Distribution and formation conditions of gibbsite in the upland soils of humid Asia: Japan, Thailand and Indonesia

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Abstract
Gibbsite is considered to be an ultimate product of weathering. However, soils in temperate regions such as Japan usually contain gibbsite, whereas some strongly weathered soils in tropical regions do not. We investigated gibbsite distribution in humid Asia (Japan, Thailand and Indonesia) and the relationship between gibbsite and soil solution to explain distribution according to soil forming factors. Clay mineralogy was determined by X-ray diffraction and differential thermal analyses. The chemical composition of soil water extract (indicative of field soil solution) was determined to evaluate minerals' thermodynamic stability. Relatively large amounts of gibbsite were found in the Japanese soils, and no or small amounts in the soils from Thailand and the Java-Sumatra and East Kalimantan region of Indonesia. In Japanese soils the distribution of gibbsite, in which $H_4SiO_4^0$ activity was high enough to be in the kaolinite stability field, was explained by 1) rapid precipitation or formation of gibbsite, and its conservation due to low temperature, which retards resilication to more stable kaolinite under a given $H_4SiO_4^0$ activity, or 2) intense leaching resulting in low $H_4SiO_4^0$ activity. In Thailand and the Java-Sumatra region, high temperatures may enhance formation of the more stable minerals kaolinite and smectite. In contrast to Thai and Indonesian soils, Japanese soils are characterized by an abundance of Al hydroxides or gibbsite, as well as amorphous Al hydroxides and interlayered Al hydroxides between 2:1 layers.

Key Words
$H_4SiO_4^0$ activity; stability diagram; soil solution; weathering.

Introduction
It is widely accepted that gibbsite is "the ultimate end product of weathering", and is usually present in high concentrations in old and weathered soils such as Oxisols and Ultisols. Gibbsite is also found commonly in young soils, i.e. Inceptisols and Andisols. The occurrence of gibbsite in these young soils is usually ascribed to the rapid desilication that occurs in very permeable materials under high rainfall or to paleoclimate. In contrast, Green and Eden (1971), Herrmann *et al.* (2007) and Vazquez (1981) have determined gibbsite occurrence in soils in the initial stages of weathering in southwest England, northern Spain and northern Thailand, respectively.

In humid Asian regions such as Japan, Thailand and Indonesia, information on gibbsite distribution is still scarce. The geological conditions of these regions, characterized by steep topography caused by intense orogenesis and small areas of Oxisols, differ significantly from those of the South American and African shield areas, and differences in gibbsite distribution patterns is to be expected. Characterizing gibbsite distribution and formation conditions will deepen our understanding of soils in these regions.

Thermodynamic analysis and weathering indices help to elucidate the formation conditions of clay minerals. Thermodynamic analysis of soil solution is useful for the theoretical understanding of clay mineral distributions and weathering trends (Watanabe *et al.* 2006). $H_4SiO_4^0$ activity controls mainly the relative stability of gibbsite, kaolinite and smectite: gibbsite is most stable under strong leaching conditions with low $H_4SiO_4^0$ activity, whereas kaolinite is stable under moderate $H_4SiO_4^0$ activity conditions and smectite is stable under restricted drainage with high $H_4SiO_4^0$ activity conditions. Among soil weathering indices, total reserve in bases (TRB) and the relative content of crystalline iron oxides are most common.

The objective of this study is to investigate soil gibbsite distribution in extensive regions of Japan, Thailand and Indonesia, and to discuss gibbsite formation conditions through thermodynamic analysis and weathering indices, which will increase our understanding of soils in these regions.

Materials and methods
Soils
We collected soil samples from Japan, Thailand and Indonesia, according to the soil distribution patterns in the respective regions based on geology and climate. Climatic conditions differ between the regions and soil

temperature and moisture regimes are mesic/thermic-udic in Japan, isohyperthermic-ustic in Thailand, and isohyperthermic-udic in Indonesia. Soil parent materials reflect their geological conditions. Parent materials of soils from Japan, where volcanic belts are distributed, include felsic igneous and sedimentary rocks, and tephra. The soils in Thailand are formed on sedimentary and felsic igneous rocks. The soils from Java and Sumatra, where volcanic belts are also distributed, are formed on andesite, tephra, sedimentary rocks, and limited areas of felsic rocks. Most of East Kalimantan, Indonesia is underlain by sedimentary rocks, there are no active volcanoes, and soils are more weathered on stable rolling landscapes.

Types of soils investigated were common in each region. Japanese soils consist mostly of Udepts, Thai soils Ustults and Humults, Java-Sumatra's Udepts and Udults, and East Kalimantan's Udults. Oxisols are restricted to very limited areas of humid Asia and were not included in the samples.

Analytical methods
Clay minerals were identified by X-ray diffraction (XRD). Gibbsite and kaolin minerals in the clay fraction were quantified by differential thermal analysis (DTA). Before DTA, iron oxides were removed by citrate-dithionite-bicarbonate treatments. Fe (Fe_o) was extracted with ammonium oxalate in the dark. Fe (Fe_d) was also extracted with citrate-dithionite-bicarbonate. Total elemental analysis was made with HF and HClO.

The weathering indices, TRB and $(Fe_d\text{-}Fe_o)/Fe_{total}$ ratio were calculated; TRB is the sum of basic cations (Ca+Mg+K+Na) and gives a chemical estimation of weatherable minerals, and the $(Fe_d\text{-}Fe_o)/Fe_{total}$ ratio indicates the relative content of crystalline iron oxides.

For thermodynamic analysis on the stability of minerals, soil water extracts, of which composition gives an indication of soil solution composition in the field, were collected by continuously shaking the soils for 1 week at 25°C and 1 atm with a soil to water ratio of 1:2. In these samples, pH and Si, Al, Ca, Mg, Na, K concentrations were determined. Inorganic monomeric Al species were determined by the method of Driscoll (1984). Ionic activities were calculated by the extended Debye-Hükel equation.

Results

Gibbsite detection by XRD and DTA
Results of XRD show that gibbsite was detected in most Japanese soils, whereas a gibbsite peak was usually very small or not detected in the other study regions (Figure 1a). In XRD analysis, a large part of Al hydroxide between the 2:1 layers remained even after heat treatment up to 350°C for Japanese, Thai and Java-Sumatra samples, while a small part remained for the East Kalimantan ones. The gibbsite content measured by DTA was high in Japanese samples, low in Thai and Java-Sumatra samples, and not detected in most East Kalimantan soils (Figure 1b).

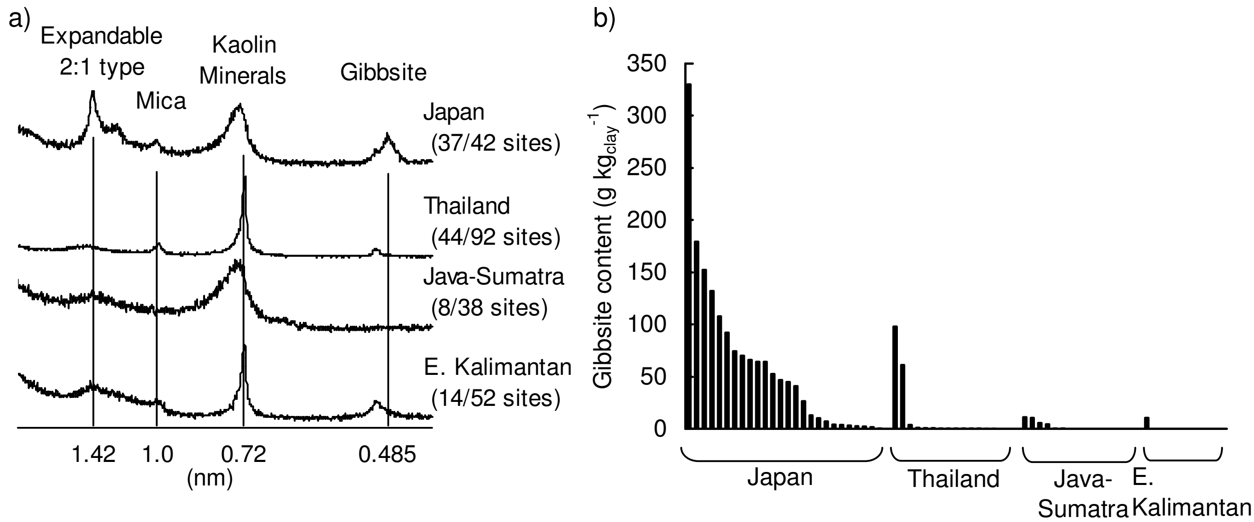

Figure 1. Gibbsite detection by X-ray diffraction (a) and differential thermal analysis (b). Number of sites where gibbsite was detected by X-ray diffraction is in the parentheses.

Weathering indices
Weathering indices indicated that Japanese and Java-Sumatra soils were younger than those in Thailand and East Kalimantan (Figure 2). The $(Fe_d\text{-}Fe_o)/Fe_{total}$ ratio, indicating the relative content of crystalline iron oxides, was low in Japanese and Java-Sumatra soils (mostly less than 0.6), and high in Thai and East

Kalimantan soils (mostly more than 0.6). TRB values, giving a chemical estimation of weatherable minerals, were high in Japanese, Java-Sumatra and Thai soils, with averages of 128, 136 and 106 $cmol_c\ kg^{-1}$, respectively. The TRB values in East Kalimantan soils were smaller than in the other regions, with an average of 69 $cmol_c\ kg^{-1}$. The high values of TRB (Figure 2) and presence of 2:1 type minerals (Figure 1a) indicate that all the investigated soils still contain some amount of weatherable minerals, and are not as strongly weathered and desilicated as Oxisols or Ferralsols.

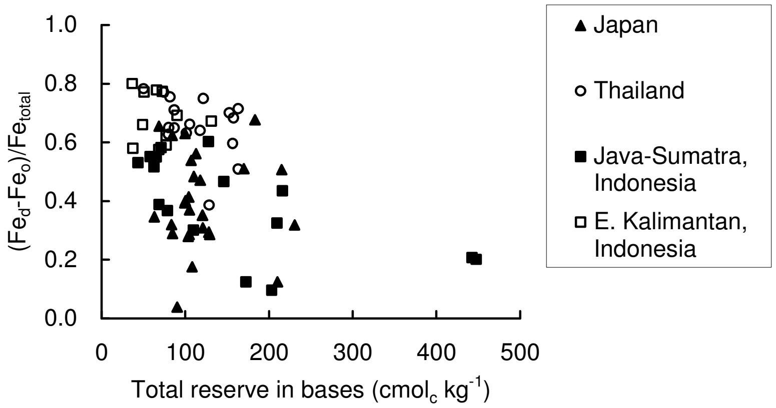

Figure 2. Weathering indices of the soils: total reserve in bases and relative content of crystalline iron oxides.

Composition of soil water extract

Most of the water extracts for Japan, Thailand and Java-Sumatra were supersaturated with gibbsite, indicating the possibility of gibbsite precipitation (Figure 3a). In contrast, East Kalimantan water extracts were undersaturated, indicating dissolution or non formation of gibbsite. Judging from $H_4SiO_4^0$ activity in the soil water extracts, kaolinite was considered to be the most stable mineral in most of the soils (Figure 3b). For the Java-Sumatra region, $H_4SiO_4^0$ activity in the soil water extracts was high and the extract compositions are close to or within the stablity field of smectite (Figure 3b). Composition of soil water extract indicated that gibbsite can form in Japanese soils where the composition is supersaturated with gibbsite (Figure 3a), but is unstable compared with kaolinite (Figure 3b).

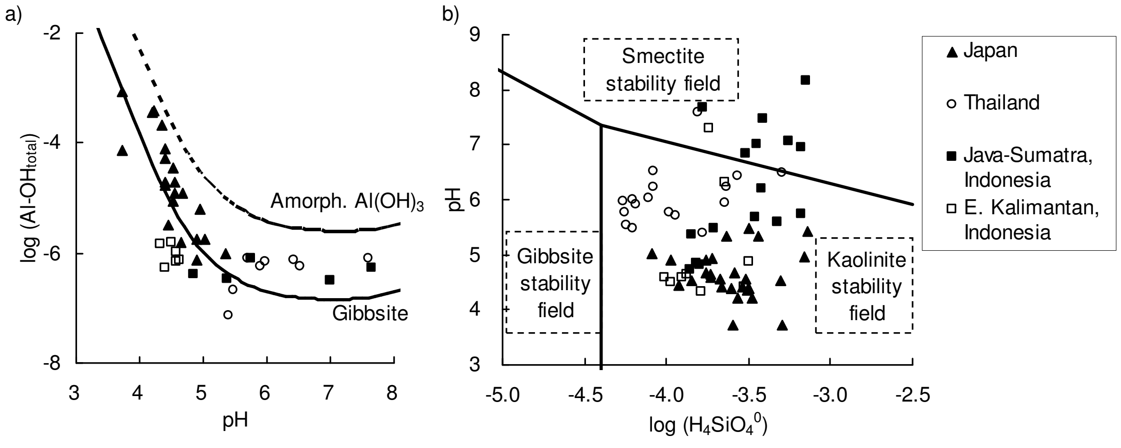

Figure 3. Composition of soil water extract plotted on a solubility diagram with gibbsite and amorphous $Al(OH)_3$ solubility lines (a) and a stability diagram representing relative stability of gibbsite, kaolinite and smectite.

Discussion

Gibbsite formation conditions in humid Asia

The presence of gibbsite in weakly weathered soils where soil water extract indicated that kaolinite or smectite is most stable can be explained by 1) a higher precipitation rate of gibbsite as a transient mineral than that of kaolinite in soil solutions supersaturated with gibbsite, or 2) low $H_4SiO_4^0$ activity due to rapid removal of soil solution or a high leaching rate. Both explain the formation of gibbsite in young soils that are not strongly desilicated. The former is demonstrated by May *et al.* (1986) as gibbsite formation under high $H_4SiO_4^0$ activity of the smectite stable range, which is explained by *Gay-Lussac-Ostwald Step Rule* (Sposito 1994). Synthesis of gibbsite in laboratory experiments is easy and rapid compared to that of kaolinite (Nagy 1995). The second factor is assumed in weathering saprolites and soils derived from volcanic ash (Huang *et al.* 2002).

Depending on gibbsite's precipitation rate, the regional differences in the amount of gibbsite between Japan and the tropical regions of Thailand and Java-Sumatra were presumably due to the difference in temperatures: high temperature in tropical regions stimulates chemical reactions and results in dominance of the most stable mineral or kaolinite, which may consume gibbsite, if present, precipitated as less stable mineral. Thus, the lifetime of gibbsite in tropical regions with high $H_4SiO_4^0$ activity, where kaolinite or smectite is stable, is short. On the other hand, the low temperatures in Japan are considered to inhibit the formation of kaolinite, and gibbsite remains as a transient mineral.

Rapid removal of soil solution resulting in low $H_4SiO_4^0$ activity did not explain well the regional distribution pattern of gibbsite. The content of gibbsite in Japanese soils is higher than that in Indonesian soils, although the leaching in Indonesian soils seems to be as strong as or stronger than Japanese soils.

The above explanations for the presence of gibbsite in young soils under cool temperature conditions seen in this study cannot be applied to the presence of gibbsite in Oxisols. The presence of gibbsite in highly weathered soils such as Oxisols on the shields in South America and Africa is supposed to be caused by strong desilication, where gibbsite is present as the most stable mineral.

Importance of Al hydroxides in Japanese soils

The occurrence of gibbsite as well as the other Al hydroxides, i.e. amorphous Al hydroxides and interlayered Al hydroxides (Watanabe *et al.* 2006) characterize Japanese soils in comparison to Indonesian and Thai soils. These Al hydroxides affect soil properties; amorphous Al and gibbsite contribute to acid neutralization in soils (Watanabe *et al.* 2008), cancel the negative charge in 2:1 layers (Funakawa *et al.* 2008), adsorb phosphorus (Huang *et al.* 2002) and accumulate soil organic matter (Imaya *et al.* 2007).

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