogen, and employed in the same manner as the deionized water. A total of 15 exchanges (three daily for 5 d) guaranteed the complete dehydration of our sediments, as evidenced by consistently high embedding quality (a firm, polishable cut surface). Specific gravity measurements can be used to track the removal of water during acetone dehydration. However, we note that water can be retained in the matrix of clay-rich sediments for several weeks, even when specific gravity measurements suggest complete dehydration. For this reason, we recommend that a test series of samples should be dehydrated and embedded using a range of acetone replacement timescales (both number and duration), to calibrate the process to the sediments in question.

Resin embedding—Spurr Epoxy Resin consistently has shown good results for soft sediment embedding (e.g., Grimm 1992; Lamoureux 1994; Pike and Kemp 1996; Lotter and Lemcke 1999), satisfying criteria such as low viscosity, long pot life, and medium hardness (Jim 1985). Formerly, the toxic Vinyl Cyclohexene Dioxide (VCD) component was used as the polymer of Spurr resin, but the suppliers have replaced this in recent years with ERL 4221. This polymer is required in greater quantities than VCD to maintain the anhydride:epoxide ratio achieved between VCD and the epoxy resin DER (Ellis 2006). The 'old'

Table 1. Components of ‘old’ and ‘new’ formulations of Spurr epoxy resin, and relative masses required to achieve firm standard texture.

Old formulation	Code	Relative Mass	New formulation*	Code	Relative Mass
Vinyl Cyclohexene Dioxide	VCD	10	Cycloaliphatic Epoxide Resin	ERL 4221	16.4
Diglycidal Ether of Polypropyleneglycol	DER 736	6	Diglycidal Ether of Polypropyleneglycol	DER 736	5.72
Nonenyl Succinic Anhydride	NSA	26	Nonenyl Succinic Anhydride	NSA	23.6
Dimethylaminoethanol	DMAE	0.4	Dimethylaminoethanol	DMAE	0.4

*Relative masses for new formulation were established by Ellis (2006).

and ‘new’ four components of the resin mixture, along with their relative quantities, are presented in Table 1. The new formulation has increased the viscosity of the resin, but this remains low enough to achieve good impregnation, even of clay-rich sediments. Toxicity of the components in the current recipe is poorly understood, but caution should be exercised during handling (e.g., use of a fume hood to prevent inhalation of vapors, safety gloves to prevent contact with skin).

Each day for 10 d, the four components were mixed on a balance, then transferred to the glove box. Once inside, the resin was thinned by the addition of acetone to guarantee infiltration into pores (replacements one through five) and purged with nitrogen overnight (all replacements) before being applied to the samples. A series of diminishing acetone:resin ratios (from 1:1 to 1:9) were used for the first 5 d, followed by five exchanges of pure resin. All exchanges were administered by syringe, with the sample tray remaining undisturbed inside the bath. The final replacement of resin was left to stand for 2 weeks before the baths were removed from the glove box and cured in a 60°C oven for 48 h.

An alternative method (Lamoureux 2001) uses a single application of undiluted resin, and a low vacuum to promote infiltration into pores. This reduces wastage of resin and can be employed if facilities are available. However, transfer from glove box to vacuum chamber should be rapid, and vacuum strength should be monitored carefully to prevent boiling of the remaining acetone in the sample, which may rupture laminations. The passive (non-vacuum) method, while using more resources, guarantees both structural preservation and no risk of oxygen invasion at any stage.

Sample surface preparation—After curing, the solid resin blocks were removed from the aluminum baths and cut with

a diamond saw (0.2 mm thickness) to reveal the interior surface of the embedded sediment. At this point, complete impregnation of resin (and thus removal of water) was confirmed by observation of a consistently firm surface. The geometry of further sample cutting, and surface preparation, should be determined by the desired analysis technique. For assessment of stratigraphy, the number of breaks should be kept to a minimum. However, many laser ablation cells have restricted dimensions and therefore require some division of the sample. We cut our trays diagonally into four smaller blocks, retaining an overlap between each. These were halved to expose the largest interior embedded surface (see Fig. 1).

One block from each pair was polished for surface scanning techniques by the following procedure: (1) Application of P800/ P1200/ P4000 silicon carbide abrasive paper in sequence (a progressively finer sequence of grits). (2) Application of 0.3 µm aluminum polish powder (as a fluid suspension between the blocks and a rotating stage). After each step, the blocks were cleaned ultrasonically to minimize surface contamination. The second block of each pair was used to craft a series of thin sections for optical microscopy.

Assessment

Our primary concern was to construct a protocol which removed brine salts but left those sedimentary components most susceptible to oxidation undisturbed. Specifically, transition metals of potential use as geochemical tracers had to be preserved. Of the stages outlined above, desalination carries the greatest risk to the inorganic phases of such metals, as the sediment is flushed with an ionic solvent which could easily dissolve oxidation products. Therefore, we analyzed the desalination leachates of test samples of three contrasting compositions, rinsed under oxic and anoxic conditions to assess the necessity

Table 2. Initial composition of three distinct sediment layers in Urania brine basin core PP44PC.

Sample*	Water wt%	C _{org} wt%	CaCO ₃ wt%	Al wt%	Fe wt%	Ba ppm	Cd ppm	Co ppm	Cu ppm	Mn ppm	Ni ppm	U ppm	V ppm
#1 Sapropel S1	64 (2)	1.9 (0.4)	0.45 (0.2)	1.0 (0.2)	1.0 (0.2)	450 (50)	0.34 (0.02)	8 (2)	22 (5)	120 (20)	35 (5)	1.2 (0.1)	35 (3)
#2 Normal sediment	45 (5)	1.0 (0.3)	2.0 (1.5)	3.7 (0.25)	2.5 (0.25)	200 (50)	0.35 (0.10)	17 (3)	70 (20)	375 (75)	105 (25)	3.2 (0.5)	90 (10)
#3 Slump	40 (2)	0.2 (0.01)	21.3 (0.3)	2.6 (0.05)	1.3 (0.01)	100 (20)	0.09 (0.01)	7 (1)	30 (5)	180 (10)	36 (3)	1.8 (0.2)	46 (3)

* Reported concentrations were measured at the depths where the test samples were taken; Bracketed numbers underneath represent the variability within each layer, based on a complete series of 3 mm resolution discrete samples through the 1 m core section.

of using a glove box. In addition, we acetone-dehydrated an organic rich sample after anoxic desalination and analyzed the acetone to assess possible metal loss during organic pigment dissolution.

Methods

The test samples were ~5cm³ cubes of wet sediment derived from three chemically distinct layers in an Urania basin core: The organic carbon-rich sapropel S1 (sediment layer #1), ‘Normal’ post sapropel brine sediment (sediment layer #2) and an allochthonous slump from outside the brine basin (sediment layer #3). The initial compositions of the layers were determined by analysis of discrete freeze-dried samples by ICP-AES (major-minor elements), Fisons NA 1500 NCS (total and organic carbon, hence inorganic carbon by deduction) and ICP-MS (trace elements). Instrumental precision was <1% (major/minor elements), and <5% (total and organic carbon, trace elements), and analysis of laboratory and in-house standards showed accuracy to be within 5%.

One series of samples (#1, #2, #3) was weighed and desalinated in the glove box as described above, another on the lab bench with oxalic rinsing water. After each 12-h rinsing period, the water was collected, filtered, acidified to 1M HNO₃, and subsequently analyzed by ICP-MS for dissolved element concentrations. The anoxic-desalinated #1 sample — the most organic-rich of the three — was then dehydrated in the glove box, and the rinsing acetone was filtered, evaporated, and acidified to 1 M HCl for ICP-MS analysis.

Results

A summary of the initial compositions of samples #1, #2, and #3 is shown in Table 2, reported as wet sediment concentrations. The ‘normal’ brine sediment (#2) contains the highest levels of Co, Cu, Mo, Ni, and V, as expected in an anoxic depositional environment in the modern ocean (e.g., Francois 1988; Brumsack 1989; Böning et al. 2004). The high water content of sapropel S1 (#1) depresses the concentrations of solid components when reported as wet sediment, but this layer also is rich in these metals when compared to the allochthonous slump (#3), which has a composition closer to surrounding oxalic Mediterranean sediments. Mn shows a similar distribution to the other investigated metals, implying unusual behavior in the anoxic brine environment. In most suboxic Mediterranean sediments, solid phase Mn is depleted by reductive dissolution of its oxides (e.g., Van Santvoort et al. 1996)

Analysis of dissolved Na in the leachates of #1, #2, and #3 confirms complete salt removal over four rinses in both anoxic and oxalic conditions (Fig. 2). Each rinse removes around 90% of the salt remaining from the previous rinse (i.e., the first rinse removes 90% of total salt, the second around 9% of total salt, etc). This logarithmic pattern implies efficient diffusion of salt ions out of the sediment matrix.

Oxalic desalination of #1 released an order of magnitude more Cd, Co, and Ni than the comparable anoxic procedure

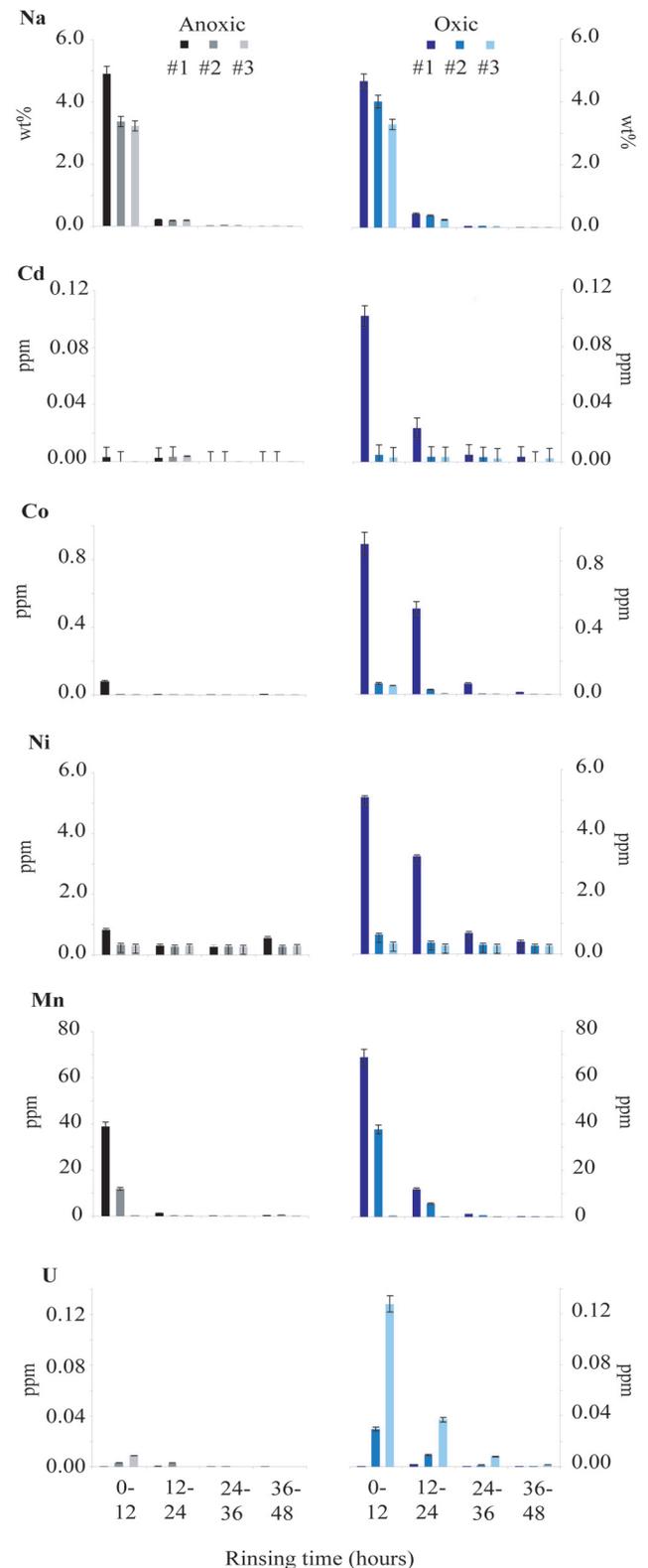


Fig. 2. Elements in anoxic and oxalic desalination leachates of samples #1, #2, and #3. Error bars represent reproducibility of duplicate samples and mean concentrations in blanks.

Table 3. Summary of elements dissolved in anoxic and oxic desalination leachates.

Protocol*	Sample	%									
		lost Al	Fe	Ba	Cd	Co	Cu	Mn	Ni	U	V
Anoxic	#1	0.15	0.24	2.3	–	1.15	1.48	34.2	5.5	0.1	2.1
	#2	0.58	0.50	0.6	–	0.06	0.45	3.4	1.1	0.3	0.7
	#3	0.10	0.11	0.4	–	0.07	0.76	0.4	3.2	0.5	1.4
Oxic	#1	0.18	0.36	0.9	40	18.7	1.18	68.4	26.7	0.2	2.0
	#2	0.30	0.09	1.6	–	0.60	0.51	11.8	1.5	1.4	0.6
	#3	0.40	0.12	0.4	–	0.90	1.52	0.4	3.2	10	2.0

*The sum of four rinses is reported as a percentage of the total elemental concentration in wet sediment (*see* Table 2). Cd concentrations were below detection limits for all samples except oxic #1.

(Fig. 2). The release of these elements was also far greater from #1 than from #2 or #3. Mn release, too, was greatest from oxic #1, with a similar order of magnitude (although lower) release from oxic #2. Mn also appears to have been released from anoxic #1 and #2 to a greater extent than the other three metals. A mass balance comparing the dissolved Cd, Co, Ni, and Mn with their total sedimentary concentrations shows that 40%, 19%, 26%, and 68% of the elements, respectively, were lost during oxic desalination of #1 (Table 3).

In contrast, release of U during oxic desalination was greatest from #3. Again, an order of magnitude more U was observed in the oxic rinses of the sample than the anoxic (Fig. 2). #2 also showed enhanced release upon oxygen exposure, although to a lesser extent.

Loss of metals during the subsequent acetone dehydration of anoxic-desalinated #1 was minimal (Table 4). Only Co and Mn clearly were elevated above the background values of a blank acetone sample, and the loss amounted to only 2.5% and 0.08% of the total concentrations of these elements, respectively. Some metals even appear to have a higher concentration in the blank than in the #1 rinse, although the values are of a similar order of magnitude, and thus very low in comparison to the total concentration of these metals in #1.

Interpretation

For Cd, Co, Ni, and Mn, it is clear that oxic desalination most severely depletes sample #1 of these metals, despite initial concentrations being lower than in #2. Highly labile forms of these elements exist, therefore, in the sapropel layer, which increases the sensitivity of the sediment to oxygen invasion.

Table 4. Summary of elements dissolved in acetone during (anoxic) dehydration of #1, reported as a percentage of the total elemental concentrations in wet sediment.

Element	Cd	Co	Cu	Mn	Ni	U	V
% lost	2.9	2.5	1.0	0.08	0.11	–	0.7
Acetone blank value (equivalent units)*	2.4	0.2	2.1	0.02	0.20	–	1.0

*A blank acetone sample also was analyzed, and elemental concentrations converted into equivalent units for a typical sample weight.

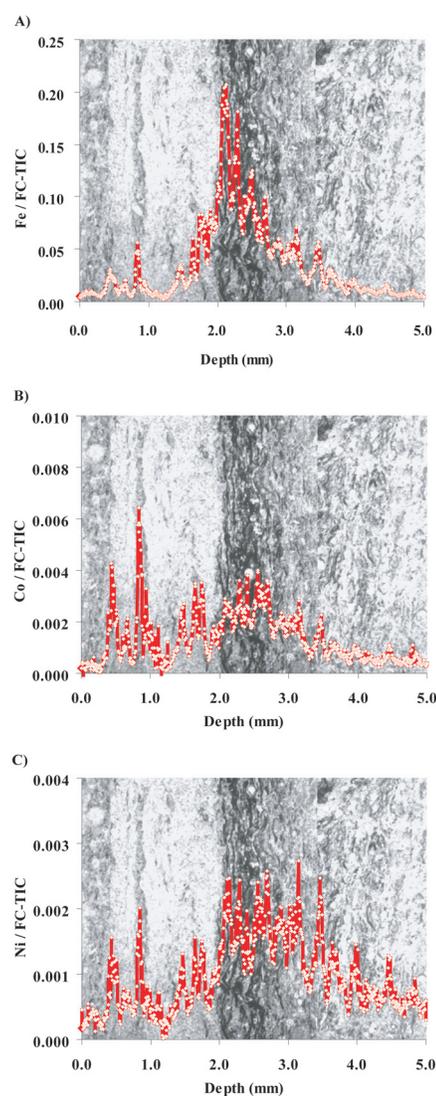


Fig. 3. LA-ICP-MS profiles of A) Iron, B) Cobalt, and C) Nickel across a band of sulfide deposition in the embedded sapropel S1. Elemental counts at the MS detector are normalized to the 'Fractionation Corrected' Total Ion Counts (FC-TIC), estimated from individual elemental fractionation factors in the standard glass NIST SRM 610. The background image shows the corresponding interval in a grayscale of a digitally imaged thin section.

Sequential extraction of sapropel S1 sediments from a formerly brine filled basin (Rutten and de Lange 2003) shows Ni to be associated with organic matter, whereas Co and Mn profiles more closely resemble those of pyrite, implying sulfide association. However, a similar proportion of total Mn also exists as Mn carbonate. No Cd data are presented, but this element commonly associates with marine organic matter in the water column (Bruland 1980; Price and Morel 1990) and in anoxic sediments from other locations. The release of all four metals in any case indicates that multiple sedimentary phases are affected by oxic desalination, and the logarithmic shape of the dissolution profiles implies total removal of the labile fractions over four oxic rinses.

The partial release of Mn during anoxic desalination of #1 and #2 is best explained by dissolution of Mn carbonate, which may occur as alkalinity decreases during desalination. As all ions – including CO_3^{2-} and HCO_3^- – are removed from the porewaters, this mechanism seems plausible. Assuming the roughly even distribution of Mn between pyrite and carbonate-associated phases described by Rutten and de Lange (2003), oxic desalination appears to remove both phases whereas anoxic desalination removes the carbonate phase but preserves pyrite-associated Mn (Fig. 2).

Dry sediment U concentrations in all three samples (converted from Table 2) are well above the detrital background (Colley and Thomson 1985), indicating the presence of authigenic U throughout the core. However, #3 clearly contains more mobile U than the other samples, and this is lost during oxic desalination (Fig. 2). From the low organic carbon content of #3, it seems more likely that this labile U is in a directly reduced form (Veeh et al. 1974) than adsorbed or complexed with organic matter (Kolodny and Kaplan 1973).

The minimal loss of metals during anoxic acetone dehydration of #1 indicates that the potential dissolution of organic pigments does not alter the metallic chemistry of the sediment substantially. A yellow staining of the acetone exchanges shows that such dissolution probably is taking place, but only Co and Mn concentrations are elevated above those in a blank acetone sample. As these elements usually are not associated with organic pigments, it is more likely that undersaturation of mineral phases during acetone dehydration is the cause of this minor release. For the metals showing higher concentrations in the acetone blank than in the #1 rinse, it is not clear whether this represents minor uptake of metals from the acetone or simply a variable dissolved concentration in different acetone batches. In any case, the magnitude of any chemical change is so small that it will not affect subsequent analyses of the sediment.

We did not investigate the effects of oxic acetone dehydration in non-hypersaline anoxic sediments (those not requiring desalination prior to acetone application). Therefore, it remains to be established whether the use of acetone alone, outside the glove box, would alter the redox-sensitive chemistry of such sediments. Given the solubility of oxygen within

acetone, some risk of alteration seems plausible, although the solubility of the oxidized metals within acetone may determine the extent of their removal from the sediment.

Clearly, the most sensitive stage of our protocol is desalination, and we have shown that anoxic sediments prepared for embedding by oxic desalination may be deficient in a number of metals. If sediments contain labile phases of Cd, Co, Ni, and U, accurate micro-analysis of these metals in embedded samples can be achieved only by the use of an oxygen-deficient atmosphere during sample preparation. The loss of Mn from the carbonate phase, which occurs even during anoxic desalination, is a potential drawback of the protocol. However, sulfide-related Mn lost during oxic desalination is shown to be preserved by the use of the glove box.

Discussion and application

Depth profiles of sedimentary elements measured by LA-ICP-MS represent an ultra-high resolution paleoclimate resource. Data at 10 μm increments can be obtained to yield inter and intra-annual accumulation signals in finely laminated sediments. The resin embedding and LA-ICP-MS combination has a number of advantages over other high resolution techniques such as wet-core (μ)XRF scanning; the embedded sample has a more even surface, there are no water or foil attenuation effects and no desiccation during scanning. The most advanced LA-ICP-MS setups can analyze major elements with sufficient accuracy to report concentrations by oxide summation, and the range of analyzable trace elements is much greater than by XRF. For hypersaline sediments, resin embedding by our preparation removes the porewater salts which dominate the wet-core signals of Na, K, Mg, and S, elements whose non-salt phase profiles may be of interest. Wet core techniques offer the advantage of speed and economy, but potentially more problematic data.

Preservation of elemental microprofiles obviously is key to subsequent interpretations, and we have shown that our protocol leaves in the sediment various elements which may be removed by existing embedding preparations. Fig. 3 shows depth profiles of Fe, Ni, and Co across a narrow (<5mm) sulfide-rich interval in an embedded sapropel S1 sample. The embedded block was mounted in an ablation chamber on a motored stage, such that a steady lateral motion carried it under the target of the laser beam. The profiles of Fe, Ni, and Co contrast markedly; although they record peaks at equivalent depths, the relative magnitudes of corresponding peaks vary from one element to another. It is impossible to prove that the microstratigraphy of these metals is undisturbed during the stages of embedding (as embedding is required to investigate this). However, their absence in anoxic desalination rinses strongly suggests that they are not mobilized, and that the profiles in Fig. 3 are genuine reproductions of their distribution in the sediment. As we have shown, preservation of Ni and Co during resin embedding of sapropel sediments is much improved by the use of our

anoxic protocol; hence the profiles of these elements in particular can be reliably investigated only after preparation by this method.

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