

THE USE OF U-SOTOPES MODELLING TO EVALUATE WEATHERING RATE AT THE MORRO DO FERRO, POÇOS DE CALDAS PLATEAU (MG), BRAZIL

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1. INTRODUCTION

The high grade thorium and rare earth elements deposit situated in Minas Gerais State, Brazil, has been investigated by Earth and Health scientists for over 40 years (Tolbert, 1955; Roser and Cullen, 1962; Wedow, 1967; Fujimori, 1982; Eisenbud et al., 1984; Bonotto, 1989; Chapman et al., 1992). It is a very interesting site for investigations of weathering rates through natural radionuclides belonging to the ^{238}U decay series, because their abundance in the area. ^{238}U is a parent nuclide of an independent decay series, which proceed as follows: ^{238}U (4.49 Gyr, α) \rightarrow ^{234}Th (24.1 d, β^-) \rightarrow ^{234}Pa (1.18 m, β^-) \rightarrow ^{234}U (2.48×10^5 yr, α) \rightarrow ^{230}Th (7.52×10^4 yr, α) \rightarrow ^{226}Ra (1622 yr, α) \rightarrow ... The isotopes ^{238}U and ^{234}U are in secular equilibrium in all minerals and rocks greater than one million years old and that are closed systems for U. The $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) is, therefore, unity in the bulk of such systems, however, rock-water interaction frequently results in AR's for dissolved uranium which are greater than unity (Osmond and Cowart, 1976; Ivanovich and Harmon, 1982). Thus, in alteration fronts, ^{234}U is preferentially mobilized to ^{238}U when rock weathers (Ivanovich and Harmon, 1982). Consequently, measurements of the $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) in rocks, soils and waters have allowed the calculation of the solution coefficient for the uranium characteristic of the region, that allows evaluate the time necessary to weather 1 m of rock under actual climatic conditions (Moreira-Nordemann, 1980, 1984). Such approach focusing the U-disequilibrium method was utilized to evaluate the velocity of alteration of rocks from an area affected by the continuous use of fertilizer-derived uranium utilized in sugar cane crops at Corumbataí River basin, São Paulo State, Brazil (Conceição and Bonotto, 2003). This paper describes the application of the technique at the main drainage of Morro do Ferro, Poços de Caldas plateau, as the area is recognized not to be dominantly affected by anthropogenic inputs of elements/compounds and there are enough data available to properly use the method and compare the results with those of previous investigations held in areas subjected to different climatic conditions taking place in Brazil.

2. GENERAL FEATURES OF THE AREA STUDIED

The Morro do Ferro deposit is located about 20 km south of the city of Poços de Caldas, an important touristic site in Minas Gerais State, Brazil, nearly in the center of the Poços de Caldas alkaline complex. This complex is circular shaped with a mean diameter of 33 km, has an area of about 800 km², an altitude between 1300 and 1600 m, and topography characterized by valleys, mountains, and gentle grass-covered hills. The plateau is a ring structure of Mesozoic age comprising a suite of alkaline volcanic and plutonic rocks, mainly phonolites and nepheline syenites. The local geology of the Morro do Ferro is characterized by hydrothermally altered country rocks termed "potassic rocks" overlain by a deep weathering cover. Dominant rock-types identified around Morro do Ferro are phonolites, tinguaïtes and foyaites mineralogically and geochemically comparable to the rocks exposed all over the Poços de Caldas plateau (Schorscher and Shea, 1992). The Th-REE ore body is a 410 m long, 215 m wide and 10-35 m thick zone of NW-SE elongated argillaceous lenses extending from the summit of the hill along its south-eastern slope (Barreto and Fujimori, 1986). The magnetite veins are the dominant features at the surface of Morro do Ferro, being concentrated in the uppermost 40 m of the hill.

Morro do Ferro is one of the highest points on the caldera, rising some 140 m above the base (Fig. 1). The hill is steep-sided and bounded by two deeply incised streams which drain the groundwater: the North stream (drains the northern side) and the South stream (curves around the south-eastern periphery). Drainage for the Morro do Ferro basin is self-contained to a distance of several kilometres, being provided mainly by South stream, where the flow during periods of no rainfall (baseflow) is sustained by groundwater seepage. The topsoil supports a thin cover of grasses, and a small densely wooded area lies along the south stream to about 750 m downstream, whereupon the stream drains into a swamp.

Several boreholes were drilled to investigate the hydrological and chemical character of the subsurface flow on the aquifer system developed in the weathered profile of the Morro do Ferro area. Nine were drilled by IPT(1982) to sample the upper part of the saturated zone, from which three in the ore body zone (SR-5, SR-7 and SR-8), four around the ore body zone (SR-2, SR-4, SR-6 and SR-9) and two distant

from the ore body zone (SR-1 and SR-3). Four other boreholes were drilled along the southeastern slope of Morro do Ferro to study the lower part of the saturated zone (Holmes et al., 1992): MF 10, situated in the ore body zone; MF 11, immediately adjacent to MF 10, to sample groundwater in the vicinity of the water-table for comparison with the deeper water sampled by MF 10; MF 12, at the bottom of the southeastern slope near the south stream, and MF 13, between boreholes MF 10 and MF 12. The water-table is a subdued replica of the topography, with recharge on the higher elevations from precipitation and discharge locally to streams. At the top of the hill, the water-table is at least 80 m below the surface and in the valley bottoms is at or near the surface, occurring as seepages or discrete springs. The borehole studied in this investigation is SR-5, which was drilled at 1473 m above sea-level on the southeastern slope of Morro do Ferro, where the ground slope is 0.22%. It is located a few metres further downhill from borehole MF 10 (Fig. 1), penetrated through the Th-REE ore body and terminated at a depth of 27.3 m. The water-table depth of SR-5 after drilling was 12.05 m and decreased 3.05 m from October 1981 to January 1982 (wet season). Such borehole was chosen due to its location within the limit of strong radioactivity at surface and relation to water flow in South stream.

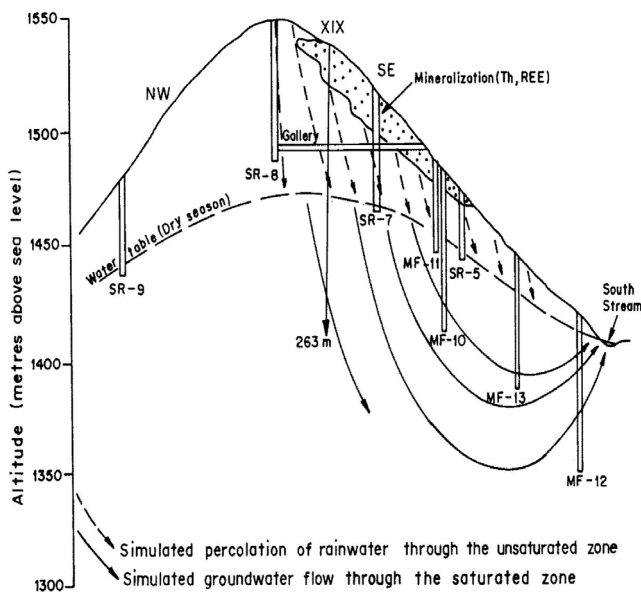


Figure 1. Profile across Morro do Ferro showing the Th-REE mineralization, the dry-season water-table, and location of the gallery and boreholes drilled during exploratory/research studies extending back to the 1950s. Adapted from IPT (1982) and Waber et al. (1992).

Because alternating wet/dry seasons are typical and weathering conditions are vigorous in the semi-tropical climate of the region, weathering of the host rock has taken place down to a depth of more than 100 m. The recovered material from borehole SR-5 consisted predominantly of a fine-grained clay-silt matrix (Fig. 2),

whose main feature is the abundance of magnetite layers of variable thicknesses which have stabilized the hill from excessive erosion, allowing a residual enrichment of Th- and REE-minerals through dissolution of the more soluble mineral phases. The ore material is mainly dark reddish-brown in color; magnetite nodules occur loosely arranged in layers and vein-like structures and also more randomly distributed throughout the matrix. Waber et al. (1992) applied the term "host rock" to the completely weathered material below the ore body whose original matrix was a carbonatite, the weathering of which led to the present supergene Th-REE deposit of Morro do Ferro. Such host rock in MF 10 varies between 22 and 75 m depth, its clay/silt material is much brighter in color, varying from yellowish-white to reddish-white and intercepted by thin dark-red/brown and black zones. Magnetite veins are much less abundant in this completely weathered host rock and because its lower boundary is still not clearly defined, the lithological description of SR-5 given in Fig. 2 is indicative that it has not been attained by drilling.

DEPTH (m)	DESCRIPTION	MAJOR MINERALS	NOTES
0	limonite in silty matrix	illite/sericite, kaolinite, gibbsite, goethite, limonite, bastnaesite, cerianite, thorianite	fragments of limonite about 5 cm in diameter, dark brown to black
3	clayey silt, with fragments of limonite	illite/sericite, kaolinite, gibbsite, goethite, limonite, bastnaesite, thorite	dark brown to reddish-brown
6	silty clay	illite/sericite, kaolinite, gibbsite, hematite, limonite, bastnaesite, cheralite	reddish-brown with fragments of limonite
9			yellowish-white
12			dark brown
15			whitish - yellow
15	dike of magnetite with the presence of limonite	magnetite, limonite	black coloured
18	silty clay	illite/sericite, kaolinite, cheralite	whitish - yellow
18	dike of magnetite with the presence of limonite	magnetite, limonite	black coloured
18	silty clay with fragments of magnetite coated with limonite	illite/sericite, gibbsite, kaolinite, goethite, limonite	whitish - yellow
21	dike of magnetite with several fragments from 0.5 to 3 cm in diameter	magnetite	black coloured
21	silty clay	illite/sericite, kaolinite, alunite group, hematite, bastnaesite	reddish - brown
24	dike of magnetite with several fragments from 0.2 to 2 cm in diameter	magnetite	black coloured
27	silty clay	illite/sericite, kaolinite, bastnaesite	whitish - yellow

Figure 2. Lithological description and mineralogy at borehole SR-5 from Morro do Ferro at Poços de Caldas plateau (IPT, 1982).

3. SAMPLING AND METHODS

Rock samples were collected and analyzed by Schorscher and Shea (1992) throughout the area, taking into account the geological context, the rock types and their abundance or spatial distribution. Several U-isotopes data referring to campaigns for sampling surface waters were reported by Grimaldi (1981). The samples were stored in polyethylene bottles, filtered through 0.45 µm membranes and preserved with HNO₃ acid. Crushed borehole spoil samples representing depth intervals from 0 to 27.3 m at borehole SR-5 were also analyzed. About 0.5 g of material was crushed to about 200 mesh, put in acid digestion bomb similar to Parr 4575 at temperatures to 150 °C and internal pressures to 1200 psig, and brought into complete solution with HF, HClO₄ and HNO₃; the samples were spiked with ²³²U equilibrated with ²²⁸Th (19.3±0.8 dpm) to measure ²³⁴U activity. U and Th were co-precipitated with Fe(OH)₃, Fe³⁺ extracted with isopropyl ether, and U separated from Th by anion exchange. The sorbed U was eluted with 0.1 M HCl and extracted with 0.4 M thenoyl-trifluoroacetone (TTA). Uranium concentration and isotopic composition of all samples were determined using standard alpha spectrometric technique (Osmond and Cowart, 1976; Ivanovich and Harmon, 1982). The ²³⁸U concentration was calculated by isotope dilution from the counting rates of ²³⁸U and ²³²U peaks, and ²³⁴U/²³⁸U AR was calculated from the counting rates of ²³⁸U and ²³⁴U peaks.

4. THE U-ISOTOPES MODELLING

The U-isotopes method to determine the weathering rate of rocks was developed by Moreira-Nordemann (1980, 1984) and applied to Preto and Salgado River basins. The quantity of weathered matter removed per unit of surface and per unit of time (*W*, ton/km²/yr) is determined by $W = E_E D/E_R S$, where: E_E =weighted average U concentration in river water, E_R =mean U concentration in rocks, D =mean discharge of the river, and S =surface of the basin. The weathering rate of rocks in the basin (v) depends on the density (ρ) of rocks and of the coefficient of dissolution (k) of uranium during weathering, according to the equation $v=W/k\rho$. The solubility coefficient for uranium may be expressed as $k=(A_R-A_S)/(A_E-A_S)$, where A_R , A_E and A_S are the mean ²³⁴U/²³⁸U ratios in rocks, waters and soils, respectively.

5. RESULTS AND DISCUSSION

The ²³⁸U concentration and ²³⁴U/²³⁸U activity ratio in the analyzed spoil samples are represented in Table 1. The average ²³⁸U concentration corresponded to 33.62 µg/g. The data also indicate that preferential removal of ²³⁴U occurred throughout the studied core up to about 27 m depth, where an average ²³⁴U/²³⁸U AR of 0.90±0.02 was generated in the solid phase, a typical result related to the effect of rock/soil water interaction (Osmond and Cowart, 1976). Consequently, uranium ratios greater than unity are expected to be found for the dissolved U, where

the enhancement of ²³⁴U in surface waters of South stream was confirmed by the average value of 1.26±0.05 for the ²³⁴U/²³⁸U AR (Grimaldi, 1981). The mean dissolved uranium content for 43 samples analyzed from June 1980 through July 1981 at the same site corresponded to 0.32µg/L (Grimaldi, 1981). Schorscher and Shea (1992) reported average values corresponding to 45.27 µg/g and 1.06±0.06, respectively, for the ²³⁸U concentration and ²³⁴U/²³⁸U AR in oxidized and reduced phonolites found at borehole MF 12 drilled at Morro do Ferro. The density of such rocks is 2.64 g/cm³ (Schorscher and Shea, 1992). The discharge data reported by Lei (1984) from May 1981 through April 1982 allow estimate a weighted mean flow in South stream corresponding to 1.53×10³ m³day⁻¹. The Morro do Ferro area drained by South Stream is estimated as 0.23 km² (Lei, 1984).

Table 1. Concentration of U and ²³⁴U/²³⁸U activity ratio in core samples from borehole SR-5 at Morro do Ferro. All analytical uncertainties correspond to 1σ standard deviation.

Depth		Average (m)	Weight (g)	U		²³⁴ U/ ²³⁸ U	
Interval (m)				(µg/g)		+/-	+/-
0.00 - 2.00	1.00	0.51	43	3	0.94	0.05	
2.00 - 3.05	2.52	0.52	28	2	0.96	0.05	
3.05 - 4.45	3.75	0.48	49	3	0.89	0.05	
4.45 - 5.50	4.98	0.50	47	3	1.01	0.06	
6.96 - 8.75	7.86	0.51	53	4	0.93	0.05	
8.75 - 10.00	9.38	0.50	32	2	0.87	0.06	
10.00-11.25	10.62	0.51	32	2	0.93	0.06	
11.25-12.10	11.68	0.53	35	2	0.94	0.05	
12.10-13.65	12.88	0.51	45	3	0.80	0.04	
14.65-16.26	15.46	0.47	12	1	0.90	0.06	
17.50-20.00	18.75	0.53	17	1	0.84	0.05	
20.00-22.30	21.15	0.47	16	1	0.97	0.08	
25.90-27.30	26.60	0.53	28	2	0.75	0.06	

The U-isotopes modeling was developed by Moreira-Nordemann (1980, 1984) considering the mean U content in weathered rocks (or in C horizons). However, there is no typical soil horizons developed at Morro do Ferro area, but only a thick weathered profile, as shown in Fig. 2. Despite this, the U-isotopes data in Table 1 are well appropriate to be used in the modeling as are a typical result related to the effect of rock/soil water interaction, i.e. the ²³⁴U/²³⁸U AR is lower than 1, within experimental errors. Thus, the ²³⁴U/²³⁸U AR data for rocks, waters and spoil samples allow estimate a solubility coefficient for uranium as $k=0.44$ in the area, which implies that 44% of the available uranium in rocks is taken into solution during the weathering process. Using all available data and applying the equation established by the U-isotopes model, it is possible estimate a value of 0.015 mm/yr for the weathering rate v . This result shows that one vertical meter of rock needs about 67 ka to be chemically weathered, under the present climatic conditions. This value is very reasonable when compared with the range between 0.015 and 0.05 mm/yr based on land surface lowering within the entire caldera (Holmes et al., 1992). It is also compatible with that corresponding to 0.013 mm/yr determined by Moreira-Nordemann (1984) for the Salgado River basin in a semi-arid

region in Bahia State, Brazil.

Thus, the modeling proved to be useful for estimating the weathering rate in a small hydrographic basin that is not subjected to the same climatic conditions occurring in the area where it was firstly applied. The value generated is reliable and increases the potential use of the method into other different areas occurring in Brazil and elsewhere.

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RESUMO

O depósito de tório e terras raras situado no Morro do Ferro no planalto de Poços de Caldas, Brasil, tem sido investigado por pesquisadores das Ciências da Terra e da Saúde durante os últimos 40 anos. Ele é um local muito interessante para investigações sobre taxas de intemperismo por intermédio de radionuclídeos naturais pertencentes à série de decaimento do ^{238}U , devido sua abundância na área. Medidas da razão de atividade $^{234}\text{U}/^{238}\text{U}$ (RA) em rochas, solos e águas tem permitido a avaliação de taxas de intemperismo. Este trabalho descreve a aplicação da técnica na drenagem principal do Morro do Ferro, uma vez que a área não tem sido predominantemente afetada por entradas antropogênicas de elementos/compostos e também porque existem dados disponíveis que permitem utilizar apropriadamente a técnica e comparar os resultados com aqueles de investigações prévias realizadas em locais sujeitos a diferentes condições climáticas ocorrendo no Brasil. Os dados de razão de atividade $^{234}\text{U}/^{238}\text{U}$ em rochas, águas e material alterado permitiram estimar um coeficiente de solubilidade para urânio na área correspondente a $k=0,44$. Usando todos os dados disponíveis e empregando a equação definida pelo modelo isotópico do urânio, foi possível estimar um valor de 0,015 mm/ano para a taxa de intemperismo. Este resultado mostra que um metro vertical de rocha necessita de cerca de 67.000 anos para ser quimicamente alterado, nas condições climáticas atuais. Este valor é compatível com taxas de 0,015-0,05 mm/ano estimadas com base em diminuição da superfície do terreno no interior da caldeira, bem como com a taxa de 0,013 mm/ano determinada para a bacia do Rio Salgado em uma região semi-árida no estado da Bahia, Brasil.