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Semi-quantitative mineralogical valuation of the non-nickeliferous weathering crusts in the northeast of Cuba

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Gerardo Orozco Melgar

Abstract
This study presents a semi-quantitative mineralogical evaluation of the non-nickeliferous weathering crusts in the areas of Baconal, El Culebro, Caimanes and Farallones in the northeast of Cuba. The main objective of this study is to determine the main mineral phases, their vertical distribution and concentration, as well as the degree of mineral transformation in the weathering profiles. Sixteen samples were analyzed by X-Ray Diffraction and the diffractograms were used in qualitative and semi-quantitative phase analyses using ANALYZE and AUTOQUAN programs. The degree of mineral transformation in relation to phase distribution and concentration as weathering progressed was evaluated using the Mineralogical Index of Alteration. The main mineral phases present in Baconal and El Culebro are Kaolinite (50-75%), Kaolinite-Montmorillonite (50-75%), Quartz (25-50%), Plagioclase, mainly Albite (25-50%) and Hematite (<10%). In Caimanes and Farallones the principal mineral phases present are Kaolinite, Hematite, Quartz, Potassic feldspars, mainly as Orthoclase, all with more than 75%, Halloysite (<10%), and Montmorillonite (<10%). Extreme primary mineral transformation is evidenced in the intermediate and upper layers in Baconal, El Culebro and Caimanes (Mineralogical Index of alteration values between 29 and 98 %). This transformation is also evidenced in the whole Farallones profile (98-99 %). In conclusion, the non-nickeliferous weathering crusts in Baconal, El Culebro, Caimanes and Farallones are mainly kaolinitic clays.

Key words
Clays, mineralogical index of alteration, mineralogy, northeast Cuba, weathering crusts.
Evaluación mineralógica semi-cuantitativa de las cortezas de meteorización no niquelíferas en la región nororiental de Cuba

Resumen
Este estudio presenta una evaluación mineralógica semi-cuantitativa de las cortezas de meteorización no niquelíferas en las áreas de Baconal, El Culebro, Caimanes y Farallones en la región nororiental de Cuba. El objetivo principal del presente trabajo es determinar las principales fases minerales, su distribución, concentración y grado de transformación de los minerales en los perfiles de meteorización. Las muestras, 16 en total, se analizaron mediante Difracción de Rayos X; los resultados se procesaron con los programas ANALYZE y AUTOQUAN. El grado de transformación de los minerales en relación con la distribución, concentración de las fases y el avance de la meteorización se determinó por el Índice Mineralógico de Alteración. Las principales fases minerales presentes en Baconal y El Culebro son caolinita (50-75%), caolinita-montmorillonita (50-75%), cuarzo (25-50%), plagioclasas, principalmente albita (25-50%) y hematita (<10%). En Caimanes y Farallones las fases principales son caolinita hematita, cuarzo, feldespatos potálicos, principalmente ortoclasa, todos en más de un 50-75%. También están presentes la halloysita (<10%) y montmorillonita (<10%). Se evidencia una transformación mineral extrema en los horizontes intermedios y superiores en Baconal, El Culebro y Caimanes (Índice Mineralógico de Alteración con valores entre 29 y 98%). Esta transformación también se observa en el perfil completo de Farallones (98-99%). Se concluye que las cortezas de meteorización en Baconal, El Culebro, Caimanes y Farallones son principalmente arcillas caoliníticas.

Palabras clave
Arcillas, índice mineralógico de alteración, mineralogía, Cuba nororiental, corteza de meteorización.
INTRODUCTION
The weathering crusts in Baconal, El Culebro, Caimanes, and Farallones, in Eastern Cuba, are developed on different types of rocks found as presented in Figure 1. Bedrocks include the Late Cretaceous volcanic rocks of the Téneme Formation in Baconal and El Culebro (Proenza et al. 2006) and volcano-sedimentary rocks of the Sabaneta Formation in Caimanes and Farallones (Orozco 2008). These areas were selected due to the large extent of the weathering crusts and that the mineralogical aspects of these crusts are not well documented in literature (Njila & Díaz-Martínez 2009, Njila et al. 2010).

Figure 1. The geographical location of the study sectors modified from Proenza et al. (2006) and Orozco (2008).

Various authors have studied the clays and the non-nickeliferous weathering crusts in Moa and surrounding areas, reaching the conclusion that these crusts are kaolinitic clays (Pons & Leyva 1996, Fadel 2005, Pons et al. 1997, Cámara 2007). There are no recent studies on the quantitative mineralogy of these weathering crusts in the Baconal, El Culebro, Caimanes and Farallones. The mineralogical phase analyses (Pons & Leyva 1996, Cámara 2007) have been
focused on the whole profile without any analysis on the mineralogical zoning down-profile.

The aim of the present paper is to present a semi-quantitative mineralogical evaluation of the non-nickeliferous weathering crusts in Baconal, El Culebro, Caimanes and Farallones areas in the northeast of Cuba with the main objective of determining the principal mineral phases, their vertical distribution and concentration, as well as the degree of mineral transformation in the weathering profiles. This analysis is based on the X-Ray Diffraction and Fluorescence techniques.

MATERIALS AND METHODS

Samples were taken from well-exposed outcrops in different sectors of the study area. In Baconal, a thick weathering crust develops on volcanic rocks with a remarkable variation in its composition, texture and colour. The upper part of the profile is composed of a clayey, fine-grained material of ochre texture and reddish in colour. The lower part differs notably from the upper; the texture is coarse, with inclusions of volcanic clasts and yellowish-brown in colour. Three samples (TNL-1, 2 and 3) were taken from the three layers from top to bottom. In El Culebro the weathering crust are approximately eight meters in thickness and are similar to the Baconal profile, with presence of red clayey material in the upper part and a brown-yellowish part at the base. The lower part of the profile is composed of a yellowish material with reddish stains and volcanic rock fragments (Figure 2), representing hard saprolite in the profile. Four samples (TNL-4, 5, 6 and 7) were taken form the profile. In Caimanes, five samples (TNL-8, 9, 10, 11 and 12) were taken using a similar method, which was also applied in Farallones, represented by four samples (TNL-13, 14, 15 and 16).

X-Ray analyses were done at the Technical University of Clausthal (TUC) in Germany using a HZG - 4 type diffractometer with CuKα radiation and goniometric speed of 2°/min.
Whole-rock chemical analysis data used in the CIA and MIA calculations were determined at the University of Barcelona using a Panalytical (Philips) PW2400 spectrometer with an Rh X-Ray tube operated at 60 KeV, 125 mA and 3000 W.

Semi-quantitative mineralogical data were determined using ANALYZE (version 2.293, copyright 1993-2002) and BGRM/AUTOQUAN (version 2.6.0.0, 2001) programs, respectively. BGRM/AUTOQUAN uses the Rietveld method for curve adjustments between selected patterns and analyzed samples.

The Mineralogical Index of Alteration (MIA; Voicu et al. 1997) was used to evaluate the degree of mineralogical weathering, i.e. the transformation ratio of a primary mineral into its equivalent alteration mineral. MIA yields values between 0 and 100, and reflects incipient (MIA<20), intermediate (MIA = 20-60), and intense to extreme (MIA>60) mineralogical transformation. The value of 100 means complete transformation of a primary mineral into its equivalent alteration product. The calculated MIA values are further used for partitioning the major oxides between the pairs of primary/secondary minerals in normative mineralogical calculations. The relation between this index and the Chemical Weathering Index (CIA; Nesbitt & Young 1982) is given by MIA= 2 x (CIA-50) (Voicu et al. 1997).

RESULTS AND DISCUSSION

In Baconal, a disordered Kaolinite and Quartz are abundant at the top of the profile. Quartz content increases down-profile while Kaolinite decreases in the same direction. Hematite is present in the upper and intermediate layers in small amounts. Towards the base, plagioclases appear, mainly as Albite, as shown in Figures 2a and 2b. Throughout the profile there are Quartz veinlets, as also observed in the underlying rock.
Figure 2a. Comparative X-Ray diffractograms of the Baconal weathering crust profile. The relative abundances of the phases are shown as percentage ranges on the top right side.

Figure 2b. Composition of the Baconal weathering crust profile and bedrock. Bedrock information is from Marchesi (2006) and Proenza et al. (2006). The relative abundances are shown as percentage ranges below the graph. Plc=Plagioclase; Cpx=Clinopyroxene; hnb=Hornblende; Opx=Orthopyroxene; Ol=Olivine; Ep=Epidote;
As in Baconal, the weathering profile in El Culebro is dominated by Kaolinite and Quartz, but with the presence of Kaolinite-Montmorillonite in the lower part of the profile. Quartz veinlets are present in the profile, concentrated mainly towards the lower part. Figures 3a and 3b show the X-Ray diffractograms and the variation in mineralogy with depth.

Figure 3a. Comparative X-Ray diffractograms of the El Culebro weathering crust profile. The abundances are shown as percentage ranges on the top right side.

Figure 3b. Lithologic, mineralogical and chemical composition of the El Culebro weathering crust profile. Bedrock data were taken from Marchesi (2006) and Proenza et al. (2006). The phase abundances in the samples are shown as percentage ranges below the graph.
In Caimanes, the underlying tuffs were altered to a weathering profile in which Hematite dominates and is present in the upper layers. Halloysite is also present in the intermediate and upper layers, while Montmorillonite appears subordinately below these layers. Quartz and K-feldspars are concentrated in the lower layers. Phase analysis results are shown in Figure 4a and 4b.

Figure 4a. Comparative X-Ray diffractograms of the Caimanes weathering crust profile. The average abundances are shown as percentage ranges on the top. Hyt=Halloysite; Mnt=Montmorillonite; Hem=Hematite; Or=Orthoclase; Q=Quartz
The non-nickeliferous weathering crusts in Farallones are mainly composed of Kaolinite and Hematite, with the presence of Halloysite, Montmorillonite and Kaolinite-Montmorillonite in the intermediate and lower layers. Figures 5a and 5b show the mineralogy changes as depth increases.
Figure 5a. Lithologic, mineralogical and chemical composition of the Farallones weathering crust profile. The relative abundances are shown as percentage ranges on top of the graph.

Figure 5b. Lithologic, mineralogical and chemical composition of the Farallones weathering crust profile. Bedrock data taken from Reyes (1997). The relative abundances are shown as percentages below the graph.
The MIA values for the four sectors studied are shown in Table 1. Figure 6 shows a graphical representation of the MIA derived from CIA values of the samples in this study and bedrock data taken from Marchesi (2006), Proenza et al. (2006) and Reyes (1997).

Table 1. Mineralogical Index of Alteration (MIA) and Chemical Weathering Index (CIA) values for Baconal, El Culebro, Caimanes and Farallones. Calculation based on molar proportions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thickness (m)</th>
<th>Depth (m)</th>
<th>CIA %</th>
<th>MIA %</th>
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<tr>
<td>Baconal</td>
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<td></td>
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<tr>
<td>TNL-1</td>
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<td>1.1</td>
<td>98</td>
<td>97</td>
</tr>
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<td>2.3</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
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<td>3</td>
<td>65</td>
<td>29</td>
</tr>
<tr>
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<td>6</td>
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</tr>
<tr>
<td>TNL-7</td>
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<td>99</td>
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<td>TNL-16</td>
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<td>TNL-13</td>
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Figure 6. The CIA and MIA plot for the 16 samples taken from Baconal, El Culebro, Caimanes and Farallones. Bedrock data taken from Marchesi (2006) and Reyes (1997). The vertices are in molar proportions. Average values of andesite, basaltic andesite and rhyolite are from Roser et al. (2002).
DISCUSSION

The volcanic rocks of the Téneme Fm are mainly composed of basalts, basaltic andesites, andesites, and minor dacites. In general, Téneme volcanic rocks underwent extensive hydrothermal processes that led to the formation of abundant quartz veins (Proenza et al. 2006). This is the reason for the presence of quartz veinlets in the weathering crusts in Baconal and El Culebro. Quartz may also be present as a relict mineral inherited from silicic igneous parent rocks, e.g. basaltic andesites, andesites, and dacites. The lower layers of these profiles may have undergone chloritization and albitionization due to hydrothermal processes evidenced by smectites and plagioclase albite appearances, of which the former may have been hydrothermal replacements of pre-existent phyllosilicates. Halloysite appears in small amounts in Caimanes and Farallones. In Caimanes it appears in the upper layers while in Farallones it is found in the lower layers.

Generally, the MIA values in Baconal, El Culebro and Caimanes show that the degree of mineral transformation decreases down-profile. The values are in the incipient transformation range for the sample taken towards the bedrock, while those for samples in the intermediate and upper layers are in the intense to extreme range. In particular, the values of this index in Farallones are almost constant in the intense to extreme mineral transformation range (MIA>60). Its presence in minute quantities (<10%) in deeply weathered crusts in Farallones suggests the abundance of silica which led to the formation of kaolinite (>75%). In Farallones and Caimanes there are no values of intermediate mineral transformation, as shown in Table 1 and Figure 6.

By chemical composition, the major elements concentrated in the upper layers of each profile are Al, Fe and Si. The alkali and alkaline-earth oxides are highly depleted in the upper layers of all the profiles. Na increases down-profile in Baconal and El Culebro, probably due to intermediate weathering of bedrock (MIA<60) which has been subjected to hydrothermal processes in marine environments.
CONCLUSIONS

The weathering crusts in Baconal and El Culebro, Caimanes and Farallones are mainly kaolinitic clays, composed of Kaolinite, Hematite, Kaolinite-Montmorillonite, with the presence of Quartz. The relative abundances of these phases are in the range of 58-85% for kaolinitic material and 2-11% hematite, showing a concentration of kaolinite towards the upper parts of the profile. Sodium smectites (10-25%) appear in the El Culebro profile. Hydrothermal processes may have affected the bedrock and the quartz veins remained unaltered in the resulting weathering products.

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