# Formation of Secondary Minerals across Topogeothermal Sequences on Ratu Crater of Tangkuban Parahu Volcano, West Java

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***Abstract*****—** *The internal environment of volcanic craters is influenced by chemical content contained in geothermal resources, in the form of fumarola and solfatara, as well as the topography and extreme fluctuating temperatures can create a specific phenomenon to the formation of secondary minerals.*

*There were 5 represent profiles samples i.e. Profile A (toeslope), Profile B , Profile D (backslope), G Profile and Profile J (summit), plotted based on the topographic gradient of Ratu Crater, Tangkuban Parahu Volcano (topogeothermal), with a steep to very steep slope grade (van Zuidam , 1985). Samples on each profile were analyzed on its mineralogical properties.*

*Mineralogical analysis showed that the sand fraction of heavy minerals (density > 2.87) are opaque, augite, and hiperstin with varying percentages, while light mineral (density < 2.87) are a volcanic glass, zeolite, andesin, labradorite, bytownite and rock fragments. Extraction with oxalic and pyrophosphate acid showed the highest mineral content of allophane (1.414 %), imogolite (0.391 %), and ferrihydrite (2,091 %) contained in the profile D (backslope). The lowest content founded in the Profile A (toeslope), which has a smaller content than the Profile J (summit).*

*XRD analysis results (without treatment) showed that in each profile (A, B, D, G, J) have almost the same reflection pattern that consists of gypsum (4.27Å), feldspar (3.1-3.25 Å, cristobalite (4.04 Å), gibsite (4.85 Å), calcite (3.03 Å), kaolinite (7.1 Å) and quartz (3.34 Å).*

*XRD analysis (Mg+glycol) on each profile mostly dominated by non-crystalline minerals (amorphous), however the Profile J (Summit) and the Profile A (toeslope) are dominated by crystalline minerals that have been developed from amorphous minerals, i.e. mineral 2:1 (smectite and chlorite) and mineral 1:1 (halloysite and kaolinite).*

***Keywords*****—** ***Crater, Secondary Mineral, Topogeothermal, Volcanic Ash.***

## I. INTRODUCTION

Tangkuban Perahu volcano is located in West Java, it is one of the active volcanoes in Indonesia. Tangkuban Perahu is a post-caldera volcano situated on the eastern rim of Sunda caldera. Some previous researcher conducted research on Tangkuban Perahu volcano. However, they only explained the geologic condition of the volcano, and the soil genesis develoved in the external system of the volcano. Crater is one of the volcanic depression form as result of the explosion, a part of volcano internal system. The mineral development inside the crater still remains unclear.

The clay mineralogy of soils formed in volcanic materials varies widely depending on such factors as the composition of the parent material, stage of soil formation, pH, soil moisture regime, and the accumulation of organic matter (Shoji et al., 1993). Poorly ordered materials such as allophone, imogolite, ferryhydrite, and Al- and Fe-humus complexes often dominate the clay size fraction of volcanic soils.

Generally, Climatic conditions and their effects on degree of leaching and soil solution chemistry also play an important role in volcanic material weathering pathways and secondary mineral neogenesis. Volcanic materials may weather directly to Short Range Order (SRO) materials or kaolins, depending on the amount of rainfall and solution silica activity (Parfitt et al., 1983). Kaolin minerals can show a wide range of structural disorder (Churchman, 1990; Soma et al., 1992; Newman et al., 1994) due primarily to Al-vacancy displacements in the octahedral sheet (Plancon and Tchoubar, 1977a, 1977b; Soma et al., 1992). These vacancies may originate from nonstoichiometric substitution of $Fe^{3+}$ for $Al^{3+}$ in the octahedral sheet (Soma et al., 1992).

Indeed, some studies have shown that crystalline clays, such as halloysite, form initially without a SRO precursor in weathering systems that exhibit high solution silica activity (McIntosh, 1979; Singleton et al., 1989). Variable effects of hydration might also add to degree of disorder in halloysite. Low rainfall or leaching promotes high solution silica activity, facilitating halloysite formation, whereas high precipitation or leaching promotes low silica activity, favoring SRO material formation (Parfitt et al., 1983). Coupled with precipitation, temperature also plays a role in the formation of SRO materials or crystalline minerals, with crystallization promoted as the soil climate becomes warmer and drier (Talibudeen, 1981; Schwertmann, 1985). Short-range ordered materials are more persistent under cool soil conditions because crystallization is hindered by low input of thermal energy, therefore we hypothesize that thermal energy radiated by sulphide existance in crater basis will affect the transformation of the mineral surrounding in the crater, beside effected by translocation process.

Therefore, the study will investigate the formation of secondary mineral across topogeothermal sequences on ratu crater of Tangkuban Parahu volcano, west java.

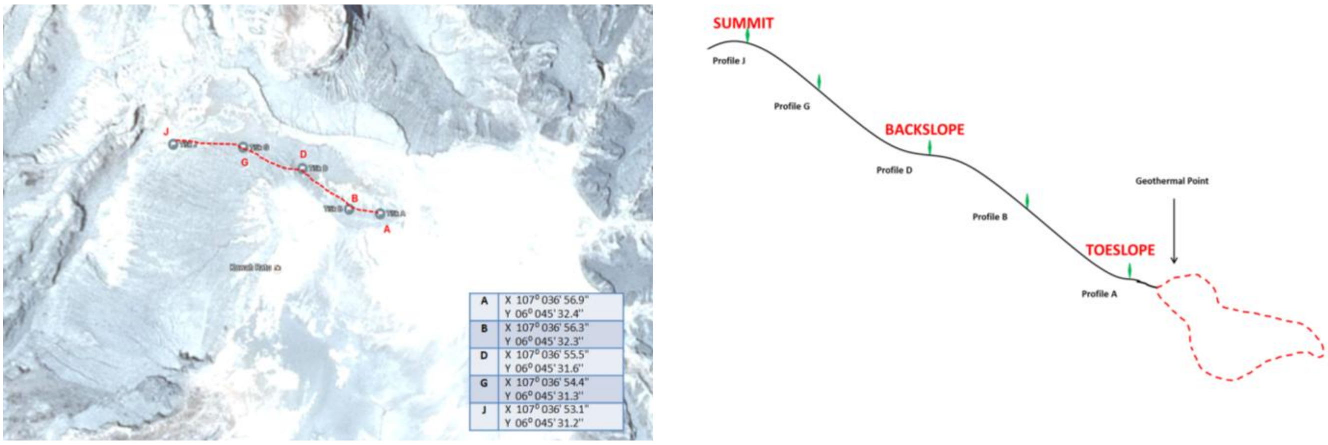
## II. MATERIALS AND METHODS

### 2.1 Environmental Setting

A series of vocanic ash material will be examined across an elevation gradient on the crater slope (topogeothermal). The transect spans a broad environmental gradient with variation in slope level.

### 2.2 Field Methods

In this study, there were 10 represent soil profiles (A-J), were taken based on the topographic gradient of Ratu Crater, Tangkuban Parahu Volcano (topogeothermal), with a steep to very steep slope grade (van Zuidam , 1985). However, the observation and discussion focused on the data were taken only from five (5) profiles, the Profile A (toeslope), Profile B, Profile D (backslope), G Profile and Profile J (summit). Samples on each profile were analyzed on its mineralogical properties. All samples were dominated by volcanic ash parent material, as the result of Tangkuban Parahu Volcano eruption.



| | |
|---|---|
| A | X 107⁰036' 56.9"<br>Y 06⁰045' 32.4" |
| B | X 107⁰036' 56.3"<br>Y 06⁰045' 32.3" |
| D | X 107⁰036' 55.5"<br>Y 06⁰045' 31.6" |
| G | X 107⁰036' 54.4"<br>Y 06⁰045' 31.3" |
| J | X 107⁰036' 53.1"<br>Y 06⁰045' 31.2" |

**FIG 1. ILLUSTRATION OF SAMPLES DISTRIBUTION ON TOPOGEOTHERMAL SEQUENCES**

### 2.3 Laboratory Methods

### 2.3.1 Physical Analysis

Samples were air-dried and crushed to pass a 2-mm sieve. Coarse (2.0–0.2 mm), fine-sand (0.20–0.02 mm), silt (0.020–0.002 mm), and clay (0.002 mm) fractions were separated by pipette and sieving following pretreatment with $H_2O_2$ to oxidize organic matter and dispersion aided by sodium hexa-metaphosphate. Water content at 1.5 MPa was determined on air-dried and field-moist 2-mm soil (Soil Survey Laboratory Staff, 1996).

### 2.3.2 Chemical Analysis

Soil pH was measured by potentiometry in soil/solution suspensions of 1:2.5 $H_2O$ and 1:2.5 1 *M* KCl. Organic C (OC) was estimated by wet digestion with a modified Walkley-Black procedure.

### 2.3.3 Mineralogical Analysis

X-ray diffraction (XRD) was performed on the clay (<2 µm), silt (2–53 µm), and very fine sand (53–100 µm) fractions for each horizon of the some pedon in observation line. Clays and silts will be collected by repeated mixing and centrifugation with dilute $Na_2CO_3$. X-ray analyses made with a Diano XRD 8000 diffractometer (Diano, Woburn, MA).

Clays and silts were oriented on glass slides with the following standard treatments: Mg saturation, Mg saturation and glycerol solvation (Whittig and Allardice, 1986). Halloysite was distinguished from kaolinite by the presence of a peak near 1.0 nm after intercalation with formamide (Churchman, 1990). Very fine sands were analyzed using random powder mounts.

Selective dissolution was performed on the fine-earth fraction by nonsequential extractions using sodium pyrophosphate, acid ammonium oxalate, and citrate–dithionite (Soil Survey Staff, 1996). Samples were shaken for 15 h with 0.1 *M* sodium pyrophosphate at pH 10 and a soil/liquid ratio of 1:100 to extract Al ($Al_p$) bound in organo–metal complexes. Samples were shaken for 4 h in the dark with a soil/oxalate ratio of 1:100 with 0.2 *M* ammonium oxalate adjusted to pH 3.0 with oxalic acid to extract Al, Fe, and Si ($Al_o$, $Fe_o$, and $Si_o$) from organic complexes and SRO Fe oxyhydroxides (e.g., ferrihydrite) and aluminosilicates (e.g., allophane and imogolite).

Citrate–dithionite extraction consisted of shaking 4 g of soil for 15 h with 2 g of sodium dithionite and 100 mL of 0.3 *M* sodium citrate to extract Fe and Al ($Fe_d$ and $Al_d$) from organic complexes, some SRO aluminosilicates, and secondary forms of Fe oxyhydroxides (Parfitt and Childs, 1988; Dahlgren, 1994). Aluminum and Fe concentrations were determined by atomic absorption spectrophotometry, and Si was determined colorimetrically (Weaver et al., 1968).

NaF pH was analysed using 1:50 1 *M* NaF to determine amorphous minerals.

All laboratory analysis are conducted at Pedology Laboratory, University of Idaho (Moscow - USA); Soil Research Institute, Bogor; Geology Laboratories, Bandung; and Laboratory of Soil Chemistry and Plant Nutrition, Padjadjaran University.

## III. RESULTS AND DISCUSSION

### 3.1 Pedon Characterization

### 3.1.1 pH

Soil pH values in $H_2O$ ranged between 2.71 and 5.51 and showed distinct trend with increasing elevation (Table 1). This is an opposite of similar elevation gradients on granite and basalt parent materials ranges, where pH steadily declined with increasing elevation (Alexander et al., 1993; Dahlgren et al., 1997a). As well as Soil pH in KCl ranged between 2.33 and 4.16 and showed similar trend with Soil pH values in $H_2O$.

Geothermal system play an important role in this phenomenon, which contains rich of sulfuric acid, indicating major amounts of exchangeable $H^+$ (Tan, 1991). Delta pH values [$\Delta pH = pH(KCl) - pH(H_2O)$] ranged between -0.38 and -1.35, indicating that all the sites were dominated by a net negative surface charge (Soil Survey Staff, 1996). The unexpectedly high pH in the upper elevation sites may result from decreased leaching, due to leaching process by precipitation and not infiltrating the soil profile.

TABLE 1
DATA OF CHEMICAL SOIL PROPERTIES DERIVED FROM RATU CRATER TOPOGEOTHERMAL SEQUENCES

| Profile | pH | | |
|---|---|---|---|
| | $H_2O$ | KCl | ΔpH |
| A | 2.71 | 2.33 | -0.38 |
| B | 3.65 | 3.05 | -0.60 |
| D | 3.68 | 3.05 | -0.63 |
| G | 4.80 | 4.16 | -0.64 |
| J | 5.51 | 4.16 | -1.35 |

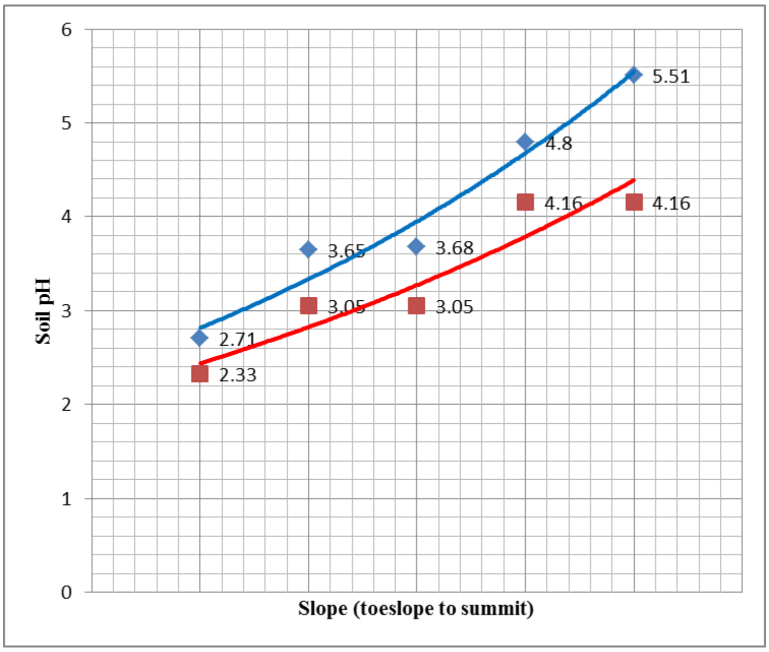


**FIG 2. SOIL PH VALUE, $H_2O$ (BLUE GRIDLINE), KCl (red gridline)**

### 3.1.2 Organic Carbon

Soil organic C content (on a mass percentage basis) on upper horizon has no clear pattern, trend decreased from Profile J (2.65%) to Profile G (0,43 %) subsequently increase at underneath point (D 0,67%). Soil C content variation across the gradient, is probably due to the presence of SRO materials that provide numerous adsorption sites for C coupled with Al–humus complexation that inhibits biodegradation of organic C (Saggar et al., 1996; Yuan et al., 2000; Parfi tt et al., 2002; Rasmussen et al., 2006).

**TABLE 2**
**DATA OF CHEMICAL SOIL PROPERTIES DERIVED FROM RATU CRATER TOPOGEOTHERMAL SEQUENCES**

| Profile | S | Fe | Pyrite ($FeS_2$) | C Org |
|---|---|---|---|---|
| | ------------------ % ------------- | | | |
| A | 0.10 | 0.02 | 0.04 | 0.73 |
| B | 0.09 | 3.04 | 0.17 | 0.63 |
| D | 0.14 | 2.13 | 0.26 | 0.40 |
| G | 0.22 | 0.07 | 0.14 | 0.43 |
| J | 0.16 | 2.18 | 0.30 | 2.65 |

## 3.2 Mineralogy

### 3.2.1 Volcanic Glass

Volcanic glass content varied substantially across the gradient and may be a function of differential weathering environments or parent material variation, or both. A point nearest of geothermal contained very high volcanic glass (< 95%) in the very fine sand fractions of surface horizons (Fig. 3). The existance suggests that glass also accumulated by leaching process from the top to bottom gradient, due either to precipitation or gravitation energy. Glass content increased significantly in A and G, where suggesting a possible accumulating threshold related to the form of slope gradient. Profile B, D, and J showed more less in glass content relative to A-1 and B-1.

The reason for this decrease is very clear, it may result from enhanced leaching due to the degree of gradient slope. It is also possible that some volcanic glass in the lower elevation soils originated from the latest volcanic eruptions, and the glass also shows the resistance to chemical weathering (Shoji et al., 1993).

Linear line in Fig. 3 shows trend clearly the increase of volcanic glass content from lower to higher gradient slope.

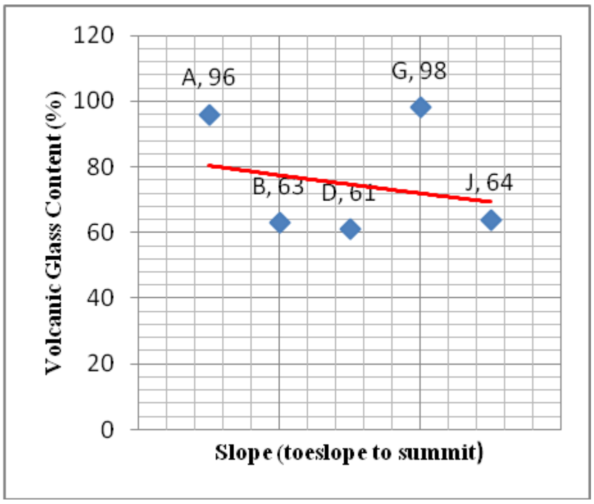


**FIG. 3. VOLCANIC GLASS CONTENT IN THE VERY FINE SAN (VFS) FRACTION OF SURFACE HORIZON ON GRADIENT FROM TOESLOPE (PROFILE A) TO SUMMIT (PROFILE J).**

### 3.2.2 X-Ray Diffraction (Clay Fraction)

Samples were selected from three point representing of extreme different gradient, i.e. Profile A as toeslope, Profile D as backslope, and Profile J as summit.

XRD analysis (without treatment) on silt and very find sand fraction results showed that in each profile (A, B, D, G, J) have almost the same reflection pattern that consists of gypsum (4.27Å), feldspar (3.1-3.25 Å, cristobalite (4.04 Å), gibsite (4.85 Å), calcite (3.03 Å), kaolinite (7.1 Å) and quartz (3.34 Å).

XRD analysis (Mg+glycol) on clay fraction in each profile mostly dominated by non-crystalline minerals (amorphous), however the Profile J (Summit) and the Profile A (toeslope) are dominated by crystalline minerals that have been developed from amorphous minerals, i.e. mineral 2 : 1 (smectite and chlorite) and mineral 1 : 1 (halloysite and kaolinite).

**TABLE 3**
**MINERAL COMPOSITION OF EACH PROFILE AS RESULTS OF XRD ANALYSIS ON SILT AND VERY FINE SAND FRACTION**

| Profile | Mineral |
|---|---|
| **A** | Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)<br>Gypsum ($CaSO_4.2H_2O$)<br>Kristobalite ($SiO_2$)<br>Quarzt ($SiO_2$) |
| **B** | Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)<br>Gypsum ($CaSO_4.2H_2O$)<br>Kristobalite ($SiO_2$)<br>Quarzt ($SiO_2$) |
| **D** | Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)<br>Gypsum ($CaSO_4.2H_2O$)<br>Quarzt ($SiO_2$) |
| **G** | Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)<br>Gibsite ($Al_2O_3.2H_2O$)<br>Gypsum ($CaSO_4.2H_2O$)<br>Quarzt ($SiO_2$) |
| **J** | Feldspar ($KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$)<br>Gibsite ($Al_2O_3.2H_2O$)<br>Gypsum ($CaSO_4.2H_2O$)<br>Calcite ($CaCO_3$)<br>Kaolinite ($Al_2O_3$ $2SiO_4.2H_2O$)<br>Kristobalite ($SiO_2$)<br>Quarzt ($SiO_2$) |

XRD analysis (Mg+glycol) on each profile (Fig. 3) mostly dominated by non-crystalline minerals (amorphous), however the Profile J (Summit) and the Profile A (toeslope) are dominated by crystalline minerals that have been developed from amorphous minerals, i.e. mineral 2 : 1 (smectite and chlorite) and mineral 1 : 1 (halloysite and kaolinite).

Based on correlation of analysis results data, the sudy shown that crystalline clays, such as halloysite, form initially without a SRO precursor in weathering systems that exhibit high solution silica activity (McIntosh, 1979; Singleton et al., 1989). Variable effects of hydration might also add to degree of disorder in halloysite. Low rainfall or leaching promote high solution silica activity, facilitating halloysite formation, whereas high precipitation or leaching promote low silica activity, favoring SRO material formation (Parfitt et al., 1983). Coupled with precipitation, temperature also plays a role in the formation of SRO materials or crystalline minerals, with crystallization promoted as the soil climate becomes warmer and drier (Talibudeen, 1981; Schwertmann, 1985). Short-range ordered materials are more persistent under cool soil conditions because crystallization is hindered by low input of thermal energy, therefore we hypothesize that thermal energy radiated by sulphide existance in crater basis will affect the transformation of the mineral surrounding in the crater, beside effected by translocation process.

Therefore, Climatic conditions and their effects on degree of leaching and soil solution chemistry (topogeothermal) also play an important role in volcanic material weathering pathways and secondary mineral neogenesis

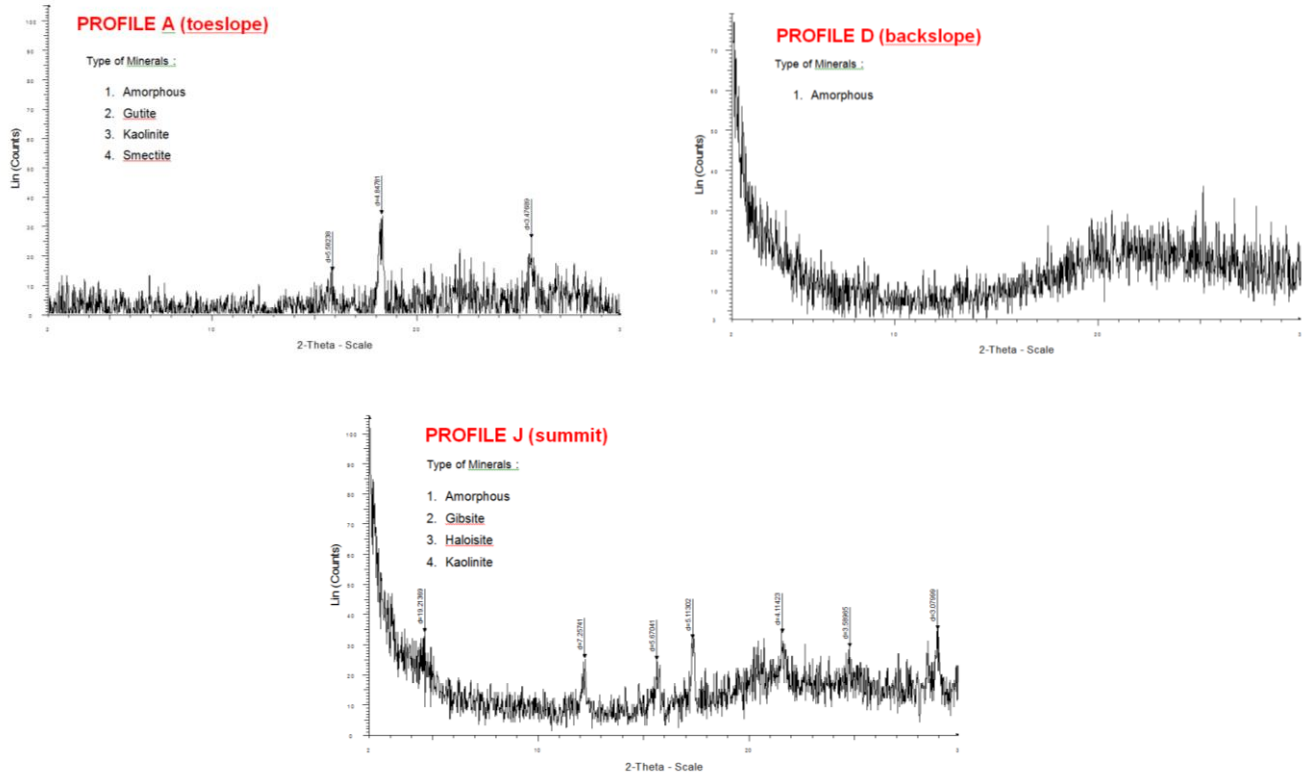


**FIG. 4. X-RAY DIFFRACTOGRAMS FOR RANDOM POWDER MOUNTS OF $Mg^{2+}$ SATURATION AND GLYCEROL SOLVATION, CLAY FRACTIONS FROM SURFACE HORIZONS ON EACH PROFILE (A, D, J)**

## IV. CONCLUSION

Based on the results of this study concluded the topography of the crater (topogeotermal) influence on the formation of secondary mineral soil with specific content indicated on each profile

Temperature and content of the geothermal source (fumarole and solfatar) influence on the formation of secondary minerals crater, secondary mineral formation in the lower profile (toeslope) dominated crystalline minerals as the effects of temperature and specific content of the crater geothermal environment.

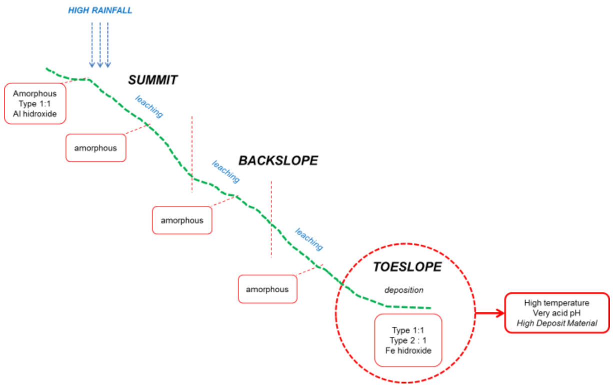


**FIG. 5. MECHANISM OF SECONDARY MINERALS FORMATION ON INTERNAL TOPOGRAPHY SEQUENCE OF RATU CRATER, TANGKUBAN PARAHU VOLCANO**

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