

# Spectral analysis of selected sediment core samples from the Chew Bahir Basin, Ethiopian Rift in the spectral range from 0.3 to 17 $\mu\text{m}$ : support for climate proxy information

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## ABSTRACT

Investigations on short ( $\leq 18.8$  m) sediment cores retrieved along a NW-SE transect across the Chew Bahir (CHB) basin, Southern Ethiopian Rift, have shown that they can provide valuable climate information<sup>1</sup>. The relationship between mineralogical and geochemical properties of the core samples is closely linked to the hydroclimate history of the region. During dry climate episodes both the illitization of the smectites and the octahedral Al-to-Mg substitution in the phyllosilicate materials has been documented. An enhanced potassium fixation during dry intervals is also linked to the increase in layer charge caused by the authigenic changes in octahedral composition<sup>2</sup>.

The ongoing work, a non-destructive spectral analysis of reflectance in a wide spectral range from 0.3 to 17  $\mu\text{m}$  on selected core samples from both wet and dry intervals from the long ( $\sim 280$  m) cores from Chew Bahir basin supports this interpretation. The spectral range from 0.3 to 6  $\mu\text{m}$  is suitable for investigating the absorption bands of OH, H<sub>2</sub>O, M-OH lattice vibrations as well as the crystal field transitions of transition metal ions. This allows a detailed examination and differentiation of various clay minerals as well as indications of single primary minerals (olivine and pyroxene). The wavelength range longward 7  $\mu\text{m}$  provides further mineralogical data such as on the presence of source minerals like feldspars and the results of the short-wave channel to be substantiated. First results show that the main mineralogical structure is characterized by clays with variable Al/Mg content (Al-rich clays mixed with Mg-phyllosilicates). Strongly variable parts of calcite are also spectrally detectable. Characteristic reflectance minima (Christiansen features) close to 8  $\mu\text{m}$  indicate the presence of Ca-rich plagioclase + clinopyroxene and/or corresponding aqueous weathering products. The high variability of a band close to 1  $\mu\text{m}$  is used together with the spectral information above 7  $\mu\text{m}$  to identify the diverse individual minerals within the olivine, pyroxene, feldspar group minerals and corresponding aqueous weathering products. The results will be further compared with  $\mu\text{XRF}$  scan data and verified by petrographic data of the rocks in the catchment. Overall, the presented spectral study (0.3 to 17  $\mu\text{m}$ ) is a suitable and non-destructive method to examine the main mineralogical components of the samples. The results can be directly compared with hyperspectral remote sensing data that are available for the Chew Bahir basin.

## STUDY AREA AND DRILL CORE SAMPLES

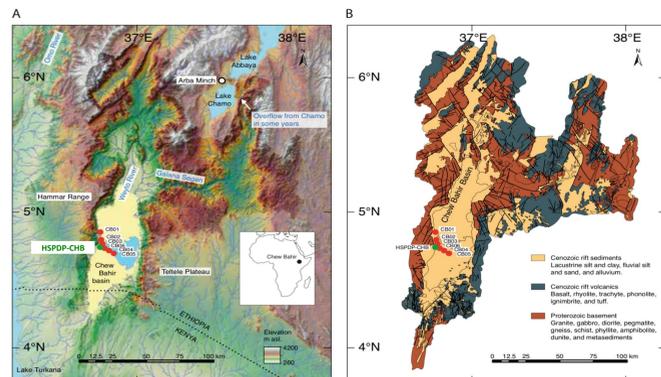


Fig. 1. Study Area: Adapted from Förster et al., 2018.

Left - Topographic map of the Chew Bahir basin showing the outline of the catchment, the drainage network, the location of the long cores (red points) large cores (HSPDP-CHB drill site, green point). Right - Geologic map of the Chew Bahir basin showing generalized rock type: Cenozoic rift sediments, Cenozoic rift volcanic, and Proterozoic basement. Compilation based on Omo River Project Map<sup>3</sup>, Geology of the Sabare Area<sup>4</sup>, Geology of the Yabello Area<sup>5</sup>, and Geology of the Agere Maryam Area<sup>6</sup>.

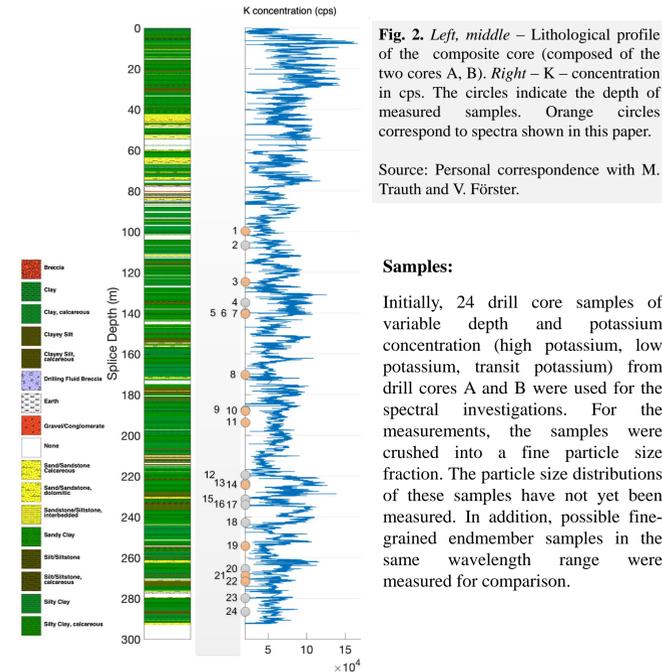


Fig. 2. Left, middle - Lithological profile of the composite core (composed of the two cores A, B). Right - K - concentration in cps. The circles indicate the depth of measured samples. Orange circles correspond to spectra shown in this paper.

Source: Personal correspondence with M. Trauth and V. Förster.

### Samples:

Initially, 24 drill core samples of variable depth and potassium concentration (high potassium, low potassium, transit potassium) from drill cores A and B were used for the spectral investigations. For the measurements, the samples were crushed into a fine particle size fraction. The particle size distributions of these samples have not yet been measured. In addition, possible fine-grained endmember samples in the same wavelength range were measured for comparison.

## MEASUREMENTS OF VIR REFLECTANCE

Method: Bi-directional spectral reflectance has been measured at atmospheric pressure between 0.3 and 17  $\mu\text{m}$  at the DLR Planetary Spectral Laboratory (PSL)<sup>7</sup> with a Bruker Vertex80V FTIR instrument at room temperature, at 15° incident and emergence angles, and with a spectral resolution of 4  $\text{cm}^{-1}$ . For the spectral data analysis continuum removals were performed in selected cases. Fig. 3 shows three typical CHB-HSPDP spectra.

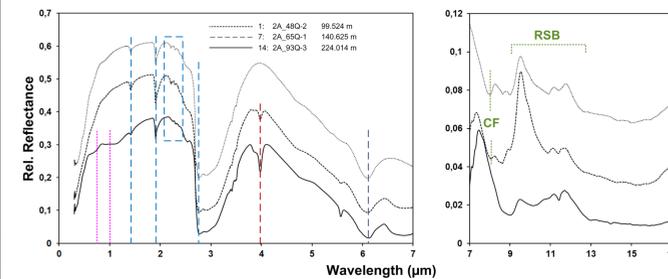


Fig. 3. Left - Typical reflectance spectra of three selected HSPDP drill core samples (different depths) in the wavelength range from 0.3 to 7  $\mu\text{m}$ . Right - 7 to 17  $\mu\text{m}$ ; from top to bottom: 2A\_48Q-2 (low K), 2A\_65Q-1 (high K), and 2A\_93Q-3 (low K). For reasons of clarity, the spectra are provided with an offset in reflectance (left and right offsets are different).

The spectra display IR absorption bands at  $\sim 1.4$   $\mu\text{m}$ ,  $\sim 1.9$   $\mu\text{m}$ ,  $\sim 2.7$   $\mu\text{m}$ , between 2.0 and 2.4  $\mu\text{m}$ , around 3.0  $\mu\text{m}$  and 6.0  $\mu\text{m}$  due to OH and H<sub>2</sub>O vibrations (see Fig. 2 - absorption bands marked with blue dotted vertical lines). The weaker bands between 2.0 and 2.4  $\mu\text{m}$  are indicative for the cation incorporation. A band at 2.2  $\mu\text{m}$  is caused by an Al-OH and at 2.3  $\mu\text{m}$  by a Mg-OH vibration. Five weak absorption bands between 1.8 and 2.7  $\mu\text{m}$  emerging together are caused by carbonates. The carbonate spectra display stronger absorption bands between 3.0 and 6.0  $\mu\text{m}$ . A band around 4.0  $\mu\text{m}$  classifies the carbonate present in the CHB spectra as calcite (see Fig. 2 - absorption band marked with a red vertical line). At about 8.0  $\mu\text{m}$  local minima, called Christiansen Features (CF), and low-contrast RestStrahlen Bands (RSB) around 10  $\mu\text{m}$  are characteristic for the silicate component. Finally, the UV-VIS spectral part is characterized by different spectral slopes and absorption bands, one close to 1  $\mu\text{m}$  (marked with a magenta dotted line), which can be caused by Fe<sup>2+</sup> associated electronic processes.

## RESULTS

Figs. 4 and 5 show reflection spectra of CHB samples from different drilling depths with high (4) and low (5) potassium concentrations. All spectra display no or very weak calcite absorption bands. The following figure 6 shows comparison spectra of possible endmember components. Fig. 7 and 8 display continuum removed reflectance spectra for a detailed spectral analysis.

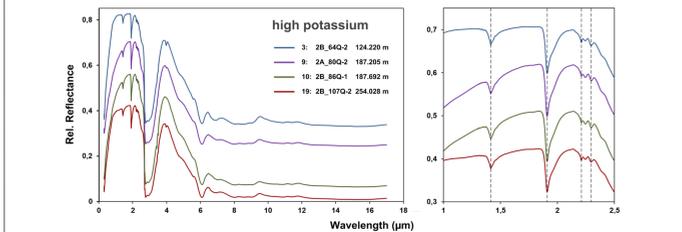


Fig. 4. Left - Reflectance spectra of HSPDP drill core samples (high potassium) in the wavelength range from 0.3 to 17  $\mu\text{m}$ . Right - Section of the spectra between 1.0 and 2.5  $\mu\text{m}$ . For reasons of clarity, the spectra are provided with an offset in reflectance.

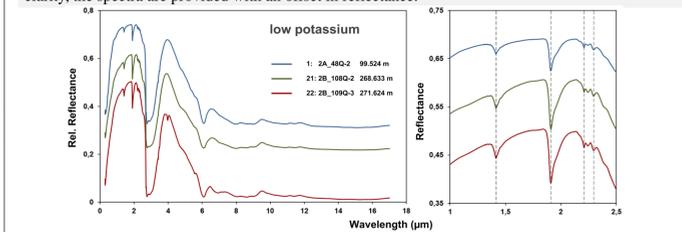


Fig. 5. Left - Reflectance spectra of HSPDP drill core samples (low potassium) in the wavelength range from 0.3 to 17  $\mu\text{m}$ . For reasons of clarity, the spectra are provided with an offset in reflectance. Right - Section of reflectance spectra (absolute values) between 1.0 and 2.5  $\mu\text{m}$ .

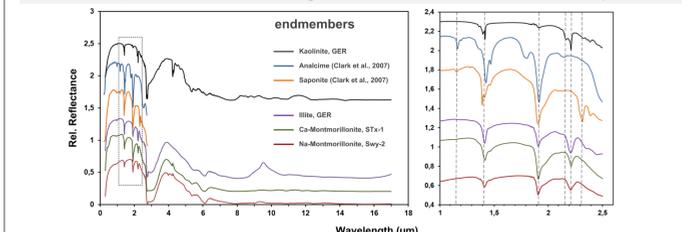


Fig. 6. Left - Reflectance spectra possible endmember minerals in the wavelength range from 0.3 to 17  $\mu\text{m}$ . Right - Section of the spectra between 1.0 and 2.5  $\mu\text{m}$ . For reasons of clarity, the spectra are provided with an offset in reflectance.

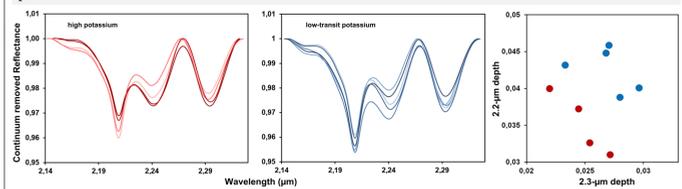


Fig. 7. Left and middle - Continuum removed CHB reflectance spectra between 2.14 and 2.33  $\mu\text{m}$  calculated from spectra shown in Fig. 3 and 4 + two additional spectra (transit K, low calcite: 2A\_82Q-1\_193.123 m and 2A\_75Q-2\_170.966 m), not shown here). Right - 2.2- $\mu\text{m}$  band depth vs. 2.3- $\mu\text{m}$  band depth.

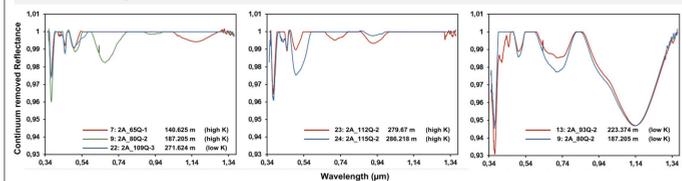


Fig. 8. Continuum removed CHB reflectance spectra between 0.35 and 1.37  $\mu\text{m}$ .

## DISCUSSION

The UV to MIR spectral reflectance measurements of large core samples show variable mean reflectance values, spectral slopes and absorption bands within the entire spectral range (see Fig. 3 and 4). Most pronounced spectral features are OH and H<sub>2</sub>O vibration bands in the range between 1 and 7  $\mu\text{m}$ . They are comparable in their form in the wavelength position with Al/Mg smectites (see Fig. 6). An absorption band at 2.2  $\mu\text{m}$  is typical for montmorillonite, while another absorption band at 2.4  $\mu\text{m}$  indicates a Mg containing clay. Obviously calcite is the major carbonate being present in a large number of analyzed samples. A 4.0  $\mu\text{m}$  absorption band of calcite enables tracking the samples carbonate content. In the MIR CHB samples poor of calcite occur local reflectance minima around 8.0  $\mu\text{m}$  and RSBs between 9.0 and 11.0  $\mu\text{m}$  that are typical for Ca-rich plagioclase + clinopyroxene and their aqueous weathering products. Large calcite contents mask the silicates' CF (see Fig. 3).

Continuum removed reflectance spectra between 2.14 and 2.33  $\mu\text{m}$  enable to correlate the Al-OH ( $\sim 2.2$   $\mu\text{m}$ ) and Mg-OH ( $\sim 2.3$   $\mu\text{m}$ ) spectral band depths (Fig. 7). The CHB spectra show a clear tendency to higher 2.2- $\mu\text{m}$  band depths of for low-transit potassium samples (blue dots, Fig. 6, right) in comparison to high potassium samples. This is in agreement with the observed Al-to-Mg substitution in phyllosilicates during dry climate phases as documented in 1 and 2 (illitization). However, this trend must be statistically verified by the inclusion of spectral measurements on further CHB samples.

The UV to NIR spectral range exhibit several weak spectral bands (see Fig. 8). Bands at 0.43  $\mu\text{m}$ , 0.9 - 1  $\mu\text{m}$  together with a band at 2.24  $\mu\text{m}$  could be associated with Ca-rich clinopyroxenes, while shallow bands at 0.64  $\mu\text{m}$  together with 0.9  $\mu\text{m}$  bands could be caused by Fe<sup>3+</sup> e.g. in ferric oxides.

## CONCLUSIONS AND OUTLOOK

### Conclusions

- The studies show differences in the reflectance spectra of the large core CHB samples with respect to continuum reflectance, spectral slopes, and spectral absorption bands. However, the spectra show evidence that Al-rich clay minerals (montmorillonite) mixed with Mg-phyllosilicates dominate the sediment mineralogy. Furthermore, calcite is a frequent representative in CHB samples of both high and low potassium content samples.
- Reflectance minima (CF) at about 8.0  $\mu\text{m}$  establish a relationship to source materials such as Ca-plagioclase feldspars and pyroxene. This is in agreement with fundamental silicate vibration bands that occur around 10  $\mu\text{m}$ . Weak absorption bands in the UV to NIR may be associated with Ca-rich clinopyroxenes and ferric oxides.
- The illitization of the samples can probably be followed by examining the band depth ratios of 2.2  $\mu\text{m}$ -to-2.3  $\mu\text{m}$ , so that an assessment of the samples of wet and dry climate periods is possible (requires further testing).

### Outlook

- Complementing the spectral measurements for denser coverage with regard to the drill core depths and better statistics.
- Comparison of the spectral measurements with the available  $\mu\text{XRF}$  and radiocarbon analyses.
- Correlations with hyperspectral remote sensing measurements.

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