REFLECTANCE SPECTRAL STUDY OF SECONDARY MINERALOGICAL EVOLUTION AND WEATHERING INTENSITY OF A THICK BASALTIC WEATHERING SEQUENCE IN HAINAN ISLAND, CHINA. J. C. Liu1, H. P. He2, J. R. Michalski1, J. Cuadros3, M. F. Zhou1, W. Tan4, Y. Z. Yao5, X. R. Qin2, S.Y. Li5, G. J. Wei5. Division of Earth and Planetary Sciences, The University of Hong Kong (cugcliu@foxmail.com), 2Guangzhou Institute of Geochemistry, CAS, 3Dept. of Earth Sciences, The Natural History Museum of London, 4Dept. of Geology, Northeastern University, Shenyang.

Introduction: Vis-IR Reflectance spectroscopy (350-2500 nm) is an efficient and effective tool to identify and semi-quantify clay minerals, ferric oxide/hydroxide, and their crystal-chemistry/structure [1-3]. Yet, systematic spectral studies of their mineralogical evolution during weathering, and theoretical analysis of spectral indices for weathering intensity are limited. In this study, reflectance spectra of a long core of a thick basaltic weathering sequence in Hainan Island and a series of intermediate transformation products from montmorillonite to kaolinite, are measured and analyzed to present spectral features associated with weathering trends. We describe general mineralogical transitions, weathering intensity, and crystal chemistry of weathering products developed on igneous rocks from reflectance spectroscopic perspective.

Materials and Method: A 53 m long core was drilled at Chengmai (CM) basaltic weathering sequence in Hainan Island. The climate of Hainan is tropical with high temperature (MAT is 23.7°C) and high precipitation (MAP is 1760 mm/yr) with obvious annual dry and wet seasons. The drill core stopped at 53 m depth because the protolith changes from basaltic material to granitic material and we were interested in weathering of the basalt. The basaltic and granitic materials at the bottom of the drill are also strongly weathered. The long drill core is divided into organic zone, completely weathered zone and semi-weathered zone according to textures and colors of the weathering products. The core samples were collected from 0.25m depth at 0.5 m intervals along the 53m long core and grounded to powder after collection. In addition, transformation experiment from montmorillonite to kaolinite was conducted with addition of Al at 250 °C and pH=5 under autogenous water pressure.

Major oxides were determined by wavelength-dispersive X-ray fluorescence spectrometry (XRF). The total organic carbon content was measured by a Leco C/S analyzer. Powder samples used for XRF chemical analysis are measured by Analytical Spectral Devices (ASD) FieldSpec-3 spectrometer with a circle detector, the diameter of which is 20 mm. Rigaku D/max-1200 X-ray diffractometer with Co Kα1 radiation at The University of Hong Kong is used for mineralogical analysis. The clay mineral composition of the fraction smaller than 2 μm was studied by X-ray diffractometer with CuKα radiation.

Results: Abrupt drops or jumps in major elements occur around 49 m, 39 m, 31.5 m and 20 m in the long core. These major shifts in chemistry are governed by changes in protolith. On the basis of geochemical and textural records, the long core is divided into one episode of rhyolite (deeper than 50 m), three episodes of basaltic lava flow, and one volcanic series (31.5-20m). In each individual episode of basaltic lava flow, there is upwards decreasing trend in concentration of Al oxide, decreasing trend in concentration of Si oxide.

The Co radiation diffractometer produce higher quality XRD patterns with lower fluorescence and better peak to noise ratio than Cu radiation diffractometer for weathered basaltic rocks, because of their relatively high Fe concentration. Weathering products from rhyolite zone and volcanic series zone have much higher quartz content than these from basaltic zones. From bottom to top, weathered basaltic rocks exhibit an decreasing trend of feldspar and goethite content, and increasing trend of quartz, hematite and clay minerals content. In the semi-weathered zone, the clay minerals include nontronite, kaolinite and mixed-layer kaolinite-smectite. In the middle sequence, the clay minerals dominated by kaolinite with minor halloysite. In the uppermost 10 m, the kaolinite content decreases, whereas the gibbsite content increase gradually.

Even though the weathering sequence is composed of several episodes of basalt lava flow, there is broadly increasing and then decreasing trend of BD2200 (Al-OH intensity), and H2165_2nd (kaolinite intensity). For the weathered basalt flow in the semi-weathered zone, there is no obvious change in BD2290 (Fe³⁺-OH intensity) and P2290 (Fe-OH position) with depth. The H2267_2nd (gibbsite intensity) increases gradually from 8 m depth to surface. The H2240_2nd (AlFe³⁺-OH intensity) increases gradually in basalt flow I but decrease gradually from 40 m to the surface. In visible to near infrared wavelength region, all samples possess Fe³⁺-related absorption features around 500 nm (absorption I) and 900 nm (absorption III). For semi-weathered zone, their Fe³⁺ peak position III is around 960 nm, and the Fe³⁺ peak position I is around 490 nm, both of which can be attributed to goethite. In completely weathering zone, the shorter Fe³⁺ peak position
III but longer Fe$^{3+}$ peak position I (> 500 nm) suggest that hematite is the dominant Fe oxide/hydroxide. The Fe$^{3+}$ peak position III of samples in organic zone and weathered basalt II is around 900 nm, larger than that of weathered basalt III. In terms of absorption intensity, BD530_2 (Fe$^{3+}$ intensity I) and BD900 (Fe$^{3+}$ intensity III) increase gradually in the lower profile and keep stable in the upper profile.

In the lower profile, BD1400/BD1900 (weathering intensity I) and BD2200/BD1900 (weathering intensity II) are small (<1.0), and show similar upwards increasing trend with CIA and index of laterization. Correspondingly, there are good correlations between BD1400/BD1900 (weathering intensity I), BD2200/BD1900 (weathering intensity II) and chemical index of alteration (CIA) when CIA is smaller than 0.98. In the upper profile where leaching is intense (CIA>0.98), the values of BD1400/BD1900 (weathering intensity I) and BD2200/BD1900 (weathering intensity II) are larger than 1.0.

For intermediate transformation products from montmorillonite to kaolinite, the BD1900 (interlayer water intensity) decreases gradually, whereas BD1400 (hydroxyl intensity) and BD2200 nm (Al-OH intensity) increase gradually with transformation degree. Correspondingly, the ratios of BD1410 to BD1910 and BD2220 to BD1900 increase.

**Discussion:** There are abrupt shifts in the values of spectral reflectance and spectral parameters at 50 m, 40 m, 32 m and 20 m, including BD900 (Fe$^{3+}$ intensity III), BD2207 (Al-OH intensity), BD2240 (AlFe$^{3+}$-OH intensity) and BD2290 (Fe$^{3+}$-OH intensity). The abrupt shifts in spectral indices are indicative of abrupt changes in mineral assemblages of powder samples. These locations are coincident with the locations of geochemical data gaps, suggesting that gaps in values of spectral reflectance and spectral parameters are the result of lithological changes rather than gradual mineralogical transition caused by leaching in an individual lithological unit. The reflectance of weathered rocks from rhyolite zone and volcanic series is enhanced by their high quartz content, which account for their stronger absorptions and larger band depth values. Therefore, reflectance spectroscopy is a quick and reliable method to identify protolith changes in weathering sequences, which is important for geological study but difficult to discern by naked eye.

The upwards gradual increase in BD2200 (Al-OH intensity) and H2165_2nd (kaolinite intensity) in the lower section imply increase in the abundance of kaolin in weathering products. In the upper profile, the gradual decrease in BD2200 (Al-OH intensity) with gradual increase in H2267_2nd (gibbsite intensity), suggesting that the gibbsite is formed by decomposition of kaolinite. The clay mineralogical transition from nontronite (TOT-type) to kaolinite (TO type) and finally gibbsite (O type) is the reflection of gradual hydrolysis of silicates, gradual leaching of alkaline (earth) elements and Si, and enrichment of Al during weathering. The Fe$^{3+}$ concentration increases gradually from 50 m to 30 m at depth, which is suggested by increasing Fe$^{3+}$ spectral intensity (BD530_2 and BD900), reflecting gradual oxidation of iron. From 40 m to 32 m depth, the disappearance of the Fe$^{3+}$-OH absorption around 2290 nm and gradual decreasing H2240_2nd (AlFe-OH intensity) but increasing BD900 (Fe$^{3+}$ intensity III) suggest release of Fe from Fe$^{3+}$-OH and AlFe$^{3+}$-OH of clays to form ferric oxide/hydroxide. The Fe$^{3+}$ peak position III (P900) in the zone is around 900 nm, implying that the ferric oxide/hydroxide is dominated by hematite with minor goethite. Between 20 m and 5 m depth, the Fe$^{3+}$ peak position III (P900) is around 890 nm, which is closer to hematite peak position, suggestive of increasing proportion of hematite.

BD1400/BD1900 (weathering intensity I) is proposed to estimate weathering intensity. BD1400 (hydroxyl intensity) is contributed by all clays, including Fe/Mg-rich clays. BD1400/BD1900 (weathering intensity I) can reflect the abundance ratio of hydroxyl and interlayer water in weathering products. The ratio increases gradually from smectites to kaolin, and finally gibbsite, owing to decrease in the proportion of interlayer and tetrahedral layer, and increase in the proportion of octahedral layer, caused by leaching of alkaline (earth) elements and Si. In addition, BD1400/BD1900 (weathering intensity I) also increase from goethite to hematite. This is why BD1400/BD1900 (weathering intensity I) increases consequentially towards surface and shows good correlation with CIA values in the Hainan weathering profile. It is important to note that the spectral index also works for non-vermiform soil from Sichuan Basin, China [4]. Therefore, it is reasonable to conclude that BD1400/BD1900 is a general spectral index of weathering intensity for weathered products.

**Conclusion:** Reflectance spectroscopy is very efficient and effective new tool to study weathering sequences, which can be used to identify not only weathering mineralogical transitions but also protoliths change. The BD1400/BD1900 of weathered rocks is good indicator of weathering intensity, when the hydrated minerals in weathered rocks are dominated by clay minerals.

**References:**