Laterite revisited: mode of formation

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Abstract: During 1800 laterite was perceived as a rock. This idea persisted until the first quarter of the twentieth century. From then on laterite was accepted as iron precipitate and the accumulated material could be remobilized under different condition, which affected its concentration. The formation of laterite is termed as laterization or lateritization. These terms are defined as the process which involves additions of iron with movement of dissolved Fe from elsewhere, in ferrous form with oxidation and precipitation to produce an iron oxide enriched material, leading to the formation of plinthite and ironstone. The mechanisms by which iron moves and is precipitated in the lateritization process are not clear and probably vary in different situations. This paper attempts to discuss these processes by introducing systematic approach to the requirements leading to the understanding of the formation of laterites. A number of laterite samples were taken from the field representing what was thought to be the various stages of laterite formation from plinthite to ironstone. The colours of the materials constituting the samples were noted. Photographs of the samples were taken as whole or cross-section. Parts of the samples were cut for thin sectioning followed by petrographical analysis. Photomicrographs of selected features in the thin section were taken. The samples were also prepared for EPMA analyses. The results of this study indicate that a number of conditions have to be satisfied before the formation of laterite can be initiated. The transformation of ferrous to ferric iron and precipitation of ferric oxides and hydroxide started to occur at the aerobic-anaerobic interface. Zones of different porosity may contribute to the formation of aerobic-anaerobic interface across which Fe must be transported either by flow or diffusion. The mechanisms for iron movement were suggested. Oxygen is the main oxidant in the redox reaction. There must also be a continuous supply of reductants (Fe$^{2+}$) for the growth of laterite and for the progressive development of plinthite to ironstone. The source of iron primarily originated outside the laterite body. Intermittent anaerobic conditions may develop in the laterite body and ferric iron is reduced back to ferrous form. It can move out and be deposited on the surfaces of vesicles and with time filling up the vesicles. Silicate minerals should be dissolved so that partial or total replacement by iron oxide could occur. Evidence of silica dissolution was given. The precipitation process may be controlled by simultaneous diffusion and oxidation reaction. The evidence for this is the occurrence of periodic precipitation also known as Liesegang banding phenomenon as detected by EPMA. As more and more iron oxide accumulates in the laterite body it becomes more compact and its porosity declines. The influence of water on the development of anaerobic condition becomes less significant. During drier periods and higher temperatures water is lost from the laterite body and it becomes hardened.

INTRODUCTION

A Historical Background

McFarlane (1976) gave a comprehensive historical review of laterite. Earlier, Persons (1970) gave an account of laterite genesis, its formation and its use from engineering perspective. During the first quarter of the twentieth century, this rock was perceived as a residuum. This idea persisted until the first weathered rock - a residuum. From about the first decade of the twentieth century there was generally less impetus put upon the residual hypothesis and more upon the precipitatory hypothesis. Nevertheless, the accumulation of the precipitator was believed to be essentially a mechanical process and the stress was primarily on the immobility of the precipitates to account for the accumulation of the residuum. Maclaren (1906) was the first to suggest that the role of groundwater in the formation of laterite was grossly underestimated. He stated that laterite is not the result of decomposition in situ of rocks, but the replacement of such decomposition products; the mechanism of the replacement being enhanced by groundwater. However it was Campbell (1917) who formulated the concept of laterite as precipitate and the accumulated material had a much greater degree of mobility which affected its concentration. From the middle of the twentieth century onwards, with the development of more refined techniques, attentions has been focussed more and more upon the physicochemical reactions believed to have occurred during the development of the many and varied types of laterite.

Lateritization

The formation of laterite is termed as laterization or lateritization. These terms are defined as the process which usually involves additions of iron with movement of dissolved Fe from elsewhere, probably in ferrous form with oxidation and precipitation to produce an iron oxide enriched material, leading to the formation of plinthite and ironstone (Fanning & Fanning, 1989). They suggested that lateritization must be coupled by the process of latosolization involving primarily complex mineral transformations and losses of silica and bases by leaching (see Table 1). Fe is a redox sensitive element where solution may be triggered by reduction (in the form of Fe(III)) and precipitation by oxidation (in the form of Fe(II)). When anaerobic condition changes to aerobic condition in the presence of oxygen, Fe(II) may be oxidised to Fe(III) and hydrolysed to Fe(III)-oxides with consequent release of proton (H+ or H3O+). The proton may attack clay minerals to release octahedral cations such as Al3+ and also silicic acids similar to the process of ferrolysis as described by Brinkman (1970) which may enhance latosolization.

The mechanisms by which iron moves and is accumulated in the lateritization process are not well understood and probably vary in different situations. In order to understand the lateritization occurring in a given soil and landscape, where plinthite or ironstone has formed or is forming, one would require to know: a) the source of the iron that has moved or is moving, b) how it is mobilised, c) how it precipitates and builds up to form plinthite or ironstone, and d) how the hardening takes place. This paper attempts to discuss these processes by introducing systematic approach to the requirements leading to the understanding of the formation of laterites.

<table>
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<tr>
<th>Constituent</th>
<th>Dolerite Rock</th>
<th>Primary Laterite</th>
<th>Lateritic Ironstone</th>
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<tr>
<td>Quartz</td>
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<td>Fe₂O₃/Al₂O₃</td>
<td>0.70</td>
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</table>

Table 1. Chemical composition of parent dolerite rock, primary laterite and associated lateritic ironstone (%). Source: Harrison (1933)

MATERIALS AND METHODS

A number of laterite samples were taken from the field representing what was thought to be the various stages of laterite formation from plinthite to ironstone. The colours of the materials constituting the samples were noted. Photographs of the samples were taken as whole or cross-section. Parts of the samples were cut for thin sectioning followed by petrographical analysis. Photomicrographs of selected features in the thin section were taken with 2.5, 5 and 10 x objective magnification, crossed nicols.

The samples were cut and dry polished for EPMA analyses. The highly automated Cameca SX100 EPMA at the Geology Department, University of Malaya, operating at 20kV beam current, was used for SE (Secondary Electron) and BSE(Back-Scattered Electron) imaging and X-ray mapping.
RESULTS

Hand specimen observation

The photographs of the various samples are shown in Figures 1 to 5.

Figure 1: Soil Clod
There were four main colours that could be observed on the clod ranging from a hue of 10R and value/chroma of 5/8 (red) to a hue of 5YR and value/chroma 8/2 (pinkish-white) according to the Munsell Notation of Colours (1975). The differences in colour should represent two redox zones - red being more oxidized than pinkish white. In the red zone the soil seemed to be more porous and less compact as compared to the pinkish-white zone. A cross-section of a root channel could also be seen here. The pinkish-white zone was more massive. The colour could be due to the soil pores were more likely to be filled with water. The redox potential was likely to be low characterizing reduced condition and ferrous iron should be predominant.

Figure 2a: Outer part (surface) of a laterite (plinthite A) nodule (5 cm diameter)
The surface of the nodule had a mixture of red (10R 5/8) and brownish yellow (10YR 6/8) ‘iron oxide’ or ‘iron hydroxide’. These surface materials are loose and can be scrape off with fingernails.

Figure 2b: Cross-section of laterite (plinthite A) nodule of Figure 2a
This cross-section is mainly red in colour (10R 5/8) and porous in nature with many quartz sand particles. The nodule is hard and unbreakable by hand. The sample is intersected by probably relic of root channel now filled with yellowish material.

Figure 3: Cross-section of Plinthite B
The nodules might have formed around cracks or...
cleavages of bedding, where oxygen can move in, creating aerobic condition, transforming ferrous to ferric iron followed by precipitation of iron oxides and hydroxides. Notice the difference in colour between the material in the cleavage and the material surrounding it. The material in the cleavage was darker in colour (2YR 3/2) as compared to the material surrounding it (2YR 4/6).

**Figure 4:** Cross-section of Plinthite C

This interesting cross-section indicated that laterite started off as nodules. Colours ranged from 7.5YR 8/2 to 2.5YR 3/5. With time these nodules grew and they 'merged' with each other to form a massive material. Water movement might carry loose clay material away leaving vesicles within the massive mass. Deposition of new precipitate might occur within the vesicles until they were filled up.

**Figure 5a:** Iron stone

The sample was a dense, massive and hard material, which could be called ironstone. Colours were mostly 7.5YR 3/2. It showed nodular features with varying sizes. These nodules merged with each other leaving vesicles near the point of contact, which could be filled up later.

**Figure 5b:** Cross-section of ironstone

This cross-section showed that the sample was massive with all vesicles being filled up. Merging nodules are mostly rounded in shapes. Ironstones are comparatively hard in nature. Transformation of hydroxide to oxide by loosing water causes the material to become hard.

**Petrographic observation**

**Figures 6a, b and c**

These photomicrographs suggest dissolution of ferric oxide, perhaps under anaerobic condition and reoxidized as ferric hydroxide. Some dissolved material might have moved out of the compact mass and re-precipitated on void surfaces as linings (Fig. 6c) and with time filling up the void (see Fig. 4 and 5b).

**Figures 7a, b and c**

The dissolution of silica in laterite is indicated by these photomicrographs. Figure 7a shows an invasion of a quartz particle by iron oxide by the action of acid produced during oxidation reaction as explained above. A more advanced invasion is shown in Figure 7b and the most advanced invasion is shown in Figure 7c.

**EPMA on laterite samples**

**Figure 8**

Figure 8 shows the X-ray map of a selected section of the polished sample. It is interesting to note that the EPMA imaging clearly indicate periodic precipitation of iron oxide intercalated with banding of Si and Al minerals. This phenomenon is called Liesegang banding (Stern, 1954; Keller & Rubinow, 1981; Venzl & Ross, 1982) which indicates that the precipitation process involved the interdiffusion of two dissolved ions, which can react with one another, in this case $O_2$ and $Fe^{2+}$, to form relatively insoluble solid, ferric oxides. This is evidence that the formation of laterite is controlled by the coupled diffusion and oxidation reactions and the exclusion of Si and Al ions.

**Figure 9**

Figure 9 is a X-ray map showing the Al and Si ions occupying the more porous portion (lower half) while the more diffusible Fe ions are concentrated in the less permeable portions (top half) forming Liesegang bandings.

**Figure 10**

Figure 10 is a X-ray map showing a channel (right) rimmed by material rich in Si and Al but devoid of the more diffusible Fe which remained in the bulk of the laterite material.

**DISCUSSIONS**

**Sources of iron**

The basic concept of lateritization is accumulation of iron oxide/hydroxide in ferric form in aerobic zones with simultaneous depletion of silica and bases (Table 1) within the laterite body. The source of iron that has moved originated from the anaerobic zones. Textural differences in soils could create differences in redox conditions caused by the interplay between water and oxygen filling the pore spaces in soils. Coarse textured soils have higher possibility to receive oxygen as compared to fine textured soils with the same amount of water. As can be seen in Figure 1, the aerobic zone in a soil clod is red in colour and was characterized by presumably higher porosity and coarser texture. Anaerobic zone with lighter colour was presumably less porous and fine textured. This light coloured zone is the zone of iron depletion (Berner, 1980). From field observation, on a larger scale, these two zones can be seen in a landscape; i.e. zone of aeration characterized by reddish soil colour is always accompanied side by side with an anaerobic zone or a depletion zone characterized by whitish soil colour.

The cross-section of Plinthite A in Figure 2b showed a porous material in which accumulation of Fe occurred, which supports this contention. There exist an interface between anaerobic and aerobic zones through which mobile $Fe^{3+}$ iron crosses and oxidized to $Fe^{2+}$ to form iron oxides and hydroxides. The existence of these two zones with different redox conditions is a prerequisite for laterite formation. After heavy rainfall aerobic zones may be filled with water getting rid of the air containing oxygen. After a period of time with persistent saturated condition, this zone can become anaerobic and reverse transformation of $Fe^{3+}$ to $Fe^{2+}$ (Fig. 6a, b and c) may occur and could move along with the receding water to other location in the laterite body or a landscape, again crossing another anaerobic/aerobic interface to be reoxidized. Porosity is an important contributing variable to the flux of the reacting ions in the redox reaction.
Figure 8. X-ray mapping indicating periodic precipitation of iron oxide intercalated with banding of Si and Al minerals, a phenomenon called Liesegang banding.

Figure 9. X-ray map showing the Al and Si ions occupying the more porous portion (lower half) while the more diffusible Fe ions are concentrated in the less permeable portions (top half) forming Liesegang bandings.

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Movement and precipitation of iron

The intricacies of the physicochemical interactions occurring at this interface may well be explained by a process called coupled diffusion and oxidation reactions as described by Ahmad (1986), Ahmad & Nye (1990) and Kirk et al. (1990). A generalised process occurring in the diffusion and oxidation reaction system can be described by considering an anaerobic zone surrounding a growing aerobic zone (perhaps a mottle), with a continuous oxygen supply (perhaps through a micro-channel, a dead root-hair), as in Figure 11. Vepraskas & Bouma (1976) used small tubings to simulate the formation of mottles in anaerobic soils for oxygen supply. After a period of time one of two extreme situations may result depending on the rate processes prevailing at the anaerobic-aerobic interface. In one situation the mottle grows relatively fast making the whole zone aerobic and in the other the mottle grows very slowly with high concentration of iron within the mottle. In the first situation the rate of diffusion of oxygen is much faster than the rate of oxidation of Fe(II). Thus the oxygen can diffuse outward into the anaerobic zone and the whole zone will become aerobic. In the second situation the rate of oxidation is much faster than the rate of diffusion of oxygen. The oxygen is consumed by the oxidation reaction before it has the chance to diffuse deeper into the anaerobic zone. As the reaction proceeds there would be a depletion of Fe(II) in the mottle creating a concentration gradient of Fe(II) across the anaerobic-aerobic interface. This results in the net movement of Fe(II) towards the aerobic mottle zone where it reacts with the oxygen or other oxidant. The main redox couples operating at the anaerobic-aerobic interface are \( \text{O}_2 - \text{H}_2\text{O} \) and \( \text{Fe(OH)}_3 - \text{Fe}^{2+} \). The slow growth of the mottle and the concentration of iron oxide within the mottle depends on the rate of diffusion of Fe(II). Many occurrences in the field show that the second situation is the most common where zone of depletion can be clearly seen. Taking an infinitesimal section of the anaerobic-aerobic interface the reactions involved is shown in Figure 12. The vertical arrows indicate the net movements of the components (\( \text{O}_2 \), Fe\(^{2+} \), and H\(^+ \)). The horizontal arrows represent the redox reactions and the interactions between ions in liquid and solid phases.

The above processes are quite similar to the authigenic processes as described quantitatively by Berner (1980). He suggested that precipitation or crystal growth involves: a) the transport of ions (atoms or molecules) to the reaction or formation sites, b) various surface reactions including adsorption, nucleation, surface diffusion, dehydration, ion exchange etc., that result in the formation of precipitate or incorporation of the ions into the crystal lattice and, c) removal of products of the reaction from the reaction site. The rate of reaction may be limited either by transport of ions, or by surface chemical reaction, or by a combination of both processes.

Figure 10. X-ray map showing a channel (right) rimmed by material rich in Si and Al but devoid of the more diffusible Fe which remained in the bulk of the laterite material.
The types of iron oxide precipitate formed depend on Fe concentration, pH, Eh and temperature, which are influenced by external environment. A comprehensive description of iron oxides pertaining to their forms and occurrence in soils, their modes of formation, and their properties relevant to soils, were given by Schwertmann & Taylor (1977).

**Breakdown of silicate minerals in laterite**

It can be seen that the oxidation of Fe$^{2+}$ produces acid. For every Fe$^{2+}$ oxidised, 2 H$^+$ are produced so that acidification occurs at the oxidation sites within the mottles. This may contribute to the breakdown of clay mineral kaolinite, commonly formed under tropical condition, residing in the aerobic mottles, according to the chemical equation:

$$\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4 \text{(kaolinite)} + 6\text{H}^+ \leftrightarrow 2\text{Al}^{3+} + 2\text{H}_2\text{SiO}_4 + \text{H}_2\text{O}. \quad (1)$$

Lindsay (1979) showed a quantitative consideration on the solubility of kaolinite in a soil system. The products of this breakdown are Al$^{3+}$ and silicic acid. These products may move out of the aerobic zone under concentration gradients or water flow. The depletion of silica in the laterite body is a process called desilication. The use of acid for the breakdown of clay mineral enhances further the oxidation and precipitation processes. With time the mottle will finally transform into ironstone.

Under normal soil condition quartz is somewhat stable and its solubility is very low. The solubility is a function of temperature, pH, particle size and most importantly, the presence of disrupted surface layer (Wilding et al., 1977). Moreover metallic ions such as Al, and Fe could be sorbed onto silica surfaces forming insoluble silicate coating. The result of the petrographic study indicated that quartz mineral could be dissolved in the laterite body (Fig. 7a, b, and c). Oxidation and precipitation of Fe produce acid. It seems possible, according to Wilding (1977) that the formation of silicate coating would be inhibited in acid condition as shown by the equation:

$$-\text{Si(OH)}_4 + [\text{Fe(OH)}_2]^+ \leftrightarrow \text{SiFe(OH)}_3 + \text{H}^+ \quad \ldots \quad (2)$$

At the disrupted surface layer of quartz particle Fe oxides could sorb the dissolved silica by the following reactions:

$$\text{Si(OH)}_3 \leftrightarrow [\text{SiO(OH)}_2]^+ + \text{H}^+ \quad \ldots \quad (3)$$

$$[\text{SiO(OH)}_3]^+ + \text{Fe(OH)}_3 \leftrightarrow \text{Fe(OH)}_3\text{Si(OH)}_3 + \text{OH}^- \quad \ldots \quad (4)$$

In such system it is suggested that Fe oxide act as a sink for soluble silica and increase the dissolution of silica. It is apparent that the reactions are pH dependent. The neutralization of acidity may enhance the dissolution of silica.
CONCLUSIONS

The results of this study indicate that a number of conditions have to be satisfied before the formation of laterite can be initiated. These are:

1. The existence of aerobic-anaerobic interface. Transformation of ferrous to ferric iron and precipitation of ferric oxides and hydroxide occur at this interface.

2. There should exist zones of different porosity. Zones of different porosity may contribute to the formation of aerobic-anaerobic interface across which Fe^{3+} must be transported either by flow or diffusion.

3. There must be a continuous supply of oxidant. Oxygen is the main oxidant in the redox reaction. Oxygen can move towards the reaction sites through soil cracks cleavages of weathered rocks and root channels, creating aerobic conditions within the soil and landscape. Other possible oxidant is NO_{3}^{-} ions by which the oxygen molecule is used for oxidation while Nitrogen gas is formed in the process of denitrification.

4. There must also be a continuous supply of reductants for the growth of laterite and for the progressive development of plinthite to ironstone. The source of iron for the formation of laterite primarily originated from the weathering and oxidation reaction. The evidence for this is the Liesegang banding phenomenon. As more and more iron oxide accumulates in the laterite body it becomes more compact and its porosity declines. The influence of water on the development of anaerobic condition becomes less significant. During drier periods and higher temperatures water is lost from the laterite body and it becomes harden.

5. Silicate minerals should be dissolved so that partial or total replacement by iron oxide could occur. Evidence of silica dissolution was given.

The precipitation process is controlled by diffusion and oxidation reaction. The evidence for this is the occurrence of periodic precipitation also known as Liesegang banding phenomenon. As more and more iron oxide accumulates in the laterite body it becomes more compact and its porosity declines. The influence of water on the development of anaerobic condition becomes less significant. During drier periods and higher temperatures water is lost from the laterite body and it becomes harden.

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