Developments in Paleoenvironmental Research 17

Ian W. Croudace
R. Guy Rothwell *Editors*

Micro-XRF Studies of Sediment Cores

Applications of a non-destructive tool for the environmental sciences

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Developments in Paleoenvironmental Research

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Editors

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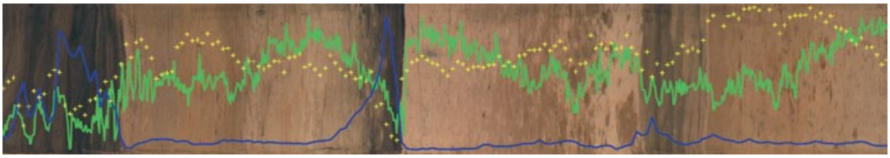
BOSCORF core (CD166-19), recovered off northwest Africa. The core shows a sequence of pelagic nannofossil oozes (cream) and clays (light to medium brown) with interbedded turbidite sands (dark brown to black). Three logging parameters, magnetic susceptibility (dark blue), ITRAX measured Ca (green) and b* colour values (yellow) are overlaid and plotted downcore. These data were obtained using the BOSCORF ITRAX, MSCL-XYZ, core loggers and MSCL-S and displayed in CoreWall.



Foreword

Over the last century, Earth sciences have evolved from disciplines mostly based on naked eye observations of rocks and sediments to a scientific field employing the most sophisticated tools developed in analytical physics and chemistry. The introduction of quantitative instrumentation has thus played a major role in enabling advances in our knowledge of Earth history and processes. Because geological archives are so unique and complex, the geoanalytical refinements have often been pushed to their ultimate limits of resolution, precision and detection limits in order to extract crucial information from objects found in nature.

High-resolution core scanners incorporating X-ray fluorescence (XRF) spectrometry are arguably one of the most useful tools that have become available to the research community. Their impact is based on their ability to rapidly, non-destructively and automatically scan sediment cores. Not only do they rapidly provide important proxy data without damaging samples, but they can obtain environmental data at decadal, annual and even sub-annual scales. Micro-XRF core scanners can indeed be used at the limit of the inherent heterogeneity of sediments linked to the presence of grains of different nature, chemical composition and mineralogy. In addition to producing geochemical profiles along the core length, these scanners also allow study of spatial heterogeneities within the sediment through optical images, X-radiography or micro-XRF 2D images of elemental composition.

In a little over a decade, micro-XRF core scanners have made a substantive contribution to paleoenvironmental research as evidenced by the exponential rise in the peer-reviewed scientific literature. For the field of paleoclimatology, the use of sediment cores from lakes and oceans had always been limited by the resolution of discrete sampling, but the introduction of XRF-scanners truly revolutionized the field allowing the study of similar details in sediments as in polar ice cores from Greenland and Antarctica. The versatility of XRF-scanners allows their application to other types of paleoclimate archives from diverse locations such as massive corals from tropical reefs, speleothems from caves and subfossil woods.

The key initial strength of XRF core scanners was their ability to scan a meter of sediment core at high resolution in about 24 hours. Ongoing instrumental developments are already leading to further enhancements in sensitivity and speed and throughput. High-resolution XRF core scanners produce a high data output, with potentially several thousand spectra acquired per meter of core.

The increasing speed of analyses has allowed researchers to dare tackling projects based on large amounts of cored material, the XRF-scanner being often the first analytical tool used after opening and splitting the cores. The resulting elemental profiles, derived from the non-destructive analysis of cores and often involving several thousand XRF spectra, are thus used for reconnaissance studies and basic stratigraphic correlations. XRF core scanners can also be used for insightful geochemical studies, provided that proper calibration is performed by means of discrete geochemical measurements with accurate techniques such as conventional XRF or ICP. Whereas with these conventional techniques, data are acquired from dry homogenized fine-grained samples, wet natural sediment cores measured with scanners present very different sample conditions. Grain-size and water content variations, core surface imperfections, presence of organic matter and water pooling on the sample surface will all impact on data quality. Hence interpretation of core scanner data is not trivial and guidance is often needed to discriminate environmentally meaningful information from data artifacts.

As outlined above, the use of XRF core scanners is characterized by an inherent simplicity in acquiring useful elemental profiles, but making the best out of these sophisticated tools also requires experience and a deep knowledge in geochemistry and physical properties of sediments. XRF-scanner facilities are now used in about one hundred institutions spread throughout Europe, North America and Asia. This gave rise to a specific community of users with diverse technical expertise and scientific expectations.

As an illustration, I will say a few words about the specific example of the XRF-scanner installed in 2008 at CEREGE in Aix-en-Provence. We became interested in such analyses in the mid-2000s because of our tradition of working on deep-sea sediments, notably the basic quantification of major phases such as carbonates, detrital minerals and organic matter, but also several detailed studies of trace elements scavenged in the water column or trapped in the sediments because of specific redox conditions. These variables were quantified with various techniques of organic and inorganic geochemistry on discrete samples. Since then, micro-XRF scanner profiles have allowed us to better understand the relationships between these various profiles and integrate them into a coherent and high-resolution framework. This truly brought a new dimension to our research in paleoceanography.

The other main consequence of our XRF-scanner acquisition was that it fostered collaboration with specialists of other sedimentary archives, notably those taken from modern and ancient lakes. Our experience is obviously not unique and it can be stated with confidence that the rise of XRF core scanning contributed to bridging the gaps between scientific communities, which were working in parallel.

Scientists of this new community often have similar needs and expectations. By considering ratios of XRF profiles it has been possible to develop proxies for particle sizes, mineralogical composition and organic matter content of sediments. Hopefully, more direct evaluation of these parameters may come from future innovations in analytical core scanning based on other electromagnetic emissions and detecting systems.

This volume edited by Ian Croudace and Guy Rothwell, two pioneers and prominent contributors in the field, presents a broad ranging view of instrument capability and points to future developments that will combine higher precision elemental data coupled with faster core analysis. It also presents specific application papers reporting on the use of XRF core scanners in a variety of marine, lacustrine and pollution studies, together with papers examining practical aspects of core scanner usage and data calibration and interpretation. It is a welcome addition to the literature and the first volume of its kind to focus specifically on this important technology. Given the importance of XRF core scanning in modern paleoenvironmental research, this is a timely publication which environmental investigators will find useful. It contains essential reading for both experienced and new researchers using XRF core scanners.

Specific Publications from CEREGE that used XRF core scanning (by date)

Gasse F, Vidal L, Van Campo E, Demory F, Develle AL, Tachikawa K, Elias A, Bard E, Garcia M, Sonzogni C, Thouveny N. (2015) Hydroclimatic changes in northern Levant over the past 400,000 years. *Quaternary Science Reviews* 111, 1–8

Tachikawa K, Vidal L, Cornuault M, Garcia M, Pothin A, Sonzogni C, Bard E, Menot G, Revel M (2015) Eastern Mediterranean Sea circulation inferred from the conditions of S1 sapropel Deposition. *Climate of the Past* 11, 855–867

Cartapanis O, Tachikawa K, Romero OE, Bard E (2014) Persistent millennial-scale link between Greenland climate and northern Pacific Oxygen Minimum Zone under interglacial conditions. *Climate of the Past* 10, 405–418

Brisset E, Miramont C, Guiter F, Anthony EJ, Tachikawa K, Poulenard J, Arnaud F, Delhon C, Meunier J-D, Bard E, Suméra F (2013) Non-reversible geosystem destabilisation at 4200 cal. BP: Sedimentological, geochemical and botanical markers of soil erosion recorded in a Mediterranean alpine lake. *The Holocene* 23, 1863–1874

Simonneau A, Chapron E, Courp T, Tachikawa K, Le Roux G, Baron S, Galop D, Garcia M, Di Giovanni C, Motellica-Heino M, Mazier F, Foucher A, Houet T, Desmet M, Bard E (2013). Recent climatic and anthropogenic imprints on lacustrine systems in the Pyrenean Mountains inferred from minerogenic and organic clastic supply (Vicdessos valley, Pyrenees, France). *The Holocene* 23, 1764–1777

Jenny JP, Arnaud F, Dorioz JM, Giguet Covex C, Frossard V, Sabatier P, Millet L, Reyss JL, Tachikawa K, Bard E, Pignol C, P, Soufi F, Romeyer O, Perga ME (2013) A spatiotemporal sediment investigation highlights the dynamics of hypolimnetic hypoxia in a large hard-water lake over the last 150 years. *Limnology & Oceanography* 58, 1395–1408

Soulet G, Ménot G, Bayon G, Rostek F, Ponzevera, Toucanne S, Lericolais G, Bard E (2013) Abrupt drainage cycles of the Fennoscandian Ice Sheet. *Proceedings of the National Academy of Science* 110 (17), 6682–6687

Doyen E, Vannière B, Berger JF, Arnaud F, Tachikawa K, Bard E (2013) Land-use changes and environmental dynamics in the upper Rhone valley since Neolithic times inferred from sediments in Lac Moras. *The Holocene* 23, 961–973

Wilhelm B, Arnaud F, Sabatier P, Magand O, Chapron E, Courp T, Tachikawa K, Fanget B, Malet E, Pignol C, Bard E, Delannoy J-J. (2013) Paleoflood activity and climate change over the last 1400 years recorded by lake sediments in the North-West European Alps. *Journal of Quaternary Science* 28, 189–199

Simonneau A, Doyen E, Chapron E, Millet L, Vannière B, Di Giovanni C, Bossard N, Tachikawa K, Bard E, Albéric P, Desmet M, Roux G, Lajeunesse P, Berger J-F, Arnaud F (2013) Holocene land-use evolution and associated soil erosion in the French Prealps inferred from Lake Paladru sediments and archaeological evidences. *Journal of Archaeological Science* 40, 1636–1645

Cartapanis O, Tachikawa K, Bard E (2012) Latitudinal variations in intermediate depth ventilation and biological production over northeastern Pacific Oxygen Minimum Zones during the last glacial period. *Quaternary Science Reviews* 53, 24–38

Wilhelm B, Arnaud F, Sabatier P, Crouzet C, Brisset E, Chaumillon E, Disnar JR, Guiter F, Malet E, Reyss JL, Tachikawa K, Bard E, Delannoy J-J (2012) 1400yr of extreme precipitation patterns over the Mediterranean French Alps and possible forcing mechanisms. *Quaternary Research* 78, 1–12

Tachikawa K, Cartapanis O, Vidal L, Beaufort L, Bard E (2011) The precession phase of hydrological variability in the Western Pacific Warm Pool during the past 400 ka. *Quaternary Science Reviews* 30, 3716–3727

Cartapanis O, Tachikawa K, Bard E (2011) North-Eastern Pacific oxygen minimum zone variability over the past 70 kyr: Impact of primary production and oceanic circulation. *Paleoceanography* 26, PA4208, 1–17

Soulet G, Ménot G, Garreta V, Rostek F, Lericolais G, Zaragosi S, Bard E (2011) Black Sea “Lake” reservoir age evolution since the Late Glacial-hydrologic and climatic implications. *Earth and Planetary Science Letters* 308, 245–258

Böning P, Bard E, Rose E (2007) Towards direct micron-scale XRF elemental maps and quantitative profiles of wet marine sediments. *Geochemistry Geophysics Geosystems (G-cubed)* 8 (5), 1–14

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About the Editors

Ian W. Croudace is a geochemist with more than 40 years research experience, is a Professor at the University of Southampton (Ocean and Earth Science) and is Director of GAU-Radioanalytical. He is a specialist in several branches of analytical geochemistry including X-ray fluorescence spectrometry, gamma ray spectrometry and radioanalytical chemistry and has published more than 135 papers in the international geochemical and chemical literature. During his career he has supervised 28 PhD students on a variety of geochemical topics. He has also co-developed an industry standard instrument for extracting tritium and C-14 (and other volatile radionuclides) from nuclear and related materials. With NOC colleague Guy Rothwell in 2000 he conceived the fundamental design of what became the prototype Itrax X-ray core scanner. He jointly obtained development funding, identified and commissioned the analytical partner (Cox Analytical Systems) and contributed to the realisation of the first Itrax core scanner that emerged in 2003.

R. Guy Rothwell is a marine sedimentologist and Curator of the British Ocean Sediment Core Research Facility (BOSCORF), the UK's national deep-sea core repository, located at the National Oceanography Centre, Southampton. He has participated in over 25 research cruises including two legs of the Ocean Drilling Program. He and colleague Ian Croudace conceived of, and secured the funds, to realise the prototype Itrax core scanner and contributed to its design. He is author of *Minerals and Mineraloids in Marine Sediments* (Elsevier Applied Science, 1989) and editor of *New Techniques in Sediment Core Analysis* (Geological Society of London Special Publication, 2006).

Explanation of Abbreviations and Acronyms

AAS	Atomic absorption spectroscopy
AMO	Atlantic Multidecadal Oscillation
AMS	Accelerator mass spectrometry
ANSTO	Australian Nuclear Science and Technology Organisation
AO	Arctic Oscillation
ArcGIS	A geographic information system for working with maps and geographic data
ASTM	American Society for Testing and Materials
AVAATECH	Commercial XRF core scanner manufactured by Avaatech Analytical X-ray Technology, Alkmaar, The Netherlands
BGS	British Geological Survey
BOSCORF	British Ocean Sediment Core Research Facility, National Oceanography Centre, Southampton, United Kingdom
BRITPITS	British Pits (British Geological Survey mines and quarries database)
BSi	Biogenic silica
CANMET	Canada Centre for Mineral and Energy Technology
CATMHS	Cumbrian Amenity Trust Mining History Society
CAT-Scan	Computerized axial tomography scan
CBCI	Cumulative biogenic carbonate inventory
CCD	Charge-coupled device
CEREGE	Centre de Recherche et d'Enseignement de Géosciences de l'Environnement (based in Aix-en-Provence)
CF:CS	Constant flux—Constant sedimentation
CIC	Constant initial concentration
CLIMATCH	Climatic and anthropogenic change in seasonal river runoff and impacting cyclones resolved by novel spectral geochemistry of giant corals in Indian Ocean catchments (Netherlands Organisation for Scientific Research Earth and Life Sciences project 2010–2014)
CMOS	Complementary metal–oxide–semiconductor
CNRS	Centre Nationale de Recherche Scientifique (French National Scientific Research Agency)

COREWALL	A US-developed stratigraphic correlation, core description, and data visualization system used by the marine, terrestrial, and Antarctic science communities
CORSAIRES	Coring Stable and Instable Realms in European Seas, European Union Concerted Action research program 1996–1998
CORTEX	Core Scanner Texel—forerunner of the AVAATECH core scanner
CPSD	Curved position sensitive detector
CRPG-ANRT	Centre de Recherches Pétrographiques et Géochimiques—Association Nationale de la Recherche Technique
CRS	Constant rate of supply
CSI	Cumulative sediment inventory
CSIC-UGR	Consejo Superior de Investigaciones Cientificas—Universidad de Granada, Spain
CSIRO	Commonwealth Scientific and Industrial Research Organisation, Australia
CSSD	Constant sample to detector distance
CT	Cryptotephra or numbers from the Hounsfield scale, a quantitative scale for describing radiodensity (in x-radiography)
CT-Scan	Computed tomography scan
DICOM	Digital Imaging and Communications in Medicine—a standard for handling, storing, printing, and transmitting data in medical imaging
DLC	Direct linear calibration
DOSSEC	Drilling, Observation and Sampling of the Earths Continental Crust not-for-profit corporation
EAGLE III	A micro-XRF elemental analyser manufactured by EDAX Inc., New Jersey, USA
ECD	Electron capture detection
EDS	Energy dispersive spectrometry
EDXRD	Energy dispersive X-ray diffraction
ED-XRF	Energy dispersive X-ray fluorescence
ENSO	El Niño Southern Oscillation
EPA	Environmental Protection Agency (USA)
EU	European Union
FT	Fourier transform
GAU	GAU-Radioanalytical Laboratories, University of Southampton, NOC, Southampton
G/B	Green/Blue colour ratio
G-BASE BGS	Geochemical Baseline Survey of the Environment, British Geological Survey
GC	Gas chromatography
GCR	Geological Conservation Review (Joint Nature Conservation Committee, U.K.)
GEOTEK	Commercial core logger manufacturer based in Daventry, U.K.
GICC05	Greenland ice core chronology 2005

GLAD800	Global Lake Drilling Initiative
GMRT	Global multi-resolution topography
GRM	Geological reference material
GV	Gray-level values
HBSMR	National Trust Historic Buildings, Sites and Monuments Record, United Kingdom
HCB	Hexachlorobenzene
HDS	Hydrodesulfurization
HSI	Hyperspectral imaging
HPLC-FLD	High performance liquid chromatography with post-column fluorescence derivatization
HU	Hounsfield unit
IAEA	International Atomic Energy Agency
ICCD	Intensified charge-coupled device
ICDP	International Continental Scientific Drilling Program
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IFREMER	Institut Français de Recherche pour l'Exploitation de la Mer (French Research Institute for the Exploitation of the Sea), Brest, France
IfSAR	Interferometric synthetic aperture radar
IMAGES	International Marine Past Global Changes Study of the Past Global Changes Project of the International Geosphere-Biosphere Programme
INRS-ETE	Institut National de la Recherche Scientifique, Eau Terre Environnement Research Centre (Research Centre on Water, Earth, and the Environment), Université du Québec, Canada
IODP	International Ocean Discovery Program, successor to ODP
IR	Infrared
IRD	Ice-rafted debris
ISI	Institute for Scientific Information
ISPRA	Istituto Superiore per la Protezione e la Ricerca Ambientale (Institute for Environmental Protection and Research), Italy
ISQG	Interim sediment quality guidelines
ITRAX	Commercial XRF core scanner manufactured by Cox Analytical Systems, Mölndal, Sweden
ItraxPlot	Software for visualising ITRAX data initially developed at the National Oceanography Centre, United Kingdom
JAMSTEC	Japan Agency for Marine Earth Science and Technology
JEOL	Commercial manufacturer of scientific instruments, headquartered in Tokyo, Japan
JGS	Japanese Geotechnical Society
KDMRS	Kendal and District Mine Research Society
LA-ICP-MS	Laser ablation inductively coupled mass spectrometry

LDHER	Lake District Historic Environment Record
LE	Light element
LIBS	Laser-induced breakdown spectroscopy
LiDAR	Remote sensing technique that measures distance by using a laser to illuminate a target and analyzing the reflected light
LOI	Loss on ignition (test to estimate organic content of a sediment)
LWIR	Longwave infrared
MCCAP	Mercury cell chlor-alkali plant
MDA	Minimum detectable activity
MIS	Marine Isotope Stage
MLC	Multivariate log-ratio calibration
MOD	BGS BRITPITS Mineral Occurrence Database
MSCL	Multi-sensor core logger
MSCL-S	Multi-sensor core logger, standard type, for automated down-core analysis, manufactured by Geotek Ltd., Daventry, United Kingdom
MSCL-XYZ	Multi-sensor core logger for automated analysis of multiple core sections, manufactured by Geotek Ltd., Daventry, United Kingdom
MSCL-XZ	Multi-sensor core logger bench-top logging track manufactured by Geotek Ltd., Daventry, United Kingdom
MSE	Mean square error
MSPE	Mean squared prediction error
MTS	Moroccan turbidite system
MWIR	Mid-wave infrared
n	Number
NAO	North Atlantic Oscillation
Nd:YAG	Neodymium-doped yttrium aluminium garnet, a crystal used as a lasing medium in solid-state lasers
NEXTMap	Commercial terrain mapping product
NGRIP	North Greenland Ice Core Project
NIOZ	Nederlands Instituut voor Onderzoek der Zee (Netherlands Institute for Sea Research), Texel, The Netherlands
NIR	Near infrared
NOCS/NOC-S	National Oceanography Centre, Southampton, United Kingdom
NPL	National Physical Laboratory, Teddington, United Kingdom
ODP	Ocean Drilling Program
OxCal	Radiocarbon calibration program developed by the Oxford Radiocarbon Accelerator Unit, University of Oxford, United Kingdom
PAH	Polycyclic aromatic hydrocarbon
PASADO	Potrok Aike Maar Lake Sediment Archive Drilling Project
PCA	Principal component analysis
PCB	Polychlorinated biphenyl
PETM	Paleocene-Eocene Thermal Maximum

PLS	Partial least squares regression
POZ	Poznan Radiocarbon Laboratory, Poland
PSD	Position sensitive detector
QSpec	Spectral analysis software for the ITRAX core scanner developed by Cox Analytical Systems, Mölndal, Sweden
Q-switched	Production of a high-powered pulsed laser
R^2	Coefficient of determination of a linear regression
REE	Rare earth element
RGB	Red, green and blue channels that constitute an image that broadly follows the colour receptors in the human eye
RRS	Radiographic reference sample
RX	X-radiography
SD	Standard deviation
SDD	Silicon drift detector
SDD-DPP	Silicon drift detector—digital pulse processing
SEM	Scanning electron microscope
SINDOCOM	Southern Indian Ocean/tropical Pacific teleconnections assessed by a coral—*in situ* ocean monitoring database (Netherlands Organisation for Scientific Research Earth and Life Sciences project 2007–2011)
SME	Small and medium-sized enterprise
SLS	Spectral luminescence scanning
STW	Sewage treatment works
SWIR	Shortwave infrared
T	Tephra
TATSCAN	Japanese-built XRF core scanner installed on the Japanese drilling vessel *D/V Chikyu* and at the Kochi/JAMSTEC/IODP Core Repository, Kochi, Shikoku, Japan
TOC	Total organic carbon
ULC	Univariate log-ratio calibration
UNEP	United Nations Environment Programme
UOS	University of Southampton
USGS	United States Geological Survey
UV	Ultraviolet
VAST	Volcanism in the Arctic System Project
VEI	Volcanic explosivity index
VIS	Visible spectrum
VNIR	Visible and near-infrared
WD-XRF	Wavelength dispersive X-ray fluorescence spectrometer
XRD	X-ray diffraction or X-ray diffractometer
XRF	X-ray fluorescence or X-ray fluorescence spectrometer
YTT	Younger Toba Tuff
Z	Symbol for atomic number

Chapter 1
Micro-XRF Studies of Sediment Cores: A Perspective on Capability and Application in the Environmental Sciences

R. Guy Rothwell and Ian W. Croudace

Abstract XRF core scanners represent a major innovation in the analysis of cored sediment sequences and have revolutionised palaeoenvironmental research over the last decade. Such scanners provide capability to rapidly and non-destructively record element proxy variations at decadal, annual and even sub-annual scales. Their use, initially by the marine science community, was soon taken up by lake core researchers, particularly after the advent of high-resolution models incorporating x-radiography, particularly suited for analysis of varved sequences. Their impact on the environmental sciences is seen in the exponential rise in research papers published since 2005 involving their use. Although their main application has been in the study of Quaternary marine and lake cores, they have also been used in the analysis of terrestrial hard rock cores in mining applications, analysis of loess cores, speleothems, cores from peat bogs and river banks and cores collected for environmental forensics and pollution studies. Further, an important cohort of papers has addressed interpretation and calibration issues, increasing the robustness of acquired datasets. In this paper we review marine and lacustrine applications of XRF core scanning, together with environmental forensics applications and research into data optimisation and calibration presented in the current volume. We provide synopses of the principal findings and a concise summary of the current work.

Keywords XRF core scanners · Core scanner publications · Micro-XRF · Sediment cores · XRF core scanner data optimisation

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Introduction

Non-destructive, high-resolution, sediment core scanners incorporating X-fluorescence (XRF) spectrometry and other sensors are now widely used in the earth and environmental sciences, and have radically improved our capacity to record environmental and process changes down to annual and even sub-annual scales. Such instruments measure down-core element variations, typically in the range Al ($Z=13$) to U ($Z=92$), with detection limits down to several ppm under favourable conditions depending on acquisition count time and X-ray tube excitation efficiency. Analysis is rapid (<50 s per increment) with typically little user intervention and samples require little preparation prior to investigation.

Marine and lacustrine sediments have long been recognised as being excellent recorders of environmental change. Such sequences may contain long records of earth processes such as climate change, local and regional events (e.g. floods, tsunamis, earthquakes, volcanic eruptions, landslides, storms) and anthropogenic changes (e.g. changing land use, pollution). A large number of element proxies have been recognised as important indicators of climate, weathering and erosion, redox conditions, organic productivity and water mass changes. Although the value of many of these proxies were recognised prior to the advent of XRF core scanners, these instruments have revolutionised our capability to extract high-resolution environmental data from sediment records.

The Development of XRF Core Scanners—A Boon to the Environmental Sciences

The recognition of climate change as a serious environmental and political concern from the 1980s onward and the growing collection of sediment cores for scientific research demanded fast, high-resolution instruments be developed to investigate environmental processes, particularly through element proxies. The origins of this new generation of instruments can be traced back to the CORTEX scanner developed by the Netherlands Institute for Sea Research (NIOZ) in the late 1980s (Jansen et al. 1998). This was commercialised as the AVAATECH core scanner by Avaatech Analytical X-ray Technology with installation at the University of Bremen and NIOZ in 2002. However, the down-core resolution of early instruments was 1 cm at best, meaning researchers could only realistically measure element proxies down to centennial to decadal timescales. Reconstruction of past environmental changes at annual or sub-annual scales, for example, through study of annual varves, needed millimetric or sub-millimetric resolution. This led to the development of high-resolution capability for the AVAATECH scanner (Richter et al. 2006). An independent enterprise headed by the Southampton Oceanography Centre (now National Oceanography Centre), United Kingdom, and Cox Analytical Systems, Gothenburg, Sweden, led to the innovative ITRAX prototype core scanner which was delivered in