

## Geochemical mapping of drill core samples using a combined LIBS and XRF core scanning system

### Abstract

A LIBS-XRF drill core scanner prototype was developed through a collaboration between Avaatech B.V. and SPECTRAL Industries B.V. This core scanner was tested on a drill core sample of a polymetallic sulphide ore originating from the historic Reiche Zeche mine in Freiberg, Germany. Comparing the LIBS and XRF data showed that both techniques produce similar results for all the major elements of which the sample is composed. Differences between the results of LIBS and XRF were also observed, which were attributed to differences in the size of the measured surface area, signal to noise ratio, and detection limits of LIBS and XRF. Additionally, XRF cannot be used to detect light elements such as oxygen or carbon, while these elements can be detected with LIBS. Another advantage of the LIBS technique is that the data acquisition speed is much higher. This is especially useful when drill core scanning is applied in large mineral exploration projects in which hundreds of kilometers of drill core samples are produced. Drill core sections that are of special interest can be further investigated using XRF, which may provide a higher precision for determining the content of certain trace elements such as arsenic.

### Introduction

Core drilling is often used in the exploration for mineral resources and other geological studies to obtain information about the Earth's subsurface. Analysis of the obtained drill core samples is traditionally performed through visual inspection and laboratory analyses, which are generally time consuming and expensive. Alternatively, sensors can be used to collect mineralogical and geochemical data at much higher speeds and lower costs.

Drill core scanners are systems that use a certain sensor or combination of sensors to gather information on drill core samples. Sensor techniques that are commonly used for drill core scanning are digital imaging and near-infrared (NIR) and short-wavelength infrared (SWIR) hyperspectral imaging. These techniques provide information on a material's visible properties and the occurrence of specific minerals (Thompson et al., 1999; Dalm et al., 2018). However, ore minerals can often not be detected, and no information is provided on the chemical composition of samples. This while the concentration of ore minerals in the rock is usually the most important parameter in mineral exploration studies.

Laser-induced breakdown spectroscopy (LIBS) is a sensor technique that provides information on a material's chemical composition. It utilizes a pulsed laser beam to ablate a small amount of material on the surface of a sample and break it down into a plasma consisting of atoms, ions and free electrons. When the plasma cools down it emits electromagnetic radiation because the free electrons release energy in the form of photons when they fall back into atomic or ionic orbits (Radziemski & Cremers, 2006). The wavelength at which these emissions are produced depends on the specific atom or ion in which the electron is captured, and the intensity of the emission is related to the concentration of that atom or ion. The composition of a material can therefore be determined by using a spectrometer to measure the radiation that is emitted by the laser-induced plasma.

X-ray fluorescence (XRF) is another technique that can be used to determine chemical composition. No plasma is produced with XRF, but electrons in the inner orbitals of atoms are ejected from their orbit by bombarding them with high energy X-rays. Electrons in higher orbitals will subsequently fall into the hole that is left behind and release energy in the form of photons (Beckhoff et al., 2007). As

with LIBS, the intensity and wavelength position of the photon emissions depend on the type of atom and its concentration in the sample. The composition of the sample can therefore be determined by measuring these emissions with a spectrometer.

One of the main differences between LIBS and XRF is that LIBS deals with emissions of the outer-shell electrons, while XRF deals with emissions of inner-shell electrons. For certain transition metals many different energy levels exist in the outer-shells on which electrons can be captured. When these transition metals occur in relatively high concentrations, their emissions may dominate the LIBS spectrum and occlude emission lines of other elements. The XRF technique does not suffer from this phenomenon because a lower number of inner-shell energy levels exist.

The disadvantage of the XRF technique, however, is that light elements are more difficult to detect because the inner-shell energy levels of these elements are relatively low and have a low penetrating power (Beckhoff et al., 2007). As a result, the emissions from light elements are more quickly absorbed by the surrounding air. This problem can be partly overcome by measuring in an environment where the air is replaced by helium or argon. However, detecting elements lighter than sodium also requires a special configuration of the XRF sensor (Beckhoff et al., 2007). Hydrogen, helium and lithium cannot be detected with XRF at all.

A comparison was made between LIBS and XRF to investigate if a combination of both techniques offers unique opportunities for fast drill core scanning in the field. This comparison is based on a test with the LIBS-XRF core scanner prototype that was developed through a collaboration between Avaatech B.V. and SPECTRAL Industries B.V.

## Experimental

Figure 1 shows a photo of the LIBS-XRF core scanner prototype that was tested in this study. This prototype was developed by integrating the LIBS instrument of SPECTRAL Industries into Avaatech's 4<sup>th</sup> generation XRF core scanner. Table 1 presents the specifications of the core scanner and the LIBS and XRF instruments.



Figure 1: LIBS-XRF core scanner prototype

**Table 1: Specifications of the LIBS-XRF core scanner prototype**

<b>Core scanning system</b>	
Dimensions	2953 x 925 x 1775 mm (L x W x H)
Weight	1450 Kg
Sample dimensions	
Core length	300 - 1600 mm
Core width	40 - 140 mm
<b>XRF instrument</b>	
X-ray tube	
Voltage range	4 - 50 KV
Current range	0 - 2 mA
Anode type	Rhodium
Tube-sample filters	Al, Pd and Cu
Tube lifetime	5000 - 8000 hours
X-ray detector	
Type	SGX Silicon drift detector
Resolution	133 eV at 5.9 KeV
Detectable element range	Mg - U
Slit system	
Downcore resolution	0.1 - 10 mm
Crosscore resolution	2 - 12 mm
<b>LIBS instrument</b>	
Laser	
Type	Litron Nano SG 150-10
Wavelength	1064 nm
Pulse length	4 - 6 ns
Max pulse energy	150 mJ
Max repetition rate	10 Hz
Spot size	100 µm
Spectrometer	
Type	SPECTRAL Industries IRIS echelle spectrometer
Detector	Deep-UV sensitive CMOS
Spectral range	180 - 800 nm

The LIBS-XRF core scanner prototype was tested on a 30 cm long drill core sample of a polymetallic sulphide ore originating from the historic Reiche Zeche mine in Freiberg, Germany. Around 800 years ago this ore was mined as a resource for zinc, lead, copper, and silver. The ore is mainly composed of the minerals pyrite, sphalerite, galena, chalcopyrite and arsenopyrite. Gangue minerals include calcite, siderite, and quartz (Bayer, 1999).

The LIBS and XRF measurements were acquired along the same line in the downhole direction of the sample. The surface area on which the XRF measurements are performed can be adjusted by changing the slit size of the instrument. The slit size was set to 0.2 mm downhole and 2 mm

crosscore for the test measurements. The spatial resolution of the XRF measurements was set at 0.2 mm. The range of elements that can be detected with XRF depends on the excitation energy that is used, which relates to the voltage that is applied to the X-ray tube. The XRF data was acquired by making one scan while operating the X-ray tube at 10 KV and one scan while operating at 30 KV. For each XRF spectrum an integration time of ten seconds was used. The total time needed to acquire the XRF data was ten and a half hours.

The surface area on which the LIBS measurements were performed was around 0.1 mm in diameter and the spatial resolution of the measurements was 0.12 mm. The LIBS measurements were gated using a delay of 2.4  $\mu$ s between plasma generation and data acquisition. LIBS spectra were acquired at 10 Hz using an integration time of 98  $\mu$ s. The laser power was set at 15 mJ per pulse. The total time needed to acquire the LIBS data was three minutes and twenty seconds. LIBS measurements were performed while flushing the instrument with argon to obtain representative data on elements occurring in the atmosphere such as oxygen and carbon.

Processing of the LIBS and XRF spectra was performed by first subtracting the baseline from the spectra. Subsequently, characteristic atomic emission lines were identified and a Voigt or Gaussian was fitted to the peaks in the LIBS and XRF spectra respectively. The line intensity of the elements was determined by calculating the area of the Voigt or gaussian profile.

## Results

Figure 2 presents the line intensities of selected element peaks in the measured LIBS and XRF spectra versus the position of the measurement. Element line intensities shown in black are based on the LIBS data and those shown in blue are based on the XRF data. Figure 2 also shows a photograph of the sample. The red rectangle on this photo indicates the line along which the LIBS and XRF spectra were measured.

All the element line intensities shown in Figure 2 are scaled to the same range and absolute intensities between elements can be different. The relationship between measured line intensity and actual element concentration is unknown for both LIBS and XRF and may be non-linear. Both techniques are subject to chemical matrix effects, which is the phenomenon in which the line intensity of an element is influenced by the other constituents of the sample. Additionally, line intensities may depend on physical matrix effects such as the surface roughness, hardness, density, grain size, or crystallinity of the material that is measured (Harmon et al., 2013; Potts & West, 2008). The influence of chemical and physical matrix effects in LIBS may be different than those in XRF.

Figure 2 shows that the LIBS data appears noisier than that of XRF. This is partly caused by instrumental noise because LIBS is subject to signal intensity fluctuations resulting from an uneven energy distribution between laser pulses and physical matrix effects (Harmon et al., 2013). However, most of the noisy appearance is likely due to the relatively small surface area that is measured with LIBS in combination with the occurrence of fine-grained minerals in the sample. This means that small-scale heterogeneity of the drill core sample itself is the main reason for the noisy appearance of the LIBS data. The influence of small-scale heterogeneity on the XRF data is lower because the surface area that is measured with XRF is larger. Compositional variations due to the occurrence of fine-grained minerals in between minerals with a larger grain size are therefore averaged out.

Figure 2 does not present any LIBS data for arsenic and XRF data for oxygen and carbon. This is because oxygen and carbon are light elements that cannot be detected with XRF and arsenic emissions were not observed in the LIBS spectra. For the elements that were detected with both LIBS and XRF, the measured line intensities presented in Figure 2 show a similar trend. However, differences between the results of LIBS and XRF can also be observed. Most of these are likely

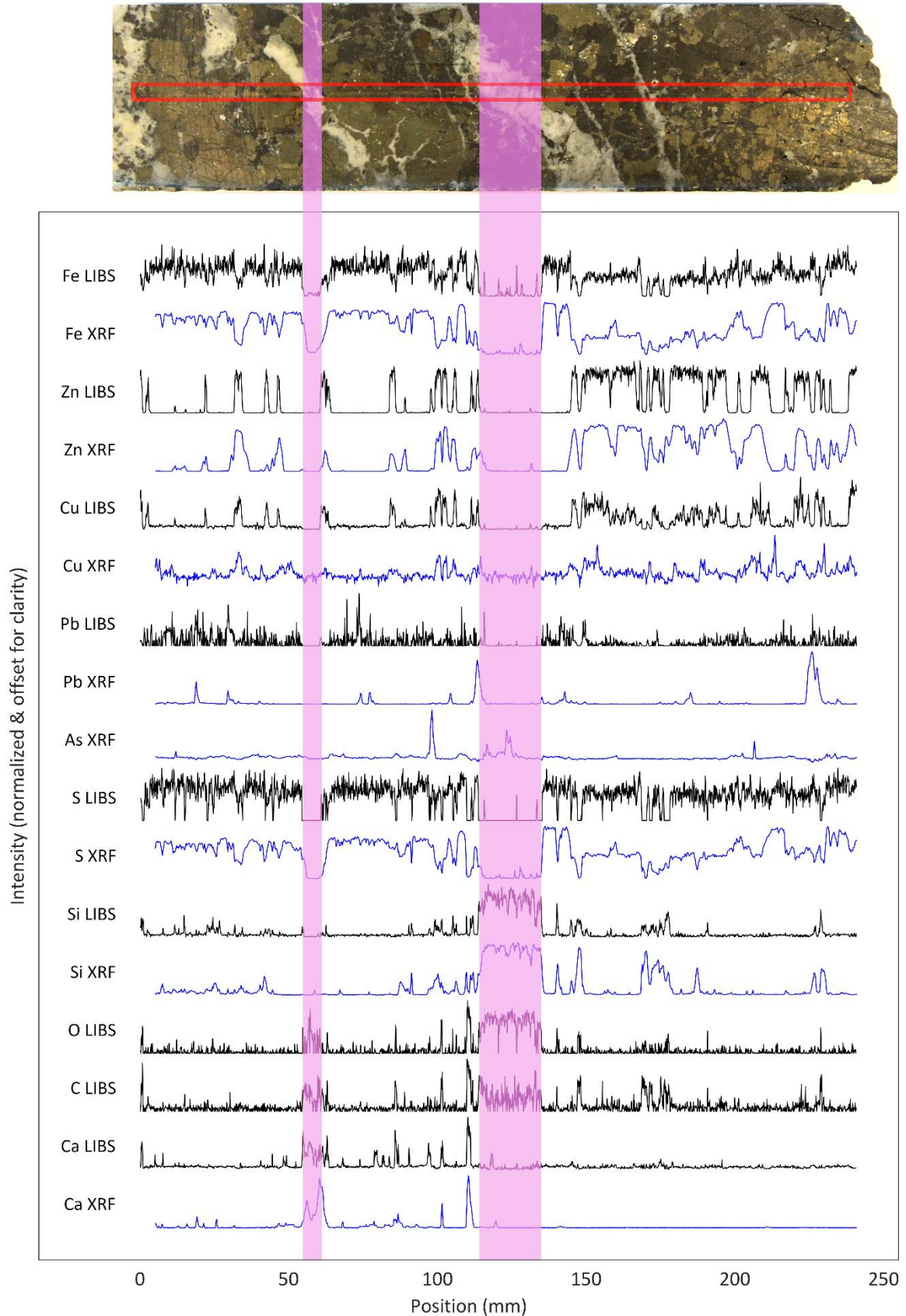
caused by differences in the surface area that is measured. Especially the field of view of the XRF instrument in the crosscore direction is much larger than that of the LIBS instrument (2 vs. 0.1 mm).

The most dominant mineralogical feature that can be observed from the data presented in Figure 2 is the occurrence of the white veins that can be seen in the photograph. The positions of two of these veins are highlighted in pink. The LIBS data shows that the white veins can be identified by using the line intensity of oxygen. This can be explained by the fact that the white veins are mainly composed of quartz ( $\text{SiO}_2$ ) and/or calcite ( $\text{CaCO}_3$ ), while most other minerals that occur in the sample are sulphides (pyrite ( $\text{FeS}_2$ ), sphalerite ( $\text{ZnS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), galena ( $\text{PbS}$ )). Based on the line intensities of Si and Ca, it can also be derived that the highlighted vein on the left mainly consists of calcite, while the one on the right mainly consists of quartz. The source of carbon in the quartz veins is somewhat unclear but might result from minor occurrences of other carbonates or small fluid inclusions containing  $\text{CO}_2$ . Fluid inclusions in quartz are common in the type of deposit from which the drill core sample originates.

The second mineralogical feature that can be seen in Figure 2 is the occurrence of pyrite ( $\text{FeS}_2$ ) versus sphalerite ( $\text{ZnS}$ ) and chalcopyrite ( $\text{CuFeS}_2$ ). In the left half of the sample pyrite is the most abundant mineral and occurrences of sphalerite and chalcopyrite can be identified from an increase in the line intensity of zinc or copper and a decrease in the intensity of iron. Occurrences of sphalerite and chalcopyrite seem to be spatially associated with each other since the line intensities of zinc and copper show similar trends. In the right half of the sample, sphalerite is more abundant and the line intensity of iron is lower than in the left half of the sample. The iron in this part of the sample is probably contained by chalcopyrite, although sphalerite can also contain iron (Awadh, 2009). It is also possible that relatively small pyrite grains occur in between those of sphalerite and/or chalcopyrite and that the measured iron is from a mixture of several minerals. This cannot be confirmed with either LIBS or XRF since measured line intensities may not be linearly related to element concentrations. A different analytical method is therefore required to confirm the source of the iron.

The third mineralogical feature that can be seen in Figure 2 is the occasional occurrence of galena ( $\text{PbS}$ ) and arsenopyrite ( $\text{FeAsS}$ ). Galena can be identified from the relatively high line intensity of lead and arsenopyrite from that of arsenic. Figure 2 shows significant differences between the results of LIBS and XRF for lead. A possible explanation for this is that the grain size of galena is relatively small. This is indicated by the fact that high line intensities for lead in the LIBS data occur over narrow ranges. Furthermore, the XRF data often still shows a small increase in the line intensity of lead at positions where the LIBS intensity of lead is high. When relatively small galena grains occur at the positions where a high intensity for lead is measured with LIBS, these will be averaged out in the XRF measurements because the surface area that was measured with XRF is larger.

Differences in the measured surface area can also create situations in which galena grains occur within the area measured with XRF, but not within the area measured with LIBS. This explains why the XRF results can show high line intensities for lead while LIBS does not. The same could apply to the arsenopyrite, which explains the absence of emission lines of arsenic in the LIBS data. However, it is also possible that the concentration of arsenic is below the detection limit for LIBS. The detection limit varies between elements and detection limits in LIBS are often different than those in XRF.



**Figure 2: LIBS and XRF results of scanning a polymetallic sulphide ore sample. The pink bands indicate the position of quartz / calcite veins.**

Finally, it was mentioned that the ore deposit from which the drill core sample originates was historically also mined for silver. With the XRF instrument silver could not be measured because the used slit contains silver, which interferes with the detected line intensities for this element. From the LIBS data no emission lines of silver were observed, but many of these lines also overlap with those of iron. It is also possible that the drill core sample used in the test was taken from a part of the deposit in which no significant amounts of silver occur.

## Discussion

The core scanning system used in this study was based on Avaatech's 4<sup>th</sup> generation XRF core scanner on which the LIBS instrument developed by SPECTRAL Industries was integrated. XRF is a well-established analytical technique with applications in many different fields. It is often used for quantitative analyses, which is possible through calibration of the instrument with calibration standards. The same approach can be used to calibrate LIBS instruments. It is therefore possible to calibrate the LIBS-XRF core scanner in order to extract full quantitative information from each measurement instead of the semi-quantitative results displayed in Figure 2. However, this does require a fairly large range of calibration standards that represents the mineralogical variability of the deposit in order to account for the matrix effects that may be associated with LIBS and XRF.

Extracting quantitative compositional information from individual LIBS or XRF measurements might not be needed for drill core scanning applications. The results in this paper showed that mineral occurrences could be inferred from the LIBS or XRF data (minerals associated with the deposit were known). This means that machine learning and multivariate classification can be used to classify measured spectra on the occurrence of certain minerals or mineral mixtures. By taking measurements at a sub-mm spatial resolution it is then possible to quantify the mineralogy on intervals in the order of tens of centimeters large by counting the number of measurements in which a certain mineral was identified. For the sample shown in Figure 2 for example, this approach would show a higher concentration of Zn- and Cu-bearing minerals over the 140-240 mm positions compared to the 0-100 mm positions. If LIBS or XRF drill core scanning is applied to hundreds of meters of drill core from an ore deposit, this approach can likely be used to accurately delineate higher and lower grade ore zones and distinguish different ore types. Furthermore, relatively small veins and fractures can be identified which may provide a better understanding of the geological processes that are associated with mineralization. This can be used to improve deposit models and better target physical sub-sampling for geochemical assay.

The main advantage of LIBS over XRF for drill core scanning is that the data acquisition speed of LIBS is much higher. The LIBS instrument that was used in the test can acquire LIBS spectra at a frequency of 10 Hz, which means that scanning a meter of drill core at 0.1 mm resolution takes about seventeen minutes. However, measurement frequencies of 1 KHz are also possible for LIBS applications (e.g. Rifai et al., 201), which would reduce the scan time for a meter of drill core to only ten seconds. The XRF instrument that was used in the test needs at least ten seconds for a single measurement and longer measurement times might be needed to acquire data on elements occurring in low concentrations. Furthermore, the range of elements that can be detected depends on the excitation energy that is used, which relates to the voltage that is applied to the X-ray tube. To obtain accurate information on the full range of elements, XRF measurements using three different excitation energies are needed. Additionally, the XRF instrument needs to be in contact with the sample during the measurement and about six seconds are needed to relocate the instrument between measurement locations. This means that scanning a meter of drill core at 0.1 mm resolution by using three excitation energies and ten seconds of measurement time takes almost six full days. However, this can be significantly reduced by decreasing the resolution and number of excitation energies at which the measurements are performed. Scanning a meter of drill core at 1 cm resolution using only one excitation energy can be done within thirty minutes.

Another advantage of LIBS is that it is possible to detect light elements. Especially the ability to detect carbon, oxygen and sulphur provides significant advantages for drill core scanning since these elements can be used to distinguish between mineral groups such as oxides, carbonates, sulphates and sulphides. Additionally, the ability to detect hydrogen could potentially be used to characterize mineral hydration, which may be relevant when investigating ore deposits associated with hydrothermal alteration.

An advantage of XRF over LIBS is that there is a lower chance that the emission lines of an element of interest overlap with the lines of other elements. As was mentioned in the introduction, certain transition metals produce many different emission lines in a LIBS spectrum which may prevent the accurate detection of other elements. Additionally, signal to noise ratios and detection limits of XRF and LIBS can be different. This means that for certain elements XRF might provide better results than LIBS and vice versa.

## Conclusions

Testing the LIBS-XRF core scanning prototype on a drill core sample of a polymetallic sulphide ore showed that LIBS and XRF produce similar results for all the major elements of which the sample is composed. By using either the LIBS or XRF data it was possible to identify and map the occurrence of economically important minerals that can be used to characterize ore grade. Differences between the results of LIBS and XRF were also observed, which can be explained by differences in the size of the measured surface area, signal to noise ratio, and detection limits of LIBS and XRF. Additionally, light elements such as oxygen or carbon that were detected with LIBS could not be detected with XRF.

Whether it is better to use LIBS or XRF for geochemical mapping of drill core samples depends on the specific goal of the application. This is mainly due to the detection limits that are associated with each technique, which depend on the mineral matrix in which an element resides (Radziemski & Cremers, 2006; Kadachi & Eshaikh, 2012). As was shown in this study, it is possible to combine LIBS and XRF in drill core scanning to allow a more complete characterization of the composition of samples.

The LIBS-XRF core scanning prototype is a transportable unit that can be operated in the field. LIBS can be used to rapidly scan drill cores because of the relatively high scanning speed that can be achieved. This is especially advantageous when drill core scanning is applied in large mineral exploration projects in which hundreds of kilometers of drill core samples are produced. Drill core sections that are of special interest can be further investigated using XRF. Especially for determination of the content of certain trace elements such as arsenic, XRF may provide a higher precision than LIBS.

## Acknowledgement

This work was supported by EIT RawMaterials Project number: CLCW-SB-2018-005.

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