THE FORMATION OF RARE EARTH ELEMENT SCAVENGER MINERALS IN WEATHERING PRODUCTS DERIVED FROM ALKALINE ROCKS OF SE-BAHIA, BRAZIL

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Weathering of nepheline- and sodalite-syenites of Upper Proterozoic age has resulted in the formation of kaolinitic and podsolic soil profiles in SE-Bahia state. Sodalite syenites of Sta. Cruz da Vitoria consist of microcline, sodalite, nepheline and arfvedsonite, latter partly replaced by biotite. Accessory minerals are calcite, apatite, zircon and ilmenite. The weathering profile consists of a narrow saprolite zone (0.5 m), grading into a kaolinitic horizon of > 4 m thickness. In the saprolite, feldspars and feldspathoids are partly preserved, while biotite gradually is altered to vermiculite. Sodalite, calcite and apatite are the first minerals to be decomposed, being followed by nepheline. The kaolinitic horizon consists of microcline relics, secondary quartz and heavy minerals, embedded in a matrix of kaolinite and goethite. In the upper part of the kaolinitic horizon, a layer of ferromanganese concretions can be observed. Heavy minerals like zircon and ilmenites have residually become enriched as a result of depletion of alkalies and silica and show slight evidence of dissolution as a result of weathering.

Mass balance calculations with TiO_2 as internal standard reveal depletion of alkali elements, Mn and Zn throughout the profile and enrichment of Rare Earth Elements (REE) in the upper profile part as well as enrichment of REE and Ba in the saprolite. Values of 560 ppm REEtot represent a 3-4 fold enrichment relative to bedrock. In the saprolite, REE and Ba are bound to hydrobiotite and vermiculite. In the surficial horizon, REE are scavanged in ferromanganese concretions.

Chondrite-normalized REE patterns of bulk weathering material of the concretionary top soil reveal relative enrichment of Heavy REE, while the REE fractionation pattern of the vermiculite-rich saprolite shows a distinct positive Ce-anomaly. In relation to the internal standard, the top horizon shows an absolute enrichment of Ce, Yb and Lu by factor 2, while the intermediate REE are enriched by approximately factor 1.2. The saprolite shows strong absolute enrichment of Ce by factor 4, while Yb and Lu are depleted. In the middle part of the profile, slight depletion of REE is observed.

Fractionation and distribution of REE in weathering material above alkaline bedrock of Sta. Cruz da Vitoria indicate at least two different phases of formation of REE-scavenger minerals : (a) the formation of REE-bearing ferromanganese concretions, consisting of crypto-crystalline Mn- and Fe-(hydr) oxides intimately intergrown with secondary silica, has occurred under conditions of restricted drainage during a subhumid-semiarid climate. In accordance with results reported by CONCEICAO *et al.* (1974), semiarid conditions in SE-Bahia were followed by a more humid climate. Weathering intensified and kaolinitic profiles have developped in a clima belt next to the coastline, which is characterized by annual precipitation of > 1500 mm (Brazil-Minesterio das Minas e Energia, 1981) ferromanganese concretions thus represent relics of an earlier weathering stage. They are still preserved in the top soil of non-truncated kaolinitic weathering profiles and act as sinks for Heavy REE and Ce^{4+}.
(b) The formation of vermiculite and hydrobiotite in the saprolite of kaolinitic profiles results from alteration of biotite contained in the sodalite syenite. Due to silicate hydrolysis and infiltration of meteoric waters, alkaline and oxidizing conditions prevail in the saprolite. Under these conditions, Ce becomes oxidized to Ce^{4+} and is scavenged in vermiculite together with Ba, as also reported by Duddy (1980). The Heavy REE are more mobile in this environment due to complexation with carbonate ions (Nesbitt, 1979) and are depleted. Conditions of restricted drainage prevail in weathering profiles above alkaline bedrock in the semiarid-subhumid zone of Palmeirao, ca. 70 km SSW of Sta. Cruz da Vitoria, where annual precipitation reaches

500-1000 mm. In these areas, podsolic soil profiles with ferromanganese concretions, siliceous duricrusts and REE-bearing Mn-Fe-Si-rich duricrusts are abundant. Neosynthesis of smectite can be observed. Podsolic soils and duricrusts are subject to degradation and erosion. Hydromorphic conditions above imper- meable duricrusts favour slight enrichment of REE relative to bedrock by maximum factor 2.

The formation of REE-bearing concretions is an indicator of restricted drainage conditions which have prevailed in different climatic zones of SE-Bahia during different time periods. REE patterns of ferromanganese concretions of different areas show variations due to the REE contents of the bedrock. In this environment significant accumulation of REE is low due to limited dissolution of REE-bearing primary minerals. High silica content of ferromanganese concretions seem to have an restrictive effect on the concentration of REE. REE enrichment is favoured by more intensive drainage, as observed in saprolite zones of kaolinitic profiles of the recent subhumid and humid zone. Here primary REE bearing minerals like apatite and biotite become sufficiently dissolved, thus mobilizing REE. Subsequently REE are scavenged under alkaline and oxidizing environment, where suitable scavenger minerals like vermiculite are present. Under these conditions, absolute enrichment of tetravalent Ce is favoured.

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