Highly sensitive non-destructive rare earth element detection by means of WD-XRF spectroscopy enabled by an energy dispersive pnCCD detector

Ella De Pauw^{1,*}, Pieter Tack¹, Miles Lindner², Antonia Ashauer², Jan Garrevoet³, Bart Vekemans¹, Gerald Falkenberg³, Frank E. Brenker², Laszlo Vincze¹

¹ X-ray Microspectroscopy and Imaging group, Department of Chemistry, Ghent University, Krijgslaan 281, B-9000 Ghent, Belgium

² Institute for Geosciences, Goethe University Frankfurt, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

³ Deutsches Elektronen-Synchrotron DESY, Notkestr. 85 22607 Hamburg, Germany

* Corresponding author information: Ella De Pauw, ella.depauw@ugent.be

KEYWORDS: *X-ray fluorescence spectroscopy, high sensitivity wavelength dispersive detection, non-destructive technique, energy dispersive full-field detector, SLcam, rare earth elements, deep Earth diamonds, Juina diamonds*

ABSTRACT: Detection of rare earth elements (REE) is commonly performed with destructive techniques such as (LA)-ICP-MS or coupled to a destructive sample preparation. When investigating unique geological samples, such as cometary, asteroidal or interstellar material from sample return missions or inclusions in deep-Earth diamonds, a non-destructive method is preferred. The presented non-destructive highly sensitive wavelength-dispersive X-ray fluorescence spectroscopy (WD-XRF) technique is designed to measure the L-lines of REE between 4.5 and 7 keV with a sensitivity down to the ppm level. REE fluorescence L- lines are often only separated by a few eV from neighboring XRF lines and cannot be resolved by an energy dispersive approach especially in the presence of transition metal K lines. In our spectrometer the characteristic X-rays emitted by the sample are dispersed by a fixed Ge(111) analyzer crystal over the active area of an energy dispersive pnCCD detector, enabling high energy resolution detection of X-rays differentiated by their corresponding Bragg angles. The use of an energy-dispersive 2D detector enables to simultaneously acquire XRF lines while eliminating any ambiguities due to potential contribution from higher order diffraction effects or other diffraction planes, and thereby increases the sensitivity by reducing the (scatter) background. This detection method shows an energy resolution of 12 eV for the Ti-K α fluorescence line and has a sensitivity down to 0.50 ppm for REE L-lines. The method was optimized specifically for the non-destructive analysis of inclusions in deep Earth diamonds, yielding *in situ* quantitative information about up-to-now inaccessible elemental (REE) composition patterns together with the more abundant transition metals like Ti, Cr, Mn and Fe. This information is of great importance to decipher the role that deep Earth plays in the global carbon and fluid cycle.

Rare earth elements (REE) are generally probed with destructive techniques such as ICP-MS¹⁻⁴, LA-ICP-MS^{5,6}, HR-ICP-MS⁷, MC-ICP-MS⁸ or ICP-AES⁹, possibly combined with specialized sample preparation methods. The destructive character of these techniques causes at least partially destroyed samples which is a major disadvantage when unique samples are examined. Synchrotron radiation induced X-ray fluorescence (SRXRF) spectroscopy on the other hand is a non-destructive, highly sensitive technique that is widely used to determine the elemental composition of various samples. SRXRF spectroscopy is for instance used for the investigation of biological systems¹⁰⁻¹³, for the characterization of new catalysts¹⁴, the visualization of elemental distributions in art and archeological objects¹⁵⁻¹⁷ and for studies in Earth and planetary science^{18,19}. Typically, an energy dispersive (ED) silicon based detector is applied for XRF detection, providing a spectral resolution of approximately 130 eV for the Mn-K α line²⁰. However, when studying rare earth elements (REE), the characteristic L-lines of the elements of interest are often separated by only a few tens of eV, preventing the interference free detection of REE in the energy range of 4.5 - 7 keV using a conventional ED approach, especially in the presence of intense transition metal K-lines. On the other hand, the K-lines of the REE are emitted in the energy range between 33 and 61 keV, requiring an incident energy of at least 63.4 keV, the K

absorption edge of Lu, to excite all REE. These high XRF energies cannot be efficiently detected by the widely used Si based SDD ED detectors due to their low quantum efficiency for energies higher than 25 keV. An additional difficulty regarding the use of REE K-line excitation is the general lack of instruments able to provide a (sub)micron, monochromatic X-ray beam at the aforementioned high excitation energies. At these high energies maintaining good peak-to-background ratios represents an additional difficulty in the presence of overlapping high intensity (multiple) Compton scatter in case of REE analysis, while at the low energy side of the spectrum an additional background contribution will rise due to Compton escape effects of high energy X-rays in the detector. Therefore, elements with characteristic radiation in either region experience increased limits of detection (LOD) due to the increase in background signal. LOD achieved for a NIST standard with K-line based REE analysis (0.5 – 1 ppm; acquisition time 1000 sec) are comparable with the higher limits achieved in this work.²¹ Although irradiating diamond inclusions with a high energetic incident beam will induce a considerably amount of scatter radiation, which will be entirely detected by the HPGe detector because the high XRF energies are incompatible with polycapillary based confocal XRF-analysis, which is often used to reduce scattering effects from geological matrices. With the presented wavelength

Figure 1 a) Setup optimized for wavelength dispersive detection; setup represented by the full-field energy dispersive detector, the aluminum adapter holding the Ge(111) crystal and the sample holder. b) Close up of the sample-adaptor geometry, optimized for detecting characteristic X-rays from the sample. c) Top view of the setup, optimized for energy dispersive detection with a Vortex EM SDD detector. As can be seen the full-field SLcam is moved out of its optimal position and the Vortex EM SDD detector is moved closer.

dispersive (WD) X-ray fluorescence detection method, it is possible to detect the fluorescence L-lines between 4.5 and 7 keV, originating from REE elements with an energy resolution of 18 eV and a sensitivity level of 0.50 ppm. This sensitivity for fluorescent L-lines is a significant improvement compared to similar WD-XRF approaches, combining a flat analyzer crystal with a CCD detector.^{22–24} The characteristic fluorescence X-rays, originating from the sample, are collected under Bragg condition by a Ge(111) analyzer crystal, dispersing the XRF radiation onto the detector chip of a full-field energy dispersive pn-charge-coupled-device (pnCCD) detector, the SLcam²⁵, rendering a spectrum with an energy resolution of 12 eV for the Ti-K α fluorescence line. The strength of this wavelength dispersive detection setup, when compared to existing wavelength dispersive setups,^{26–32} is a consequence of the use of an energy dispersive 2D full-field detector; by using the energy dispersive character of the SLcam higher order diffractions or diffractions from other crystal planes of the analyzer crystal are separated in the energy domain from the first order diffractions resulting in an interference free, low-background detection yielding considerably higher sensitivity than that reported earlier. A similar setup was described by Radtke et al., where the SLcam is combined with a flat LiF(200) analyzer crystal.³³ However in this approach the sample is illuminated by a pencil X-ray beam, and spatially resolved information is obtained after the implementation of an X-ray optic in front of the SLcam, rendering this method selective for only one narrow energy bandwidth at a time on a microscale.

Detecting and quantifying REE patterns is of vital importance in understanding various geological processes,^{34–36} like the evolution of meteoritic materials^{36,37} and to obtain information about the role of deep Earth processes regarding the global carbon and fluid cycle.³⁸ The wavelength dispersive detection technique is tested by measuring inclusions trapped in so-called super-deep natural diamonds.^{18,39,40}

Such inclusions may include a collection of high-density fluids, high-pressure minerals and even small rock fragments, which are trapped within the diamond during its growth. Because the inclusions are shielded from the reactive mantle environment during the transport of the diamond towards the surface, the elemental composition and structure of the

minerals is preserved, providing us the opportunity to study the Earth's mantle to depths reaching even the lower mantle (>670 km).⁴¹ Recently an inclusion of hydrous ringwoodite trapped in a super-deep Juina diamond has been found representing the first ever detected carrier of a hydrous component from one of Earth's most important depth regions, the transition zone (TZ).¹⁸ Combined with recent detailed geophysical studies of the Earth's mantle beneath North America it has been demonstrated that high amounts of fluids exist within the TZ and the upper part of the lower mantle. The nature and origin of this hydrous reservoir, which contains water at least the amount of today's surface oceans, is still unknown. The study of the REE content and pattern will help to better decipher its geological history.

Figure 2 Top: Schematic top view of the working principle of the wavelength dispersive detection technique. The X-rays dispersed by the crystal are energy specific. D and θ_0 (Eq. 2) are indicated. Bottom: The Al adapter to mount the crystal a) back view with the exit aperture towards the pnCCD chip. b) front view with entrance aperture c) top view with inserted Ge(111) crystal.

MATERIALS AND METHODS

The wavelength dispersive detection method (Fig. 1; Fig. 2a) is based on the use of a Ge(111) analyzer crystal built into a high purity Al adapter and an energy dispersive full-field pnCCD detector, the SLcam. A Vortex EM SDD detector with an added polycapillary optic was used for energy dispersive confocal-XRF measurements.

P06 Beamline.⁴² The characterization and testing experiments of the technique were performed at the microprobe end station of beamline P06 at PETRA III, DESY, Hamburg, Germany. For the experiment the undulator beam was set to 10.8 keV by a multilayer monochromator with an energy bandpass of $2 \times 10^{-2} \Delta E/E$. The beam was focussed by Kirkpatrick-Baez mirrors (JTEC, Japan) to 1×1 micrometer at the sample position at a flux of 1×10^{11} ph/s as determined by knife-edge scans and a calibrated Si pin diode.

Analyzer Crystal. The analyzer crystal is a flat symmetrically cut single crystal Ge(111) crystal, purchased from Saint-Gobain Crystals, having dimensions of 36 x 30 mm (HxW), with a thickness of 2 mm. Ge(111) has a d-spacing value of 3.2664 Å. The Ge(111) crystal does not diffract even order spectral lines, which is an advantage when used in wavelength dispersive XRF spectrometry, where typically only the first order diffraction signals are of interest. The Ge(111) analyzer crystal is positioned in an in-house developed and manufactured high purity aluminum adapter (Fig. 2b) under an angle of 69° with respect to the detector plane. This adapter has an optimal geometry to detect incoming fluorescent X-rays in the energy range from 4.5 to 7 keV, which is ideal when detecting lanthanide X-ray emission L-lines.

Based on Bragg's law (Eq. 1), the angles required to diffract at energies of 4, 6, and 8 keV, or respectively a wavelength of 3.098, 2.065, and 1.549 Å, are 28.308°, 18.429°, and 13.716° with respect to the Ge(111) crystal surface.

$$2d \sin\theta = n\lambda \quad (1)$$

The adapter is designed in such a way, that the Ge(111) crystal disperses the incident XRF radiation originating from a point source at the sample position over the detector chip with a Bragg-angle range of 13.7° to 28.3°, corresponding to the desired energy range of detection.

The Ge(111) analyzer crystal disperses the XRF radiation corresponding to the following energy calibration over the central row of pixels on the chip:

$$E = E_0 \frac{\sqrt{1 + \left(\frac{x}{D}\right)^2}}{1 + \frac{x}{D} \cdot \cot(\theta_0)} \quad (2)$$

Where $E_0 = 5.293$ keV, the selected energy corresponding to the ray impinging on the center of the pnCCD chip, D is the total pathlength of the central ray connecting the illuminated spot on the sample and the center of the pnCCD chip (estimated to be 55 to 60 mm), x is the distance along the horizontal axis of the chip measured from its center and θ_0 is the glancing (Bragg) angle of the central ray, calculated to be 21°. (D and θ_0 indicated on Fig. 2)

The energy resolution as a function of distance measured from the chip center along the central row of pixels can be written as:

$$\Delta E = \left| \frac{\partial E}{\partial x} \right| \Delta x \quad (3)$$

Where Δx is the horizontal pixel size (48 μm) of the chip and:

$$\frac{\partial E}{\partial x} = \frac{E_0}{D\sqrt{1 + (x/D)^2}} \frac{x/D - \cot(\theta_0)}{(1 + x/D \cdot \cot(\theta_0))^2} \quad (4)$$

As calculated by Eq. 4, the theoretical energy resolution along the chip varies from approximately 26 eV at 8 keV ($x = -6.35$ mm, first column of the chip) to 7 eV at 4 keV ($x = 6.35$ mm, last column). This ideal energy resolution can only be achieved if the size of the analyzed heterogeneity is comparable to the CCD pixel size measured along the direction of the exciting beam. If the penetration depth of X-rays within the inclusion is significantly larger than the pixel size, the diffraction lines will be broadened on the pnCCD chip proportionally to the sampled information depth within the excited sample at a given incident energy, resulting in the reduction of the achievable energy resolution. This is a modification to the point source assumption made for this derivation.

The columns, or more correctly, the arcs formed by the pixels representing a given diffraction angle (corresponding to an energy channel) subtend a (horizontal) angle of acceptance of approximately 0.87 mrad, which is considerably larger than that of the Darwin width of the Ge(111) crystal, varying from 0.072 to 0.175 mrad in the energy range of 4.5 to 7 keV. This results in the reduction of the average solid angle subtended by the pnCCD pixels representing a given energy channel of 2×10^{-4} sr by a factor of 5 - 12, depending on the energy, limiting the achievable sensitivity of the method based on the use of Ge(111). A change of crystal or an increase of the crystal mosaicity could improve the sensitivity of this technique.

Full-Field pnCCD Detector.²⁵ The diffracted X-rays are detected by a 2D energy dispersive back-illuminated detector chip of the SLcam, a full-field pnCCD detector. The pnCCD chip has 528 x 264 pixels of 48 x 48 μm pixel size, where only the central 264 x 264 pixels are in operation for the detection of X-rays, the left and right border pixels function for sideward depletion of the high resistivity silicon (dark frame storage). A fully radiated sensitive thickness of 450 μm results in a 95% quantum efficiency between 3 and 10 keV.²⁵ The detector has a frame rate of 400 Hz, a pixel readout speed of 28 Mpixel/s and a charge transfer efficiency of > 0.99995 . The pnCCD chip is cooled down to a temperature of -25 °C by aid of water-assisted Peltier cooling and is encased in a vacuum housing with a protective 50 μm thick beryllium window situated 6.2 mm from the detector chip.

Measurement. The region of interest of the sample is determined by scanning in a traditional micro-XRF approach using an (confocal) energy dispersive detection method by a Vortex EM SDD detector. After performing visualization of the elemental distributions and locating the points of interest to be analyzed, the ED detector is moved out and the SLcam with the Ge(111) crystal is moved into place; both detectors

Figure 3 a) dispersed XRF line-spectrum as detected on the chip of the SLcam with fixed 2 - 20 keV energy window of detection b) line-spectrum as detected by the SLcam chip with a fixed energy window spanning over 4.5 - 7 keV c) Post-processing with a moving energy window across the relevant range of 4.5 - 7 keV, demonstrating the removal of interfering diffraction lines. d) Wavelength dispersive result after the line spectrum in c is integrated e) Energy dispersive result, acquired for 600 s, and comparison of detected range and energy resolution.

reproducible positioning of the detectors. During these experiments the ED and WD techniques were used sequentially on a given sample position due to geometrical limitations posed mainly by the extended dimensions of the SLcam detector head and due to the large difference in acquisition times required by the two detection techniques, rendering simultaneous detection impractical. The WD detection system is positioned at a (central) angle of detection of approximately 110° with respect to the incoming photon beam in the plane of polarization, reducing the detected scatter background as much as possible given the boundary conditions defined by the detector geometry. To fit the geometry of the setup, the additional confocal ED-XRF detector is positioned at an angle of 45° with respect to the incoming beam. A given point of interest on the sample is analyzed using an acquisition time of 3600 s (or longer in case of too low count rate) in WD detection mode and the resulting raw data is processed using a dedicated in house developed software based on Interactive Data Language (IDL, Harris Geospatial Solutions). A 2D line spectrum is obtained (see Fig. 3a), through visualization of the pixel intensities (counts) on the 2D SLcam chip for the full exposure time. The energy range visualized by the detector chip corresponds to 4.5 - 7 keV, this can be seen as the X-axis on Fig 3a-d. The energy dispersive pnCCD detector has the ability to tune the energy range detected on the chip. This property can be used to optimize the detected scatter background and eliminate interfering diffraction orders or diffractions originating from other crystal-planes. The result when the corresponding 4.5 - 7 keV range is selected from the full 2 - 20 keV range of the SLcam can be observed in Fig 3b. It can be seen that there are still some interfering lines present, although the angled lines appearing in the top left corner of the image correspond to higher energy dispersed X-rays. To solve this inconvenience it is possible to derive the diffraction lines with a so-called moving energy range on the SLcam when post-processing the data: when a diffraction line is derived, the integrated energy range of the SLcam is set to the corresponding energy of the diffraction line (± 300 eV).

This procedure results in Fig 3c. Finally, a vertical integration of the 2D dispersion image (Fig. 3c) as a function of the XRF dispersion angle is performed, the WD XRF spectrum is obtained (Fig. 3d) and the resulting spectrum is calibrated. The XRF lines are subsequently identified and the background and peak shapes are fitted with a linear and a Gaussian or Lorentzian function, respectively, based on a nonlinear least-squares fitting procedure. This procedure effectively removes the background contribution and eliminates peak overlap. The raw 2D pnCCD spectrum in the energy range of 2 - 20 keV, the detected 2D spectrum in the energy window of 4.5 - 7 keV and a comparison with an energy dispersive spectrum can be seen in Fig. 3. The additional energy dispersive XRF mapping and point measurements were processed using dedicated software packages based on AXIL⁴³ and microxrf2⁴⁴, converting the raw spectra into elemental intensities using a nonlinear least-squares fitting procedure, correcting for the background and eliminating peak overlap.

Materials. The calibration and characterization of the WD-XRF method was performed using different types of reference materials. A pellet pressed from lanthanides incorporated in an Y_2O_3 -matrix with cellulose (1 w% $La(NO_3)_3 \cdot 6H_2O$,

are mounted on high precision XYZ-motor stages, which allow

Figure 4 a) overview of the SL09 diamond, black graphite coating is due to the polishing of the diamond. b) Close-ups of the investigated inclusion. c) Overview of the diamond. The reported inclusion is indicated in red.

$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in an $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ matrix (all products from Sigma Aldrich)), a 100 μm thin MPI-DING (Max-Planck Institute-Dingwell)

Atho-G⁴⁵ and a NIST SRM 611 (1 mm and 100 μm). The lanthanum, europium, gadolinium, erbium- Y_2O_3 powder pellet is employed for straightforward energy calibration. A thin (100 μm) NIST 611 standards was used in order to avoid the potential broadening of detected WD XRF-lines, causing the deterioration of energy resolution, which can in some cases be observed for thicker samples as a result of the finite penetration depth. LOD values were calculated based on a NIST SRM 611 (all elements have a concentration approximately 500 ppm and are embedded in a Si-, Ca-, Na-, and Al-oxide matrix), which was measured for 1 hour. The applicability of the spectrometer to analyse geological samples was demonstrated using measurements on inclusions in deep Earth diamonds: inclusions in Sao Luis (SL) and Juina (J) diamonds, originating from alluvial deposits of the Sao Luis river and the Juina region, located in the northwest Mato

Grosso area in Brazil, South America.^{46–48} This region lies within the Rio Negro-Juruena geochronological province (RNJP) which resamples the 1.8 - 1.55 Ga old rock unit of the Amazonian craton. The bedrock of the RNJP is composed almost completely of granite-gneisses and granitoids with granodioritic and tonalitic composition.⁴⁹ The Juinea region borders the northern part of overlying Phanerozoic sediments, leading to complex assemblages of volcanoclastic deposits.⁵⁰ The Kimberlite magmatism in the Juinea region was dated at 92 - 95 Ma with U - Pb ages of zircon grains derived from kimberlitic host rocks.⁵⁰ The intrusive and volcanoclastic kimberlitic rocks, as well as the younger diamondiferous sediment units are believed to be the source of the alluvial diamonds,⁵⁰ however it is not clear if the yet known localities are the origin of all alluvial diamonds recovered in this region. The reported sample is an SL09 (Sao Luis) diamond, which is approximately 4.5 mm high, 2 mm deep, and 3 mm wide. The investigated inclusion is situated in a polished part of the diamond, which can be observed in Fig. 4. To obtain a sufficient yield of X-rays escaping the diamond, it is of high importance that the inclusion is as close to the surface as possible.

RESULTS AND DISCUSSION

Analytical Characterisation. The obtained spectrum from NIST SRM 611 is shown in Fig. 5. In the range of 4.5 up to 7 keV, 34 different emission lines could be distinguished, which are indicated in the table next to the spectrum. The LOD values are calculated according to Eq. 5, where for a given element i , $I_{b,i}$ and $I_{p,i}$ represent the intensity of the background and the peak, respectively, and C_i corresponds to the certified concentration value in parts per million by weight. The achieved LOD are shown in Fig. 5c, reaching values of 0.05 and 0.40 ppm for fluorescent K- and L-lines respectively.⁵¹

$$\frac{3 \cdot \sqrt{I_{b,i}}}{I_{p,i}} \cdot C_i = LOD_i \quad (5)$$

Figure 5 a) The integrated and fitted NIST SRM 611 XRF spectrum, with indicated lines, identified in the columns next to it (b). The numbers of the characteristic K-lines have been indicated with a red circle. c) the calculated LOD obtained from the measured spectrum calculated for both post-processing modes. LOD are shown under the graph, ranging between 0.05 and 0.68 ppm for the fixed energy window 4.5 to 7 keV and between 0.03 and 0.42 ppm for the moving energy range, both with an acquisition time of 1 hour. Errors are 3 sigma and were calculated using Poisson counting statistics.

Figure 6 Results of the ED-XRF scan. a) Representation of the elemental distribution (intensity in counts) in the SL09 diamond inclusion. The inclusion is characterized by calcium, manganese, and iron and shows 4 hotspots rich in titanium, chromium, cerium and neodymium. A pattern of high intensity spots in argon was detected; these spots originate from the Ar ion-beam used to polish the diamond. b) RGB-image of the inclusion picturing iron (red), calcium (green), and titanium (blue). c) Titanium hotspots in the diamond inclusion.

The width of the background under the peak has been calculated based on a $\pm 3 \sigma$ confidence interval, depending on the selected peak shape (Gaussian or Lorentzian) which translates in the case of $\text{La-L}_3\text{M}_5$ and $\text{Dy-L}_3\text{M}_5$ to a background width of 27.68 and 43.29 eV respectively in the NIST SRM 611 WD-XRF spectrum. For a complex matrix the LOD are strongly dependent on the background surrounding the region of interest. The results obtained in this paper represent a significant improvement compared to similar WD-XRF approaches, combining a flat analyzer crystal with a CCD detector.^{22–24,33} The mentioned setups mostly focus on the detection of K-lines, which have a higher elemental yield using an excitation energy of 10.8 keV and consequently also a lower LOD compared to L-lines. The energy resolution was calculated as the full width at half maximum (FWHM) for different XRF-lines for the NIST SRM 611 and for an inclusion spectrum (Ti hotspot 4). In the NIST spectrum the energy resolution for $\text{Cr-K}\alpha_1$, $\text{Mn-K}\alpha_1$, and $\text{Cr-K}\beta_1$ is 32.1, 31.8, and 22.2 eV, respectively. In the Ti hotspot spectrum the

$\text{Ti-K}\beta_1$ and $\text{Nd-L}_2\text{M}_4$ lines have an energy resolution of 11.5 and 18.5 eV respectively.

Demonstration of REE analysis of inclusions in diamond.

To visualize the region of interest in the diamond, the inclusion is positioned into the focal spot by means of an optical microscope and subsequently scanned in the YZ directions across the beam by confocal X-ray fluorescence. In the example shown in Fig. 6 the measurement allowed to image an area of 200 by 250 μm including the inclusion in a non-destructive manner. The elemental distributions of the elements of interest are presented in Fig. 6a together with a red-green-blue image of the complementary regions exhibiting considerable amounts of calcium, iron, and titanium (Fig. 6b). Although preliminary Raman-spectroscopic work indicate that the studied inclusion mainly consists of a single CaSiO_3 -walstromite phase⁵², the lower part of the Ca region of the inclusion shows a lower intensity. This might result from different mineral structures in this region

Figure 7 a) An energy dispersive spectrum of the titanium hotspot 4, acquisition time of 600 s (Fig. 6). Visible peaks indicated are argon, calcium, titanium, cerium, neodymium, chromium, promethium, europium, gadolinium, iron, dysprosium and zinc. b) The region between 4.5 – 7 keV is represented by the wavelength dispersive detection measurement of the same spot. Indicated peaks are identified in the columns next to the spectrum. Some signals could not be identified, their origin is unknown.

or more likely as a result from the interaction of a complex shape of the inclusions at different depths. This shift in intensity is also slightly visible in the Mn and Fe map. The highlighted Ti hotspots are also located in the Ca region, which could indicate yet another mineral phase. Additionally an Ar rich region was detected on the surface of the diamond, which is the result of an argon ion beam used for previously performed polishing. After the points of interest are identified (see Fig. 6c) point measurements are performed using both the energy dispersive Vortex EM SDD detector and the wavelength dispersive detection setup. The points of interest were measured for 600 s and for 3600 s in the energy dispersive and wavelength dispersive setup respectively and the resulting point scan spectra for Ti hotspot 4 can be seen in Fig. 7. The differences in acquisition time compensate for the different efficiencies of both detection methods and the long measurement time for the WD-XRF method is necessary to obtain sufficient counting statistics which are consequently mandatory to quantify major, minor and trace elements in the point of interest. One can observe that the wavelength dispersive setup achieves high energy resolution, which is clearly demonstrated by the large number of distinguishable X-ray fluorescence lines. It is definitely possible to separate the abundant fluorescence K-lines from the lanthanide L-lines, which is not the case when conventionally obtained energy dispersive spectra are examined. Although in some cases it is possible to identify some L-lines based on the energy dispersive signals, it is essentially impossible to deconvolute a complex ED-XRF spectrum to the various XRF signals originating from the different constituent elements. In addition to this, the LOD in the ED spectra are higher due to the excessive amount of background produced by the large amount of detected but to a large extent indistinguishable L-lines.

Quantification. The obtained wavelength dispersive results from the point measurements were quantified using a fundamental parameter based^{53–55} quantification method with Poisson counting statistics⁵⁶ based error handling. Quantitative results were corrected for X-ray absorption due to the diamond matrix. The thickness of the diamond between the incoming X-ray beam and the inclusion was estimated using computed tomography data of the SL09 diamond and the inclusion was polished to the surface resulting in a free exit path for the characteristic X-rays. The obtained quantitative values for the detected elemental concentrations in the titanium rich positions (designated as hotspot 2, 3, and 4, (Fig. 6c)) are given in table 1 together with the corresponding absolute errors. Titanium hotspot 1 did not show any REEs above the detection limit. It can be seen that the low and mid REEs are higher in concentrations compared to the high REEs. After normalization with known REE values from Earth's crust, the REE pattern shows a negative Dy anomaly, which could indicate the presence of the mineral Dolomierite.⁵⁷

CONCLUSION

Based on the presented work, it can be concluded that high sensitivity REE detection was achieved with LOD lower than 0.50 ppm for characteristic L-lines and a factor 10 lower for detected K-lines. The wavelength dispersive detection method can be considered as a valuable addition to confocal XRF

measurements when high sensitivity measurements with a high energy resolution are required.

Table 1. Quantified results for Ti hotspot 2, 3, and 4 in ppm $\pm$ absolute error. ND: not detected

Element	Hotspot 2	Hotspot 3	Hotspot 4
Ti	216.7 $\pm$ 7.4	1337.1 $\pm$ 40.2	1888.0 $\pm$ 56.7
V	10.2 $\pm$ 1.0	108.2 $\pm$ 10.8	21.8 $\pm$ 2.2
Cr	13.5 $\pm$ 1.1	19.1 $\pm$ 1.5	77.2 $\pm$ 6.2
Mn	41.7 $\pm$ 7.8	ND	5.7 $\pm$ 0.4
Fe	29.2 $\pm$ 1.4	ND	8.7 $\pm$ 0.4
La	38.2 $\pm$ 6.1	171.7 $\pm$ 27.5	203.7 $\pm$ 39.7
Ce	101.7 $\pm$ 12.8	450.1 $\pm$ 57.1	571.4 $\pm$ 97.2
Pr	20.8 $\pm$ 3.4	74.2 $\pm$ 22.3	37.1 $\pm$ 3.4
Nd	125.3 $\pm$ 10.9	248.1 $\pm$ 22.3	299.6 $\pm$ 47.9
Sm	34.0 $\pm$ 1.6	ND	61.4 $\pm$ 3.1
Eu	ND	ND	13.1 $\pm$ 1.5
Gd	32.9 $\pm$ 2.0	ND	87.9 $\pm$ 5.3
Tb	ND	ND	14.3 $\pm$ 0.7
Dy	8.4 $\pm$ 0.4	ND	10.9 $\pm$ 0.4
Ho	2.4 $\pm$ 0.1	ND	3.4 $\pm$ 0.2

The strengths of the presented technique are clearly demonstrated by the performed experiments; a wide range of energies could be detected simultaneously (4.5 - 7 keV) by making use of a single detector position and a fixed analyzer crystal geometry. The scatter background and undesirable signals from other crystal planes or different diffraction orders could be effectively filtered out by making use of the energy dispersive ability of the SLcam, resulting in unambiguous high sensitivity and energy resolution XRF spectra in the energy range relevant to the detection of REE L-lines. Rare diamond samples were used to demonstrate the working principle of this technique, showing the potential of the approach to obtain highly valuable information on the concentration of REEs in geological sample material.

AUTHOR INFORMATION

Corresponding Author

* Email: ella.depauw@ugent.be

ORCID

Ella De Pauw: 0000-0001-7490-9573

ACKNOWLEDGMENT

The authors acknowledge the financial support by (1) Funds for Scientific Research Flanders (FWO), Belgium, Grant nr. G099817N and G1502819N, (2) Ghent University, Geconcerteerde Onderzoeksacties BOF 2017, and (3) DFG, Grant BR2015/26-1. Parts of this research were carried out at the light source PETRA-III at DESY, a member of the Helmholtz Association (HGF), Germany. The research leading to this result has been supported by the project CALIPSOplus

REFERENCES

- (1) Squadrone, S.; Brizio, P.; Stella, C.; Favaro, L.; Rugna, C. Da; Florio, D.; Gridelli, S.; Abete, M. C. Feathers of Humboldt Penguin Are Suitable Bioindicators of Rare Earth Elements. *Sci. Total Environ.* **2019**, *678*, 627–631.
- (2) Jeans, C. V.; Wray, D. S.; Williams, C. T. Redox Conditions in the Late Cretaceous Chalk Sea: The Possible Use of Cerium Anomalies as Palaeoredox Indicators in the Cenomanian and Turonian Chalk of England. *Acta Geol. Pol.* **2015**, *65* (3), 345–366. <https://doi.org/10.1515/agp-2015-0015>.
- (3) Gueriau, P.; Mocuta, C.; Bertrand, L. Cerium Anomaly at Microscale in Fossils. *Anal. Chem.* **2015**, *87* (17), 8827–8836. <https://doi.org/10.1021/acs.analchem.5b01820>.
- (4) Kang, J.; Jeong, K.-S.; Cho, J. H.; Lee, J. H.; Jang, S.; Kim, S. R. Post-Depositional Redistribution Processes and Their Effects on Middle Rare Earth Element Precipitation and the Cerium Anomaly in Sediments in the South Korea Plateau, East Sea. *J. Asian Earth Sci.* **2014**, *82*, 66–79. <https://doi.org/10.1016/j.jseas.2013.11.019>.
- (5) Liao, X.; Hu, Z.; Luo, T.; Zhang, W.; Liu, Y.; Zong, K.; Zhou, L.; Zhang, J. Determination of Major and Trace Elements in Geological Samples by Laser Ablation Solution Sampling-Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* **2019**, *34* (6), 1126–1134. <https://doi.org/10.1039/c9ja00027e>.
- (6) Fadel, A.; Žigaitė, Ž.; Blom, H.; Pérez-Huerta, A.; Jeffries, T.; Märss, T.; Ahlberg, P. E. Palaeoenvironmental Signatures Revealed from Rare Earth Element (REE) Compositions of Vertebrate Microremains of the Vesiku Bone Bed (Homerian, Wenlock), Saaremaa Island, Estonia. *Est. J. Earth Sci.* **2015**, *64* (1), 36. <https://doi.org/10.3176/earth.2015.07>.
- (7) in Stromatolites---I. Evidence that Modern Terrestrial Stromatolites Fractionate Rare Earth Elements During Incorporation from Ambient Waters, R. E. E. Karen H. Johannesson and Katherine Telfeyan and Darren A. Chevis and Brad E. Rosenheim and Matthew I. Leybourne. *Evol. Archean Crust Early Life, Mod. Approaches Solid Earth Sci.* **2014**, *7*, 385–411.
- (8) Ma, Q.; Yang, M.; Zhao, H.; Evans, N. J.; Chu, Z.-Y.; Xie, L.-W.; Huang, C.; Zhao, Z.-D.; Yang, Y.-H. Accurate and Precise Determination of Lu and Hf Contents and Hf Isotopic Composition at the Sub-Nanogram Level in Geological Samples Using MC-ICP-MS. *J. Anal. At. Spectrom.* **2019**, *34* (6), 1256–1262. <https://doi.org/10.1039/c9ja00034h>.
- (9) Zybinsky, A. M.; Kolotov, V. P.; Karandashev, V. K.; Kordyukov, S. V. Determination of Rare-Earth and Accompanying Elements in Niobium-Rare-Earth Ores by Inductively Coupled Plasma Atomic Emission Spectrometry Using Model Calibration and a Mathematical Approach for Resolving Spectral Interferences. *J. Anal. Chem.* **2019**, *74* (3), 213–225. <https://doi.org/10.1134/s1061934819030146>.
- (10) Carmona, A.; Zogzas, C. E.; Roudeau, S.; Porcaro, F.; Garrevoet, J.; Spiers, K.; Salomé, M.; Cloetens, P.; Mukhopadhy, S.; Ortega, R. SLC30A10 Mutation Involved in Parkinsonism Results in Manganese Accumulation within Nanovesicles of the Golgi Apparatus. *ACS Chem. Neurosci.* **2019**, *10*, 599–609.
- (11) De Samber, B.; Meul, E.; Laforce, B.; De Paepe, B.; Smet, J.; De Bruyne, M.; De Rycke, R.; Bohic, S.; Cloetens, P.; Van Coster, R.; et al. Nanoscopic X-Ray Fluorescence Imaging and Quantification of Intracellular Key-Elements in Cryofrozen Friedreich's Ataxia Fibroblasts. *PLoS One* **2018**, *13* (1), 1–24. <https://doi.org/10.1371/journal.pone.0190495>.
- (12) Schreiber, I.; Hesse, B.; Seim, C.; Castillo-Michel, H.; Villanova, J.; Laux, P.; Dreier, N.; Penning, R.; Tucoulou, R.; Cotte, M.; et al. Synchrotron-Based μ -XRF Mapping and μ -FTIR Microscopy Enable to Look into the Fate and Effects of Tattoo Pigments in Human Skin. *Sci. Rep.* **2017**, *7* (1), 11395.
- (13) Bourgeois, D.; Burt-Pichat, B.; Goff, X. Le; Garrevoet, J.; Tack, P.; Falkenberg, G.; Hoorebeke, L. Van; Vincze, L.; Denecke, M. A.; Meyer, D.; et al. Micro-Distribution of Uranium in Bone after Contamination: New Insight into Its Mechanism of Accumulation into Bone Tissue. *Anal. Bioanal. Chem.* **2015**, *407* (22), 6619–6625.
- (14) Ruiz-Martinez, J.; Beale, A. M.; Deka, U.; O'Brien, M. G.; Quinn, P. D.; Mosselmans, J. F. W.; Weckhuysen, B. M. Correlating Metal Poisoning with Zeolite Deactivation in an Individual Catalyst Particle by Chemical and Phase-Sensitive X-Ray Microscopy. *Angew. Chemie* **2013**, *125*, 6099–6103.
- (15) Bertrand, L.; Robinet, L.; Thoury, M.; Janssens, K.; Cohen, S. X.; Schöder, S. Cultural Heritage and Archaeology Materials Studied by Synchrotron Spectroscopy and Imaging. *Appl. Phys. A Mater. Sci. Process.* **2012**, *106*, 377–396.
- (16) Monico, L.; Janssens, K.; Hendriks, E.; Vanmeert, F.; der Snickt, G. Van; Cotte, M.; Falkenberg, G.; Brunetti, B. G.; Miliani, C. Evidence for Degradation of the Chrome Yellows in Van Gogh's Sunflowers: A Study Using Non Invasive In Situ Methods and Synchrotron-Radiation-Based X-Ray Techniques. *Angew. Chemie* **2015**, *54* (47), 13923–13927.
- (17) Curado, J. F.; Radtke, M.; Buzanich, G.; Reinholz, U.; Rieseemeier, H.; Guttler, R. A. S.; Rizzutto, M. A. μ -SRXRF Characterization of Brazilian Emeralds. *J. Phys. Conf. Ser.* **2014**, *499*, 12016.
- (18) Pearson, D. G.; Brenker, F. E.; Nestola, F.; McNeill, J. C. R.; Nasdala, L.; Hutchison, M. T.; Matveev, S.; Mather, K.; Silversmit, G.; Schmitz, S.; et al. A Hydrous Mantle Transition Zone Indicated by Ringwoodite Included within Diamond. *Nature* **2014**, *507*, 221–224.
- (19) Westphal, A. J.; Stroud, R. M.; Bechtel, H. A.; Brenker, F. E.; Butterworth, A. L.; Flynn, G. J.; Frank, D. R.; Gainsforth, Z.; Hillier, J. K.; Postberg, F.; et al. Evidence for Interstellar Origin of Seven Dust Particles Collected by the Stardust Spacecraft. *Science* (80-.). **2014**, *345* (6198), 786–791.
- (20) Garrevoet, J.; Vekemans, B.; Bauters, S.; Demey, A.; Vincze, L. Development and Applications of a Laboratory Micro X-ray Fluorescence (MXRF) Spectrometer Using Monochromatic Excitation for Quantitative Elemental Analysis. *Anal. Chem.* **2015**, *87*, 6544–6552.
- (21) Vincze, L.; Janssens, K.; Vekemans, B.; Adams, F. Monte Carlo Simulation of X-Ray Fluorescence Spectra: Part 4. Photon Scattering at High X-Ray Energies. *Spectrochim. Acta Part B At. Spectrosc.* **1999**, *54*, 1711–1722.
- (22) Tesaro, P.; Mando, P. A.; Parrini, G.; Pecchioli, A.; Sona, P. A Compact Flat-Crystal X-Ray Spectrometer for External Beam PIXE Measurements. *Nucl. Instruments Methods Phys. Res. B* **1995**, *108*, 197–204.
- (23) SATO, Y.; HAYAKAWA, S.; NISHIDA, Y.; HAMAMOTO, A.; SUZUKI, M.; HIROKAWA, T. Development of a Wavelength Dispersive X-Ray Fluorescence Spectrometer Using an X-Ray CCD. *Anal. Sci.* **2001**, *17*, 1201–1203.
- (24) Mihalić, I. B.; Fazinić, S.; Tadić, T.; Cosic, D.; Jakšić, M. Study of Ion Beam Induced Chemical Effects in Silicon with a Downsized High Resolution X-Ray Spectrometer for Use with Focused Ion Beams. *J. Anal. At. Spectrom.* **2016**, *31* (11), 2293–2304. <https://doi.org/10.1039/c6ja00276e>.
- (25) Scharf, O.; Ihle, S.; Ordavo, I.; Arkadiev, V.; Bjeoumikhov, A.; Bjeoumikhova, S.; Buzanich, G.; Gubzhokov, R.; Günther, A.; Hartmann, R.; et al. Compact PnCCD-Based X-Ray Camera with High Spatial and Energy Resolution: A Color X-Ray Camera. *Anal. Chem.* **2011**, *83*, 2532–2538.
- (26) Kvashnina, K. O.; Scheinost, A. C. A Johann-Type X-Ray Emission Spectrometer at the Rossendorf Beamline. *J. Synchrotron Radiat.* **2016**, *23* (3), 836–841. <https://doi.org/10.1107/S1600577516004483>.
- (27) Krishna, A. K.; Murthy, N. N.; Govil, P. K. Multielement Analysis of Soils by Wavelength-Dispersive X-Ray Fluorescence Spectrometry. *At. Spectrom.* **2007**, *28* (6), 202–214.
- (28) Margu'í, E.; Hidalgo, M.; Queralt, I. Multielemental Fast Analysis of Vegetation Samples by Wavelength Dispersive X-Ray Fluorescence Spectrometry: Possibilities and Drawbacks. *Spectrochim. Acta Part B At. Spectrosc.* **2005**, *60* (9–10), 1363–

1372. <https://doi.org/10.1016/j.sab.2005.08.004>.
- (29) Sakurai, K.; Eba, H.; Inoue, K.; Yagi, N. Wavelength-Dispersive Total-Reflection x-Ray Fluorescence with an Efficient Johansson Spectrometer and an Undulator x-Ray Source: Detection of 10-16 g-Level Trace Metals. *Anal. Chem.* **2002**, *74* (17), 4532–4535. <https://doi.org/10.1021/ac025720y>.
- (30) Longerich, H. P. Analysis of Pressed Pellets of Geological Samples Using Wavelength-Dispersive x-Ray Fluorescence Spectrometry. *X-ray Spectrom.* **1995**, *24* (3), 123–136.
- (31) Culhane, J. L.; Hiei, E.; Doschek, G. A.; Cruise, A. M.; Ogawara, Y.; Uchida, Y.; Bentley, R. D.; Brown, C. M.; Lang, J.; Watanabe, T.; et al. The Bragg Crystal Spectrometer for SOLAR-A. *Sol. Phys.* **1991**, *136* (1), 89–104. <https://doi.org/10.1007/bf00151696>.
- (32) Szlachetko, J.; Cotte, M.; Morse, J.; Salomé, M.; Jagodzinski, P.; Dousse, J. C.; Hozzowska, J.; Kayser, Y.; Susini, J. Wavelength-Dispersive Spectrometer for X-Ray Microfluorescence Analysis at the X-Ray Microscopy Beamline ID21 (ESRF). *J. Synchrotron Radiat.* **2010**, *17* (3), 400–408. <https://doi.org/10.1107/S0909049510010691>.
- (33) Radtke, M.; Buzanich, G.; Guilherme, A.; Reinholz, U.; Riesemeier, H.; Scharf, O.; Scholz, P.; Guerra, M. F. Double Dispersive X-Ray Fluorescence (D2XRF) Based on an Energy Dispersive PnCCD Detector for the Detection of Platinum in Gold. *Microchem. J.* **2016**, *125*, 56–61.
- (34) Fadel, A.; Zigaite, Z.; Blom, H.; Perez-Huerta, A.; Jeffries, T.; Marss, T.; Ahlberg, P. E. Palaeoenvironmental Signatures Revealed from Rare Earth Element (REE) Compositions of Vertebrate Microremains of the Vesiku Bone Bed (Homerian, Wenlock), Saaremaa Island, Estonia. *Est. J. Earth Sci.* **2015**, *64* (1), 36–41.
- (35) Emsbo, P.; McLaughlin, P. I.; du Bray, E. A.; Anderson, E. D.; Vandenbroucke, T. R. A.; Zielinski, R. A. Rare Earth and Critical Elements in Ore Deposits: Rare Earth Elements in Sedimentary Phosphorite Deposits: A Global Assessment. *Rev. Econ. Geol.* **2016**, *18*, 101–113.
- (36) Drake, M. J.; Boynton, W. V. Partitioning of Rare Earth Elements between Hibernite and Melt and Implications for Nebular Condensation of the Rare Earth Elements. *Meteoritics* **1988**, *23* (1), 75–80. <https://doi.org/10.1111/j.1945-5100.1988.tb00898.x>.
- (37) Kagi, H.; Takahashi, K. Relationship between Positive Cerium Anomaly and Adsorbed Water in Antarctic Lunar Meteorites. *Meteorit. Planet. Sci.* **1998**, *33*, 1033–1040.
- (38) Brenker, F. E.; Vollmer, C.; Vincze, L.; Vekemans, B.; Szymanski, A.; Janssens, K.; Szaloki, I.; Nasdala, L.; Joswig, W.; Kaminsky, F. Carbonates from the Lower Part of Transition Zone or Even the Lower Mantle. *Earth Planet. Sci. Lett.* **2007**, *260*, 1–9.
- (39) Anzolini, C.; Angel, R. J.; Merlini, M.; Derzsi, M.; Tokár, K.; Milani, S.; Krebs, M. Y.; Brenker, F. E.; Nestola, F.; Harris, J. W. Depth of Formation of CaSiO₃-Walsstromite Included in Super-Deep Diamonds. *Lithos* **2016**, *265*, 138–147.
- (40) Harte, B. Diamond Formation in the Deep Mantle: The Record of Mineral Inclusions and Their Distribution in Relation to Mantle Dehydration Zones. *Mineral. Mag.* **2010**, *74* (2), 189–215.
- (41) Brenker, F. E.; Vincze, L.; Vekemans, B.; Nasdala, L.; Stachel, T.; Vollmer, C.; Kersten, M.; Somogyi, A.; Adams, F.; Joswig, W.; et al. Detection of a Ca-Rich Lithology in the Earth's Deep (>300 Km) Convecting Mantle. *Earth Planet. Sci. Lett.* **2005**, *236*, 579–587.
- (42) Schroer, C. G.; Boye, P.; Feldkamp, J. M.; Patommel, J.; Samberg, D.; Schropp, A.; Schwab, A.; Stephan, S.; Falkenberg, G.; Wellenreuther, G.; et al. Hard X-Ray Nanoprobe at Beamline P06 at PETRA III. *Nucl. instruments methods Phys. Res.* **2010**, *616*, 93–97.
- (43) Vekemans, B.; Janssens, K.; Vincze, L.; Adams, F.; Vanespen, P. Analysis of X-Ray-Spectra by Iterative Least-Squares (Axil) - New Developments. *X-ray Spectrom.* **1994**, *23*, 278–285.
- (44) Vekemans, B.; Janssens, K.; Vincze, L.; Aerts, A.; Adams, F.; Hertogen, J. Automated Segmentation of Micro-XRF Image Sets. *X-ray Spectrom.* **1997**, *26*, 333–346.
- (45) Jochum, K. P.; Stoll, B.; Herwig, K.; Willbold, M.; Hofmann, A. W.; Amini, M.; Aarburg, S.; Abouchami, W.; Hellebrand, E.; Mocek, B.; et al. MPI-DING Reference Glasses for in Situ Microanalysis: New Reference Values for Element Concentrations and Isotope Ratios. *Geochemistry, Geophys. Geosystems* **2006**, *7* (2). <https://doi.org/10.1029/2005GC001060>.
- (46) Hayman, P. C.; Kopylova, M. G.; Kaminsky, F. V. Lower Mantle Diamonds from Rio Soriso (Juina Area, Mato Grosso, Brazil). *Contrib. to Mineral. Petrol.* **2005**, *149*, 430–445.
- (47) Kaminsky, F. V.; Zakharchenko, O. D.; Davies, R.; Griffin, W. L.; Khachatryan-Blinova, G. K.; Shiryayev, A. A. Superdeep Diamonds from Juina Area, Mato Grosso State, Brazil. *Contrib. to Mineral. Petrol.* **2001**, *140*, 734–753.
- (48) Harte, B.; Harris, J. W.; Hutchison, M. T.; Watt, G. R.; Wilding, M. C. Lower Mantle Mineral Associations in Diamonds from Sao Luiz, Brazil. *Mantle Petrol. F. Obs. High Press. Exp. A* **1999**, *6*, 125–153.
- (49) Tassinari, C. C. G.; Macambira, M. J. B. Geochronological Provinces of the Amazonian Craton. *Episodes, J. Int. Geosci.* **1999**, *22* (3), 174.
- (50) Heaman, L.; Teixeira, N. A.; Gobbo, L.; Gaspar, J. C. U-Pb Mantle Zircon Ages for Kimberlites from Juina and Paranatinga Provinces, Brazil. *Int. Kimberl. Conf. Ext. Abstr.* **1998**, *7* (1), 322–324.
- (51) Strelt, C.; Wobrauschek, P.; Meirer, F.; Pepponi, G. Synchrotron Radiation Induced TXRF. *J. Anal. At. Spectrom.* **2008**, *23* (6), 792–798. <https://doi.org/10.1039/b719508g>.
- (52) Bindl, L.; Brenker, F.; Nestola, F.; Koch, T.; Prior, D. J.; Lilly, K.; Krot, A. N.; Bizzarro, M.; Xie, X. Discovery of Asimowite, the Fe-Analogue of Wadsleyite, in Shock-Melted Silicate Droplets of the Suizhou L6 and the Quebrada Chimborazo 001 CB3.0 Chondrites. *Am. Mineral.* **2019**.
- (53) Omote, J.; Kohno, H.; Toda, K. X-Ray Fluorescence Analysis Utilizing the Fundamental Parameter Method for the Determination of the Elemental Composition in Plant Samples. *Anal. Chem. Acta* **1995**, *307* (1), 117–126.
- (54) Schoonjans, T.; Silversmit, G.; Vekemans, B.; Schmitz, S.; M., B.; Riekel, C.; Brenker, F.; Vincze, L. Fundamental Parameter Based Quantification Algorithm for Confocal Nano-X-Ray Fluorescence Analysis. *Spectrochim. Acta Part B* **2012**, *67*, 32–42.
- (55) Schoonjans, T.; Brunetti, A.; Golosio, B.; del Rio, M.; Armando Solé, V.; Ferrero, C.; Vincze, L. The Xraylib Library for X-Ray-Matter Interactions. Recent Developments. *Spectrochim. Acta Part B* **2011**, *66*, 776–784.
- (56) Stigler, S. M. Poisson on the Poisson Distribution. *Stat. Probab. Lett.* **1982**, *1*, 33–35.
- (57) Lugli, S.; Morteani, G.; D., B. Petrographic, REE, Fluid Inclusion and Stable Isotope Study of Magnesite from the Upper Triassic Burano Evaporites (Secchia Valley, Northern Apennines): Contributions from Sedimentary, Hydrothermal and Metasomatic Sources. *Miner. Depos.* **2002**, *37* (5), 480–494.