

Chapter 27

Future Developments and Innovations in High-Resolution Core Scanning

Ian W. Croudace and R. Guy Rothwell

Abstract The rapid expansion of palaeoclimate research from the late 1990s onward stimulated the introduction and subsequent use of non-destructive XRF core-scanning systems worldwide. As a result these scanners now exist in approximately 90 international institutions and they must rank as one of the most useful analytical screening tools in the geosciences. Their development has contributed to an analytical revolution in palaeoclimate and environmental research due to their overall capability, speed and spatial resolution. From the 1990s to the present time five separate commercial XRF core scanners have been available with two being dominant in the academic research sector. Up to the current time the two market leaders have been Avaatech Analytical X-Ray Technology (Netherlands) and Cox Analytical Systems (Sweden; manufacturers of the ITRAX). Other manufacturers include Geotek (United Kingdom) who are developing a growing international presence while Jeol Ltd. (Japan; manufacturers of the Tatscan) is largely limited to Japan. The Avaatech core scanner, which evolved from the Dutch CORTEX instrument, firmly established itself in the marine research sector but has also served the lake and Pre-Quaternary research community. The Itrax core scanner (Cox Analytical Systems) has been widely used by both the marine and lake sediment community. Its integration of a high power X-ray tube, X-ray capillary wave-guide, advanced silicon-drift detectors and radiographic imaging proved of great interest to users (particularly the lakes community) requiring high-resolution elemental analysis and radiographic imaging of fine sediment layers. In the last few years Geotek have expanded their core logging instrument expertise to include XRF analysis. With their user base they are likely to become a significant competitor in the XRF core scanning sector. Looking to the next decade geoscientists are likely to see extended capability arising from the addition of new or enhanced sensors to existing systems or to the appearance of new dedicated systems carrying out specific scans. Some system developments that are just becoming available involve the enhancement of existing components that allow greater analytical speed with no loss of spectral

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data quality. Future development will likely involve addition of other non-contact technological sensors perhaps exploiting investments made in the *in-situ* extra-terrestrial sector. Fertile areas for development could be based on lasers (LIBS, dispersive Raman), hyperspectral imaging (reflectance spectrometry in the VNIR, SWIR and NIR wavelength regions), X-rays (simultaneous XRD) and magnetic susceptibility. Overall, future non-destructive scanning instrument are likely to provide improved sensitivity and additional high-resolution proxy records from natural materials including sediment and rock cores, speleothems and tree rings.

Keywords Itrax core scanner · Hyperspectral imaging · Laser-induced breakdown spectrometry · Simultaneous X-ray diffraction

Introduction

The papers presented in this volume demonstrate the impressive breadth and depth of applications involving high-resolution X-ray core scanners that have arisen in a little over a decade. With their ability to simultaneously and non-destructively measure thirty or more elements (and other co-registered properties such as magnetic susceptibility and a radiographic image), X-ray core scanners have made a significant contribution to the study of marine, estuarine and lacustrine sedimentary sections as well as rocks, coal, speleothems and tree rings (e.g. Croudace et al. 2006; Rothwell et al. 2006; Thomson et al. 2006; Croudace and Rothwell 2010; Rothwell and Croudace 2015; Croudace et al. 2015; Kelloway et al. 2015). Many of the existing XRF core scanners originated as concepts or prototypes in marine science establishments (universities and research institutions in Holland, UK and Japan) from the 1990s through to the early 2000s. Following from these early initiatives, the leading prototypes became commercialized by specialist instrument companies who responded to institutional demand created by the international expansion in paleoclimate research. The clear success of core scanner technology is an exemplar for how funding streams from research institution, combined with scientific demand, stimulated opportunities for specialist SMEs. The success of the instruments is graphically demonstrated by the exponential rise in publications over the last decade (see review by Rothwell and Croudace (2015)) and shows that they have become one of the most powerful analytical screening tools available to geo- and environmental scientists.

There are currently around 90 XRF core scanners worldwide that up to now are dominated by Avaatech and Itrax instruments (Table 27.1). The early development and success of these two main core scanners represents a kind of technological Darwinism where they became the dominant market leaders. Going forward, however, as new companies compete within the XRF core scanner market, positions may change with institutions choosing instruments on the basis of reputation, capability, suitability-for-purpose and cost. For example, Geotek Ltd, an established leader in traditional core logging technology is now competing in the XRF core scanning market. All available core scanners have a robust core-handling platform with asso-

Table 27.1 General locations of known XRF core scanners (*italicized text indicates known instruments installed on ships*)

Avaatech	ITRAX	Geotek XRF	Tatscan
MARUM, Bremen, Germany	National Oceanography Centre, Southampton, UK (2003)	14 Olympus—based units	<i>DV Chikyu, Japan</i>
NIOZ—Netherlands	Woods Hole Oceanographic Institution, USA (2004)	4 new-type Units	Kochi Repository, Japan
Alfred-Wegener Institute, Germany	Université de Quebec INRS, Canada (2004)	—	Mie University, Japan
IFREMER, Brest, France	University of Wales, Aberystwyth, UK (2005)	—	—
Kiel University, Germany	Istanbul Technical University, Turkey (2006)	—	—
University of Tromsø, Norway	University of Minnesota LLO, USA (2006)	—	—
EDYTEM-CNRS, Université de Savoie, France	University of Stockholm, Sweden (2007)	—	—
EPOC-CNRS, Université Bordeaux 1, France	University of Bremen, Germany (2007)	—	—
University of Cambridge, U.K.	University of Vigo, Spain (2007/2008)	—	—
University College, London, U.K.	Universität zu Köln, (2007)	—	—
Universitat de Barcelona, Spain	University of Bergen, Norway (2008)	—	—
E.T.H Zurich, Switzerland	CEREGE, Aix-en-Provence, France (2008)	—	—
BGR, Hannover, Germany, 2012	University College Dublin, Geology (2008)	—	—
Texas A&M University, College Station, USA	Second Institute of Oceanography, Hangzhou, China (2009)	—	—
Scripps Institution of Oceanography, USA	First Institute of Oceanography, Qingdao, China (2009)	—	—
University of North Carolina, USA	National Taiwan University, Taipei, Taiwan (2009)	—	—
Rosenstiel School, Miami, USA	KIGAM, Daejeon, S. Korea	—	—
University of Wisconsin, Madison, USA	China University of Geology, Beijing, China. (2010)	—	—
KIGAM, Daejeon, S. Korea	University of Rostock, Germany (2010)	—	—
State Key Lab of Marine Geol, Tongji Uni, China	Helmholtz-Centre, Potsdam. (2011)	—	—
Nanjing University, China	<i>Korea Polar Research Institute, RV Araon (2011)</i>	—	—

Table 27.1 (continued)

Avaatech	ITRAX	Geotek XRF	Tatscan
University of the Philippines, Philippines	University of Massachusetts, Amherst, USA (2011)	–	–
University Lanzhou, China	ANSTO, Lucas Heights, Sydney, Australia (2011)	–	–
Yunnan Normal University, China	Institute of Mineral Resources, Beijing, China (2012)	–	–
Xiamen University, China, 2012	Institute of Tibetan Plateau Research, Beijing, China (2012)	–	–
Nanyang Technological University, Singapore	University of Aarhus, Denmark (2012)	–	–
The Australian National University, Canberra	State Key Laboratory of Geol. Proc. & Mineral, Wuhan, China	–	–
–	Kuwait Petroleum Institute, Kuwait Inst. Scientific Research	–	–
–	University of New South Wales, Australia	–	–
–	State Key Laboratory of Continental Dynamics, Chengdu, China	–	–
–	GSI RV Samudra Ratnakar, Mumbai, India	–	–
–	University of Bern, Switzerland	–	–
–	Korean Institute of Ocean Science & Technology, S. Korea	–	–
–	Guangzhou Marine Geological Survey, China	–	–
–	University of Copenhagen, Natural History Museum of Denmark	–	–
–	McMaster University, Hamilton Canada (2014)	–	–
–	KCC Kochi University, Japan (2014)	–	–
–	University of Köln, Itrax core scanner No. 2 (2014)	–	–
–	Oregon State University (2014)	–	–

ciated precision motor drives. Onto this basic platform have been added a range of specialized components developed by (external) original equipment manufacturers (OEMs producing X-ray tubes, X-ray detectors, CCD cameras, optical spectrometers etc). Several of these XRF corescanning systems have been successfully deployed on research vessels but so far the best analytical data are acquired in a stable terrestrial laboratory environment.

Software developments are crucial in strengthening the capability of core scanners. The manufacturers have generally provided most core scanner instrument control software. Spectral analysis software has either been developed by the manufacturer (e.g. QSpec for the ITRAX) or has used proprietary software from other providers (Canberra WinAxil for Avaatech and Geotek). Future developments in core scanning technology may arise when other high-resolution sensors are integrated into existing XRF core scanners or when new companies enter the market stimulating competition and innovation. The co-registration of core data on a single instrument (e.g. Itrax's elemental, magnetic susceptibility, radiography) is always likely to be attractive to users subject to affordability. Possible additional technical developments that may eventually be incorporated into current non-destructive core scanners are likely to be based on lasers excitation (LIBS—laser-induced breakdown spectroscopy and Dispersive Raman Spectroscopy), optical illumination (hyperspectral imaging), X-ray excitation (X-ray diffraction, XRD) and magnetics (Fig. 27.1).

In this paper we review a range of possible hardware and software developments that could become incorporated into future core scanners. The ultimate value of any of these technologies, beyond those currently available, needs to be established through systematic investigation using previously studied, well-understood cores. Relatively new sensors could emerge from other areas of investigation. For example, there may be spin-offs from the significant investment made in planetary research programmes where non-contact (standoff) sensors are being evaluated.

Hardware Developments

X-ray Based Techniques

Improved SDD Detectors and MCAs The continued improvement of silicon drift detector technology and associated digital pulse processing (SDD-DPP) with multi-channel analysers (MCAs) is already leading to significant performance enhancements for X-ray core scanners. Over the last ten years detector count-rate capability has increased by a factor of 10–30 based entirely on developments in SDD-DPP technology. It is now possible to achieve up to 1 Mcps input count rates, with virtually no degradation of peak resolution. Fifteen years ago count-rates needed to be kept below 0.01 Mcps to ensure X-ray energy resolutions were not adversely affected. The clear benefit of these SDD-DPP improvements is the provision of shorter analysis times and improved precision, especially important for less efficiently excited elements (such as Al and Si).

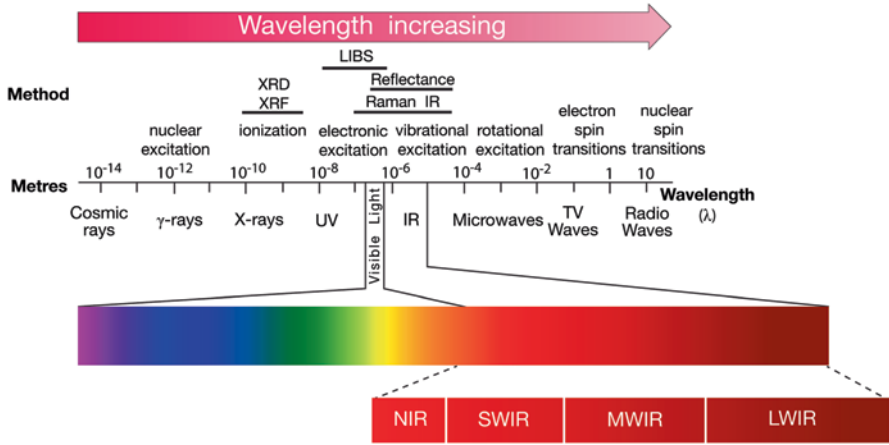


Fig. 27.1 The electromagnetic spectrum showing the spectral regions and methods used by current core scanning technologies

Twin X-Ray Detector Systems The Itrax uses a medium power (2–3 kW) X-ray generator and allows users to select a range of X-ray tubes (Cr, Mo, Rh) to optimize their analysis. The choice of tube determines elements that can be effectively measured (based on the varying excitation efficiencies) and for the broadest range of elements it is necessary to use more than one tube, currently involving a sequential scan. Changing of X-ray tubes is time consuming and inconvenient. To improve efficiency it might be possible to use two X-ray tubes on a single scanning system. In the case of the Itrax a low power X-ray tube (with a different anode from the main system) and associated detection system could be integrated. The incorporation of an additional close-coupled, low power X-ray tube with its own SDD could reduce the analytical overhead by acquiring data simultaneously using two separate, co-mounted XRF systems. Such a technical development seems feasible but would require research funding or company investment.

X-Ray Diffraction Sediment layers may comprise mixtures of minerals derived from a wide variety of sources such as local re-working, biogenic materials, terrigenous material derived from terrestrial erosion etc. The mineralogical composition can provide valuable insights into environmental processes and may be inferred from the geochemistry measured by the XRF core scanner, or it may be determined directly using a method such as X-ray diffraction analysis (XRD). Mineralogical analysis at high speed using X-ray diffraction would require the use of simultaneous acquisition systems such as curved position sensitive detector (CPSD) technology. These XRDs can simultaneously measure a 110° 2θ diffraction angle pattern (Fig. 27.2, Table 27.2), are capable of resolving 0.04 degrees-2θ FWHM (full width at half maximum) and can analyze sample areas as small as ten microns. These CPSDs replace older mechanical scanning goniometers used by traditional XRD manufacturers. Instruments using CPSDs are now well established although currently promoted by only a small number of companies (e.g. www.inel.fr). Modern CPSDs use a robust "knife edge" alloy blade anode in place of the older, more

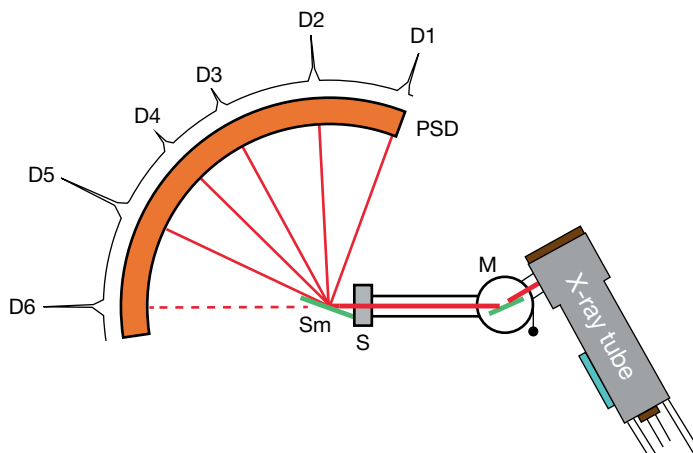


Fig. 27.2 Schematic of Inel™ Curved Position-sensitive detector (PSD) for simultaneous XRD. These systems have no moving parts and eliminate the need for mechanical scanning devices such as complex scanning goniometers used in conventional scanning XRD Systems using goniometers. *M* monochromator, *S* Slit, *Sm* sample, *PSD* Position sensitive detector, D1–D6 are possible diffraction lines produced when Sample *Sm* is irradiated with CuK α

fragile wire anode detectors. Curved Position-sensitive XRDs allows dynamic (simultaneous) measurement of diffraction data in real-time at very high resolution.

Energy-Dispersive-XRD An alternative non-destructive XRD technology offering some potential is EDXRD (Feng et al. 2004; Escarate et al. 2009; Beck et al. 2014; O'Dwyer and Tickner 2008) where simultaneous mineralogical information is obtained following on-line development for the minerals industry (Fig. 27.3). This technology has some technical challenges that need to be overcome but there is some application potential. The prototype EDXRD technique of O'Dwyer and Tickner (2008) used much higher X-ray energies (up to 120 keV) and is a transmission method compared with conventional reflection XRD that uses 10–30 keV.

EDXRD is also capable of measuring material tens of millimetres in thickness due to the use of higher energy X-rays whereas a conventional reflection mode XRD analyser measures a small amount of material on the surface of the sample. Important factors in EDXRD use are:

- Sample preparation is less critical in EDXRDs that use higher-energy X-rays because micro-absorption effects are reduced.
- EDXRD analysers have no moving parts
- EDXRD data acquisition times can be short as the complete diffractogram is collected simultaneously
- Mathematical techniques are needed to deconvolve complex diffractograms
- The main disadvantage of EDXRD is its relatively low d-spacing resolution compared to conventional XRD. This resolution stems almost entirely from the relatively wide collimator openings required to achieve sufficient counting statistics in an acceptable measurement time.

Table 27.2 Summary of existing and future possible non-destructive methods for investigating sediment cores

Method	Property measured	Principle	Sensitivity	Non-destructive capability, data type	Analysis time scale per increment	Typical sample spatial resolution	Potential for non-destructive core scanning
<i>XRF</i>	Elements Mg-U	X-ray fluorescence following orbital transitions An x-ray source generates fluorescent x rays in the sample that are detected by an energy discriminating detector	Low ppm for selective elements	Yes Semi-quantitative to quantitative	1 s for major elements 10 s for trace elements	>50 μm	Established, but detection enhancements regularly occurring
<i>XRD</i> Simultaneous XRD using position sensitive detector	Mineralogy identified via X-ray diffraction	X rays are directed through the sample and a diffraction pattern is collected using an energy discriminating detector	>1 wt% of mineral	Yes Semi-quantitative	>100 s likely	1000 μm	Offers potential
<i>XRD</i> Simultaneous XRD via EDXRD	Mineralogy identified via X-ray diffraction	Monochromatic X rays are directed through the sample and a diffraction pattern is collected	>1 wt% of mineral	Yes Semi-quantitative	>1000 s likely	1000 μm	Offers potential
<i>X-radiography</i>	Density variations; textural features	X-ray absorption, radiography	Sensitive to small changes	Yes Semi-quantitative	Seconds	>50 μm	Established

Table 27.2 (continued)

Method	Property measured	Principle	Sensitivity	Non-destructive capability, data type	Analysis time scale per increment	Typical sample spatial resolution	Potential for non-destructive core scanning
<i>FT Raman Dispersive Raman</i>	Mineralogy, organic compounds	Vibrational spectroscopy—Laser light scattered from the surface is detected. The wavelength of the Raman scattered peaks are mineral-specific	High	Yes Semi-quantitative	Seconds	>50 μm	Offers potential
<i>LIBS</i>	Elements	Atomic emission spectrometry—a short pulse from a high power laser initiates a high T plasma. As the plasma cools optical emission spectra from excited atomic states are recorded	ppm for selective elements	Laser ablation, micro-pitting Use on soft sediment may be problematic Semi-quantitative	Seconds	>500 0.5 mm	Potentially good for some elements
<i>Hyperspectral imaging</i>	Mineralogy, organic compounds	Optical reflectance spectroscopy	Highly variable	Yes Semi-quantitative	Seconds	>50 μm	Established
<i>Magnetic susceptibility</i>	Ferromagnetic minerals	Magnetic susceptibility using Bartington sensor	Ferromagnetism 50 μg	Yes	Seconds	>1000 μm	Proven at ~5 mm resolution

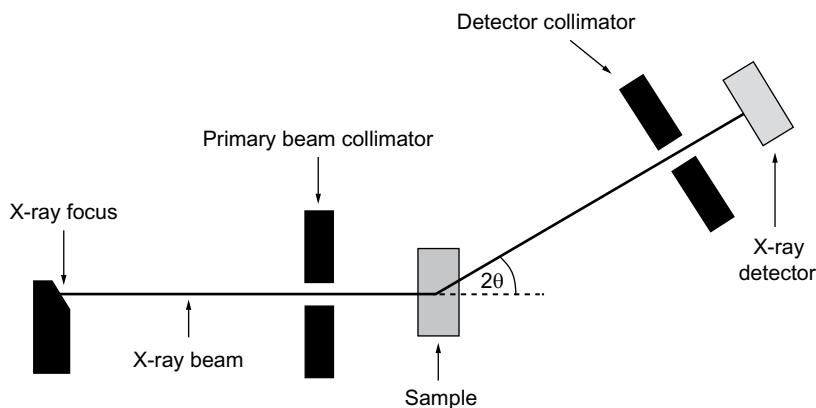


Fig. 27.3 Schematic representation of an EDXRD spectrometer. (From O'Dwyer and Tickner 2008)

Both of the XRD techniques discussed above could be added to a scanning platform with few technical obstacles, and either could become incorporated into a core scanning system if there was a sufficiently strong user driver.

Optical Methods

Hyperspectral Imaging (HSI) Hyperspectral imaging is a passive, non-destructive, surface analytical technique that only requires illumination of the sample and detection of the reflected light spectrum. Measurements can be made *in-situ* with virtually no sample preparation, except where high magnification imaging is the focus of attention. Hyperspectral imaging collects and processes information from across the electromagnetic spectrum (typically near the red part of the visible light spectrum) and its purpose is to obtain a spectrum for each pixel in the image of a scene, with the purpose of identifying compositional variations in materials. Whereas the human eye sees visible light in three colour bands (RGB), hyperspectral imaging divides the spectrum into many more bands and the recorded high-resolution spectra extend over a wide range of wavelengths. The key measuring component of a hyperspectral scanning system is the spectroscopic camera (incorporating a CCD, ICCD or CMOS) that acquires reflected light intensity for a large number of spectral bands.

Reflectance spectrometry, the basis of the HSI technique, relies on the property that when molecules are exposed to energy they vibrate with stretching and rotating of their chemical bonds. Changes at the molecular and atomic level result in selective absorption of incident and reflected light at specific and unique wavelengths.

Table 27.3 Main regions of the visible spectrum

Range	Abbreviation	Range (nm)	Minerals showing a reflection spectral response
Ultraviolet	UV	200–400	–
Visible-near infrared	VIS	500–700	–
	VNIR	400–1000	Iron oxides and hydroxides manganese oxides
Short-wave infrared	SWIR	1000–2500	Hydroxyls, carbonates, sulphates micas
Mid-wave infrared	MWIR	3000–6000	–
Long-wave infrared	LWIR	6000–12000	Carbonates, silicates, quartz, feldspar

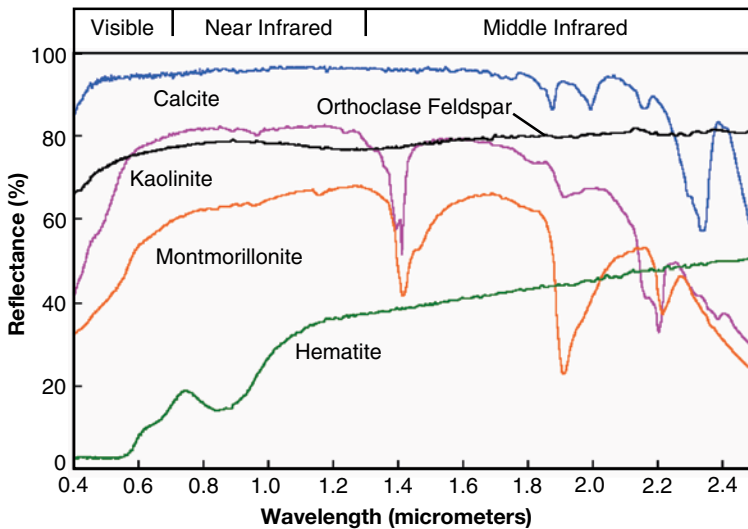


Fig. 27.4 Reflectance spectra of some representative minerals (adapted from Smith 2012). In the spectrum of hematite, the strong absorption in the visible light range is caused by ferric iron (Fe³⁺). In calcite, the major component of limestone, the carbonate ion (CO₃²⁻) is responsible for the series of absorption bands between 1.8 and 2.4 micrometers (μm). The clay minerals, kaolinite and montmorillonite, have a strong absorption band near 1.4 μm (hydroxide ions, OH⁻) and a weaker band at 1.9 μm (bound water molecules)

The infrared region is effective for mineral detection as many minerals provide spectral responses across different IR wavelengths (Table 27.3 and Fig. 27.4). For example, iron oxides and pyroxenes can be detected in the VNIR spectral range (400–1000 nm; so requiring a VNIR spectral camera), while micas, clays and many other minerals produce responses in the SWIR region (1000–2500 nm; so requiring a VNIR spectral camera).

Hyperspectral imaging is already established in some geoscience sectors (e.g. as portable or laboratory-based scanning devices in mineral exploration; CSIRO 2014; Huntingdon et al. 2004; Huntingdon 2007; Roache et al. 2011) and is used to derive compositional information (minerals or other components) or it can be used to present compositional maps derived by combining digital imaging and spectroscopy (Specim, Finland; see Fig. 27.5 and Table 27.4).

Hyperspectral Imaging

Covalent bonds in chemical components can absorb particular wavelengths of the visible and near visible light spectrum and can be measured using one or more specialist cameras that combine imaging and spectroscopy (see www.specim.fi). Hydroxyl and carbonate bond-related vibrations are typically measured in the shortwave infrared (SWIR). Phyllosilicate and carbonate minerals are commonly identified across the SWIR region. Clay minerals, micas, chlorites and different carbonate species are detectable. Longer wavelength ranges are necessary to detect the fundamental vibrations related to aluminosilicate minerals, e.g. in the long-wave (thermal) infrared (LWIR) region quartz, feldspar and other silicate minerals can be detected and identified.

With a standard digital camera, the lens system projects the image onto the focal plane array. In a hyperspectral imaging system a high quality imaging spectrograph is installed between the camera lenses and the focal plane array. The lens images the object at the entrance slit of the spectrograph which produces a spectrum on the focal plane array, preserving the location of respective points on the slit. Consequently, each line of the focal plane array is an image of the slit, containing one wavelength. One frame produced with the hyperspectral imager contains full spectral information of a single line of the image. The entire image (called the data cube) is produced line by line, each frame representing a consecutive line. Capturing the full image takes just seconds. Standard spectroscopic analytical methods are applied to analyze the image.

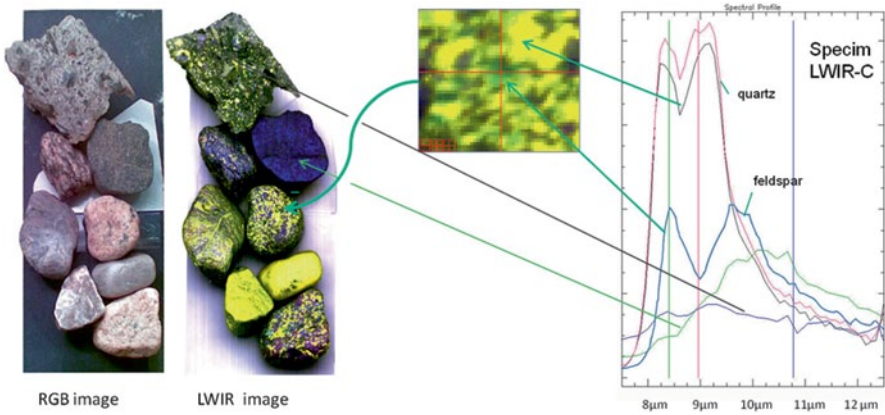


Fig. 27.5 Example of a hyperspectral mineral map a set of rock pebbles produced using a Specim LWIR-C imager. Every pixel of the LWIR image encompasses a full infrared spectrum range from 7.7 to 12.4 μm . Based on the different characteristics, minerals such as quartz and feldspar spectra are clearly recognizable

Table 27.4 Single core hyperspectral scanner, SisuSCS (Specim, Finland)

	VNIR	SWIR*
Spectral range	400–1000 nm	1000–2500 nm
Number of spectral bands	96–768 (adjustable by binning)	288
Spectral sampling	0.78–6.27 nm/pixel	5.6 nm/pixel
The number of spatial pixels	up to 1312	384
Pixel size on target	0.04–0.09 mm (1312 pixels)	0.130–0.312 mm (384 pixels)
Sample scanning	Single scan	
Scan speed (50 mm FOV)	~2.5 mm/s up to 6.7 mm/s with binning)	13 mm/s (at 100 Hz frame rate, up to 400 Hz possible)
Scan speed (120 mm FOV)	~6 mm/s (up to 16 mm/s with binning)	31 mm/s (at 100 Hz frame rate, up to 400 Hz possible)
Scan time for 1.5 m long sample	~4 min (90 s with binning)	~ 50s
Field of view (FOV)	50–120 mm	50–120 mm
Imagery	High resolution hyperspectral images	
Principle	Spectral reflectance spectrometry provides molecular compositional information	
Typical applications	Minerals in sediment or rocks	Organic compounds in sediment
Max sample size	130 × 1 500 × 75 mm (L × W × H)	
System dimensions	3 210 × 522 × 1 000 mm (L × W × H)	
Operating conditions	Laboratory environment	
Camera output format	Digital 12 bit	Digital 16 bit
Instrument calibration	Spectral calibration. Normalization using internal referencing	

*These are the characteristics of the new generation SWIR spectral camera introduced in the middle of 2014

Class	Mineral	VNIR Response	SWIR Response	LWIR Response
Wavelength		400-1000 nm	1000-2500 nm	8000-12000 nm
Silicates	Amphibole	Poor	Good	Moderate
Silicates	Pyroxene	Good	Moderate	Good
Silicates	Tourmaline	Poor	Good	Moderate
Silicates	Garnet	Moderate	Poor	Good
Silicates	Olivine	Good	Poor	Good
Silicates	Epidote	Poor	Good	Moderate
Silicates	Mica	Poor	Good	Moderate
Silicates	Chlorite	Poor	Good	Moderate
Silicates	Illite	Poor	Good	Moderate
	Kaolinite	Poor	Good	Moderate
Silicates	Orthoclase	Poor	Poor	Good
	Albite	Poor	Poor	Good
Silicates	Silica	Poor	Poor	Good
Carbonates	Calcite	Poor	Moderate	Good
Carbonates	Dolomite	Poor	Moderate	Good
Hydroxide	Gibbsite	Poor	Good	Moderate
Sulphate	Alunite	Moderate	Good	Moderate
Sulphate	Gypsum	Poor	Good	Good
Borate	Borax	Poor	Moderate	Uncertain
Chloride	Halite	Poor	Uncertain	Uncertain
Phosphate	Apatite	Moderate	Poor	Good
Hydrocarbons	Bitumen	Uncertain	Moderate	Uncertain
Oxide	Haematite	Good	Poor	Poor
Oxide	Chromite	Poor	Poor	Poor
Sulphide	Pyrite	Poor	Poor	Poor

Good – Minerals that produce a good response in the infrared region.

Moderate – Minerals that can be identified in the IR region. These minerals may not have high contrast responses or are not easily distinguished from some minerals if the system resolution is low.

Poor – Non-diagnostic responses observed for these minerals across the specific infrared regions.

Uncertain – Uncertain response for these minerals across these regions of the infrared.

Adapted from Geospectral imaging (Johannesburg, SA; www.geospectral.co.za) and Specim (Oulu, Finland; www.specim.fi)

Specialised HSI camera systems acquire reflectance spectra from rock or sediment surfaces over a spectral range determined by the camera. As an example, the currently available SisuSCS sediment/rock core scanner (Specim Ltd, Finland) uses one of two demountable cameras that are sensitive over the range 400–1000 nm or 1000–2500 nm (Table 27.4). The choice depends on the intended application such as investigation of rock or wet sediment. Wet sediment investigations can be challenging because water in the samples will cause interference effects in the SWIR, which is the preferred region for mineralogical detection. For wet sediment a VNIR sensitive camera has been used (Grosjean et al. 2014). In some cases it may be possible to temporarily dry the sample surface to acquire useful mineralogical data in the SWIR. Trachsel et al. (2010), Butz et al. (2013) and Grosjean et al. (2014) examined lake sediments and identified useful variations at a sub-varve scale using a SisuSCS (Fig. 27.6).

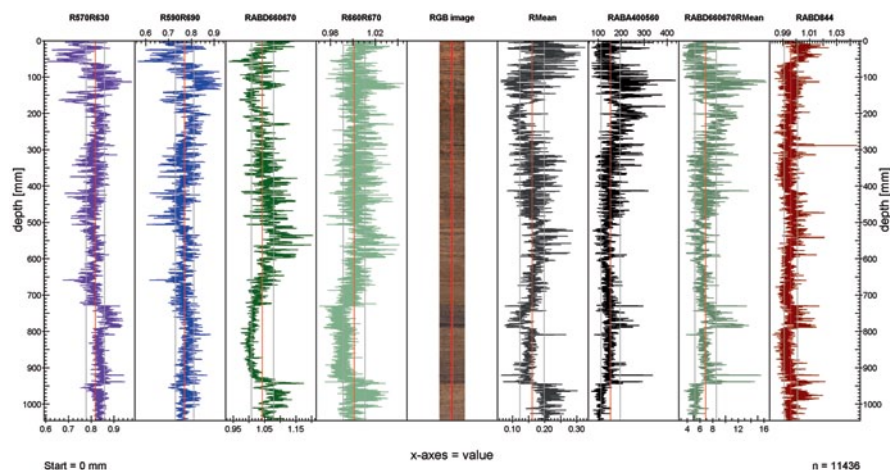


Fig. 27.6 Spectral indices derived from a hyperspectral scan of a 1 m long lake sediment core from Lake Jaczno (Poland) using a Specim SiSuSCS system. Butz et al. 2013, 2014 (Image courtesy of C. Butz and M. Grosjean)

R570/630 and R590/690 (band ratios) are used in minerogenic sediments to evaluate the amount of clay minerals (e.g. chlorite, illite) against the amount of organic material present. RABD660670 (Relative absorption band depth) is a relative measure for concentrations of chlorophylls and derivative products in marine sediments and freshwater lakes. R660/R670 (band ratio) is an index showing the degree of chlorophyll diagenesis. RMean is the mean of all spectral bands and indicates the total brightness of the sediment. RABA400560 (Relative Absorption Band Area) is the area of absorption in the blue spectrum indicative of total organic carbon content in marine sediments. RABD660670/RMean reflects red absorption of pigments.

Laser-Based Methods

Molecular Spectroscopy Raman spectroscopy is a type of vibrational spectroscopy that uses a monochromatic laser light source to irradiate a sample and is non-destructive, does not normally require sample preparation and provides information-rich data. Raman is a light scattering technique, and normally all that is required for spectrum collection is to place the sample in the excitation beam and analyse the scattered light. There are several varieties of the technique, termed Dispersive Raman (Smith and Clark 2004; Izake 2010), FT-Raman (Fourier Transform Raman; Cangemi et al. 2010; Kristova et al. 2013) and Time-resolved Raman spectroscopy (Fig. 27.7) (Blacksberg and Rossman 2010). Raman and FT-Raman are complementary techniques resulting in acquisition of very similar spectral information. Generally, dispersive Raman provides more information from microscopic applications due to its higher sensitivity, but FT-Raman is more suitable for bulk material analyses due to their lack of fluorescence.

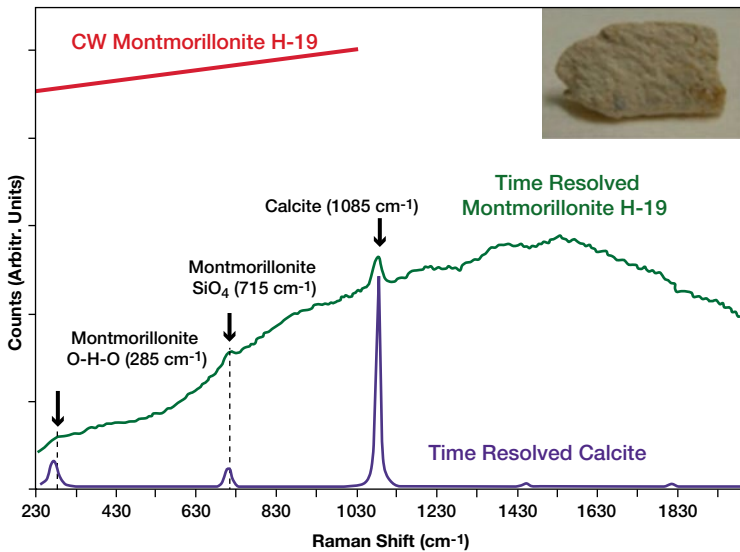


Fig. 27.7 Example of a time-resolved Raman spectrum showing the benefits of fluorescence removal (Blacksberg et al. 2014). Raman spectra of montmorillonite obtained using pulsed and CW Raman. Under CW illumination, the fluorescence saturates the CCD detector. A pulsed Raman spectrum of calcite is shown revealing that a minor phase of calcite is likely present. (Reproduced with permission from the Optical Society)

Raman Spectroscopy

1. Raman spectroscopy acts as a molecular fingerprint containing unique, reproducible, detailed features and provides the possibility of highly selective determinations.
2. The Raman fingerprint is independent of the excitation wavelength. This allows the use of any laser excitation wavelength.
3. Raman spectroscopy can be applied to virtually any sample, of any size that is capable of absorbing the laser excitation beam and where the scattered photons can be detected.
4. Solid, liquid and gaseous samples can be measured as well as transparent or non-transparent samples. Wet samples present no special technical problems.
5. No special pre-scanning preparations of the sample are necessary.
6. Scanning is non-destructive, non-invasive and response is rapid.
7. Raman spectroscopy instruments can be highly compact and portable and their overall characteristics make them suitable as an instrument for extreme environments (e.g. in-situ planetary studies).

Minerals are often Raman sensitive, but most have a native color (i.e. are not white or transparent) and often display high fluorescence when excited by visible lasers. Thus, it can be difficult to measure them using conventional Raman measurements. With one proprietary system (Bayspec, San Jose, CA, USA) using a 1064 nm laser, IR sensitive detector and volume-phase-grating, Raman spectra can be measured with high signal:noise without fluorescence interference.

Dispersive Raman—usually employs visible laser radiation with typical laser wavelengths of 780 nm, 633 nm, 532 nm, and 473 nm although others are common (1064 nm). One advantage of using shorter wavelength lasers is the enhancement in the Raman signal that occurs at shorter wavelengths. The efficiency of Raman scatter is proportional to $1/\lambda^4$, so there is a strong enhancement as the excitation laser wavelength becomes shorter. However, sample fluorescence becomes a problem at shorter excitation wavelengths and in some cases even minor fluorescence can overwhelm the desired Raman measurement.

FT-Raman—An FT-Raman spectrometer uses a laser in the near infrared (1064 nm) and at this wavelength fluorescence is almost completely absent, however because of the $1/\lambda^4$ relationship between Raman scattering intensity and wavelength, the Raman signal is weak. In addition, silicon CCD detectors cannot be used in this region of the spectrum. FT-Raman spectroscopy is particularly well-suited for bulk sample analysis.

Time-resolved Raman Spectroscopy—Raman scattering occurs instantaneously in time, while fluorescence occurs on longer time scales. Minerals can contain as many as 25 luminescence centers, each with different decay times from nsec to msec. The distinct timing differences of Raman and fluorescence can be used to separate them. This allows fluorescence-free Raman spectra to be acquired using traditional visible laser excitation (532 nm) and simultaneously measure time-resolved fluorescence spectra for the detection of trace ionic components. Through the combined use of these techniques, the probability of successful mineral identification is greatly increased. Time-resolved pulsed Raman spectroscopy is ideal for fluorescence rejection, since the Raman signal is collected simultaneously with the laser pulse, and photons emitted after the laser pulse can be rejected. Laser pulse widths of the order of 10 ns are typically combined with an intensified charge-coupled device (ICCD) based gated detection system. Most of the fluorescence signal can be rejected by electronic gating so as to detect only photons emitted during the laser pulse.

Adapted from Thermo-Nicolet; BaySpec (San Jose, USA); Smith and Clark (2004); Izake (2010); Blacksberg et al. (2014)

Blacksberg et al. (2014) note that the Raman technique offers clear advantages for non-destructive analysis but there are challenges when investigating complex multi-mineralic systems like soils and rocks. The presence of organic matter also causes difficulties in that fluorescence can overwhelm Raman signals when using 532 nm laser excitation. The use of time resolved Raman helps to reduce the high background signal caused by fluorescence because Raman scattering is an instantaneous process while fluorescence processes are associated with decay times that vary from picosecond to millisecond. In geological materials there can be several fluorescent phases, leading to both long lifetime (mineral) and short lifetime (organic) fluorescence.

Atomic Spectroscopy An analytical technology that shows some potential for rapid core scanning is Laser-Induced Breakdown Spectroscopy (LIBS), described as an emerging technology for more than ten years. This is a type of atomic emission spectroscopy in which a single, dual or triple pulse of laser energy is used as the excitation source. It is a high-speed non-contact and virtually non-destructive method of elemental analysis and provides data of semi-quantitative quality. However, generating quantitative data from a complex wet sediment matrix remains a major challenge at present. The output of a pulsed laser, such as a Q-switched Nd:YAG type, is focussed onto the surface of the sample. For the duration of the laser pulse (typically 10 ns) the power density at the surface of the sample can exceed 1 GW per cm² using a compact laser device and simple focusing lenses. At such high power densities, several micrograms of material may be vapourised from the sample surface through laser ablation after a laser shot (or multiple shot) that generates a short-lived but luminous plasma having a temperature up to 10,000 K. A wide range of volatilised elements in the plasma from the sample will initially exist as excited ionic and atomic species that upon cooling emit characteristic optical radiation as they return to lower energy states. The emitted light can be readily measured using a sensitive CCD device, often via the same fibre optic bundle that delivered the excitation laser. LIBS therefore provides potential to qualitatively, and possibly quantitatively, identify elements in a sediment sample with high sensitivity (Barbinia et al. 2002; Cremers and Radziemsk 2013). However, in soft sediments, the laser excitation pulses used during a LIBS single point analysis may produce an ever-deepening pit that can limit the light collected by the CCD.

Magnetic Methods

High-Resolution Magnetic Devices Bartington magnetic susceptibility sensors are already included on some core scanners as options and have long been used on Geotek MSCL systems (Geotek, Daventry, UK). The current resolution is typically 5 mm but it may be possible to increase resolution to 1 mm. Such measurements require flat samples and close coupling. It remains to be seen whether further developments take place leading to higher resolution measurements.

Numerical and Software Developments

Efficient quantification of core scanner data will continue to develop and is a key requirement in the evolution of core scanner technology. Many researchers continue to use either count or count-rate data as supplied by the instrument's software or they may adopt a semi-empirical approach by analyzing a small number of sub-samples using WD-XRF, ED-XRF or ICP-OES to calibrate their data (e.g. Boyle et al. 2015; Croudace et al. 2015). A more advanced approach based on the use of multi-variate statistics is described by Weltje et al. (2015) and represents a significant advance that could become increasingly used. Further developments in data quantification are likely. Instrument manufacturers are tending to move toward more integrated and comprehensive quantification software (e.g. Cox Analytical Systems have recently developed a package called Q-quant which offers improved peak fitting, calibration and calculation procedures for ITRAX data). Data Analysis and data visualization is already quite well developed (e.g. ItraxPlot, RediCore software etc.) but there is scope for further enhancements depending on application. At least one core scanner manufacturer is working on a software solution to infer mineralogy and mineralogical distribution from elemental data (e.g. Cox Rock-Core, Cox Analytical Systems, Gothenburg) using multivariate statistical analysis.

Conclusion

The commercial development of non-destructive, high-resolution core scanners from the year 2000 to the present has contributed to a rapid expansion of palaeoclimate and environmental research. Recent application of these scanners to mineral exploration has expanded the market and led to innovation and competition among instrument manufacturers. The international scale of these research enterprises has been marked by an exponential rise in published output from 1995–2015. Other areas benefitting from the high-resolution capability of these scanners include dendrochemistry, environmental forensics, environmental geochemistry and more recently mineral exploration. The impact of these instruments could grow if new sensors and data processing options are added to existing platforms. Some of these sensors may emerge from R&D associated with studies of extreme environments. The significant investment made in planetary research programmes (such as the Mars Science Lab Rover), where there has been a focus on producing non-contact (standoff) sensors, could also be adapted for core scanners. Inclusion of some of these developments on current core scanner models will depend on their analytical value, user interest and company investment. Alternatively, specialist instrument manufacturers may develop specific sediment/rock scanning instruments (several already exist) that would complement existing XRF core scanners.

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