SPECTROPHOTOMETRY ANALYSIS OF DEEP-SEA SEDIMENTS ALONG THE MAIN PATHWAY OF THE INDONESIAN THROUGHFLOW: SPATIAL VIEW

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ABSTRACT

Deep-sea sediment is the primary marine archive for reconstructing climate of the past millennia. With an array of geochemical analyses and more techniques to be developed, conservative sample usage is necessary. This study presents spectrophotometry analysis as a non-intrusive approach on deep-sea sediment samples retrieved along the main pathway of the Indonesian Throughflow in the Makassar Strait. Sediments from 25 sites including: Eastern Kalimantan, western Sulawesi, south Makassar Strait, southern Sulawesi and northern Bali are scanned as wet and dried samples over the visible spectra (400-700nm). After taking first derivatives of the raw data to accentuate the signals, R-mode factor analysis is applied to reveal three factors that explain 96.99% variance. Factor 1, which explains 53.94% variance, is characterized as halite. Factor 2 (30.89%) is carbonate and Factor 3 (12.18%) is kaolinite or clay mineral. XRD analysis reveals the presence of calcite, quartz, halite, plagioclase and aragonite, with the first three being the most prevalent minerals. Spatial distribution map of Factor 1 (halite) shows higher values in eastern Kalimantan, south Makassar Strait and western Sulawesi. Factor 2 (carbonate) is relatively high in eastern Kalimantan, southern Sulawesi and northern Bali; with similar observation at the first two sites from accompanying carbonate content analysis. Relatively high Factor 3 (kaolinite) in eastern Kalimantan is consistent with its proximity to the Mahakam River delta. Characteristics of each region are further discussed herein. Taken together, this information lays a foundation for applying the non-intrusive spectrophotometry downcore to study past climate change in the Makassar Strait.

Keywords: paleoclimate, deep-sea sediment, spectrophotometry, ITF, factor analysis

INTRODUCTION

Paleoclimate archives such as deep-sea sediments, corals, speleothems and ice cores, have been providing key information for understanding past global climate change. Paleoclimate records serve to extend the temporal coverage of modern instrumental data that combined help to refine climate model outputs on future climate projection. Indeed, paleoclimate records have been an integral part of the International Panel on Climate Change reports in understanding the rate and physical mechanisms of the ongoing anthropogenic climate change (e.g. IPCC, 2014).

Deep-sea sediment remains the primary marine paleoclimate archive in providing records over the past millennia. A suite of geochemical (e.g. isotopic, trace metals) measurements have been applied to understand past regional climate by reconstructing sea-surface temperature and salinity (Zuraida *et al.*, 2009; Newton *et al.*, 2011; Setiawan *et al.*, 2015) as well as ocean productivity (Murgese *et al.*, 2008; Lückge *et al.*, 2009) to name a few. Also, novel techniques continue to be developed to provide more robust results with reduced uncertainties. With such array of geochemical analyses, conservative sample usage is necessary. Whenever possible, non-intrusive analyses that keep samples intact would be helpful.

An avenue for expanding non-intrusive measurements on deep-sea sediments is through the perception of color. For instance, lighter and reddish colors may indicate high carbonate and iron contents, respectively. However, the perception of color contains huge subjectivity, making manual color change estimation an unreliable one. Well-categorized colors have been catalogued in order to reduce the subjectivity in perceiving color such as the Munsell color system (Cleland, 1921). However, the technique is very time consuming and it can only be done at a low resolution along sediment core.

These problems give rise to the application of spectrophometer, which is an instrument to quantitatively measure diffuse spectral reflection (or color) of an object. Mix *et al.*, (1992; 1995) developed a prototype Split Core Analysis Tract (SCAT) for automated core scanning of reflectance 455-945nm on the Ocean Drilling Program (ODP) Leg 138 to estimate biogenic calcite, biogenic opal and non-biogenic contents. A revised SCAT with an improved signal-to-noise ratio and wider frequency band (250-950nm) was later developed (Harris *et al.*, 1997). However, SCAT are stationary and costly than handheld spectrophotometer such as the Minolta CM that also has better resolution (10nm) compared to SCAT (0.68nm). Beginning with ODP Leg 154, shipboard core scanning has become a routine using the Minolta spectrometer that measures visible spectral range (400-700nm).

The objective of this study is to explore the application of spectrophotometry analysis as a non-intrusive method on deep-sea sediments retrieved along the Makassar Strait, Indonesia. The study site represents the main pathway of the Indonesian Throughflow, an important ocean current connecting the Pacific with the Indian Oceans, whose variations influence the Indo-Pacific climate (Gordon, 2005; Sprintall *et al.*, 2014). This paper aims to lay a foundation for applying the method downcore, by first understanding the spatial view from coretop sediment samples.

MATERIALS AND METHODS

Study Sites and Material

This study analyzes 25 coretop deep-sea sediment samples taken from several sites along the Makassar Strait (Figure 1).

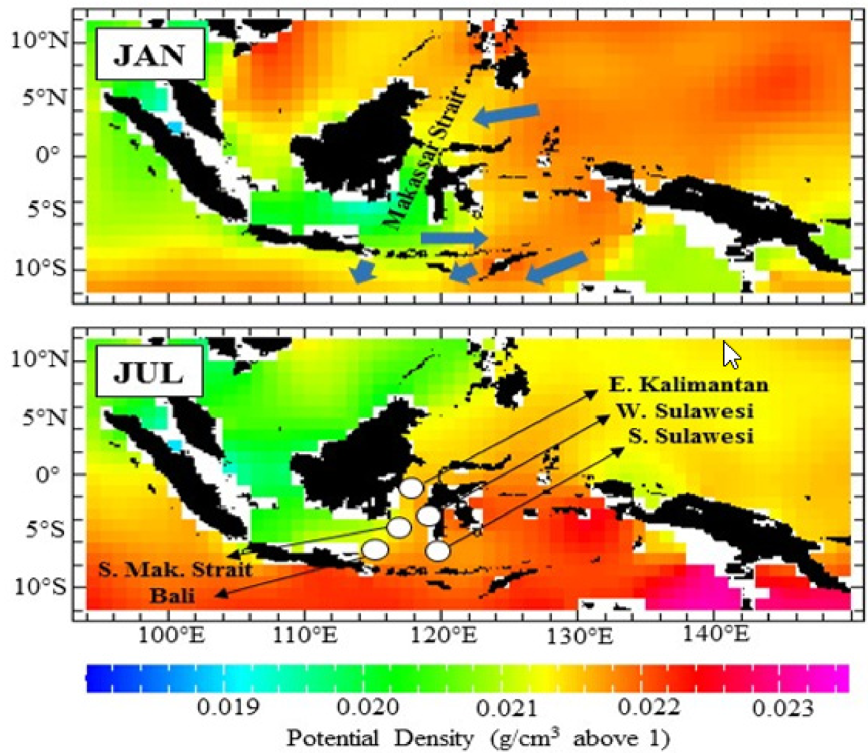

Figure 1. (Top) Sea-surface density during the NW monsoon. The arrows denote flow directions of the ITF. **(Bottom)** Similar with above, but for during the SE monsoon. Sample locations are shown.

Climate and oceanography in the study sites are influenced by the Indo-Australian monsoon on seasonal timescales. During the northwest (NW) monsoon that peaks around January, the ITF is slower compared to the southeast (SE) monsoon that peaks around July due to the advection of low density waters from western Indonesia (Gordon *et al.*, 2003).

The samples analyzed herein represent five regions along the Makassar Strait. From north to south, they are: Eastern Kalimantan (1 core), western Sulawesi (15 cores), south Makassar Strait (2 cores), southern Sulawesi (6 cores) and northern Bali (1 core).

The samples were retrieved using a multicorer deployed from the R/V Baruna Jaya VIII of the Research Center for Oceanography-LIPI (Indonesian Institute of Sciences) in July 2003. The multicorer, which consists of a group of plastic barrels installed on a multicore tripod, slowly penetrated the seafloor. Then, the top and bottom of each core barrel were sealed to hold on to the sediment samples before the tripod left the seafloor.

Groundtruth Data: Carbonate Content and X-Ray Diffraction (XRD) Measurements

To provide groundtruth for the spectrophotometry approach, carbonate content is analyzed on all the samples using a coulometer and their mineral composition is determined via XRD on eight representative samples (1 from eastern Kalimantan, 3 western Sulawesi, 1 south Makassar, 2 southern Sulawesi and 1 northern Bali samples)

The coulometer measures the amount of carbonate content on CO_2 concentration as the reaction product of carbonate in the sediment and acid. The measurement is calibrated by running a blank sample to get a base number. Thus:

% CaCO3 = [Value- Blank] x 8.333 x 100   (Eq.1)

where 8.333 value is a stoichiometric recalculation factor.

Spectrophotometry Analyses

The samples are analyzed using a handheld spectrophotometer (Minolta CM 2022) over visible spectrum range (400-700nm) under three circumstances: (i) wet, (ii) dried and under thicker plastic cover, and (iii) dried and under thin plastic cover. The spectrophotometer measures the amount of visible light transmitted or absorbed by sediments, which is a distinctive function of different chemical species such as minerals. While the instrument is held perpendicular to the surface, the spectral sensors are aligned at an 8 degree angle to the vertical axis. This geometry is referred to as the d8 observer frame of reference.

The measurements are taken after performing zero (black) and white calibrations. The instrument is warmed up for at least 30 minutes prior to calibration and measurement to avoid drift. Then, zero calibration is performed by taking measurement of blank space, which could be done by holding the instrument to waist level with no object underneath. White calibration is performed by measuring a white ceramic standard. Post measurement using the white calibration plate is also performed to check for drift during measurement process. Measurements are taken using three averaged data points automatically calculated by the instrument.

Data Processing: R-mode Factor Analysis

Data analysis of the spectrophotometry data involves several steps in order to accentuate the signal, identify compositional information and create distribution map of each prevalent element via factor (principal component) analysis.

The first step is by taking the first derivative of the raw data that are smooth and featureless. First derivative values peak where the slope of the percent reflectance curves changes rapidly. And the position of a first derivative peak for any mineral is a function of the concentration of that mineral.

The next step is to extract and identify compositional information from the spectra via R-mode factor analysis using SPSS© statistical software. The analysis operates based on the extraction of the eigenvalues and eigenvectors from a square matrix produced by multiplying a data matrix by its transpose. Rotated factor loadings of each factor across wavelengths are analyzed by comparing them against groundtruth data (carbonate content and XRD measurements) and mineral spectral library.

Spatial distribution map for each factor is constructed by calculating their factor scores and presented using ArcMap GIS software. Balsam and Deaton (1991) recommends factor analysis as the most appropriate statistical analysis for spectral studies for a number of reasons. First, it estimates the value of the independent variables with a few assumptions about them. Second, it easily handles bimodal spectral responses and is not hindered by assumptions involved with spectral band ratios. Third, it allows the results to be tested by examining the factor loadings.

RESULTS

Carbonate Content and XRD Measurements

The groundtruth measurements of carbonate content and XRD show varying compositions of the Makassar Strait sediments (Figure 2). Carbonate content analysis on the 25 samples shows markedly higher content in southern Sulawesi and uniformly lower values in western Sulawesi, while other regions have carbonate contents that are in between.

XRD analysis on the eight representative samples reveals the presence of calcite, quartz and halite being the three most prevalent minerals. Plagioclase is present in one of the three western Sulawesi samples and the northern Bali sample. And aragonite is present in one of the two southern Sulawesi samples.

Spectrophotometry Analysis

Spectrophotometry analysis highlights the importance of making measurements on dried samples and taking the first derivative values to enhance the raw signals. Figure 3 shows raw data taken under three circumstances (wet, dried under thick plastic cover, and dried under thin plastic cover), with its first derivative curve for the northern Bali site as an example. Spectrophotometry analysis conducted under three circumstances yield higher reflectance on dried samples. Most wet samples yields about 5-10% reflectance, with an exception of a sample from southern Sulawesi that shows 15% reflectance (and has the highest or 56.2% carbonate content via the coulometer). Whereas, dried samples show values around 15-40%. Furthermore, most samples show higher

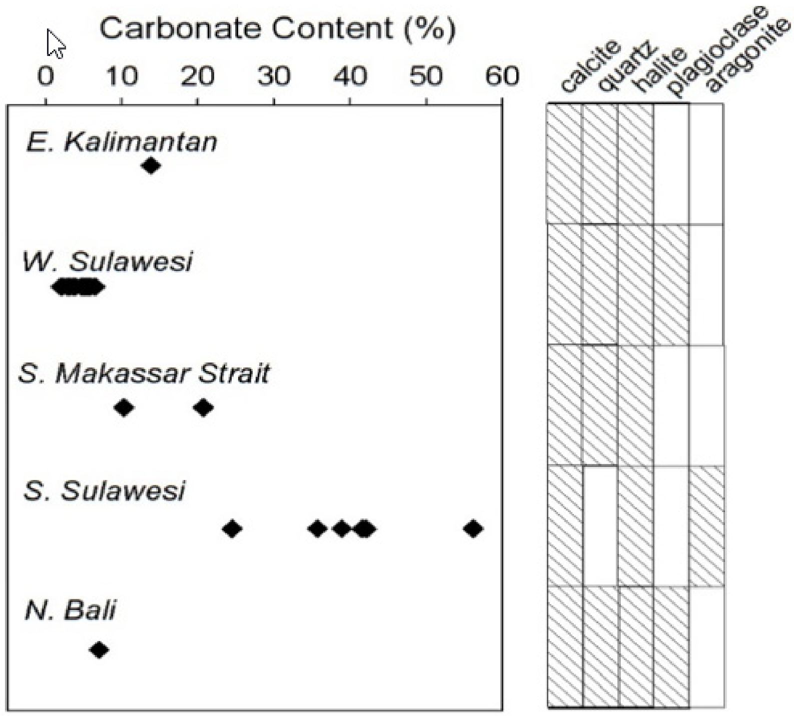

Figure 2. (Left) Carbonate content (in %) in sediment samples along the Makassar Strait (from north to south). **(Right)** XRD results showing five minerals present in the samples.

reflectance with the thinner cover; but some show the opposite or no difference. Calibration checking shows 1-3.2% error range associated with the instrument.

The factor analysis extracts three influencing factors that vary along the Makassar Strait. These three factors have eigenvalues higher than 1. And combined, they explain 96.99% of variance within first derivative values of the visible spectrum bands (Figure 4). Spatial distribution maps of these factors are shown in Figure 5.

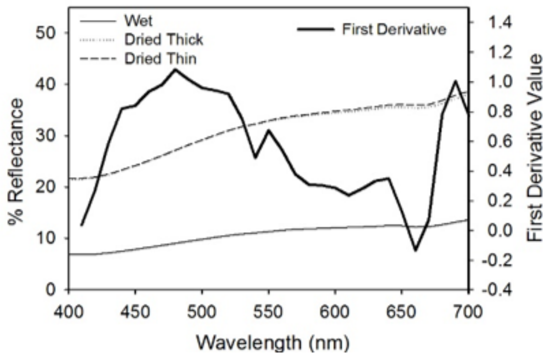

Figure 3. Raw values of wet, dried & under thick plastic cover, and dried & under thin plastic cover, with its first derivative curve.

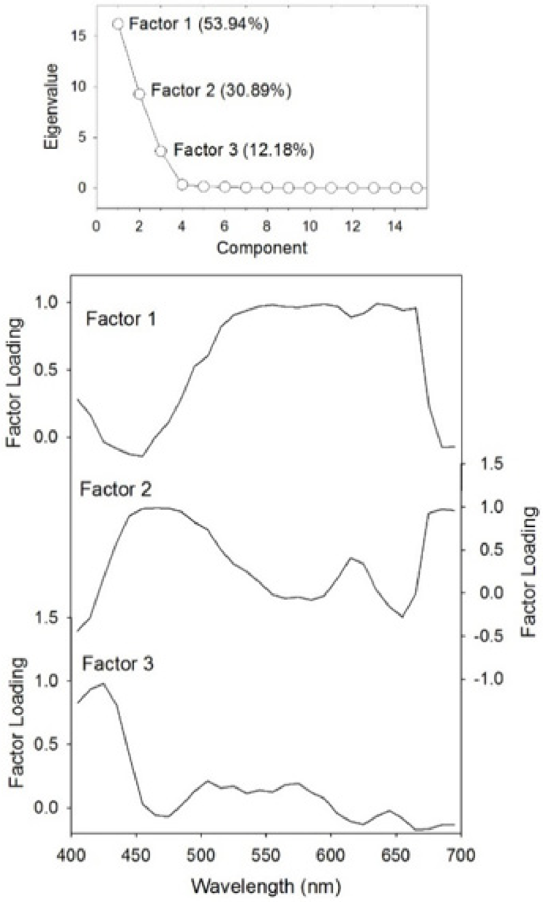

Figure 4. (**Top**) Eigenvalue and variance of the three most influencing factors. (**Bottom**) Factor loading of the actors across spectra.

Factor 1, which explains 53.94% variance, is relatively high in eastern Kalimantan, south

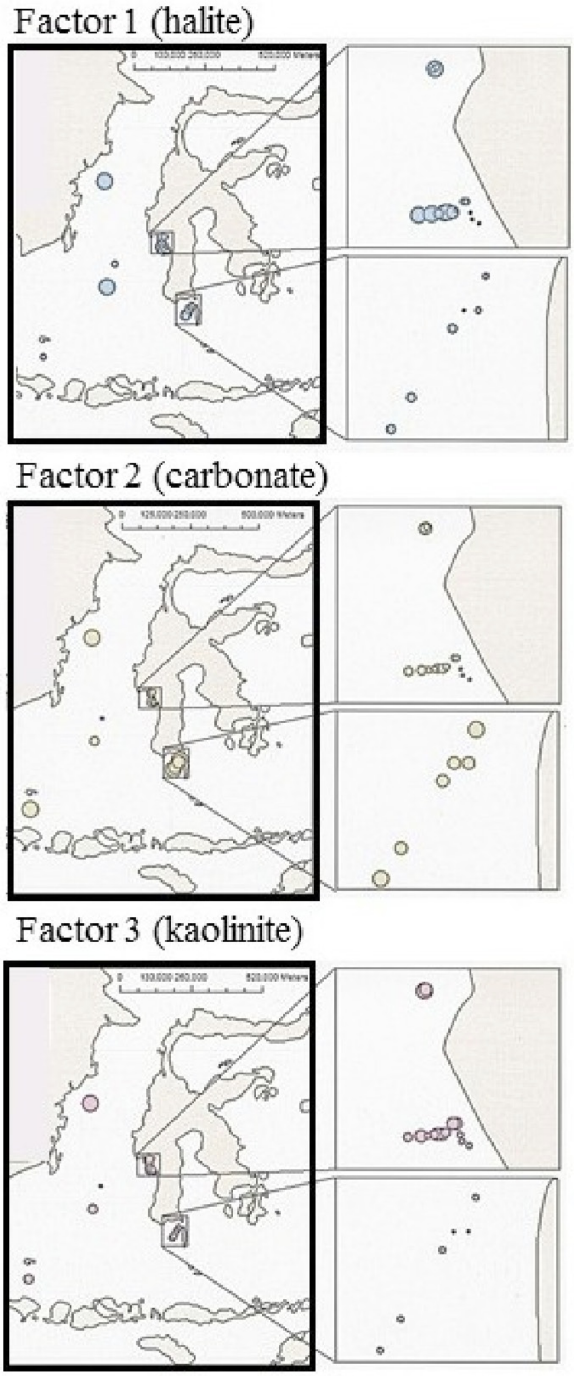

Figure 5. Spatial distribution of Factors 1-3 along the Makassar Strait. Figures modified from Nurhati (2005).

Makassar Strait and western Sulawesi. It is interpreted as halite (rock salt) considering that XRD analysis of samples with high influence of Factor 1 strongly indicate the presence of halite, which do not occur in sites where Factor 1 is weak. This approach is in line with Balsam and Deaton (1991) that suggests using mineral assessment and comparing the composition of samples with low factor scores against those with high factor scores.

Factor 2, which explains 30.89% variable, is relatively high in Eastern Kalimantan, Southern Sulawesi and N. Bali. It is interpreted as carbonate from its a positive correlation with the carbonate content data. Moreover, high Factor 2 values in Eastern Kalimantan and Southern Sulawesi are in line with high carbonate content results in these sites. The distribution of Factor 2 in Southern Sulawesi is fairly uniform.

And Factor 3, which explains 12.18% variance, is relatively high in Eastern Kalimantan. It is interpreted as kaolinite as determined by the spectral shape of kaolinite.

DISCUSSION

Spatial distribution map of the three factors reflects their environmental settings.

1. The eastern Kalimantan site scores high in all factors, is a site with high fluvial input from the Mahakam River that flows 650 km through a mountainous rainforest before emptying into the Makassar Strait. Consequently, sample close to this delta shows low carbonate content dilution and high in kaolinite. Indeed, a clay mineral distribution study on surface sediments between Indonesia and NW Australia shows kaolinite as the dominant clay mineral in the region (Gingele *et al.*, 2001). Kaolinite, however, does not show strong XRD signal due to its characteristics.

2. Western Sulawesi sediments are influenced by numerous small drainage systems. The terrigenous influence is reflected by low carbo

3. South Makassar sediments, which are about 150 km away from any island, show high carbonate and less kaolinite.

4. Southern Sulawesi sediments have high carbonate influence, and minimal terrigenous input as supported by low kaolinite and the absence of quartz (an indicator of terrigenous influences).

5. Northern Bali sediment has high terrigenous input as suggested by various mineral including plagioclase with no particularly dominant mineral as shown by the XRD.

Terrigenous factor is an influencing factor on sediment composition along the Makassar Strait, particularly by influencing the presence of carbonate and kaolinite. Future studies are advised not to sample too close to the shore particularly in high sedimentation areas as it could complicate interpretation of sediment composition. The identification of minerals via factor analysis can go both ways, in the sense that we can predict minerals that may be present in sediment samples by recognizing their first-derivative spectra (for example, compare Figure 3 with Figure 4-Factor 2).

The advantage of the non-intrusive spectrophotometry method is that it allows sediments to be analyzed without harming the cores. Considering that most of the paleoclimate analyses require taking sub-samples from the core, non-intrusive techniques would give way to more other measurements on sediment core samples.

CONCLUSION

This study explores the application of spectrophotometry analysis as a non-intrusive approach on deep-sea sediments retrieved along the main pathway of the Indonesian Throughflow in the Makassar Strait. Sediments from 25 sites covering eastern Kalimantan, western Sulawesi, southern Sulawesi, south Makassar Strait and northern Bali are scanned as wet and dried samples over the visible spectra (400-700nm). The wet vs. dried measurements highlight the importance of taking spectrophotometry analysis on dried samples.

After taking first derivatives of the raw data to accentuate the signal, R-mode factor analysis is applied to reveal three factors that explain 96.99% variance. Factor 1, which explains

53.94% variance, is characterized as halite. Factor 2 (30.89%) is carbonate and Factor 3 (12.18%) is kaolinite or clay mineral.

Carbonate content analysis of these samples shows high values in southern Sulawesi sites and the opposite in western Sulawesi sites. The XRD analysis reveals the presence of calcite, quartz, halite, plagioclase and aragonite, with the first three being the most prevalent minerals.

Spatial distribution map of Factor 1 (halite) shows higher values in eastern Kalimantan, south Makassar Strait and western Sulawesi. Factor 2 (carbonate) is relatively high in eastern Kalimantan, southern Sulawesi and northern Bali. And Factor 3 (kaolinite) is relatively high in eastern Kalimantan.

Taken together, this information lays a foundation for applying the non-intrusive spectrophotometry downcore to study past climate change around the Makassar Strait.

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