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Elemental and strontium isotopic geochemistry of the soil profiles developed on limestone and sandstone in karstic terrain on Yunnan-Guizhou Plateau, China: Implications for chemical weathering and parent materials

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ABSTRACT

The limestone and yellow sandstone soil profiles from SW China were measured for chemical and Sr isotope compositions of the bulk soils and their sequential leachates (labile, carbonate, and residue or silicate fraction), aiming to characterize the parent materials of the soils, to understand the soil weathering and formation processes, and to discuss the origin of the red residua (terra rossa). The studied yellow sandstone soil, yellow limestone soil, and black limestone soil show different pH values, SiO_2 contents, Rb/Sr abundance ratios, and $^{87}Sr/^{86}Sr$ ratios. The sequential leachates of different soil types also have different $^{87}Sr/^{86}Sr$ and Ca/Sr ratios. The major chemical compositions of the studied soil profiles suggest that all the sandstone and limestone soils are developing at a stage that feldspar is exhausting and the clay minerals are changing from smectite to kaolinite and gibbsite. As compared with the red residua distributed in the karst region, the soils studied here show lower CIA values (58–84), but both higher Na_2O/K_2O (0.9–2.7) and Na_2O/Al_2O_3 concentration ratios (0.07–0.26) on average, suggesting a lower weathering intensity than that of the red residua. The depth profiles of soil CIA values, Na_2O/K_2O and Rb/Sr ratios, and $^{87}Sr/^{86}Sr$ ratios indicate that the weathering intensity is slightly lower for the upper and higher for the deeper soils, which suggest that the sandstone and limestone soil profiles were formed through both accumulation and weathering of in situ weathering residue and input of external detritus or soil from upper land. During weathering of the soils, preferential release of Ca and retention of Sr in soil result in higher Ca/Sr ratios in both labile and carbonate fractions than those in the residue fractions of all soil profiles. The co-variations of Hf/Nb and Zr/Nb ratios, together with those Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of limestone soils, sandstone soils, and the red residua, demonstrate that their parent materials are distinct, and support the point that the widely distributed red residua is originated from the weathering residua of both carbonate and silicate clastic rocks, and further weathering of the weathering residua resulted in intensive release of Si, Na, Ca and relative enrichment of Al, K and other immobile elements in the red residua.

1. Introduction

Research on the identification of soil parental materials, chemical weathering of rocks and pedogenesis holds significance in the study of river basin erosion, element transportation to oceans, elemental biogeochemical cycling at the interface of rock–soil–vegetation system (Taylor and Velbel, 1991; Taylor and Lasaga, 1999; Vance et al., 2009). In addition, rock weathering processes provide inorganic nutrients in soils, buffer watershed acidification, and affect the global carbon cycle and long-term climate change (White and Brantley, 1995; Dessert et al., 2003; Clow and Mast, 2010), which relate themselves with critical societal concerns on the living environment of human beings to a deep extent. The karst area of southwest China is characterized by rare soil distributions, low soil-formation rate, along with serious water loss and soil erosion, all of which result in a fragile ecosystem (Liu, 2009). To recover and improve the deteriorating ecosystem in karst area of southwest China, a better understanding of elemental biogeochemical cycling in the interface of rock–soil–vegetation is imperative, and a systematic study on rock weathering and pedogenesis is of key importance.

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Different from the silicate weathering, carbonate dissolution takes place over large scales at a rapid rate, but leaves small quantities of material for soil formation in karst areas. In the karst areas of southwest China, soil layers are usually thin, about 20–30 cm thick on average. The rock–soil profile in karst areas generally has a nearly clear-cut soil–rock interface, and is absent of the gradual weathering zones that are composed of weathering frontier, saprolite, and pedogenic front in most in situ rock weathering profiles (Ruxton and Berry, 1957; Sequeira Braga et al., 2002; Kirschbaum et al., 2005; Ma et al., 2007). Yellow soil (developed on both sandstone and limestone) and limestone soil (developed from limestone weathering) are the two main types of soil in this area, and their source materials and formation processes still remain controversial. In particular, the origin of the thick and widely distributed yellow or reddish-yellow soil layer or mantle developed on carbonate rocks, also called red residua or terra rossa (Ji et al., 2004; Feng et al., 2009b), has been attracting wide and intense interests from both geochemists and pedologists for many years.

The red residua is a type of red clay soil produced by the weathering of limestone (Durn et al., 1999). When limestone weathers, the clay contained in the rocks is left behind, along with any other non-soluble rock material. Under oxidizing conditions, when the soils are above the water table, iron oxide (rust) forms in the clay. This gives it a characteristic red to orange color. However, the origin of the red residua is still on the debate about their parent material sources. As reviewed by Feng et al. (2009b), there are at least six theories describing the origin of the worldwide distributed reddish-yellow soil at present, which are *the residual theory* (Moresi and Mongelli, 1988; Ji et al., 2004), *the allochthonous theory* (Hall, 1976; Olson et al., 1980; Prasad, 1983), *the non-carbonate rock weathering theory* (Driese et al., 2003; Cooke et al., 2007), *the eolian theory* (Syers et al., 1969; Macleod, 1980; Mee et al., 2004), *the iso-volumetric weathering theory* (Stephenson, 1939; Monroe, 1986; Li and Wang, 1988; Merino and Banerjee, 2008), and *the poly-origin theory* (Yaalon and Ganor, 1973; Jackson, 1982; Durn et al., 1999). In all of the theories, the principal debate regards the source material of the soil.

The studies carried out recently on the origin of the red residua on the Yunnan-Guizhou Plateau support the residual theory, suggesting that the red residua with underlying carbonate rocks is in situ weathering solum, and originates mostly from insoluble residues of the parent carbonate rocks (Wang et al., 1999; Ji et al., 2004; Feng and Zhu, 2009; Feng et al., 2009a). Their arguments for the residual origin stems mostly from the studies of quartz content, size distribution of quartz grains, mineral composition, surface micro-texture and crystal morphology of quartz, oxygen isotope ratios of quartz, and other tracers. Nevertheless, the red residua (terra rossa) is unlikely to have been formed from in situ weathering of carbonate rocks due to mass budget problem, because the carbonate rocks generally contain a small amount (on average, at most 5% in mass fraction of carbonate rocks) of insoluble silicate materials. Moreover, the geochemical evidence supporting the origin of the in situ weathering of carbonate rocks is still insufficient, and more evidence such as the major and trace element, Sr and other isotope evidence is needed. In particular, more systematic comparison studies on the geochemical features of different soil profiles developed on clastic rocks such as sandstone, shale, and carbonate rocks are necessary to document the origin relationship between the vastly distributed yellow soil, limestone soil, and the red residua in karst area.

Major and trace elements, as well as Sr isotopes are powerful tools in the studies of rock weathering and pedogenesis, especially when applied to source material identification, characterization of soil formation pattern, and rock weathering degree (Worden and Compston, 1973; Kronberg et al., 1987; Maynard, 1992; Nesbitt et al., 1996; Malpas et al., 2001; Stewart et al., 2001; Ma et al., 2007, 2010). This study first focuses on the major and trace element, and Sr isotope geochemistry of the yellow sandstone soil as well as both black and yellow limestone soil profiles in central Guizhou province, southwest China. A three-step sequence extraction procedure was also carried out on the soil samples. Ca and Sr contents, along with $^{87}Sr/^{86}Sr$ ratio were determined for different phases to provide further information of chemical weathering and soil formation processes. Combined with a large number of previous work published on red residua in this area (Sun et al., 2002; Wang et al., 2002, 2007; Ji et al., 2004; Liu et al., 2004), the results obtained here may provide insight into the origin of the red residua, in addition to the weathering and pedogenesis of sandstone and limestone in the karst area on Yunnan-Guizhou Plateau, China.

2. Regional lithology and geography

Guizhou Province is located in the west of the Yangtze Platform. The Yangtze Platform spread from the east of Sichuan province, alone Changjiang river, and to the east part of south China. It was in a marine environment from Sinian to the middle of Triassic and received a thickness of more than ten thousand meters of continuous sedimentary rocks. In Guizou Province, the carbonate deposition reached a total thickness of approximately 8500 m. More than 70% of the outcropped rocks there are carbonate rocks (both limestone and dolomite) and the rest are mainly clastic rocks, with piecemeal igneous and epi-metamorphic rocks. The strata distributed in Guizhou Province, together with in eastern Yunnan, southern Sichuan and western Guangxi Province are of Precambrian and Triassic ages for carbonate rocks and of Permian age for arenaceous shale. The carbonate rocks are commonly interbedded with clastic rocks (Fig. 1). The widely distributed carbonate rocks in southwest China form one of the largest continuous distributions of karst landform in the world, with an area of about 500,000 km^2 (Young and Nesbitt, 1998).

As a main part of the Yunnan-Guihzou Plateau, Guizhou Province has a mean annual temperature of 8–12 °C and a mean annual rainfall of 850–1600 mm. More than 50% of the rainfall occurs during June and August. Guizhou is located in the transition zone of the second and third tread of Chinese hypsography, with an average altitude of about 1100 m, displaying a topography slopping from west to the east within the province. Carbonate mesa, peak cluster and forest, basins and hills dominate the types of landforms in Guizhou.

The yellow and limestone soil are the major soil types in this region, occupying 46.5% and 17.6% of total soil area of Guizhou province (Liu and Zhang, 1997). Additionally, red residua, generally with a thickness of 8–10 m, extensively developed in karst area. The distribution of the red residua is controlled mainly by karst geomorphological, hydrological, and ecological environments (Zhu and Li, 2004).

3. Soil profiles and analytical methods

3.1. Soil profiles

To study the rock chemical weathering processes occurring in karstic areas and the formation of soils on sandstone and limestone rocks, three soil profiles developed on limestone and two soil profiles on sandstone were chosen. Since the carbonate rocks (both limestone and dolomite) and sandstone rocks are the main rocks in karst areas, the geochemical features of the soil profiles developed on these two types of rocks will provide important insights into the origin of the widely distributed red residua.