Mineralogy and geochemistry of some Thai acid sulfate soils

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Abstract
This research contributes to the understanding of the mineralogy and geochemistry of Thai acid sulfate soils (ASS). Twenty ASS profiles representing former, actual and potential ASS located in inland and coastal areas of the Central Plain and Southeast Coast of Thailand were investigated. Mottles of distinct colors were separated and analyzed by x-ray diffraction (XRD), SEM/EDS and chemical analysis. The mineralogy of the soils is dominated by quartz, feldspars, kaolinite and illite. The coastal ASS often contain more quartz, feldspars and halite than those inland. Various amounts of hematite, goethite, lepidocrocite, akaganéite, gypsum and pyrite (framboidal and single crystal) are also present. Using principal component and classification analysis, it could be demonstrated that the texture of soil parent materials has the strongest influence on variations in geochemical properties.

Keywords
Mineralogy, geochemistry, acid sulfate soils, Thailand

Introduction
Acid sulfate soils (ASS) in Thailand cover approximately 8,800 km^2 (Land Development Department, 2006) mostly occurring in sediments on the Lower Central Plain with small areas located in the Southeast Coast and Peninsular Thailand (Land Development Department, 2006; Janjirawuttikul et al., 2010). The sediments developed during fluctuations of sea level in the Holocene epoch (Sinsakul, 2000). The region represents a complex interplay of alluvial, fluvial and deltaic environments of the Chao Phraya River and its tributaries (Dheeradoloke et al., 1992; Sinsakul, 2000). The small interconnected marine and brackish water alluvial plains of the Southeast Coast and Peninsular regions have been derived from igneous rocks including granites (Department of Mineral Resources, 2007). The ASS are used extensively for agriculture and support dense populations. According to their drainage status and soil morphological characteristics, these soils may be divided into 3 types: former acid sulfate soils (FASS), actual acid sulfate soils (AASS) and potential acid sulfate soils (PASS). The focus of this research was to develop an understanding of the mineralogical and geochemical characteristics of these three types of ASS.

Materials and Methods
Twenty ASS profiles representing former, actual and potential ASS in the Central Plain and Southeast Coast Thailand were collected by auger to the maximum depth of 2 meters, they were packed in sealed plastic containers and immediately cooled to 4° C in order to prevent oxidation of sulfidic materials. A novel preparation procedure involving a biocide was used to limit oxidation during subsequent processing.

Mottles of various types were picked from the soil profile by hand and kept at low temperature until they were analyzed by x-ray diffraction (XRD). Their morphology and composition were examined by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). Before XRD analysis, the abundant quartz particles were removed from hand-picked materials under a dissecting microscope as quartz diluted the samples. Whole soils were analyzed using a combination of ICP-OES (aqua regia digestion) and X-ray fluorescence (XRF) to determine chemical composition. Principal component and classification analysis were used to interpret data.

Results
Mineralogical properties
Mottled materials from inland and coastal areas consisted mainly of quartz, feldspars and clay minerals (kaolinite and illite) (figure 1 and 2 respectively). Coastal ASS often contain more quartz, feldspars and halite than do inland ASS because this coastal region is associated with granite which contributes much quartz and feldspars to sediments with halite originating in sea water (Charusiri et al., 1993). Former and

actual ASS from both inland and coastal regions (particularly from the inland region) where liming had been a common practice contain gypsum in the soil matrix and in some yellow and red mottles (figure 3b).

An important geochemical feature of oxidized ASS is the abundance of iron minerals, especially secondary ferric oxyhydroxides and meta-stable oxyhydroxy sulfate minerals (Sullivan and Bush, 2004). Red mottles contain hematite and goethite, yellow mottle and mottles in root zones contain goethite and jarosite (figure 3c). Goethite and lepidocrocite were present in topsoils from inland PASS (figure 3a) and akaganéite occurs in salty soils. Electron microscopy showed that single crystal and framboidal pyrite are present in reduced horizons of FASS, AASS and PASS (figure 3d).

Geochemical properties

Ninety nine ASS soil samples were analysed for thirty three elements (Al, As, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Gd, K, La, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, S, Sc, Si, Sr, Th, Ti, V, Y, Zn and Zr). Principal component and classification analysis were used to identify affinity groups of elements with texture being included in the data set (figure 4). Only 41% of the variation in data for the soils is explained by the first two factors which is indicative of the diverse nature of these soils (figure 4a and 4b). The data from each region were separately analyzed using factor analysis (data not shown). Attributes could be allocated into two affinity groups. The first group consists of Si and Zr and is indicative of sand. This group is related to ASS from the Southeast Coast area which are derived from granitic sediments and mainly consist of quartz and feldspars (figure 4a) (Charusiri et al., 1993). The second group is diffuse consisting of clay, Al, As, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Gd, K, La, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, S, Sc, Sr, Th, Ti, V, Y, and Zn. This group relates to the clay content of the soils as these elements are mostly constituents of clay minerals and oxides. Some elements probably occur as adsorbed species and in sulfur minerals (Deng et al., 1998; Prakongkep et al., 2008; Toivennen and Österholm, 2011). Former, actual and potential ASS from both regions have quite similar geochemical properties. Most coastal ASS have more Na, S and sand (Si,Zr) than do inland ASS.

Chemical data for topsoils of inland PASS, AASS and FASS tend to be grouped together in the factor diagram because they are relatively organic rich and contains higher amounts of rare earth elements which may have been applied in phosphatic fertilizer (figure 4b) (Hu et al., 1998; Kabata-Pendias, 2011). It is evident that the large variation in chemical composition of these Thai ASS mostly reflects the texture of soil parent materials.

Conclusions

ASS from both regions are mostly dominated by quartz, feldspars, kaolinite and illite. Other minerals occur depending on the development status of the soils as indicated by mottles and different coloured soil materials. Red mottles, particularly in FASS, contain hematite and goethite. Jarosite and goethite are the main secondary iron minerals present in yellow mottles and in mottles along root zones. Goethite and lepidocrocite were present in topsoils of inland PASS. Single crystal and framboidal pyrite are present in reduced horizons of FASS, AASS and PASS. Principal component and classification analysis of chemical properties showed that the texture of soil parent materials has the strongest influence on chemical compositions.

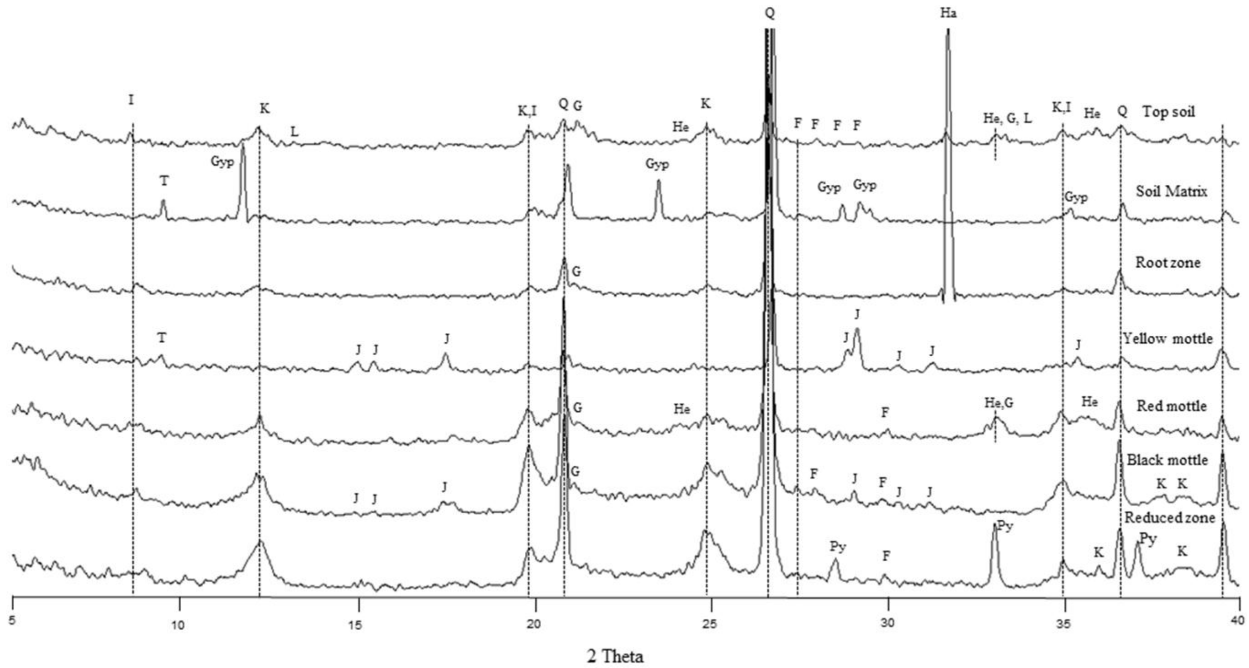

Figure 1: XRD patterns of mottled and other soil materials separated from inland acid sulfate soils (Q = Quartz, F = Feldspars, I = Illite, K = Kaolinite, G = Goethite, He = Hematite, L = Lepidocrocite, Py = Pyrite, J = Jarosite, Gyp = Gypsum and Ha = Halite)

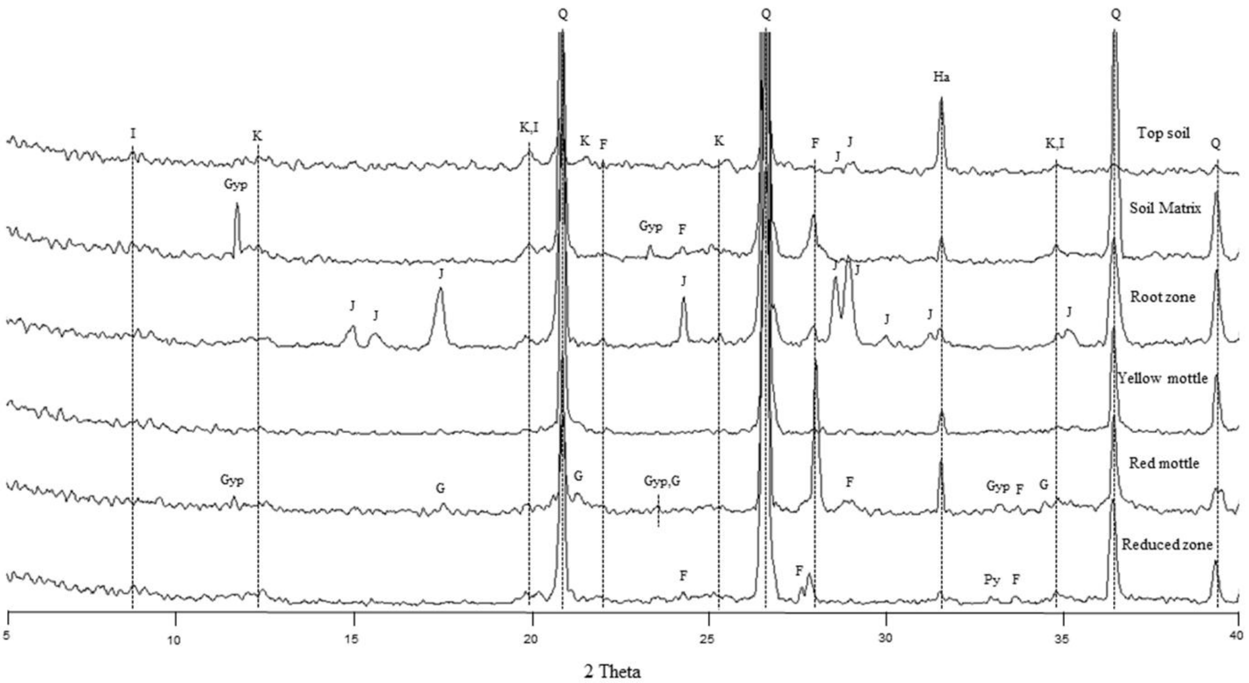

Figure 2: XRD patterns of mottled and other soil materials separated from coastal acid sulfate soils (key as for figure 1)

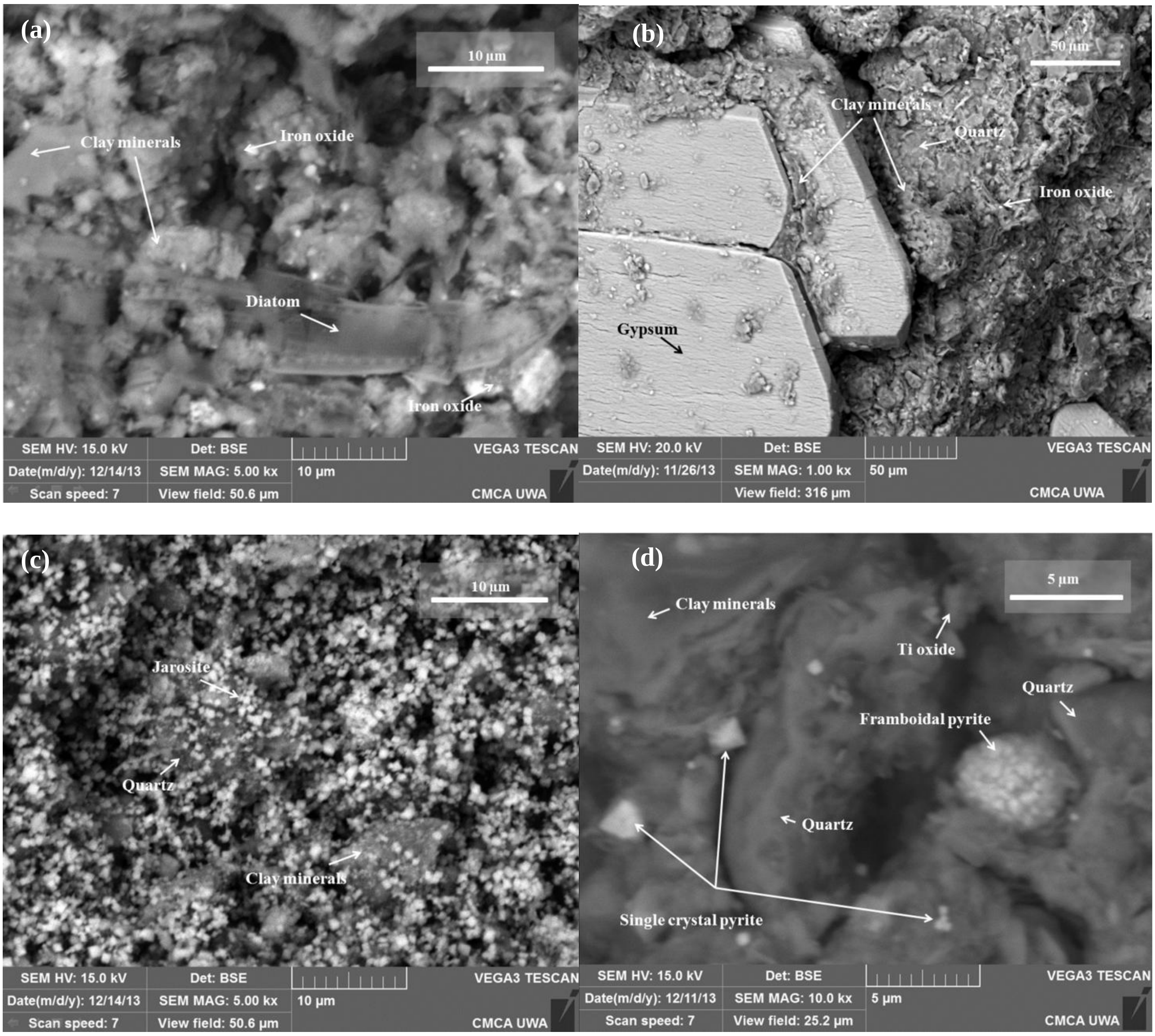

Figure 3: Backscattered electron images of (a) iron oxide, diatom and clay minerals (kaolinite and illite) in red surface soil horizon of inland PASS, (b) gypsum, quartz, iron oxide and clay minerals in soil matrix of inland AASS, (c) jarosite, quartz and clay minerals in yellow mottle of inland AASS and (d) framboidal and single crystal pyrite in a reduced horizon of an inland PASS.

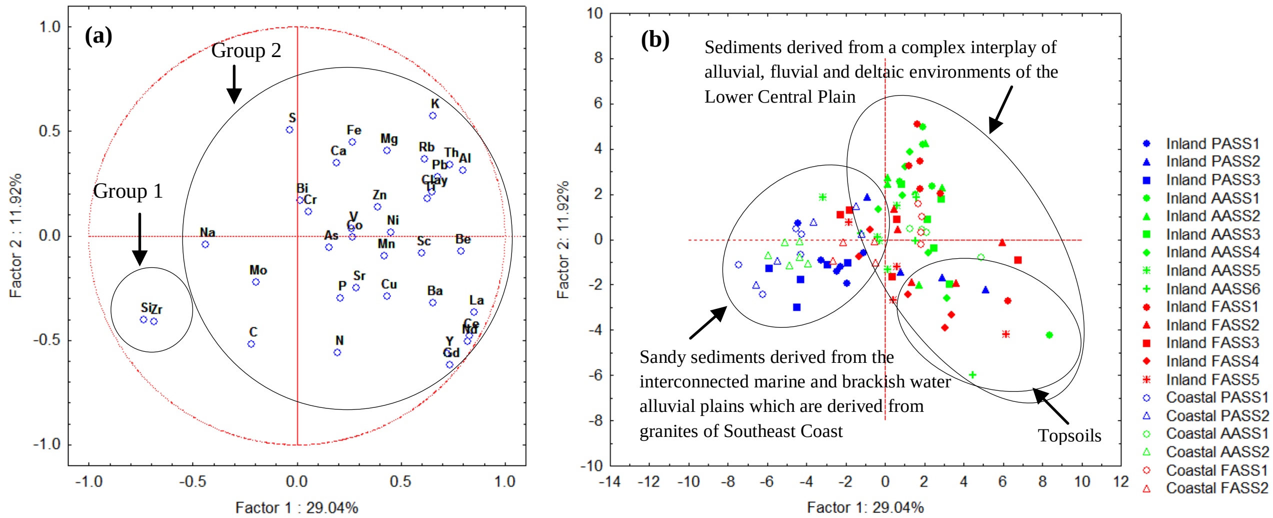

Figure 4: Factor analysis based on chemical properties of bulk samples of Thai ASS (a) distribution of chemical properties (variables) and (b) distribution of samples (cases) (PASS = Potential acid sulfate soils, AASS = Actual acid sulfate soils and FASS = Former acid sulfate soils)

References

Charusiri, P., Clark, A.H., Farrar, E., Archibald, D., Charusiri, B. 1993. Granite belts in Thailand: evidence from ^{40}Ar/^{39}Ar geochronological and geological syntheses. *Journal of Southeast Asian Earth Science* **8**, 127-136.

Deng, H., M. Åström, A. Björklund. 1997. Geochemical and mineralogical properties of sulfide-bearing fine-grained sediments in Finland. *Environmental Geology* **36,** 37-44.

Department of Mineral Resources. 2007. Geology of Thailand. Department of Mineral Resources, Ministry of Natural Resources and Environment, Thailand (In Thai).

Dheeradilok, P., Wongwanich, T., Tansathien, W., Chaodumrong, P. 1992. An introduction to geology of Thailand. In: Piacncharoen, C. (Ed.), National Conferences on “Geologic Resources of Thailand: Potential for Future Development”. Department of Mineral Resources, Bangkok, Thailand, pp. 141-167.

Hu, Y., F. Vanhaecke, L. Moens, R. Dams, P. del Castilho, J. Japenga. 1998. Determination of the aqua regia soluble content of rare earth elements in fertilizer, animal fodder phosphate and manure samples using inductively couples plasma mass spectrometry. *Analytica Chemica Acta* **373**, 95-105.

Janjirawuttikul, N., M. Umitsu, and P. Vijarnsorn. 2010. Paleoenvironment of acid sulfate soils formation in the lower central plain of Thailand. *Research Journal of Environmental Science* **4**, 336-358.

Johnston, S.G., Burton, E.D., Busg, R.T., Keene, A.F., Sullivan, L.A., Smith, D., Mcelnea, Al., Ahern, C.R., Powell, B. 2010. Abundance and fractionation of Al, Fe and trace metals following tidal inundation of a tropical acid sulfate soil. *Applied Geochemistry* **25**, 323-335.

Kabata-Pendias, A. 2011. Elements of Group 3. In Trace Elements in Soil and Plants (4th edition). Broken Sound Parkway, New South Wales, pp. 147-166.

Prakongkep, N., A. Suddhiprakarn, I. Kheoruenromne, M. Smirk, R.J. Gilkes. 2008. The geochemistry of Thai paddy soils. *Geoderma* **144**, 310-324.

Sinsakul, S. 2000. Late Quaternary geology of the Lower Central Plain, Thailand. *Journal of Asian Earth Science* **18**, 415-426.

Sullivan, L.A., Bush, R.T. 2004. Iron-precipitate accumulations associated with waterways in drained coastal acid sulfate soil landscapes of Eastern Australia. *Marine and Freshwater Research* **55**, 727-736.

Toivenen, J., P. Österholm. 2011. Characterization of acid sulfate soils and assessing their impact on a humic boreal lake. *Journal of Geochemical Exploration* **110**, 107-117.

Notes