

Understanding mud: The importance of sediment biogeochemistry

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Sediment biogeochemistry is an exciting field which aims to improve our understanding of element cycling in aquatic systems. Sediments play a key role in the cycling of many elements in lakes and the oceans, acting both as sources and sinks on various timescales.

A detailed understanding of the chemical reactions taking place in sediments, how these are mediated by the sediment microbial community, and how the rates of these reactions vary in response to environmental change, are at the heart of sediment biogeochemistry. This information is especially important in the management of human-

influenced aquatic systems such as eutrophied lakes and seas, in estimates of carbon burial and greenhouse gas exchange, and in the interpretation of sedimentary sequences as archives of past environments.

The driver of most chemical reactions in sediments is organic matter (Canfield *et al.* 2005). Residual organic material which escapes recycling in the water column of aquatic systems accumulates in the underlying sediments, where it undergoes respiration by the microbial community. A vertical zonation is often observed in sediments, in which respiration pathways of progressively lower energy yield are observed progressively deeper in the sediment column (Fig. 1).

Oxygen is by far the most energy efficient electron acceptor for the microbial respiration of organic matter. In many open marine systems, where the water column is several kilometers long and primary production is low, the carbon flux to the sediments may be vanishingly small. Under these conditions, almost all organic matter remineralization occurs by the aerobic pathway (Middelburg *et al.* 1993), and the excess of oxygen over carbon may be so great that dissolved oxygen penetrates several meters into the seafloor.

Many coastal marine and freshwater systems are at the opposite end of this scale, being relatively shallow and often highly productive. Here, oxygen may be exhausted within the upper millimeters of the sediments, well before all reactive organic material has been remineralized. In the most extreme cases, for example in stratified systems such as the Baltic Sea and the Black Sea, oxygen is fully consumed in the water column itself (Conley *et al.* 2009, Eckert *et al.* 2013).

Anaerobic pathways of organic matter remineralization yield less energy than aerobic respiration and proceed at a slower rate, but can account for a large fraction of total remineralization in systems where organic matter is quickly buried below the zone of oxygen penetration. Due to the abundance of the sulfate ion (SO_4^{2-}) in seawater, the most important pathway of anaerobic respiration in marine sediments is sulfate reduction (Jørgensen 1982). In freshwater systems, denitrification, reduction of metal oxides and methanogenesis become quantitatively more important (Mason 2013).

Pore water chemistry

The prevailing pathways of organic matter remineralization in sediments have a strong influence on the chemistry of the pore waters (Fig. 1), which impacts on fluxes of dissolved

species across the sediment-water interface, and on the potential for precipitation and dissolution of mineral phases. This can be of critical importance to the management of eutrophied aquatic systems. For example, fluxes of phosphate from sediments into the water column of aquatic systems may sustain primary production and a high oxygen demand. These fluxes are often referred to as 'internal loading' and can be responsible for the delayed recovery of eutrophied systems long after external nutrient loading has been reduced.

In the case of phosphate, anoxic conditions favor a strong release from sediments for two main reasons. Firstly, when anaerobic respiration proceeds by the reduction of iron and manganese oxides, their dissolution liberates associated phosphate ions (Mortimer 1941). Secondly, when anaerobic respiration proceeds by sulfate reduction, the release of phosphorus from organic matter is more efficient than the release of carbon and nitrogen (Ingall *et al.* 1993). Both of these effects are observed in the sediments of the Baltic Sea (Jilbert *et al.* 2011). Consequently, a large annual surplus of phosphate is present in the water column of the Baltic, which is conducive to blooms of cyanobacteria in the summer months (Vahtera *et al.* 2007).

Vertical fluxes of dissolved chemical species can be accurately calculated from pore water data. Whenever a concentration gradient is observed in a porewater profile, a corresponding vertical flux can be estimated (Schulz 2006). A steeper gradient i.e. a greater change in concentration over a given depth interval indicates a stronger flux. This principle can be applied at all depths in the sediment column, where different reactions produce and consume dissolved chemical species (see Fig. 1), but is most often used to estimate fluxes across the sediment-water interface. The

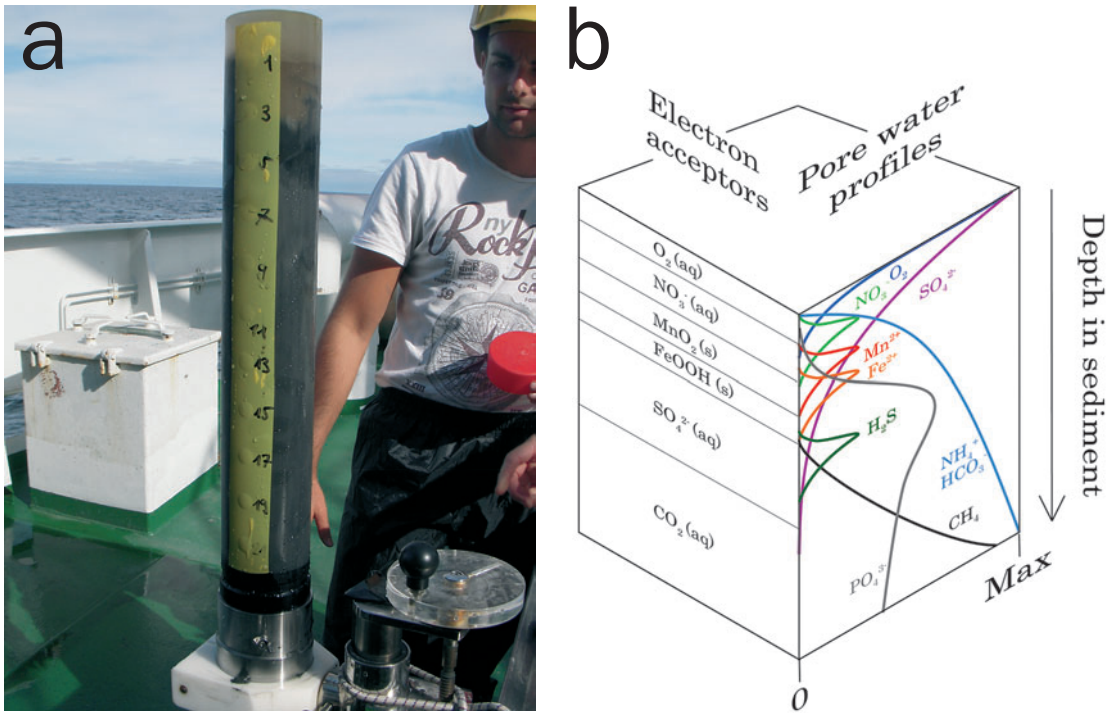


Figure 1. (a) GEMAX coring is the preferred method for sampling the upper ~50 cm of sediments in the Baltic Sea. Pore waters can be sampled using Rhizons™ or open syringes on pre-drilled core tubes, or by centrifugation of wet sediment slices. (b) Biogeochemical processes in the upper sediments display a distinct vertical zonation. The dominant electron acceptors used in the respiration of organic matter and other substrates vary according to the free energy of the reaction, from highest (O_2 , i.e., aerobic respiration) to lowest (CO_2 , i.e., methanogenesis). Pore water profiles of dissolved species reflect these zones. Dissolved species produced in one zone may diffuse into another and be consumed by other processes. For example Fe^{2+} produced in the zone of Fe oxide reduction diffuses upwards to react with O_2 (re-forming Fe oxides) and downwards to react with H_2S (forming Fe sulfides).

Kuva 1. (a) GEMAX kairausnäytteenottoalaite on hyvä menetelmä pintasedimenttinäytteenottoon. Huokosvettä voi kerätä Rhizons™ ruiskujärjestelmällä tai sentrifugoimalla sedimenttiviipaleita. (b) Biogeochemialliset prosessivyöhykkeet sekä aineiden pitoisuusgradientit sedimentissä ja huokosvedessä. Orgaanisen aineen hajoamisprosesseihin vaikuttaa saatavilla olevan vapaan energian määrä. Prosessit, joissa vapautuu suhteessa enemmän energiaa, kuten aerobinen respiraatio, tapahtuvat pintasedimenteissä, kun taas prosessit, joissa vapautuu vähemmän energiaa, kuten metanogeneesi, tapahtuvat syvemmällä sedimentissä. Vapautuneet aineet hajautuvat sedimenttiin diffuusion kautta, ja ne voivat osallistua reaktioihin muissa vyöhykkeissä.

advantage of this approach, over for example incubation methods, is that the underlying process driving the flux can be understood.

An example is given in Fig. 2. At Time 1 in both sediments, the phosphate flux from the sediments to the water column is equal. However, one sediment is rich in organic

matter and the flux is driven primarily by release of phosphate during organic matter remineralization; meanwhile, the other sediment is organic-poor but contains a surface layer rich in Fe oxides which is undergoing transient dissolution due to changing oxygen conditions. Here, the flux is driven by the

release of phosphate from dissolution of Fe oxides. By Time 2, the entire pool of Fe oxides has been dissolved. Consequently, the phosphate fluxes from the two sediments differ markedly. Extrapolating the results of an incubation experiment at Time 1 would overestimate the mean flux from the organic-poor sediments. In contrast, the pore water profiling approach would identify these sediments as a transient source of phosphate, warning against such an extrapolation.

Carbon cycling and mineral authigenesis

Sediment biogeochemistry is also critical to the understanding of carbon burial and greenhouse gas fluxes. Carbon burial in sediments is the key vector for permanent storage of carbon and hence plays a critical role in modulating Earth's climate. Carbon burial in marine systems is regulated by sedimentation rates and by grain size (Hedges and Keil 1995), but also by the prevailing redox conditions, due to the slower rates of anaerobic respiration processes. A recent study showed that 11 % of marine carbon burial occurs in (mainly anoxic) fjord sediments (Smith *et al.* 2015), signaling a large upwards revision of previous estimates. Since carbon that is buried is not converted to CO₂, efficient carbon burial may act as a brake on climate change. However, in eutrophic lake environments, efficient carbon burial is often accompanied by high rates of methanogenesis. If conditions are favorable for the release of this methane to the atmosphere, the radiative forcing effect of carbon burial may be offset.

For sedimentary geologists, understanding syn- and post-depositional geochemical processes is essential to the proper interpretation of sedimentary records. This is particularly true in the case of authigenic mineral formation, which can alter both the

chemistry and texture of sediment sequences. The principal groups of authigenic minerals formed during early diagenesis in aquatic sediments are carbonates, sulfides and phosphates. Carbonates may form even in environments of low biogenic carbonate flux to the sediments, due to the abundance of inorganic carbon released during the breakdown of organic matter (Fig. 1). For example Baltic Sea sediments are characterized by high concentrations of Mn-Ca carbonate minerals despite the absence of major carbonate-based primary producers in the water column. Instead, high rates of sulfate reduction in the anoxic sediments produce bicarbonate (HCO₃⁻), which precipitates as carbonates under the high dissolved Mn concentrations often found in the deep basins of the Baltic (Huckriede and Meischner 1996).

Modeling sediment biogeochemistry

A more advanced understanding of the suite of reactions taking place in sediments can be achieved by means of reactive transport modeling. 1D models are used to replicate the pore water and solid-phase concentration profiles observed in real data, and to derive rates for the various reactions occurring in the sediments (Reed *et al.* 2011). Both primary (remineralization of organic matter) and secondary reactions (further redox processes, mineral precipitation and dissolution) can be modeled simultaneously. The big advantage of the modeling approach is that once the processes in the system are understood, the impacts of changing boundary conditions can be simulated. These may include changes in temperature, the annual cycle of organic matter accumulation, or long term eutrophication. For example, the seasonal release of phosphate due to transient dissolution of Fe oxides can

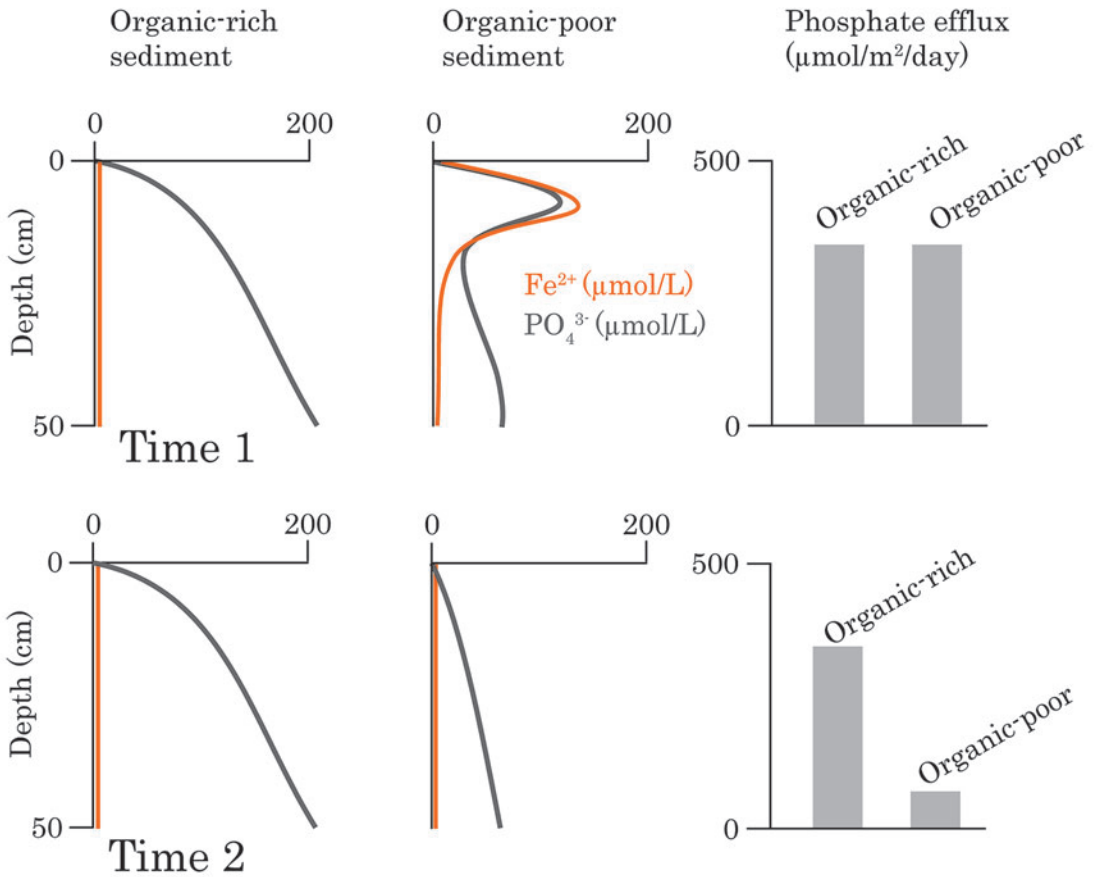


Figure 2. Pore water profiling can be used to estimate effluxes of phosphate from sediments to the water column, and to identify the underlying mechanisms. The efflux is proportional to the gradient of the phosphate (PO_4^{3-}) concentration across the sediment-water interface (i.e. the gradient of the grey lines at 0 cm depth). At Time 1, these gradients are equal for both the organic-rich and organic-poor sediment. However, the coincident peaks in Fe^{2+} and PO_4^{3-} in the upper zone of the organic-poor sediment show that the phosphate flux here is mainly derived from transient dissolution of Fe oxides, which has expired by Time 2. In contrast, the organic-rich sediment does not contain reducible Fe oxides and all the phosphate in the pore waters is derived directly from organic matter remineralization. Here, the phosphate efflux is constant.

Kuva 2. Huokosvesiprofiileista voidaan arvioida, kuinka paljon fosfaattia vapautuu sedimentistä vesipatsaaseen ja selvittää, mitkä prosessit ovat niiden takana. Vapautunut fosfaatin määrä on verrannollinen fosfaattipitoisuuden sedimentti-vesipatsas -rajapinnassa. Ajankohtana 1 (Time 1) fosfaattipitoisuus on sama sedimentissä, jossa orgaanista ainesta on paljon kuin siinä, jossa sitä on vähän. Nämä samankaltaiset pitoisuudet syntyvät kuitenkin eri prosessien tuloksena: sedimentissä, jossa orgaanista ainetta on paljon, fosfaatin vapautuminen sedimentistä liittyy orgaanisen aineen hajoamiseen, kun taas sedimentissä, jossa orgaanista ainetta on vähän, vapautuminen liittyy rautaoksidien liukenemiseen pintasedimentistä. Ajankohtana 2 (Time 2) kaikki rautaoksidit ovat liunneet, minkä vuoksi fosfaatin vapautuminen sedimentistä on vähäistä.

be modeled and integrated to a net annual value (see example in Fig. 2).

As with all modeling approaches, a prerequisite is that the processes being modeled are properly understood. In the case of sediment biogeochemistry, reactive transport models are continuously being improved as new knowledge of processes is developed. A current area of intense research concerns the processes occurring in the methanogenic zone of sediments. Methane is a simple form of reduced carbon, produced by low-energy yield processes such as reduction of CO₂ and acetate disproportionation in the deepest reactive zone of the sediment column (Fig. 1). Traditionally, it has been thought that methane diffusing

upwards from the methanogenic zone is consumed only by reaction with sulfate at the so-called sulfate-methane transition. However, microbes may theoretically derive energy from the oxidation of methane by a range of electron acceptors, providing these are available in the sediments. Recent studies have shown that in sediments with especially high concentrations of Fe and Mn oxides, a fraction of these minerals may escape dissolution in the upper sediments and become utilized in the oxidation of methane deeper in the sediment column (e.g. Egger *et al.* 2015a). This process was recently included for the first time in a reactive transport model for sediments from the Bothnian Sea (Rooze *et al.* 2016), and is found

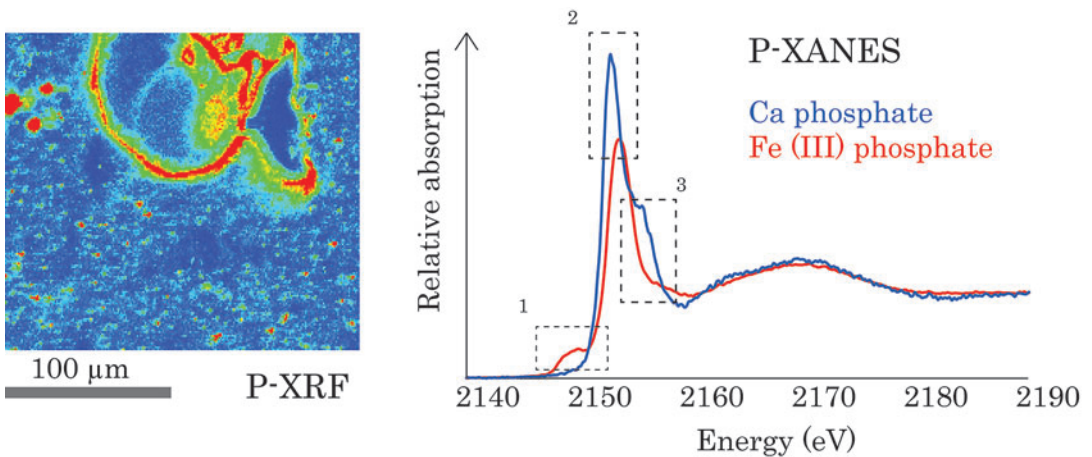


Figure 3. (left) Example of synchrotron-based Micro X-Ray Fluorescence (XRF) mapping of resin-embedded sediments from the Baltic Sea, showing the distribution of phosphorus (P). (right) Example of X-Ray Absorption Near Edge Spectroscopy (XANES) data across the P absorption edge, which can be used to identify phosphate mineralogy in sediments on the micro scale. Each pixel of the image on the left could theoretically be analyzed for such spectra. Pre-edge features (1), white line position (2) and post-edge features (3) in the spectra differ between phosphate minerals. Data from project ES45 at beamline ID21, ESRF (Tom Jilbert, 2013).

Kuva 3.(vasemmalla) Esimerkki hartsiin upotetulle Itämeren sedimentille tehdystä sykrotroni-pohjaisesta mikro-XRF (mikro-röntgen-fluoresenssi, engl. X-Ray Fluorescence) -kartoituksesta, josta nähdään fosforin jakauma. (oikealla) Esimerkki XANES-tekniikasta (engl. X-Ray Absorption Near Edge Spectroscopy), jota voidaan käyttää sedimentin fosfaatin mineralogisten piirteiden selvittämiseen mikro-mittakaavassa. Periaatteessa jokainen pikseli vasemmassa kuvassa voitaisiin analysoida vastaavalla tavalla. Spektrien (1, 2, 3) ominaisuuksia voidaan käyttää fosfaattimineraalien tunnistamiseen. Kuvassa käytetty aineisto on projektista ES45, beamline ID21, ESRF (Tom Jilbert, 2013).

to be extremely important for rates of Fe cycling in these sediments.

Microanalysis: the future of sediment biogeochemistry

The quest for improved understanding of sediment biogeochemistry has also led to a boom in the use of state of the art analytical techniques within the field. These include Laser Ablation-ICP-MS (Jilbert and Slomp 2013), SIMS (Virtasalo *et al.* 2013), Micro XRF and XANES (Fig. 3). The latter two techniques were recently used to elucidate the mechanisms of phosphate mineral authigenesis in Bothnian Sea sediments (Egger *et al.* 2015b). At the most advanced level, NanoSIMS facilitates mapping of the incorporation of labeled chemical substrates into sedimentary microbes (Polerecky *et al.* 2012), allowing biogeochemical processes to be directly studied. The Finnish research community has access to several of these techniques through its own resources and through international collaborations (e.g., participation in *NORDSIM* and the European Synchrotron Radiation Facility *ESRF*). Coupled to a growing level of expertise in the discipline, this infrastructure means that Finland is well placed to maintain a strong profile in sediment biogeochemical research in the coming years.

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Tom Jilbert was appointed Assistant Professor (Tenure Track) in Aquatic Biogeochemistry at University of Helsinki Department of Environmental Sciences in January 2016. His position is co-funded by Vesijärvi Foundation. Tom's current research areas include phosphorus burial in the sediments of eutrophied

lakes and the role of iron and manganese in boreal carbon cycling.

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Tiivistelmä

Sukellus pohjamutaan: sedimenttien biogeokemian merkityksestä

 Sedimenttien biogeokemia tarjoaa tärkeää tietoa akvaattisten ympäristöiden rehevöitymisestä sekä hiilen ja kasvihuonekaasujen kiertokulusta. Monet sedimentissä tapahtuvat kemialliset reaktiot liittyvät orgaanisten aineiden hajoamiseen ja vaikuttavat ravinteiden

vapautumiseen sedimentistä. Sedimenttien kemiallisia on ratkaisevassa roolissa myös prosesseissa, jotka määrittävät, millaisia mineraalifaaseja sedimentissä muodostuu.

Hiilen kiertokulku toimii eri tavoin erilaisissa akvaattisissa ympäristöissä. Avomerisedimenteissä hapen saatavuus on suuri verrattuna merenpohjaan laskeutuvan hiilen määrään. Siten melkein kaikki hiili hajoaa nopeasti pintasedimentin aerobisissa prosesseissa, ja kerrostuminen sedimenttiin on erittäin vähäistä. Rannikkoalueilla ja järvissä, missä sedimentti on hapettunutta vain muutaman millimetrin syvyydeltä, aineiden hajoaminen tapahtuu usein anaerobisten prosessien kautta. Meressä sulfaatin pelkistyminen on tärkein orgaanisten aineiden anaerobinen hajoamisreitti, kun taas järvissä meta-nogeneesi eli hiilidioksiidin ja orgaanisten aineiden pelkistyminen metaaniksi on merkittävää.

Huokosvesianalyysien avulla on mahdollista määrittää, kuinka paljon aineita ja ravinteita sedimenteistä vapautuu vesipatsaaseen, ja mitkä prosessit vaikuttavat vapautumiseen. Näiden biogeokemiallisten tapahtumaketjujen ymmärtäminen on tärkeää vesistöjen kunnostustoimenpiteiden suunnittelussa, sillä ne vaikuttavat olennaisesti vesistön tilaan. Esimerkiksi prosessilintamisen avulla on mahdollista arvioida ympäristönmuutoksen vaikutusta ravinteiden ja aineiden kiertoihin sedimentissä.

Innovaatiiviset analyysimenetelmät ja tekniikat ovat viime aikoina mahdollistaneet uudet tutkimussuuntaukset varsinkin kiinteiden sedimenttiaineiden mittauksissa. Esimerkiksi laserablaatio-ICP-MS, mikro-XRF ja nano-SIMS ovat uusia menetelmiä, joiden käyttö on yleisesti lisääntynyt. Lähitulevaisuudessa myös suomalaisilla tutkimusryhmillä on omien resurssiansa ja kansainvälisten yhteistyöverkostojen kautta monia mahdollisuuksia laajentaa toimintaansa sedimentin biogeokemiallisessa tutkimuksessa.