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Clay transformation and pedogenic calcite formation on a lithosequence of igneous rocks in northwestern Iran

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ABSTRACT

Knowledge about the pathways of pedogenic calcite formations and clay transformations on igneous rocks in semiarid regions plays a vital role in the commentary of soil development on these rocks. The present study was conducted to explore the weathering stages and pathways for the formation of pedogenic calcite in soils developed on selected plutonic and volcanic rocks in a semiarid climate in north-western Iran. The soils developed on plutonic rocks were found to be in the primary stage of weathering with very few pedogenic calcites, except for soil developed on alkali granite which contained few calcitic pedofeatures. Calcitic crystallitic b-fabrics and calcitic pedofeatures were found in all soils developed on volcanic rocks. In situ weathering of Ca-bearing minerals such as plagioclases, amphiboles and pyroxenes could be the possible explanation for the accumulation of pedogenic calcite in the absence of calcareous parent rocks in the studied area. Micritic calcite was observed to be the dominant form in most of the soils developed on volcanic rocks, indicating a rapid precipitation of calcium carbonate. Smectite, kaolinite and mica (illite) were present in the soils developed on plutonic rocks and the clay content in these soils was less than that of the volcanic rocks. Feldspars plus mica were supposed to be the most likely source minerals for the formation of pedogenic illite which could be consequently transformed into smectite in these semi-arid environments. Smectite, mica (illite) and kaolinite were the most abundant clay minerals in the soils developed on dacite and andesite rocks, while a minor quantity of vermiculite occurred only in andesite derived soils. Smectite, as the dominant mineral, and some kaolinite with fairly constant variation in content with depth were observed in the soils formed on hornblende andesite and pyroxene andesite. This could indicate that the smectite had the authigenic origin and was formed most likely from the weathering of plagioclase, hornblende and pyroxene. In general, in situ crystallization of pedogenic carbonates and high quantities of smectite in the clay fraction confirmed that the soils formed on volcanic rocks were more developed than those on plutonic rocks in the studied semiarid region. Moreover, our results showed that releasing calcium from Ca-bearing minerals in igneous rocks in conjunction with biological activities resulted in pedogenic calcite formation.

1. Introduction

Igneous rocks are unstable when raised to the earth surface; therefore soils can be considered as a transition phase formed when the igneous rocks are altered to more stable chemical states (Bohn et al., 1985). Soils play a major role in the biogeochemical cycles, including weathering, as well as the rest of soil functions. Chemical weathering is the partial dissolution of bedrock by surficial fluids and the removal of soluble ions such as Ca^{++}, Mg^{++}, K^{+}, and, Na^{+} in solution (Von Blanckenburg, 2005). Furthermore, chemical weathering includes the process of mineral alteration and transformation to different secondary clay minerals (Schroeder et al., 2000). Clay minerals are mostly formed from pre-existing minerals in rock-forming silicates during transformation, and/or neoformation, where rocks are exposed to water, air, or steam (Galan, 2006).

The weathering rate is influenced by the parent material as well as the climate condition at the beginning of the process (Muhs et al., 2001). The main factors affecting the types of clay minerals following chemical weathering are the chemical composition of the weathered rock and the water/rock ratio (Galan, 2006). The weathering of crystalline rocks commonly produces kaolinite and dioctahedral smectite.

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These two clay minerals, in addition to the products of the micaceous rock-forming mineral degradation (i.e., illite), commonly constitute the bulk of the weathering products. These species are thermodynamically stable with respect to the chemical composition of the soil solution (Galan, 2006).

Among the climate factors, the weathering rate is more dependent on precipitation than temperature (Egli et al., 2003). Moreover, secondary clay mineral compositions vary with precipitation within a specific temperature regime. Under warm, arid and semiarid conditions, soils usually consist of secondary minerals comprising crystalline Fe-oxyhydroxides and phyllosilicates that go from dioctahedral smectite to mixed-layer smectite–kaolinite and kaolinite or dehydrated/hydrated halloysite, with increasing the annual rainfall (Egli et al., 2008; Graham and Franco-Vizcaino, 1992; Mirabella et al., 2005). Under warm, wet and tropical conditions, soils generally exhibit secondary mineral fractions dominated by kaolinite and Al–Fe (hydro) oxides as the response to the high rates of desilication (Galan, 2006; Kleber et al., 2007).

Overall, clay type and content, organic matter, color, depth of leaching and accumulation of calcium carbonate in soils are closely associated with climate (Birkeland, 1999). Calcium carbonate accumulation requires sufficiently wet conditions for the release of calcium from minerals, providing sufficient dry conditions to assure the precipitation of $CaCO_3$ (Durand et al., 2007). Semiarid conditions are the ideal setting for calcite genesis, since carbonate can be solubilized during the wet autumn/winter and re-precipitated during the dry summer (Durand et al., 2007). Secondary calcium carbonate can be autochthonous or allochthonous. Autochthonous carbonates are d from the parent material either directly (being present within that material or inherited) or indirectly (formed from the composition of the parent material or mineral alterations such as plagioclase and hornblende) (Durand et al., 2006). Allochthonous origin involves calcium derived by the lateral movement of Ca at landscape scale from neighboring calcium-rich source-rocks via the lateral flow of ground waters or from aeolian dust addition (Alonso et al., 2004; Durand et al., 2006; Gunal and Ransom, 2006).

Little work has been carried out on calcium carbonate formation in non-calcareous parent materials such as igneous rocks (Ducloux et al., 1990; Durand et al., 2006; Shankar and Achyuthan, 2007). Moreover, no attempt has been made to study the genesis and micromorphological characteristics of calcite pedofeatures and secondary clay minerals in soils developed on the igneous parent rocks of semiarid regions of Iran. Our hypothesis was that pedogenic calcite formed on the igneous rocks in the studied area might originate from the weathering of Ca-bearing primary minerals present in the rocks. Therefore, the objectives of this study were (i) to describe the morphological properties of the various calcium carbonate accumulations in soils developed on different igneous parent materials, (ii) to identify the roles of different igneous parent rocks in the development of calcite accumulated horizons, and (iii) to characterize their clay mineralogy in a semiarid region of north-western Iran.

2. Materials and methods

2.1. Site description and sampling

The study area is located in northwest Iran, in the western zone of the Tertiary Alborz magmatic belt (Ahar–Arasbaran volcanic belt (AHAVB)) (Fig. 1). AHAVB mainly consists of andesitic to rhyodacitic lavas and numerous granitoid bodies with calc-alkaline affinity. This zone is separated from the Urumieh–Dokhtar magmatic belt by a narrow fragment of the central Iran block (Jamali et al., 2010).

Nine soils developed on the igneous rocks, including plutonic and volcanic rocks of AHAVB in the northwest of Iran, were studied (Fig. 1). Plutonic rocks included intermediate (monzodiorite), intermediate-felsic (alkali granite and granodiorite), and intermediate-mafic compositions (syenite and pyroxene diorite). Also, three volcanic intermediate (andesite, hornblende andesite, and pyroxene andesite) and a volcanic intermediate-felsic (dacite) were studied. All studied soils were formed on the backslope positions, except soil developed on pyroxene diorite, which was on the summit position. Lithologic continuity was carefully examined in field by the ratio of immobile elements in soil horizons and parent rocks for the studied soils (Yousefifard et al., 2012). Lithological discontinuities were not observed in the selected pedons, confirming their in situ formation from the weathering of different parent materials. Mean annual precipitation and temperature in the study area are 350 mm and 10 °C, and the soil moisture and temperature regimes are xeric and mesic, respectively.

The description of the morphological properties of the soil horizons was carried out by the standard method of Soil Survey Staff (1993). Their field descriptions are summarized in Table 1. Bulk samples were taken from pedogenic horizons and parent rocks. The oriented and undisturbed samples of soil horizons were also collected and vertical thin sections of the blocks were made for micromorphological observations.

Selected soils had already been characterized in Yousefifard et al. (2012) for chemical and physical properties. The soil samples had low organic matter (4.3 to 35.4 g kg^{-1}). CEC varied from 12.8 to 42.2 cmol + kg^{-1}. The highest CEC values corresponded to soil horizons on volcanic parent rocks. All horizons had neutral to moderately alkaline pH values (7.07 to 8.03). All soils developed on volcanic rocks were calcareous and pedogenic carbonate varied from 92.5 to 322 g kg^{-1}. On the contrary, the soils developed on plutonic parent rocks showed insignificant content of pedogenic carbonates (Table 2).

According to the Soil Survey Staff (2010), the soils developed on plutonic igneous parent rocks, except alkali granite (Calcic Haploxerepts), are classified as Typic Haploxerepts. The soils on volcanic igneous rocks and andesite rock were classified as Typic Calcixerepts and Calcic Haploxerepts, respectively. Soil thickness was often less than 100 cm for the profiles developed on plutonic igneous rocks, except the one on alkali granite, but it was more than 100 cm for all the soils developed on volcanic rocks (Table 1). Most of the soils developed on plutonic and volcanic parent rocks had a sandy loam, and clay or clay loam texture, respectively (Table 2). A decrease in the grain size could have a concomitant effect on weathering (physical breaking down of coarse particles and chemical–mineralogical transformation) (Egli et al., 2008), so the grain size distribution has been used as an indicator for the soil development (Burt et al., 2003; Caspari et al., 2006). Aluminosilicate clays are usually the products of chemical weathering; therefore, clay and clay loam textures in the soil developed on volcanic rocks suggest a dominant chemical weathering process, while sandy loam textures in plutonic rocks rather indicate a physical weathering process. The highest clay content was found in the soils developed on the hornblende andesite and pyroxene andesite (Table 2).

2.2. Laboratory analysis

Chemical cementing agents (organic matter, carbonates and free iron forms) were removed prior to the separation of the clay fraction according to Kittrick and Hope (1963) and Jackson (1975). Oriented specimens on glass slides were analyzed by an X-ray diffraction instrument (Bruker D8 advanced) using Cu-Kα radiation, 30 mA, and 40 kV. Samples were scanned from 2 to 35°2θ, at a scan speed of 2° (2θ) min^{-1}. The following treatments were performed: Mg and K saturation and ethylene glycol (EG) solvation and heating for 2 h at 550 °C on Mg and K treatments, respectively. The relative abundance of each clay mineral was estimated on the basis of peak intensity ratio (Moore and Reynolds, 1997).

For micromorphological studies, the thin sections were prepared from air-dried, undisturbed and oriented clods using standard techniques with polyester resin. The thin sections were described according to Stoops (2003) and Bullock et al. (1985). They were studied with an Olympus BX51 polarizing microscope.