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Chemical weathering in hardened volcanic horizons (tepetates) of the State of Mexico

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ABSTRACT

Weathering is one of the most important phenomena that affect the balance dynamics of the Earth's crust. The chemical composition of soil samples and hardened horizons from seven profiles (P1 to P7) of the State of Mexico was compared to detect the degree of alteration by means of weathering indices. In hardened horizons, the dominant elements are SiO_2, Al_2O_3, Na_2O, K_2O and TiO_2, corresponding to 86.8 % of the total oxides. The weathering indices based on the mobility and immobilization of alkaline and alkaline earth elements reveal that the B horizons and the hardened horizons of profiles P4, P5, P6 and P7 are generally more altered than the surface horizons, therefore they have a greater pedogenic development. Profiles P1, P2 and P3 show incipient weathering. The geochemical indices and chemical relationships used in this study to evaluate weathering and associated basic alteration processes showed consistent results. These coincide in indicating incipient to moderate weathering acting in the seven profiles, with variable intensity in all the hardened horizons. The intensity variation defines a sequence of chemical weathering for the hardened horizons: P6> P4> P5> P7> P2> P3> P1, where P6 has the highest degree of weathering in the indices: CIA, CPA, CIA-K, CIW, PIA, IPark, V.

Key words: Volcanic tuff; chemical weathering; pyroclasts; total oxides; tepetate; Mexico.

RESUMEN

La meteorización es uno de los fenómenos más importantes que afectan la dinámica de equilibrio de la corteza terrestre. Se comparó la composición química de muestras de suelo y horizontes endurecidos de siete perfiles (P1 a P7) del Estado de México para detectar el grado de alteración mediante índices de meteorización. En horizontes endurecidos, los óxidos dominantes son SiO_2, Al_2O_3, Na_2O, K_2O *y* TiO_2, *correspondientes al 86.8 % del total de óxidos. Los índices de meteorización basados en la movilidad e inmovilización de elementos alcalinos y alcalinotérreos revelan que los horizontes B y los horizontes endurecidos de los perfiles P4, P5, P6 y P7 están generalmente más alterados que los horizontes superficiales, por lo que tienen un mayor desarrollo pedogénico. Los perfiles P1, P2 y P3 mostraron una meteorización incipiente. Los índices geoquímicos y las relaciones químicas utilizados en este estudio para evaluar la meteorización y los procesos de alteración básica asociados mostraron resultados consistentes. Estos coinciden en indicar una meteorización incipiente a moderada interactuando en los siete perfiles, la cual presenta diferente intensidad en todos los horizontes endurecidos. La variación en la intensidad permitió establecer una secuencia de meteorización química para los horizontes endurecidos: P6> P4> P5> P7> P2> P3> P1, donde P6 presenta el grado más alto de meteorización en los índices: CIA, CPA, CIA-K, CIW, PIA, IPark, V.*

Palabras clave: toba volcánica; meteorización química; piroclastos; óxidos totales; tepetate; México.

INTRODUCTION

The name tepetate refers to hardened, compacted, or cemented horizons, found in volcanic landscapes, underlying soils, or surface outcrops. In Mexico, hardened horizons known as "tepetates" take up nearly 30 % of the total surface of the Mexican Republic (Pajares-Moreno *et al.*, 2010). These are layers of volcanic material (tuff) with pedological secondary depositions, which adopt physical and chemical properties in accordance with the nature of the different mineralogical components. They are characterized by their hardness, low porosity, limited biological activity and low fertility level. All these features represent a limiting factor in regard to plant development, restricting root penetration, which devaluates or impedes its agricultural use. Pyrogenic materials mainly form hardened horizons: volcanic glass, quartz, pyroxene, mica, plagioclase, alkali feldspar and iron oxide, as well as authigenic minerals: halloysite, kaolinite, montmorillonite, allophane, hydrated iron oxides and aluminum and silicon sesquioxide, among others (Acevedo-Sandoval *et al.*, 2003, 2012; Gama-Castro *et al.*, 2007).

The usefulness of this study is because the presence of tepetates deteriorates, to different degrees, the natural aptitude of the soil to function within the limits of an ecosystem, which generates risks to the other elements in its environmental context. These hardened horizons are common in the Trans-Mexican Volcanic Belt, occurring mainly in the foothills of the volcanic mountain ranges. From an

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agricultural point of view, the clayey soils that cover the tepetates have low fertility, which is why the peasants abandon them, initiating intense erosion. Consequently, the surface tepetates present a highly degraded landscape, without vegetation cover, without soils and with little possibility of rehabilitating the system, since there is no water recharge in the aquifer given that runoff is stronger than minimal infiltration. Rehabilitating such a system is expensive and time consuming.

Weathering is one of the most important processes affecting the dynamics of the Earth´s crust balance (Jayawardena and Izawa, 1994; Ramos-Vázquez and Armstrong-Altrin, 2019). The weathering processes are one of the first mechanisms that control the material recycling system on the Earth surface, playing a very important role in the generation of a great variety of geological products (Ohta and Arai, 2007).

Che *et al.* (2012) defined chemical weathering as the mineralogical, textural, and geochemical changes in rocks through dissolution, leaching, precipitation, enrichment and/or formation of secondary minerals at different scales, which reduces rock hardness. The factors interfering with chemical weathering are the same five factors that control soil development, that is to say: weather, parent material, relief, organic activity and time (González *et al.*, 2004; Le Blond *et al.*, 2015; Ramos-Vázquez and Armstrong-Altrin, 2019; Armstrong-Altrin *et al.*, 2021). Tzozué and Yongue-Fouateu (2017) reported that the main chemical components that control rock weathering are: solution pH, parent material composition and crystallinity, microenvironment, oxidation-reduction potential, temperature and ionic strength.

Fiantis *et al.* (2010) and Abbaslou *et al.* (2013) described that evaluating the geochemical components and weathering indices improves the understanding of soil formation and pedogenetic processes. Le Blond *et al.* (2015) reported that pedogenesis is a process where weathering alters the rock constituents through the loss of the most mobile elements (Mg, Ca, Na and K) and the enrichment of the less mobile elements (Si, Al, Fe) combined with the alteration and formation of new secondary minerals and the accumulation of organic matter.

Price and Velbel (2003), Fiantis *et al.* (2010), Le Blond *et al.* (2015) and Taboada *et al.* (2016) reported that the chemical weathering indices are used to measure and compare pedogenesis of soils, to evaluate the fertility, and to determine the origin of soil nutrients, as well as to demonstrate the impact of weather on rock disintegration, to predict the origin of soil minerals, the weathering associated with neotectonic lineaments, to quantify the engineering properties of regoliths, and/or to simply recognize element mobility during weathering. Besides, they are employed to interpret the alteration of modern and ancient sediments. Souri *et al.* (2006) reported that all the information relevant to soil weathering is essential to a great number of research topics in the agricultural and environmental fields.

Weathering indices are based on the molecular proportion of mobile oxides against immobile oxides; it is assumed that the distribution of the elements through the profile is mainly regulated by the weathering degree (Che *et al.*, 2012). It is also mentioned that the chemical weathering indices, in addition, assume that the content of ignition losses along the eroded profiles is also regulated by the degree of weathering (Baldermann *et al.*, 2021).

The bibliography reports different indices employed to measure the degree of chemical weathering in rocks (Armstrong-Altrin *et al.*, 2019; Armstrong-Altrin *et al.*, 2021; Baldermann *et al.*, 2021). In Mexico, the information about weathering processes in hardened horizons is extremely poor (Armstrong-Altrin *et al.*, 2019; Ramos-Vázquez and Armstrong-Altrin, 2019; Armstrong-Altrin *et al.*, 2021) and for this reason, the aim of the study is to present a general view of the variability in the values of chemical weathering indices of the hardened horizons (tepetates) of the State of Mexico, seeking to improve the understanding of the weathering processes in regard to the formation and evolution of hardened volcanic soils.

MATERIALS AND METHODS

Study area

The study zone is located between the following coordinates: 19°36’53” and 19°38’51”N and 99°16’25” and 99°21’34”W, at an altitude between 2350 and 2600 m a.s.l., in the municipality of Nicolás Romero, State of Mexico. The region is part of the Trans-Mexican Volcanic Belt. The studied soils and hardened horizons are located at the Tarango Formation, which is constituted by volcanic ash, pumice, lava, and dacitic tuff deposits (Pliocene-Pleistocene). The most important minerals present in the soils are quartz, feldspar, chlorite, calcite, volcanic glass, and lithic fragments in the clay fraction (Acevedo-Sandoval *et al.*, 2002, 2003). The morphological description of the seven profiles is presented in Table 1.

Climate C(W_2)(W)bi is temperate to sub-humid with rainfall regime during summer, a winter rainfall average of less than 5 % of the annual total and an annual rainfall of 604.8 mm; isothermal, with annual temperature fluctuation of less than 5 °C. The average annual temperature is of 13.9 °C, while the soil humidity regime is udic, and the temperature regime is isomesic (Soil Survey Staff, 1995).

Profile selection was based on previous photo-interpretation studies (Zuidam and Zuidam, 1979), through the use of panchromatic aerial photographs (black and white) on a 1:75000 scale model, together with support cartographical material and several reconnaissance trips to study zone. Seven profiles located at different altitudes were selected (Figure 1): Site 1 (2450 m) in induced grassland with a slope between 15 and 20 %; Site 2 (2300 m) in an *Opuntia* and *Agavaceae* species field with a slope between 6 and 10 %; Site 3 (2480 m) in induced grassland with a slope of 10 %; Site 4 (2500 m) in a forest ground (*Quercus* sp.) with a slope between 5 and 7 %; Site 5 (2600 m) in induced grassland with a slope of 12 %; Site 6 (2600 m) in a forest ground (*Quercus* sp. and *Pinus* sp.) with a slope between 15 %; and Site 7 (2350 m) in an area reforested with *Eucalypthus* sp. with a slope between 10 and 12 %. The study zone is characterized by the influence of human activities and presents hardened horizons through the profiles, which were morphologically described by Vela-Correa *et al.* (2012). Soil profiles 1, 2 and 3 were classified in the Entisols order and soil profiles 4, 5, 6 and 7 in the Alfisols order.

With the purpose of conducting a geochemical analysis of the hardened horizons, the total chemical composition was determined by X-Ray fluorescence spectrometry employing a PERKIN-ELMER equipment (model 3110). Different indices and chemical reactions were calculated in accordance with this information, in order to estimate the weathering degree. Table 2 shows the chemical weathering indices proposed by several authors that were used in the current study.

RESULTS AND DISCUSSION

The soil elemental composition can be inherent to the parent material, and it can gradually change as a result of the influence of the predominant pedogenetic processes. Nevertheless, the rate of accumulation depends on the susceptibility of the rock or mineral components to the effect of weather, climate and human activities (Abbaslou *et al.*, 2013).

Taking as reference the environmental conditions, particularly the climate (relation between temperature and humidity) represents an extremely important element, which is used to determine the kind and intensity of the alteration and disintegration processes acting on the rock. It can be seen that, at 13.9 °C (average annual temperature) and 604.8 mm (annual rainfall), the climatic factors of the study area indicate that the chemical weathering intensity is moderate (González *et al* 2004), the climatic harshness index calculated for the study zone is of 93.06 which is interpreted as low.

In Figure 2a–2c, three characteristic profiles of the evaluated soils are shown. Figure 2a groups profiles 1-3 showing incipient weathering, < 60 cm, Typic Fragiudalfs, one or more horizons within 60 cm from the mineral soil surface, and redox depletions, with a chroma of 2 or less. Figure 2b groups profiles 4, 5 and 7 showing moderate to high weathering, > 60, Typic Dystrochrept, soils with ocric horizon and with cambic subsurface horizon, well drained, very deep. Finally, Figure 2c shows Profile 6, Typic Eutrocrepth, high content of amorphous or low crystallinity materials.

The chemical composition of the seven hardened horizons (Table 3) indicates that these are felsic materials, where the most prevailing components are silicon, aluminum, and sodium oxides, the last one related to plagioclase feldspar (andesine and albite) (Acevedo-Sandoval, *et al*., 2012). Surface horizons show a slight decrease in the SiO_2 concentration with increase in the weathering degree (Table 3), except for profiles 4 and 5, in which values increase. In hardened horizons, the content of Al_2O_3 varies from 4.45 to 21.21 %, while in surface horizons it varies from 13.27 to 15.80 % as a result of high plagioclase content. Manga *et al*. (2013) reported that the relative enrichment of Al (secondary clay minerals, kaolinite, and gibbsite formation) and the loss of Ca and Na are typical processes of weathered rocks and soils (Okewale and Grobler, 2021).

In surface horizons, the content of Fe_2O_3 is higher than in hardened horizons except for profiles 4 and 5. These results indicate that oxidation is an important weathering process for Fe minerals as biotite, which is commonly found in pyrogenic materials. Acevedo-Sandoval *et al*. (2002) concluded that the solubility of Fe, Al and Si oxides varies in hardened layers because of the edaphic processes.

The content of TiO_2 varies from 0.63 to 6.0 %, sharply increasing in surface horizons in relation to hardened horizons. In soils, these values are above the world average for soils (0.67 %) (Abbaslou *et al*., 2013). The increase in the TiO_2 content is originated by the weathering of amphiboles and pyroxenes identified through petrographic analysis

Table 1. Morphological description of the seven soil profiles under study.

Profile	Depth (cm)	Structure	Consistence moist	Consistence dry	Horizont boundaries	Textural class	PDI	HDI	Colour dry	Colour moist
1	0–20	sbk/de/fi	VFI	SHA	A/S	SCL	0.21	0.38	10YR6/2	10YR7/1
	20–32	sbk/mo/me	VFI	HA	A/S	CL		0.36	2.5Y7/0	2.5Y5/2
	30–50	sbk/mo/me	VFR	SHA	A/S	SCL		0.30	2.5Y8/0	2.5Y6/2
	> 50	ma	FI	VHA	A/S	CL		0.21	2.5Y8/0	2.5Y7/2
2	0–17	sbk/we/fi	VFR	LO	C/W	CL	0.16	0.28	7.5YR5/2	7.5YR3/2
	17–31	sbk/mo/me	VFR	SHA	C/W	SCL		0.29	7.5YR4/2	7.5YR2/0
	31–43	sbk/we/me	FR	HA	A/W	L		0.29	7.5YR7/2	7.5YR5/2
	> 43	ma	VFI	VHA	A/S	LS		0.16	7.5YR8/2	7.5YR6/2
3	0–8	sbk/mo/fi	FR	HA	A/W	SCL	0.18	0.19	10YR6/3	10YR3/3
	8–19	sbk/mo/me	FR	SHA	A/W	SCL		0.24	10YR7/3	7.5YR5/4
	19–40	sbk/mo/fi	FR	HA	A/S	LS		0.37	10YR8/4	10YR4/4
	> 40	ma	FI	HA	A/S	LS		0.20	2.5Y8/2	2.5Y5/4
4	0–6	sbk/we/me	VFR	LO	C/W	L	0.22	0.11	10YR6/3	10YR3/4
	6–18	sbk/mo/me	VFI	HA	C/W	L		0.26	10YR6/4	10YR3/3
	18–36	sbk/mo/me	VFR	HA	C/W	CL		0.21	10YR7/2	10YR5/4
	36–59	sbk/mo/co	FR	HA	C/W	C		0.38	10YR6/4	10YR4/3
	59–73	sbk/mo/me	FR	HA	C/W	C		0.37	10YR8/6	10YR4/4
	> 73	ma	VFI	EHA	C/S	C		0.18	10YR8/6	10YR5/8
5	0–13	sbk/mo/me	VFR	SHA	A/W	L	0.15	0.16	10YR5/2	10YR3/3
	13–27	sbk/mo/me	VFR	HA	A/W	L		0.21	10YR6/1	10YR3/2
	27–57	sbk/we/co	FR	HA	A/S	L		0.27	10YR6/3	10YR4/4
	> 57	ma	VFI	HA	A/S	L		0.18	10YR7/3	10YR4/4
6	0–12	sbk/mo/fi	VFI	HA	C/W	L	0.20	0.14	10YR6/3	10YR3/4
	12–29	sbk/mo/me	VFR	SHA	A/W	L		0.33	10YR6/6	5YR4/4
	29–48	sbk/mo/co	FR	HA	A/W	C		0.37	7.5YR3/4	5YR2/2
	48–72	sbk/mo/me	VFR	VHA	A/W	L		0.36	5YR7/3	5YR4/6
	> 72	ma	VFI	VHA	A/W	C		0.18	5YR7/3	5YR4/4
7	0–12	sbk/mo/co	FR	SHA	A/W	CL	0.16	0.16	10YR4/3	10YR3/2
	12–56	sbk/mo/me	FR	SHA	A/W	CL		0.21	10YR5/6	10YR4/4
	56–62	sbk/mo/fi	VFR	HA	A/S	C		0.44	10YR6/3	10YR4/2
	> 62	ma	FR	SHA	A/S	LS		0.19	10YR7/3	10YR5/6

Soil structure: sbk, subangular blocky; ma, massive. Grades of structure: we, weak; mo; moderate. Size classes: me, medium; co, coarse; fi, fine. Consistence dry: LO, loose; SHA, slightly hard; HA, hard; EHA, extremely hard. Consistence moist: VFR, very friable; FR, friable; FI, firm; VFI, very firm. Textural classes: LS, loamy sand; C, clay; CL, clay loam; L, loam; SCL, sandy clay loam. Horizon boundaries: A, abrupt; C, clear; S, smoothW, wavy. PDI: profile development index; HDI, horizon development index. Values between 0.00 (no development) and 1.00 (maximum development) (Birkeland *et al*., 1991).

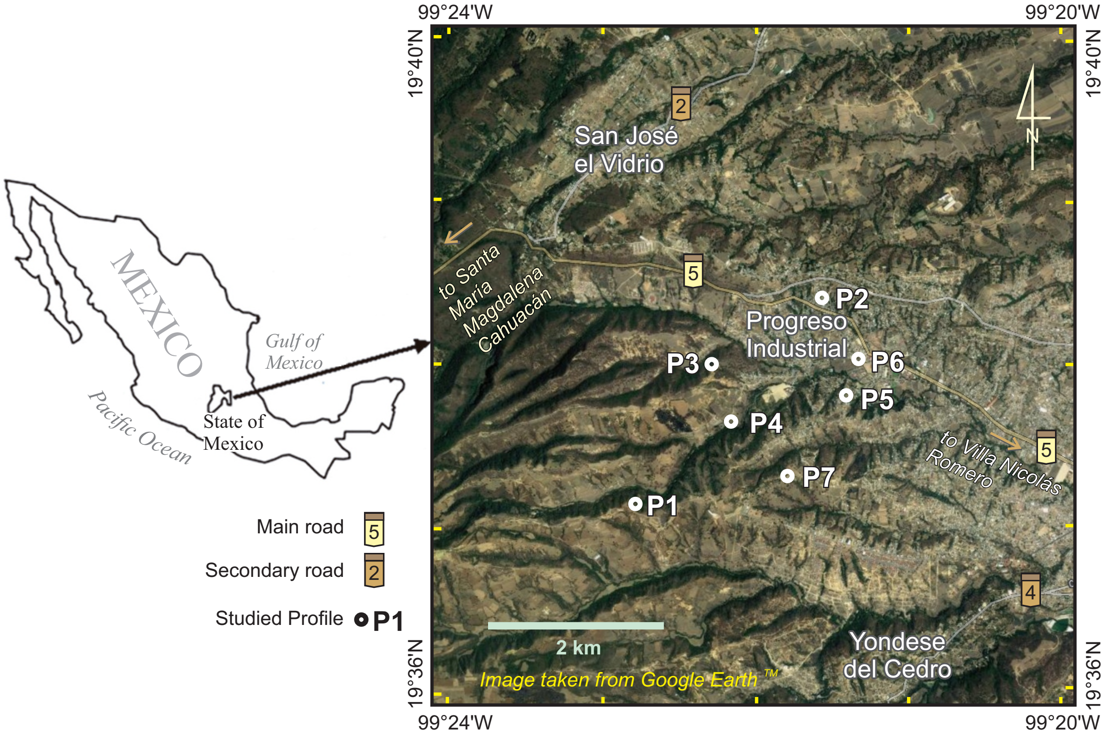


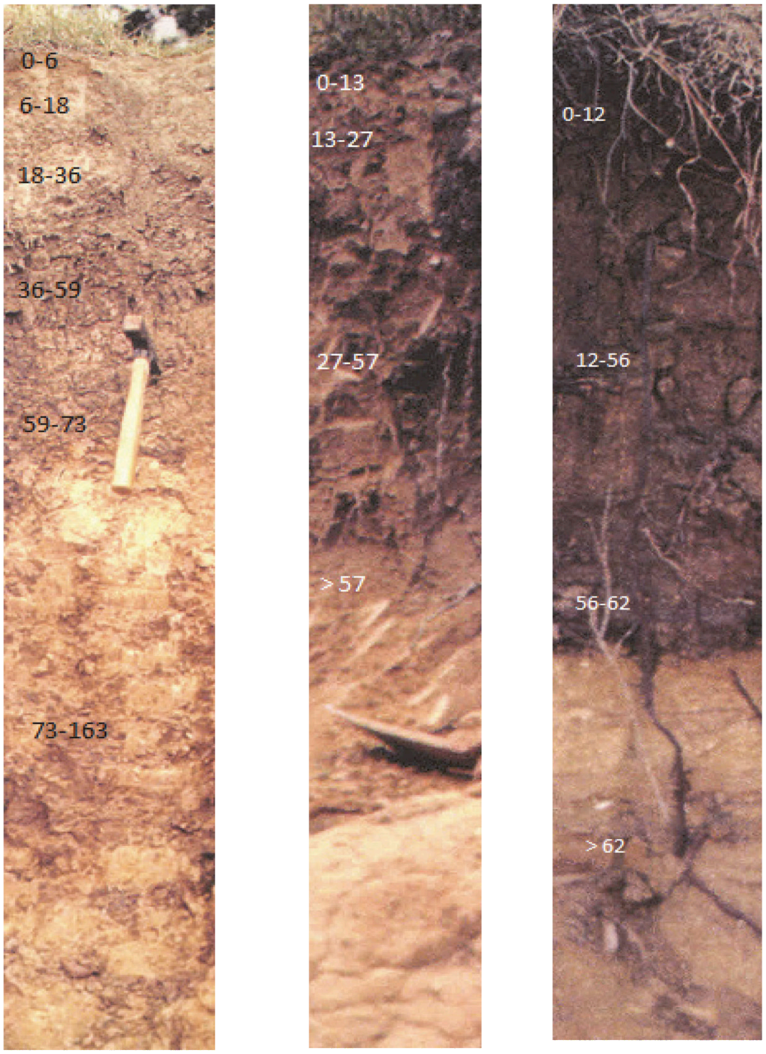
Figure 1. Location of sampling sites in the municipality of Nicolás Romero, State of Mexico.

(Acevedo-Sandoval *et al*., 2003). During the early stages of weathering, the amount of CaO, Na_2O and MgO increases in surface horizons of profiles 4, 5 and 6 in relation to hardened horizons. On the other hand, in profiles 7 and 3, the average content of CaO, Na_2O and MgO decreases in upper horizons in relation to hardened horizons. Khanlari *et al*. (2012) stated that feldspar alteration may result in a direct loss of CaO, Na_2O and SiO_2 and that during the weathering process, FeO is oxidized transforming into Fe_2O_3, with the amount of Fe_2O_3 increasing with the weathering degree in granitic rocks.

The low values of Na, K and Ti correspond to an early stage of soil development, reflecting a low degree of alteration in the material. Tsozué and Yongue-Fouateu (2017) pointed out that feldspar

Table 2. Weathering indices used in this study. All ratios refer to molecular proportions (Che *et al*. 2012; Tzozué *et al* 2017; Aristizábal *et al* 2009; Munroe *et al*. 2007; Raczyk *et al*. 2015).

Index	Formula	Reference
Imob	$(Mob_{fresh} - Mob_{weathered})/Mob_{weathered.}$ where Mob=(K_2O+Na_2O+CaO)	Irfan (1996).
CIA	$100*Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)$	Nesbitt and Young (1984).
CIA-K	$100*((Al_2O_3)/(Al_2O_3+CaO^{sil}+Na_2O))$	Bowen *et al*. (2013).
CIW	$((Al_2O_3/(Al_2O_3+CaO+Na_2O))*100$	Harnois (1988).
PIA	$(100)(Al_2O_3-K_2O)/(Al_2O_3+CaO+Na_2O-K_2O)$	Fedo *et al*. (1995).
PI	$100*(SiO_2)/(TiO_2+Fe_2O_3+SiO_2+Al_2O_3)$	Reiche (1943); Souri *et al*., (2006).
IPark	$100*(2Na_2O/0.35+MgO/0.9+2K_2O/0.25+CaO/0.7)$	Parker (1970).
V	$(Al_2O_3+K_2O)/(Na_2O+CaO+MgO)$	Vogt (1927); Roaldset (1972).
MWPI	$100*((Na_2O+K_2O+CaO+MgO)/(Na_2O+K_2O+CaO+MgO+SiO_2+Al_2O_3+Fe_2O_3))$	Reiche (1943, modificado por Vogel, 1975).
MIA	$2*(CIA-50)$	Voicu *et al*. (1997).
WPI	$100*((Na_2O+K_2O+CaO-H_2O^+) / Na_2O+K_2O+CaO+MgO+SiO_2+Al_2O_3+Fe_2O_3+TiO_2))$	Reiche (1943).
Fes	$(Fe_2O_3)/(Fe_2O_3+SiO_2)$	Escamilla-Sarabia *et al*. (2002).
Si/Ti	$(100)((SiO_2/TiO_2)/(SiO_2/TiO_2)+(SiO_2/Al_2O_3)+(Al_2O_3/TiO_2))$	Jayawardena and Izawa (1994).
CPA	$(100)(Al_2O_3)/(Al_2O_3+Na_2O)$	Cullers (2000).
KnA	$((SiO_2+CaO+K_2O+Na_2O)/(Al_2O_3+SiO_2+CaO+K_2O+Na_2O))$	Nesbitt and Young (1984).
KnB	$((CaO+K_2O+Na_2O)/(Al_2O_3+CaO+K_2O+Na_2O))$	
S/SAF	$(Al_2O_3)/(SiO_2+Al_2O_3+Fe_2O_3))$	Hill *et al*. (2000).
S/A	SiO_2/Al_2O_3	Ruxton (1968).
B/A	$(K_2O+Na_2O+CaO+MgO)/(Al_2O_3)$	Birkeland (1999).
Si/Ses	$SiO_2/(Al_2O_3+Fe_2O_3)$	Birkeland (1999).



a) b) c)

Figure 2. Hardened horizons (tepetates) of the State of Mexico. a) Profiles 1, 2 and 3 show incipient weathering, < 60, typic fragiudalfs, one or more horizons within 60 cm of the mineral soil surface, redox depletions, with a chroma of 2 or less. b) Profiles 4, 5 and 7 show moderate to high weathering, > 60, Typic dystrochrept, soils with ocric horizon and with cambic subsurface horizon, well drained, very deep. c) Profile 6, typic eutrocrepth, high content of amorphous or low crystallinity materials.

degradation and the concomitant formation of clays constitutes a dominant process during the chemical weathering of the Earth's crust. Generally, calcium, sodium and potassium are removed from feldspars increasing the proportion of alumina to alkalis in the weathering product.

The concentration of K_2O (1.93 to 3.13 wt.%) and Na_2O (0.93 to 10.98 wt.%) correlates with the presence of alkali feldspars, while the values of MgO (0.6 to 3.62 wt. %) show the differences between the horizons. These values are caused by the presence of biotite, a mineral commonly found in tepetates formed from volcanic tuff. González *et al*. (2004) reported a greater release of alkali and alkaline earth cations during the initial transition of the rock into soil. The mineralogy of these seven profiles does not change in a significant way with depth. SiO_2, Al_2O_3, Na_2O, K_2O and TiO_2 are the dominant oxides, which represent 86.87 and 87.35 percent of the total hardened and the surface horizon, respectively (horizons average value). In accordance with these results, the seven profiles are located in the first stages of weathering (González *et al*., 2004).

Weathering patterns analysis

To establish the geochemical evolution of the materials during weathering, the following diagram proposed by Nesbitt and Young (1989) was used: A-CN-K. The diagram was employed to examine the weathering patterns and their products: clay minerals. Other authors (Armstrong-Altrin *et al*., 2019) have demonstrated that regardless the different composition of rocks, the weathering processes follow similar trends, which are simple and common and are not affected by the climatic conditions under they were originated.

The most intensively weathered samples plot in the upper corner of the diagram (Figure 3a), reflecting the presence of alumina clay minerals. The analyzed samples lie in a trend parallel to the A-CN axis, as plagioclase is more susceptible to weathering than potassium feldspars. This pattern meets the A-K axis once the entire plagioclase has been eliminated. The weathering pattern continues towards the A vertex, once the K has been extracted, preferably to A, from the residual materials. The results coincide with the information reported by Aristizábal *et al.* (2009).

Table 3. Total chemical composition (wt%) of the soils and the hardened horizons. Hz horizon.

	Profile 1			Profile 2			Profile 3			Profile 4			Profile 5			Profile 6			Profile 7		
Hz	**A_{11}**	**AC**	**Cqm**	**A_{11}**	**AC**	**Cqm**	**A_{11}**	**AC**	**Cqm**	**A_{11}**	**B_{t1}**	**Cd**	**A_{11}**	**Bw**	**Cqm**	**A_{11}**	**Bt**	**Cd**	**A**	**BW_1**	**Cqm**
Depth	**0–32**	**32–50**	**50+**	**0–31**	**31–43**	**43+**	**0–19**	**19–40**	**40+**	**0–18**	**18–73**	**73+**	**0–27**	**27–57**	**57+**	**0–29**	**29–72**	**72+**	**0–12**	**12–62**	**62+**
SiO_2	66.98	75.56	84.37	60.42	55.28	65.87	62.43	64.78	62.32	65.15	60.82	52.34	60.48	61.61	59.70	58.89	57.89	58.14	51.56	54.11	53.15
TiO_2	2.18	1.33	0.63	2.01	1.83	1.58	3.00	2.43	2.39	5.81	4.92	3.34	3.90	3.30	2.81	2.96	3.28	2.66	2.56	3.98	2.28
Al_2O_3	14.21	8.03	4.45	15.18	13.67	14.56	15.52	15.51	14.86	13.44	16.76	21.21	15.44	17.20	17.36	16.25	15.23	18.17	14.75	17.42	17.75
Fe_2O_3	2.54	2.20	1.30	2.40	1.71	1.91	3.15	2.59	2.78	3.43	3.97	3.90	2.75	2.78	2.85	2.82	2.83	2.52	3.11	3.74	2.62
FeO	2.28	1.98	1.17	2.16	1.54	1.72	2.83	2.33	2.50	3.08	3.57	3.51	2.47	2.50	2.56	2.53	2.55	2.27	2.80	3.36	2.36
MgO	2.15	2.09	1.24	2.06	1.77	1.79	2.46	2.25	3.62	1.72	1.32	0.60	1.05	0.91	1.06	0.90	0.99	0.65	1.28	2.25	2.40
MnO	0.52	0.17	0.18	0.62	0.72	0.69	0.73	0.55	0.71	0.66	1.10	0.59	0.50	0.35	0.57	0.65	0.63	0.48	0.79	0.80	0.73
CaO	1.94	1.33	1.13	2.41	4.31	2.29	2.13	1.99	2.69	1.65	1.05	0.64	1.56	1.47	1.52	1.41	1.21	0.91	1.41	1.89	2.21
Na_2O	9.24	5.09	4.51	8.84	6.96	7.68	7.77	8.04	8.03	6.23	4.86	0.93	3.01	3.21	3.01	2.68	2.68	1.74	2.68	3.28	3.30
K_2O	2.89	2.65	2.41	3.13	2.89	2.89	2.77	2.89	2.97	2.65	2.49	2.25	2.41	2.65	2.41	2.53	2.53	2.25	1.93	1.93	1.93
P_2O_5	0.11	0.25	0.12	0.48	0.23	0.34	0.12	0.21	0.31	0.19	0.19	0.23	0.22	0.25	0.12	0.36	0.32	0.23	0.14	0.13	0.26
H_2O^+	1.79	5.56	5.17	2.42	3.66	3.16	2.08	2.29	1.28	2.42	4.02	4.89	2.24	2.45	3.41	3.79	3.07	6.29	5.29	2.76	4.70

Figure 3a shows the CIA values for the different soil profiles within the study area. Profiles 1, 2 and 3 present a low chemical weathering with values of less than 60, while profiles 4, 5, 6 and 7 are moderate to high, with values of more than 60, indicating that calcium and sodium are increasingly removed from the plagioclase, while the proportion of alumina and potassium increase in the weathering products. The values located near the A-CN axis, indicate a greater proportion of plagioclase in relation to potassium feldspars.

In the Plagioclase Index of Alteration (PIA) diagram (Figure 3b), the plagioclase decomposition trend in profiles 1, 2 and 3 indicates a low chemical weathering, while in profiles 5 and 7 it is moderate, and in profiles 4 and 6 it is high. The composition in profiles 1, 2 and 3 is rich in albite-anorthite, nevertheless as the PIA values increase, the sediments present low Na_2O values and high Al_2O_3 values, indicating that the chemical weathering increase causes a gradual albite impoverishment and certain enrichment in secondary Al minerals.

According with the Si-Al-Fe ternary diagram modified by Hill *et al.* (2000) (not shown), the results of the analyzed surface horizons and hardened layer samples indicate that profiles 1, 2 and 3 are made of fresh material, while alteration in profiles 4, 5, 6 and 7 in the study zone is related to kaolinization.

When plotting the seven hardened horizons in the TAS diagram of LeMaitre *et al.* (1989) (not shown), it is possible to observe that the samples are in a series of subalkaline volcanic rocks, except for profiles 2 and 3, which appertain to the alkaline series. The profiles with the highest geochemical evolution degree are those formed by andesite (profile 5 and 6) and basaltic andesite (profile 4 and 7) parent material, while profile 1 (rhyolite) and 2 and 3 (trachyte) present a minor pedological evolution degree.

Weathering intensity analysis

Commonly, weathering indices are used to compare the chemical alteration degree in different materials. These are based on the principle that the proportion between the mobile elements concentration (SiO_2,

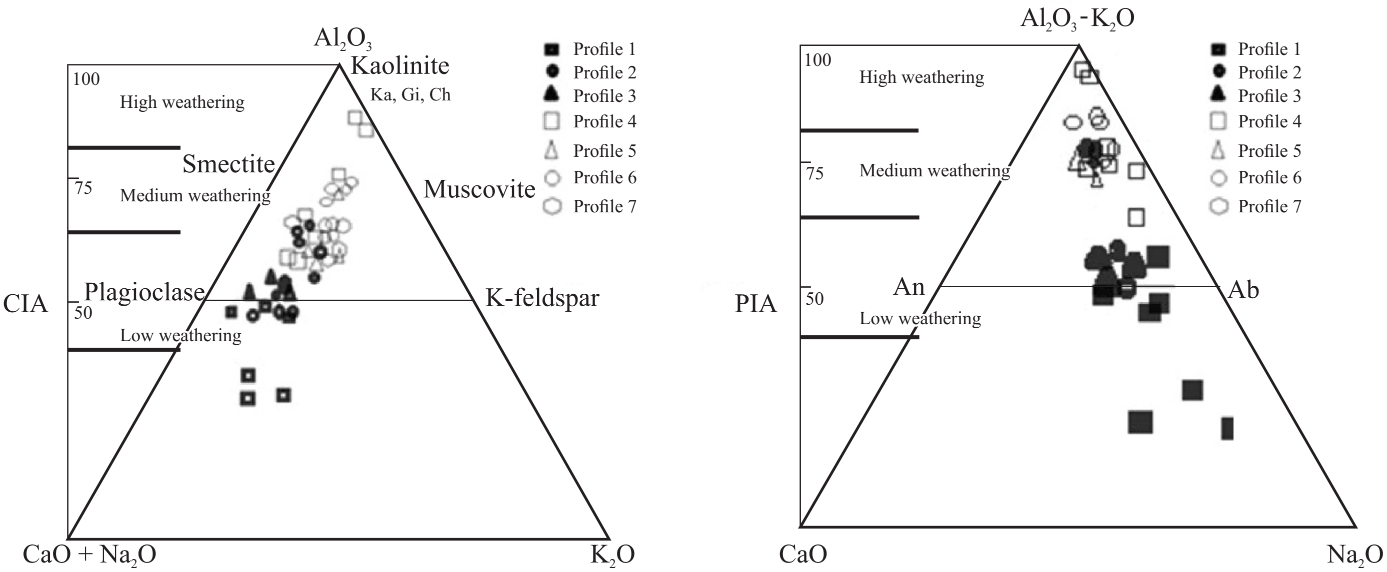


Figure 3. a) Ternary Diagram A-CN-K showing the trend of the studied soil profiles and the weathering degree according to the values of the Chemical Index of Alteration (CIA). b) A-C-N ternary Diagram. showing the chemical composition and the values of the Plagioclase Index of Alteration (PIA) of the sediments An: anortite, Ab: albite.

CaO, MgO and Na_2O) and immobile elements concentration (Al_2O_3, Fe_2O_3, and TiO_2) may decreases with time as lixiviation advances (Munroe *et al*., 2007 and Manga *et al*., 2013). Fiantis *et al*. (2010) and Abbaslou *et al*, (2013) reported that while assessing the geochemical components and weathering indices it is possible to understand the soil formation and its pedogenetic processes.

Price and Velbel (2003) and Haskins (2006) indicated that certain indices may increase their values due to the chemical weathering progress (V, CIA, CIW, PIA, CPA, S/SAF, MIA, Imob: Mobility index), which is attributed to mobile cations loss and to the alteration of the crystalline structure of primary minerals, besides an increase in the hydroxyl water content; whilst other indices diminish with a weathering increase (IPark, Si/Ti, SA, WPI, PI, B/A, Si/Ses, WR, MWPI), indicating the loss of silica.

With the aim of determining the weathering degree, Irfan (1996) proposed the mobility index (Imob). This index is based on the loss of CaO, Na_2O and K_2O of parental rocks and weathering products. Imob is defined as a molecular relationship where the weathered material is normalized to the parental rock, and this is used to determine the alteration degree of feldspars in rocks. Table 4 shows that the Imob varies from 0 to 0.27, which is translated into an incipient feldspar weathering degree and poor mobility of CaO, Na_2O and K_2O caused by a bad drainage in the profile (Aristizábal *et al*., 2009) and other weather conditions in the studied zone.

Price and Velbel (2003) reported that the Chemical Index of Weathering (CIW), Chemical Index of Alteration (CIA), Parker (IPark) and Plagioclase Index of Alteration (PIA) may be applied to evaluate the weathering degree of feldspars into clay. This index is widely used in various studies (Ramos-Vázquez and Armstrong-Altrin, 2019).

Duzgoren-Aydin *et al*. (2002) established that when the CIA values oscillate between 50 and 60, this indicates the presence of incipient weathering; if the values fluctuate between 60 and 80 this characterizes intermediate weathering, and when they are of more than 80, extreme weathering is revealed. According to the results of the current study, surface horizons of profiles 1, 2, 3, 4 and 5 show slight weathering (fresh material) revealing a low alteration of silicates (feldspars) and little removal of labile cations. Baumann *et al*. (2014) pointed out that low CIA values are caused by the absence or low chemical weathering, as a result of cold or arid climatic conditions. The hardened layers of profiles 4, 5, 6 and 7 are characterized by an intermediate alteration (Table 4). If the intensity of the chemical weathering process increases, the content of Ca, Na and K mobile ions diminishes, and the CIA value increases. For kaolinite, the CIA index is approximately of 100, representing the greatest weathering degree (Raczyk *et al*, 2015). The highest values of the CIA were determined for horizon B of profiles 4, 5, 6 and 7 in relation to surface horizons, and for this reason these are considered to have a higher pedogenetic development. The chemical weathering sequence (greater to lesser) of hardened horizons for the CIA index is: P6>P4>P5>P7>P2>P3>P1. Values of 90 to 100 have been reported for CIA in soil or saprolite; Bowen *et al*. (2013) suggested values of less than 50 for unaltered regolith and values of 70 to 100 for high weathered samples. Burke *et al*. (2007) pointed out that at values lower than 75, chemical weathering is lower.

In surface horizons, the Chemical Index of Alteration without potassium (CIA-K) varied from 46.30 to 68.83, while in hardened layers it varied from 31.96 to 80.09, presenting the highest values in profiles 4, 5, 6 and 7, indicating a moderate chemical weathering with the following sequence in hardened horizons: P6>P4>P5>P7>P2>P3>P1, while in surface horizons, P2 presented less weathering (Table 4). Bowen *et al*. (2013) outlined that values over 90 suggest high weathering and describe a high correlation between the CIA and CIA-K values (R^2=0.994), indicating that it is a younger soil. The result coincides with the results presented in the current work (y=1.0832x+1.117, R^2=0.9945).

Le Blond *et al*. (2015) reported that andosol soils with values of the Chemical Index of Weathering (CIW) that fluctuate between 37 and 45 are slightly weathered, while from 50 to 77 these are considered as highly weathered and values from 70 to 100 are presented in heavily altered volcanic soils (laterite). These values are developed in humid climate, which is often found in Brazil and China. In the current study, profiles 1, 2, and 3 presented CIW values of less than 48 (slightly weathered), while in profiles 4, 5, 6 and 7 horizons are heavily weathered, obtaining the greatest values in hardened horizons. Le Blond *et al* (2015) concluded that values of less than 42 for CIA and CIW represent the least-altered rocks. Senol *et al*. (2016) found that unaltered basaltic rocks presented CIW values of 43.36; while in soil samples it varied from 44.46 to 80.43. The present study shows that surface horizons values range from 46.3 to 68.8. Hardened horizons present the following sequence: P6>P4>P5>P7>P2>P3>P1, where P6 has the highest weathering intensity.

The CIA values from 26.9 to 72.3 and CIW values from 31.9 to 80.0 show a slight difference between the indices, establishing that alkali feldspars dominate over plagioclase (Abbaslou *et al*., 2013).

Plagioclase is a mineral that can be found in silicate rocks and dissolves in a relatively rapid way. To evaluate their chemical weathering, it is necessary to employ the Plagioclase Index Alteration (PIA). In the current study the values varied from 16.27 to 77.7 (Table 4), suggesting a low to moderate weathering intensity with the following sequence in hardened horizons: P6>P4>P5>P7>P2>P3>P1, where P1 presents the smaller plagioclase alteration. Baumann *et al*. (2014) reported that low values of CIA, CIW and PIA indices indicate the absence of chemical weathering under cold or arid climate conditions.

The Product Index (PI) is employed for silicate rocks, and it is adequate for monitoring the change in the content of the least mobile elements (Souri *et al*., 2006 and Senol *et al*., 2016), including several chemical components, pointing out that it is more trustable than a simple index. In this way, it represents a good indicator of the weathering state of rocks in terms of the remaining alkali materials after the weathering process (Khanlari *et al*., 2012), whereby the PI value decreases as the weathering degree increases reducing the content of silica (Haskins, 2006 and Senol *et al*., 2016). In the present work, the loss of silica is minimal and the PI average in the seven profiles was of 80.44±4.16, suggesting a low chemical weathering.

The Parker index (IPark) is suitable for determining the mobility of alkali and alkaline earth elements from volcanic ash deposits (Fiantis *et al*., 2010). It is extremely sensitive for calculating the loss of bases as result of weathering (Souri *et al*., 2006). This index is applied to intermediate and basic acid rocks, considering that the hydrolysis of primary minerals represents the beginning of the alteration process in silicates (Haskins, 2006). Shi *et al* (2011) mentioned that the IPark is based on the proportion of alkali and alkaline earth materials (Na, K, Mg and Ca) and its bond strength with oxygen (0.35, 0.9, 0.25 and 0.7, respectively) in order to determine the weathering of a given soil. Bowen *et al*. (2013) reported that values of more than 100 in IPark correspond to unaltered fresh rock, while weathered samples present values near zero. In the present work, the upper horizons values varied from 48.2 to 115.8, (average 74.81±27.8), while in the hardened layers it varied from 39.26 to 116.09 (average 70.31±29.4) (Table 4). High values indicate a low removal of alkali and alkaline earth mobile elements, suggesting a low to moderate chemical weathering degree in hardened layers, with the following sequence P6>P4>P5>P7>P1>P2>P3, where P6 presents the highest weathering in relation to other profiles. Souri *et al*. (2006) described those smaller values obtained from the IPark as corresponding to unbasified samples and sometimes it can be assumed

Table 4. Weathering indices calculated for the soils and the hardened horizons. Hz horizon.

Hz	Depth	Imob	CIA	CIA-K	CIW	PIA	PI	Iparker	V	MWPI	MIA	WPI	Fes	Si/Ti	CPA	KnA	KnB	S/SAF	S/A	B/A	Si/Ses
P1A$_{11}$	0–20	0.11	61.48	66.38	66.38	63.47	78.68	57.62	1.35	6.59	22.97	1.98	0.03	67.50	76.35	0.86	0.39	0.16	5.27	0.95	4.64
P1A$_{12}$	20–32	-0.35	42.39	46.97	46.97	40.54	83.70	103.90	0.80	5.03	-15.22	4.20	0.02	75.04	52.43	0.91	0.58	0.11	8.23	1.76	7.28
P1AC	32–50	-0.12	37.02	42.66	42.66	32.35	90.19	78.58	0.68	5.08	-25.96	-11.27	0.01	78.49	48.95	0.95	0.63	0.06	15.97	2.36	13.59
P1Cqm	50+	0.00	26.92	31.96	31.96	16.27	94.87	68.35	0.56	4.39	-46.17	-10.46	0.01	82.52	37.49	0.97	0.73	0.03	32.17	3.42	27.12
P2A$_{11}$	0–17	-0.05	41.98	46.30	46.30	40.14	82.51	115.88	0.83	4.61	-16.04	4.67	0.01	76.60	51.93	0.89	0.58	0.13	6.88	1.70	6.26
P2A$_{12}$	17–31	-0.15	39.11	42.86	42.86	36.80	81.71	123.90	0.72	4.73	-21.78	6.89	0.02	75.30	50.24	0.89	0.61	0.13	6.63	1.92	6.01
P2AC	31–43	-0.11	37.88	41.48	41.48	35.34	82.95	104.57	0.71	4.63	-24.23	1.22	0.01	75.95	54.42	0.89	0.62	0.13	6.86	1.97	6.35
P2Cqm	43+	0.00	42.22	46.43	46.43	40.50	84.67	106.12	0.83	4.49	-15.56	1.31	0.01	78.81	53.54	0.90	0.58	0.11	7.68	1.68	7.08
P3A$_{11}$	0–8	0.10	44.11	48.48	48.48	42.81	80.99	106.12	0.81	5.37	-11.79	5.28	0.02	72.77	55.34	0.89	0.56	0.12	6.91	1.68	6.11
P3A$_{12}$	8–19	0.07	44.12	47.98	47.98	43.00	80.36	108.60	0.81	5.26	-11.75	5.03	0.02	70.83	54.34	0.89	0.56	0.13	6.74	1.65	5.98
P3AC	19–40	0.07	43.71	47.94	47.94	42.36	82.34	109.94	0.83	4.91	-12.58	4.49	0.01	74.57	53.97	0.89	0.56	0.12	7.09	1.65	6.40
P3Cqm	40+	0.00	41.08	45.08	45.08	39.15	81.99	116.09	0.66	5.40	-17.85	9.02	0.02	74.30	52.94	0.90	0.59	0.12	7.12	2.05	6.36
P4A$_{11}$	0–6	-0.47	46.04	51.13	51.13	45.06	80.17	86.69	0.95	5.29	-7.92	0.63	0.02	60.39	57.22	0.90	0.54	0.11	8.07	1.50	6.99
P4A$_{12}$	6–18	-0.51	44.91	49.61	49.61	43.72	80.10	91.07	0.91	5.62	-10.18	2.44	0.02	59.17	56.25	0.91	0.55	0.10	8.39	1.55	7.16
P4Bt$_{1}$	18–36	-0.42	50.67	56.27	56.27	50.84	79.66	81.06	1.18	5.57	1.34	-2.87	0.02	62.98	61.21	0.90	0.49	0.11	7.62	1.21	6.55
P4Bt$_{21}$	36–59	-0.16	62.85	69.73	69.73	66.01	76.44	57.44	1.81	6.31	25.70	-10.33	0.03	64.66	75.11	0.87	0.37	0.14	6.09	0.79	5.23
P4Bt$_{22}$	59–73	-0.40	58.02	63.03	63.03	59.54	75.04	78.37	1.52	5.48	16.05	-8.20	0.02	66.62	67.33	0.85	0.42	0.16	5.10	0.89	4.51
P4Cd	73+	0.00	72.06	78.57	78.57	76.44	72.94	48.30	3.24	5.68	44.13	-15.40	0.03	69.45	82.11	0.82	0.28	0.19	4.19	0.46	3.75
P5A$_{11}$	0–13	-0.05	58.75	65.19	65.19	60.91	80.34	57.33	1.63	5.57	17.50	-1.46	0.02	69.23	74.60	0.88	0.41	0.13	6.68	0.88	6.00
P5A$_{12}$	13–27	0.04	60.80	67.80	67.80	63.61	79.63	52.85	1.83	5.62	21.59	-1.87	0.02	66.58	76.87	0.88	0.39	0.13	6.62	0.81	5.94
P5Bw	27–57	-0.05	61.38	68.38	68.38	64.31	79.63	58.36	1.96	5.50	22.76	-2.17	0.02	70.95	76.51	0.87	0.39	0.14	6.08	0.76	5.51
P5Cqm	57+	0.00	62.71	69.23	69.23	65.66	79.32	55.01	1.92	5.65	25.41	-6.56	0.02	72.57	77.81	0.87	0.37	0.14	5.84	0.75	5.28
P6A$_{11}$	0–12	-0.29	61.81	68.83	68.83	64.84	79.72	51.81	1.90	5.86	23.62	-6.64	0.02	72.27	78.18	0.87	0.38	0.14	6.23	0.78	5.56
P6A$_{12}$	12–29	-0.28	63.36	71.09	71.09	67.07	79.72	52.73	2.23	5.53	26.71	-10.89	0.02	71.12	79.11	0.87	0.37	0.14	6.08	0.70	5.52
P6Bt	29–48	-0.27	61.69	69.76	69.76	65.21	80.10	52.97	2.01	5.69	23.38	-4.80	0.02	70.60	77.62	0.88	0.38	0.13	6.52	0.78	5.83
P6BCd$_{1}$	48–72	-0.24	62.28	69.76	69.76	65.63	79.55	50.99	1.95	5.59	24.56	-7.50	0.02	69.30	77.47	0.87	0.38	0.13	6.38	0.77	5.71
P6Cd	72+	0.00	72.33	80.09	80.09	77.70	78.89	39.26	3.34	5.78	44.65	-21.99	0.02	72.94	86.39	0.85	0.28	0.15	5.43	0.47	4.99
P7A	0–12	0.27	61.94	67.90	67.90	64.49	78.49	48.22	1.65	5.82	23.89	-17.45	0.02	71.93	76.99	0.87	0.38	0.14	5.93	0.83	5.23
P7BW1	12–56	0.04	60.60	65.47	65.47	62.45	76.11	58.18	1.31	6.55	21.19	-2.23	0.02	67.51	75.52	0.86	0.39	0.15	5.48	0.98	4.81
P7BW2	56–62	0.07	62.36	67.27	67.27	64.47	75.06	57.06	1.38	6.65	24.71	-4.83	0.03	67.48	77.16	0.85	0.38	0.16	5.07	0.93	4.47
P7Cqm	62+	0.00	60.61	65.26	65.26	62.37	77.84	59.06	1.28	6.06	21.22	-11.59	0.02	73.49	76.58	0.85	0.39	0.16	5.08	0.99	4.64

that these are the most ancient. This index points out a small loss of bases, and at the same time reveals the possible rejuvenating influence in surface horizons caused by new volcanic material deposits. The results were similar to those obtained by Taboada *et al*. (2016).

The Vogt (V) index is a geochemical method for evaluating the sediments maturity (Jayawardena and Izawa, 1994). Che *et al*. (2012) reported that this index allows separating the profiles from lesser to greater degree of weathering, where the highest values indicate a chemical alteration increase. In hardened horizons of profiles 4, 5, 6 and 7, weathering is moderate; while in profiles 1, 2, and 3 values of less than 0.83 are considered as fresh material (Che *et al*., 2012, Price and Velbel 2003). In general, in the studied profiles the intensity of chemical weathering is low. The hardened horizon sequence is as follows: P6>P4>P5>P7>P2>P3>P1. Burke *et al.* (2006) concluded that this index is not so effective for granitic soils in Point Reyes California, USA.

In accordance with the Modified Weathering Potential Index (MWPI) of Vogel (1975), the values of the seven profiles varied from 4.49 to 6.65 (Table 4) with an average value of 5.49±0.58, indicating that the alteration intensity in the study zone is low. Lower values indicate a higher weathering process.

Tzozué y Yongue-Fouateu (2017) reported that the Mineralogical Index of Alteration (MIA) is used to evaluate the mineralogical weathering degree. The values obtained in profiles 1, 2, and 3 (Table 4) indicate that the mineralogical alteration is incipient, while in hardened horizons of profiles 4, 5, 6 and 7 it is considered as weakly developed (Tsozué and Yongue-Fouateu, 2017).

The Weathering Potential Index (WPI) can be considered as a good indicator of alteration in hardened horizons, as it includes different mobile alkaline earth elements, which can be more trusted than a simple index that depends on one or two components. The current study presented negative values for profiles 1, 4, 5, 6 and 7 due to an increase in the hydroxyl water content (Table 4). Similar results were obtained by Jayawardena and Izawa (1994) for residual soils or volcanic material, favoring the formation of allophane (Acevedo-Sandoval *et al*., 2002) retaining a greater water amount (thixotropism) or the presence of secondary materials, formed during weathering, that incorporate water (hydrated phases) (Khanlari *et al*.,2012, Haskins, 2006, Che *et al*., 2012). Generally, profiles may present a slight weathering intensity. Che *et al* (2012) concluded that pyroclastic materials can be more altered than lava flows of the same age, under the climatic conditions of the study zone, not favoring the pyroclastic materials weathering. Jayawardena and Izawa (1994) described that the content of H_2O^+ is low (less than 1 %) in fresh rocks, and increases with residual soils weathering, concluding that H_2O^+ can be used in rocks as a good chemical weathering indicator.

The Fes relation depends on the content of amorphous minerals, and it establishes the difference between amorphous silica and amorphous iron. The current study shows values of less than 0.03 (Table 4) and for this reason the seven profiles are considered to have a week pedogenetic weathering caused by the climatic conditions presented in the study zone. Escamilla-Sarabia *et al*. (2002) reported that Fes values near zero are considered characteristic of underdeveloped young soils with large amounts of allophane, which coincides with the reports included in this study.

The silicon/titanium relation (Si/Ti) represents the less mobile group of elements, which low values reveal more weathered materials (Price and Velbel 2003). In the current study, these values varied from 62 to 82 (average value 71.03±5.24, Table 4) indicating a slight chemical weathering in the seven profiles.

The changes in the Chemical Weathering Indices values (IPark, CIA, CIW, PIA, and Si/Ti) in relation to depth are not gradual and systematic, and these may indicate the presence of new materials due to the continued volcanic activity in the study zone. These continuous rejuvenating processes are common in volcanic soils areas (Taboada *et al*., 2016).

Chemical Proxy of Alteration (CPA) is an indicator mainly used to determine the weathering degree in silicates, aluminum silicates and plagioclase (Raczyk *et al*., 2015). In the identified sequence P6>P4>P5>P7>P2>P3>P1, the hardened horizon of profile 1 presents the lesser alteration of silicates (Table 4) and this sequence indicates that hardened horizons of profiles 4, 5, 6 and 7 is a plagioclase-rich tuff, which is extremely weathered in relation to horizons of profiles 1, 2 and 3.

Kronberg indicators (KnA and KnB) show the degree of silicate hydrolysis and the accumulation of aluminum and silica sesquioxides, with simultaneous release of alkali and alkaline earth metals. This process links the transformation of easily altered primary materials with new products formation and residual oxides accumulation during the alteration processes.

KnA explains the relative enrichment of Al and Si oxides phases and Na, K and Ca lixiviation. The selective Al and Si accumulation provides information about chemical weathering (Al enrichment) when the calculated index is near zero, or physical weathering (Si enrichment) when the calculated index is near one (Baumann *et al*., 2014). In the current study, the KnA values varied from 0.82 to 0.97 showing Si enrichment. All the above lead us to conclude that there is certain pyroclastic material deposition in the study zone. The low values of KnA indicate small changes in the weathering intensity, due to the stable temperature and humidity conditions present in the study zone.

The KnB index evaluates the feldspars alteration degree and clay minerals formation. As a result of this, as weathering increases, the index diminishes. Profiles 4, 5, 6 and 7 present a greater soil development (Table 4). The average value of the S/SAF relation for the seven profiles is of 0.13±0.03, indicating a low weathering intensity and suggesting that the pyroclastic material is of recent deposition. Che *et al*. (2012) considered that S/SAF values of 0.21 appertain to fresh rocks, while the silica-aluminum relation (SA) also known as Ruxton index is a good indicator of chemical weathering in volcanic rocks and soils, emphasizing the kind of soil and clay minerals abundance (Duzgoren-Aydin *et al*., 2002). As these values decrease, the loss of silica increases. It is assumed that the loss of silica is equal to the total number of lost elements (Jasso-Castañeda *et al*., 2012). In the current study, the SA values range from 4.19 to 32.17 for hardened horizon, while in surface horizons these varied from 5.27 to 8.07. Overall, a slight primary minerals weathering may be considered (Table 4). The hardened horizon sequence is represented as follows: P4>P7>P6>P5>P3>P2>P1, where P4 is the most weathered horizon. Burke *et al*. (2007) reported that this index is a good chemical weathering indicator in granitic rocks presenting good drainage, in an acid and humid medium where the final product is represented by kaolin minerals. These conditions do not prevail in the study zone. The SA relation is not suitable in developed profiles of mafic igneous rocks (basic).

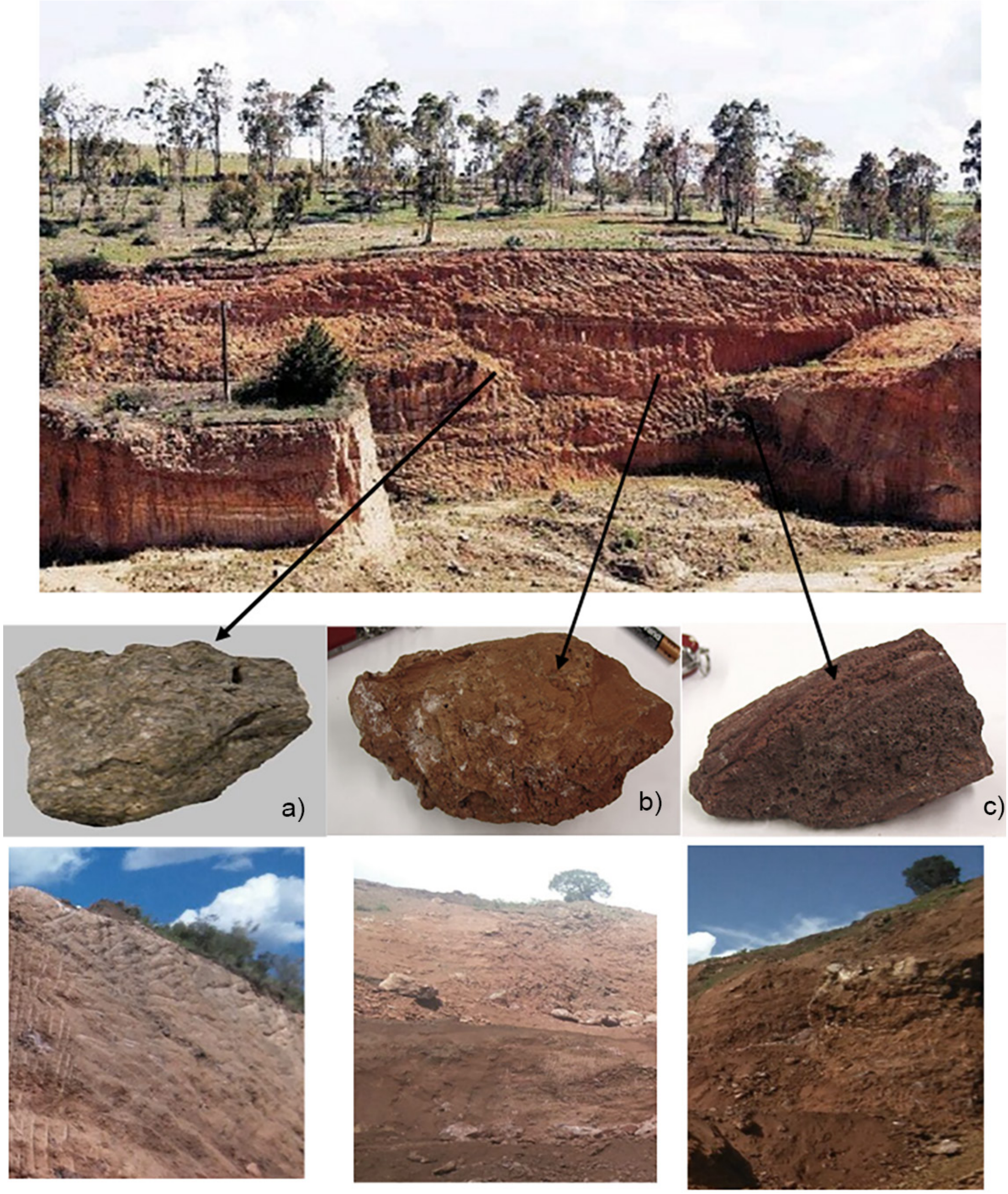
For the base/aluminum relation (B/A), values that are higher than the unit indicate a weak soil development. In the present study, profiles 1, 2, and 3 are considered as weak developed soils, while the other profiles are considered as low to moderate chemical weathered (Table 4) with a greater pedogenetic development and Al enrichment (Escamilla-Sarabia *et al*., 2002).

The silica/sesquioxide relation (Si/Ses) is high during the initial stages of weathering and extremely low at the beginning of the final stages of development, as the soil has lost most of its cations and presents neutral or acid pH values (Escamilla-Sarabia *et al*., 2002). In the current study, the average value of the Si/Ses index was 6.67±4.13, indicating low weathering in the seven profiles.

Melke (2007) reported that the numeric values of the weathering indicators show that the upper horizons of the studied soils are characterized by a high intensity in comparison to other genetic horizons. This condition cannot be observed in the current work, as the highest weathering is presented in hardened horizons of profiles 4, 5, 6 and 7. Munroe *et al*. (2007) obtained similar results in Alpine soils in Vermont, USA. Possibly, these results are caused by the presence of paleosoils in the study zone. In the volcanic zones of Mexico, it is frequent to find paleosoils that have been buried by variable materials associated to the eruptive activity (pyroclastic flows, ash fall, lahars, avalanches, among others) (Jasso *et al*. (2002).

The calculated values for the weathering indices (Table 4) indicate that in the zone study there are landscape stability periods and pedological processes, allowing an evolution degree which ranges from incipient to moderate.

The chemical weathering of the studied profiles causes the disintegration of minerals present in the volcanic tuff (mainly plagioclase) transforming them into a thin profile of soil formed by halloysite, cristobalite, montmorillonite and plagioclase (Acevedo-Sandoval *et al*., 2012). For this reason, the current study considers that the studied soils derive from the chemical weathering of pyroclastic material. Somehow it is concluded that there are certain significant differences between the seven profiles studied, grouped into three main types; Figure 4 graphically shows these differences.



Figures 4. Photographic images showing the different colorations observed in the hardened horizons, which allowed to group the seven evaluated profiles into three main types.

Taboada *et al.* (2016) pointed out that in order to execute a chemical weathering comparison between different rocks in the simplest way, the value of some of these indices must be normalized in accordance to this value in the parent material. The values near zero will indicate a low degree of weathering. In the current study the values varied from 0.63 to 2.28, indicating a low alteration degree in the profiles with the following sequence: P1(2.28) <P3(1.07) <P7(1.02)<P2(0.99) <P5(0.93)<P6(0.85)<P4(0.63), where P1 presents a lesser degree of pedogenetic development.

CONCLUSION

Weathering indices are suitable quantitative indicators, employed for describing the weathering degree in profiles of volcanic tuffs (tepetates), giving rise to a chemical weathering with the following sequence: P6>P4>P5>P7>P2>P3>P1, where P6 presents the highest weathering.

The different chemical weathering indices show that the seven soil profiles present a low geochemical and pedological evolution, associated to temperature and humidity conditions, low rainfall in the study region, slight lixiviation of the alkali and alkaline earth elements, Al_2O_3, Fe_2O_3, TiO_2 enrichment, iron oxidization, water incorporation during weathering, and a possible rejuvenating influence in the surface horizon caused by Si enrichment and recent pyroclastic material, in accordance to the values of the KnA, KnB, IPark, CIA, CIW, PIA, Si/Ti indices.

The hardened horizons in volcanic tuffs of profiles 4, 5, 6 and 7 present moderate chemical weathering in relation to surface horizons for the following weathering indices: S/A, CIA, PIA, PI, V, Si/Ses, B/A, CIA-K, Si/Ti, S/SAF, CPA, CIW. These values indicate that volcanic tuff wheathering of silicates, aluminum silicates and plagioclase is low. Besides, forest vegetation soils (profiles 4, 6 and 7) present a greater chemical weathering in comparison to the ones developing pasture.

The chemical weathering indices expose the existence of gradual or repeatedly buried soils processes and pyroclastic material deposition in different cycles, which cause a vertical variation in the profiles as well as the presence of younger materials in the soil surface (profiles 1, 2 and 3) revealing a juvenile stage of pedogenesis.

Weathering indices studied in the current research are optimal quantitative indicators employed to describe weathering degree in hardened horizons.

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