

Use of Low Molecular Weight Organic Acids for Agricultural Improvement of Ecuadorian Volcanic Soils

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ABSTRACT

The main objective of this paper is to promote the use of organic acids applied in enriched organic amendments and inoculated seeds for agricultural improve volcanic Ecuadorian soils. The physical, chemical and biological properties of soils derived from volcanic ash are strongly influenced by the degree of weathering of the pyroclastic materials, the Ecuadorian andisols are soils derived from volcanic ash materials, which unique characteristic is the presence of amorphous and easily weathered silicate minerals. The presence of the indigenous microorganisms in the soil such as Pseudomonas spp., Rhizobium spp., Burkholderia spp., Achromobacter spp., Agrobacterium spp., Aereobacter spp., Flavobacterium spp., Yarowia spp., Streptosporangium spp. and Erwinia spp. plays an important role on the rate not only of carbon and nitrogen stabilization but also of mineral stabilization, since they have the capacity to produce low molecular weight organic acids; which end up forming stable humified materials in andisols.

Keywords: Amorphous Materials, Weathering, Mineral Stabilization, Carbon Stabilization, Nitrogen Stabilization

INTRODUCTION

Low molecular weight organic acids (LMWOAs) are distributed widely in nature, they are mainly derived from the decomposition of organic matter and secretion of plant roots and microbes (Wang et al., 2012), these are vital intermediate products during metabolic pathways of organic matter and participate in the tricarboxylic acid cycle during life activities, and are prevalent on the earth's surface (Xiao et al., 2014), for

agriculture proposes LMWOAs play important roles in the soil-forming process and the cycling of nutrients, especially nitrogen (N), phosphorous (P) and sulphur (S) (Li et al., 2012), moreover the potential influences of LMWOAs on the dissolution of soil minerals, and the stabilization of organic compounds by complexation with minerals or weathering products are well characterized (Heckman et al., 2013).

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The most common LMWOAs identified in soils are oxalic, succinic, tartaric, fumaric, malic, citric, sinapic, caffeic, syringic, salicylic, gallic, p-coumaric, gentisic, protocatechuic, vanillic, p-hydroxybenzoic, and ferulic (Kaurichev et al., 1963), specifically organic acids, such as malate, citrate and oxalate, have been proposed to be involved in many processes operating in the rhizosphere, including nutrient acquisition and metal detoxification, alleviation of anaerobic stress in roots, mineral weathering and pathogen attraction (Jones, 1998) .

The LMWOAs in the root system has been explained by the fact that these compounds can influence on the solubility of essential and nonessential elements directly through acidification, chelation, precipitation, and oxidation-reduction processes in the rhizosphere, and so indirectly on the soil physical properties and the dynamics of root growth by the effects on microbial activity (Baetz et al., 2014; González et al., 2008), these compounds have recently come to attention because conventional approaches to sustainable agriculture largely rely on increasing efficient use of external nutrient sources, and research has shown that even in the presence of sufficient macronutrients, crop production and soil fertility may be deficient, emphasizing the need to understand broader ecological dynamics in soil to ecologically intensify agriculture (Wood et al., 2018).

In another hand, it's known that about 600 volcanoes have had known eruptions recording, while about 50-70 volcanoes are active (erupting), and about 20 volcanoes can erupting in any time (Pfeiffer, 2014), these eruptions have formed approximately 124 million hectares (0.84% of the earth's land surface) of volcanic ash soils cover (Tsai et al., 2010), a significant part of this surface is on Central and South America (Espinosa, 2004) , and most of this soils have been classified as Andisols (Delmelle et al., 2015). This soils developed from volcanic ash deposits vary extremely in physical and chemical soil properties and are known to degrade easily through erosion or soil compaction, which

limits intensive utilization (Bachmann et al., 2020).

The Andisols represent the 30% of the Ecuadorian soils, which are located mainly in the highland area mainly and used to crop barley, oat, wheat, corn, quinoa, amaranto, and Andean tubers such as potato, mashua, melloco, ocas, among others. There are many studies about Ecuadorian soils; however, the mineralogy and the physical and chemical properties of Ecuadorian Andisols still need to be investigated, the lithological, geomorphologic and bioclimatic characteristics of Ecuador, and the time and space variation are able to condition the development of formation factors for Andisols, so that the pedogenetic processes are the result of the combination of these factors and determine the geographic distribution of the different type of soils in the landscape (Villegas et al., 2007), and the andolization process (Espinosa et al., 2018).

Although the effects of organic acids are diverse, there is strong evidence that organic acids accelerate the dissolution of some minerals (Lawrence et al., 2014), the great interest on the role of organic acids in mineral dissolution has continued to grow, especially with the increased popularity of a surface-reaction-controlled model for dissolution kinetics. Also, the research on organic acids and weathering has been stimulated by the question of the effect of plants and mineral weathering on the global carbon cycle (Drever et al., 1994), so that, the main objective of this paper is to promote the use of organic acids applied in enriched organic amendments and inoculated seeds for agricultural improve volcanic Ecuadorian soils. The search for scientific papers was performed between april 2019 and march 2020, at Universidad Autónoma Chapingo Mexico, considering publications on agroforestry systems with a horticultural component, using SCOPUS, Web of Science and SciELO databases.

Ecuadorian volcanic ash soils: Volcanic ash is chemically/mineralogically distinct from most other soil parent materials (Grunwald,

2015), soils formed from volcanic ejecta have many distinctive physical, chemical, and mineralogical properties that are rarely found in soils derived from other parent materials. These distinctive properties are largely attributable to the presence of noncrystalline materials (e.g., allophane, imogolite, ferrihydrite and complex humus-Al) containing variable surface charge colloids, and the accumulation of organic matter. Formation of noncrystalline materials is directly related to the properties of volcanic ejecta as a parent material, namely the rapid weathering of glassy particles (Dahlgren et al., 2004).

Adicionally, the environmental conditions, notably vegetation and soil moisture regime together with chemical composition (Al:Si ratio, base status, pH, etc.) strongly influence weathering pathways of volcanic glass (Asio, 2014; Espinosa et al., 2015). The composition of the colloidal fraction forms a continuum between pure aluminum–humus complexes and pure allophane/imogolite, depending on the pH and organic matter characteristics of the weathering environment. For soil management purposes, volcanic soils are often divided into two groups based on the colloidal composition of the surface horizons: 1) allophanic soils, which are dominated by allophane and imogolite, and 2) nonallophanic soils dominated by aluminum–humus complexes and 2:1 layer silicates (Dahlgren et al., 2004).

Allophane, imogolite and humus complexes are generally transformed under leaching conditions, in Si-rich environments, halloysite formation is favored; under more basic conditions gibbsite is favored. In non-allophanic ashes, 2:1 clays occur although their pathways of formation are not well-defined. Soil moisture regimes influence transformation rates. Crystalline clay formation is favored under regimes that include dry seasons and moist regimes favor persistence of amorphous complexes (Espinosa et al., 2015).

Fundamentally, the formation factors determine the spatial distribution of the

different types of soils in Ecuador, particularly the parent materials that originated the soils (García et al., 2004), however, this distribution is independent of the natural regions into which the country is divided. From the point of view of soil classification, the Ecuadorian Sierra is divided into three regions:

a) Sierra Norte: correspond to soils that have recently received contributions of ash and lapilli, contributing to the formation of soils of volcanic origin (Cordova et al., 2001), derived from andesite and basalt classified as Andisols, are dominated by allophane, imogolite and humus-Al complexes and are characterized by being black colored soils, with medium texture, low average fertility and slightly acidic, located on the internal and external flanks of the mountain ranges and the interior nodes, while the valleys, pits and Basins are formed by colluvial alluvial materials of different granulometry and of medium and low fertility (Moreno et al., 2016), in their formation and development, the formative factors such as parental material and climate, and the formation processes, transformations and losses are of paramount importance, because they are what regulate the specific process of andolization (Espinosa et al., 2015). These soils are characterized by possessing amorphous type minerals with X-ray diffraction such as allophane, ferrihydrite and imogolite (Gardi et al., 2014; Neculman et al., 2013), and have a high capacity to fix phosphorus (P), for this reason, this nutrient must be applied in each crop cycle, which makes production more expensive (Gómez, 2013).

b) Sierra Central: are soils that have not received recent contributions of volcanic materials and that have developed from metamorphic rocks that have been transformed into a variety of soils depending on altitude; In the highest altitude sectors, Ultisols can be found; in the middle sections, Molisols and Vertisols; and in the lower part, poorly developed soils such as Inceptisols and Entisols.

c) Sierra Sur: are very irregular surface soils formed on granite deposits and metamorphic

formations along with colluvial deposits. Finally, the central Sierra and towards the south of the country have evolved a diversity of non-volcanic soils, generally clayey, randomly distributed dominated by ferrous complexes and 2: 1 type clays such as montmorillonite and vermiculite. The fertility of these soils varies with the dominant clay type (Moreno et al., 2016).

Soils derived from volcanic ashes have peculiar properties resulting, in fact, from their high SOM content and the presence of amorphous clays material (allophane and imogolite) (Broquen et al., 2004), the large amount of stabilized SOM observed on soils derived from volcanic ash apparently resides in the formation of Al-humus complexes and the adsorption of humic substances to the allophane and imogolite (Matus et al., 2014).

Organic acids of low molecular weight:

Organic acids of low molecular (LMWOAs) weight compounds are released into the ground by any type of organisms (López et al., 2012), and are characterized by the possession of one or more carboxyl groups (Fox et al., 1990; Xiao et al., 2014), these compounds are intermediate products during metabolic pathways of organic matter (Table 1), participate in the tricarboxylic acid cycle during life activities, and provide food and energy to the microorganisms (González et al., 2008), and a range of LMWOAs are produced in soils from the decomposition of organic matter, root exudates, and microbial metabolites (Bolan et al., 1994), it is known that up to 40% of the photosynthetically fixed C can be released by plants as root exudates (Baetz et al., 2014), and that plant roots exude an enormous range of compounds composed mainly of LMWOAs (González et al., 2008).

The LMWOAs such as oxalic, citric, butyric, malonic, lactic, succinic, malic, gluconic, acetic, glyconic, fumaric, adipic, indolacetic y 2-cetogluconic, can be produced by the rhizobacteria is one of the most widely known mechanisms of soil phosphate solubilization, a process that makes phosphorus available for plant nutrition. Also, among the organisms with the capacity to

produce organic acids that are nutrients soluble bacteria are *Pseudomonas*, *Rhizobium*, *Burkholderia*, *Achromobacter*, *Agrobacterium*, *Aerobacter*, *Flavobacterium*, *Yarowia*, *Streptosporangium* and *Erwinia* (Beltrán, 2014; Van Hees et al., 2000; Paredes et al., 2010).

The LMWOAs are broken down slowly by microorganisms producing an accumulation in the soil. So consequently, these compounds exist in dynamic balance; rapidly produced and consumed by microorganisms. Concentrations of organic acids are generally highest in the organic layer at the top of the soil profile and decrease with depth (Drever et al., 1994), moreover, the concentration of organic acids in the soil solution is regularly low, it varies between 1 to 50 μM and they have one or more carboxylic groups. Depending on the properties of dissociation and the number of carboxylic groups, the organic acids have a negative charge, for this reason they can form complex metallic cations and displace the anions from the soil solution (Fox et al., 1990; Sagoe et al., 1997), additionally, moreover the release of organic acids from roots can operate by multiple mechanisms (Jones, 1998).

Mineral andisols weathering: The andisols are dominated by short-range-order compounds (e.g. allophane, imogolite), including organo-metallic complexes, ferrihydrite, and aluminosilicates, that are formed largely *in situ* (Herrera et al., 2007), which high buffer capacity due to mineral and organic colloids resulting from the weathering of volcanic ash (allophane, imogolite and complex humus-Al); and have variable surface charge, so changes in pH modified their ion exchange capacity (Qafoku et al., 2004), weathering products such as Al, iron (Fe), and non-crystalline aluminosilicates stabilize humic substances and render them recalcitrant to decomposition, i.e., humic acids are accumulated (humification). Aluminum and Fe-humus complexes are only sparingly soluble and therefore they accumulate at the surface, forming dark thick surface horizon especially under grass vegetation and humid

climate (histic or melanic epipedons). The formation of Al, Fe-humus complexes is associated with a change in soil color (black

color - organic matter), which is called melanization (Grunwald, 2015).

Table 1: Organic acids in some organism and their biosynthetic routes

Organism producer	Type of organic acid	Biosynthetic routes	Reference
bacteria			
<i>Acetobacter aceti</i> , <i>Gluconobacter oxydans</i> and <i>Pseudomonas fluorescens</i>	acetic	Incomplete oxidation of sugars (fermentation acetic)	(Paredes et al., 2010)
<i>Bacillus liqueniformis</i> and <i>Bacillus amyloliquefaciens</i>	lactic	(Glycolysis) Fermentation primary lactic	(Bano et al., 2003)
<i>Pseudomonas fluorescens</i>	oxalic	Tricarboxylic acids	(Paredes et al., 2010)
<i>Erwinia herbicola</i> and <i>Yarrowia lipolytica</i>	citric	Tricarboxylic acids	(Vassileva et al., 2000)
<i>Bacillus liqueniformis</i> and <i>Bacillus amyloliquefaciens</i>	butyric	Anaerobic oxidation of pyruvate	(Paredes et al., 2010)
<i>Pseudomonas putida</i> and <i>Pseudomonas fluorescens</i>	succinic	Glyoxylate and acid cycle tricarboxylic	(Liu et al., 1992)
<i>Bacillus megaterium</i>	malic	Tricarboxylic acids	(Paredes et al., 2010)
<i>Erwinia herbicola</i> , <i>Pseudomonas cepacia</i> and <i>Burkholderia cepacia</i>	gluconic	Direct oxidation of the glucose	(Paredes et al., 2010)
<i>Pseudomonas aeruginosa</i>	fumaric	Tricarboxylic acids	(Harrison et al., 1972)
<i>Rhizobium leguminosarum</i> , <i>Rhizobium meliloti</i> and <i>Bacillus firmus</i>	2-Cetoglucónico	Direct oxidation of the glucose	(Anderson et al., 1985)
Fungus			
<i>Talaromyces flavus</i> (S73), <i>T. flavus</i> var <i>flavus</i> (TM), <i>Talaromyces helicus</i> (L7b) y <i>T. helicus</i> (N24), <i>Penicillium janthinellum</i> (PJ) y <i>Penicillium purpurogenum</i> (POP)	gluconic acid citric and valeric, malic, succinic, fumaric, and lactic acids		(Scervino et al., 2010)
Actinobacteria			
<i>Streptomyces</i> , <i>Kitasatospora</i> and <i>Streptacidiphilus</i>	oxalic acid, citric acid and gluconic acid		(Prada, 2013)
Plant			
<i>Zea mays</i>	citric, malic Amino acids: Aspartic and glycine	Ciclo de Krebs (ciclo del ácido cítrico o ciclo de los ácidos tricarboxílicos).	(Ibarra, 2011; Nigam et al., 2001; Srivastava et al., 1999)
<i>Festuca rubra</i>	Amino acids: histidine, proline, valine, alanine, glycine, aspartic acid, arginine, tyrosine, methionine. Carbohydrates: mannose, galactose, glucose, glucuronate, xylose and arabinose, cítrico, oxálico, málico, malónico, maléico, fumárico, tartárico and succínico		(Ibarra, 2011)

Allophane and imogolite are common early-stage residual weathering products of volcanic glass and both have poorly-ordered structures. Allophane forms inside glass fragments where silica concentration and pH are high and has a characteristic spherule shape. Imogolite tends to form on the exterior of glass fragments under conditions of lower pH and silica concentration, and has a characteristic thread-like morphology. Both allophane and imogolite may complex with organic matter. In some instances, where organic matter is rapidly accumulating, neither allophane or imogolite form in large amounts. Instead, opaline silica and aluminum-humus complexes are formed, which appear to inhibit allophane and imogolite formation (Grunwald, 2015; Levard et al., 2012; Parfitt, 2009).

Mechanisms for increasing rates of weathering involve formation of “surface complexes” with ions on the surface of the mineral, and lowering of the pH of the soil solution. However, neither mechanism is likely to have a significant effect on the dissolution rates of primary minerals of granitic rocks, but may have an effect on more mafic rock types. There will also be significant effects in the microenvironments around rootlets or fungal hyphae, where organic acid concentrations may be much higher than in bulk soil solution (Drever et al., 1994).

The addition of organic matter to the soil can improve the development of soil microbiology, increase production of root exudates, and therefore enhance the presence of LMWOA (Cama et al., 2006), Soil organic matter (SOM) represents the main edaphic reserve of carbon (C). It has molecules with properties and differentiated composition, which makes to SOM responsible for fundamental activities in the soil. The relationship of SOM within and with edaphic life creates a group of emergent properties that generate resilience, and promote fertility and biodiversity in the soil, nowadays, the multi functionality of SOM in agro-ecosystems has been recognized and use to improve their management (Labrador, 2012; Zunino et al., 1985).

Organic matter importance: The thick A horizon of Andisols contains large quantities of soil organic matter. The principal reason for the extraordinary accumulation of organic matter in Andisols has been explained by the stable combination of soil organic matter with amorphous materials such as allophane (Ishizuka et al., 1977), Under the changes in land management, soil has historically played the roles of both source and sink of carbon (Torbert et al., 1997), protection of organic matter occurs through adsorption of organics on mineral surfaces, complexation of organics with metals in solution, the formation of soil aggregates and/or other processes that limit the microbes’ access to organic compounds or increase the energy required to initiate decomposition (Six et al., 2002; Sollins et al., 2007; Sollins et al., 1996).

The organic matter subjected to microbial decay in soil comes from several sources. Vast quantities of plant remains and forest litter decompose above the surface. Subterranean portions of the plant and the above-ground tissue that are mechanically incorporated into the soil body become food of the microorganisms. Animal tissue and excretory products are also subjected to attack. In addition the cells of the microorganisms serve as a source of carbon and nitrogen for succeeding generations of the microscopic population (Kögel-Knabner et al., 2018), and the organic matter affects the majority of the soil chemical, physical and biological properties that are linked with its quality, sustainability, and productive capacity (Carter, 2002; Martínez et al., 2008; Sanchez et al., 2004).

The increase in stability of SOM has been hypothesized to be gained from the protection of SOM from mineralizing agents, thus increasing C mean residence time, up to millennial time periods. The amount of SOM stabilized by soil minerals is known to be influenced by the mineral size, surface functional groups, specific surface area and porosity of the minerals involved. However, there is still a lack of understanding of the mineralogy and chemistry of organic-mineral compounds, and the stabilizing mechanisms

involved in the protection of SOM in-situ (Han et al., 2016; Jones et al., 2014; Kögel-Knabner et al., 2008).

DISCUSSION

Soil properties are a result of interaction between nature and behavior soil components: minerals (45%), water (25%), and air (25%), soil organic matter (5%), microorganisms (0,01%), organic matter in soil requires processes of carbon stabilization, which have been explained by soil aggregation as a physical mechanism, and by chemical and biochemical means, where the dominant presence of carboxylic groups plays a key role in the formation of complex and recalcitrant carbon compounds, as well as, in the level of interaction with mineral colloids (Six et al., 2002; Larson et al., 1990).

Biological inputs and organic matter cycling have long been regarded as important factors in the physical and chemical development of soils. In particular, the extent to which LMWOA, such as oxalate, influence geochemical reactions has been widely studied (Lawrence et al., 2014), the mineral weathering is enhanced through several processes including ligand promoted dissolution; the influence of organic-metal complexation on dissolution reaction affinity; and/or the changes in soil pH resulting from organic acid dissociation and the production of carbon dioxide (CO₂) through the decomposition of organic products. Organic acids affect the mineralogy of soils mostly through their ability to complex and transport Fe and Al, resulting in a characteristic profile development of humid regions. There is considerable controversy as to whether organic acids at natural concentrations significantly accelerate the rate of dissolution of primary silicate minerals (Drever et al., 1994).

The Al in volcanic ash soils forms stable bonds with SOM, which enhances with the increase of humification. The accumulation mechanism of humus is attributed to the interaction clay-humus specifically allophane-humus (Broquen et al., 2004; Cascaredo et al., 2001), these processes are very important

during the formation of melanic and fulvic horizons (Shoji et al., 1990; Shoji et al., 1994; Takahashi et al., 2002). Moreover, the high buffer capacity (resistance to pH change) of Andisols is due to the fact that the clays resulting from the weathering of volcanic ash (allophane, imogolite and humus-Al complexes) have a very reactive surface, and small changes in pH increase cation exchange capacity (CIC); for this reason, these soils are known as variable load soils (Fox, 1985; Uehara et al., 1985).

One of the most important characteristics of Andisols is their capacity of fixing phosphate, so that is nutrient is in a plant-unavailable form. The highest P fixation is found in those Andisols that are fine-textured and have relatively high Al/Si ratios. The phosphate is apparently bound by the Al via an anion exchange for hydroxyl that acts as a chelating agent (Espinosa et al., 2015), phosphorus (P) immobilize (fix) on the surface of amorphous minerals. This is perhaps the main chemical limiting factor of the Andisols, however, the Andosols' P-fixing capacity varies with the type of clay present, a condition that in turn seems to be determined by the height at which the ash deposits that formed the soil are found. The mechanisms of P fixation in allophane and imogolite include processes such as chemisorption, structural silicon (Si) displacement, and precipitation. So, the importance of humus-Al complexes in this process has been recognized (Espinosa, 2008).

In another hand, nitrogen is one of the most important nutrients in the ecosystems and often its availability limits net primary production as well as stabilization of SOM. The long term storage of N on SOM was classically attributed to chemical complexity of plant and microbial residues that retarded microbial degradation. Recent advances have revised this framework, with the understanding that persistent SOM consists largely of chemically labile, microbial processed organic compounds (Kögel-Knabner et al., 2018).

The potential transformation of these amorphous materials from one form to another

under varying environmental conditions, and to other clays has been extensively debated in the literature. The generally accepted model would be that “short range order clays” SROCs are intermediary steps between the hydrolysis of volcanic glass and feldspars to more ordered clay mineral like halloysite, kalolinite, gibbsite and montmorillonite (Neall, 2009).

The clay fraction of volcanic soils is dominated by the presence of non-crystalline aluminosilicate-type minerals in which allophane, imogolite, ferrihydrite, and complexes of humus-aluminum. The study of the physical, chemical and biological properties of these soils is essential to search for sustainable management alternatives that allow increasing yields (Cascaredo et al., 2001). So that, root exudates and microbial communities drive mineral dissolution and the formation of nano-size minerals in soils, which are critical for soil C storage (Yu, 2018).

On the other hand, a lot of research has been done on soil aggregate stability; elucidating that microorganisms are capable of generate substances, like organic acids and its components, to promote soil aggregation and consequently improving soil structure. The implementation of soil conservation practices, such as no tillage, has been developed in order to control, or at least, minimize the agricultural soil loss, by increasing SOM and so enhancing soil structure, improving water availability, and reducing soil erosion (Mikha et al., 2013).

Major mature Andisols are so highly weathered that their clay content often reaches to about one-half of total soil mass. Most of special properties of Andisols are a consequence of the characteristics of amorphous materials, main mineral silicate of clay fraction in this type of soils is allophane, with some other minerals such as imogolite and halloysite, clay mineral fraction of Ecuadorian Andisol was dominated (>85%) by amorphous materials with allophane being predominant and is more stable under rainfall impact than an Colombian Oxisol and a Mollisol from USA; which was explained by greater aggregate stabilization of the Andisol

due to the strong interaction between amorphous materials and high stable soil organic matter (Larson et al., 1990; Espinosa, 1991).

CONCLUSION

For agronomic goals, the application of organic acids via organic amendments and inoculated seeds may influence on the solubility of essential and nonessential elements (especially nitrogen, phosphorous and sulphur) directly through acidification, chelation, precipitation, and oxidation-reduction processes in the rhizosphere in consequently accelerating the weathered and stabilization process of volcanic soils of Ecuador. we propose to promote the use of microorganisms are capable of generating substances, like organic acids and its components, to promote soil aggregation and consequently improving soil structure. The presence of the indigenous microorganisms in the soil such as *Pseudomonas spp.*, *Rhizobium spp.*, *Burkholderia spp.*, *Achromobacter spp.*, *Agrobacterium spp.*, *Aerobacter spp.*, *Flavobacterium spp.*, *Yarrowia spp.*, *Streptosporangium spp.* and *Erwinia spp.* plays an important role on the rate not only of carbon and nitrogen stabilization but also of mineral stabilization, since they have the capacity to produce low molecular weight organic acids; which end up forming stable humified materials in andisols.

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