Alteration and alterability of the anorthosite from Angola

Joaquim Simão & Zenaide C. G. Silva


ABSTRACT

Key words: Anorthosite; dimension stone; alteration; polluted environment; acid rain.

Siliceous rocks are widely used as dimension stone but the last decades have registered an increase rate of their alteration when exposed to polluted environments. Anorthosites were treated by acidified solutions of HCl, HNO₃ and H₂SO₄ simulating acid rain and the response was recorded through different experiments such as on the surface of the polished rock and on the surface of uncovered thin sections. The main components, plagioclase and olivine, both responded in similar ways to each acid solution, although following different trends; while plagioclase develops a thin layer which acts as protection to the mineral, olivine at first undergoes alteration due to leaching of magnesium and iron and in a following stage, is mechanically removed from the rock. The action of warm water on the rock was tested through the use of the Soxhlet extractor which caused changes on the rock colour and leaching of several cations from its components.

RESUMO

Palavras chave: Anortosito; rocha ornamental; alteração; ambientes poluídos; chuva ácida.

As rochas siliciosas são amplamente usadas como rocha ornamental tendo, nas últimas décadas, registado um aumento do grau de alteração quando expostas a ambientes poluídos. O tratamento de anortositos com soluções de HCl, HNO₃ e H₂SO₄ simulating chuvas ácidas foi desencadeado de modo a permitir a observação dos estados progressivos de alteração, tanto na superfície da rocha polida como na superfície de lâminas delgadas não cobertas. Os componentes principais da rocha, plagioclase e olivina, responderam de modo semelhante à acção de cada solução ácida apresentando, no entanto, aspectos diferentes; enquanto a plagioclase desenvolve uma película na superfície, que actua como protecção do mineral, na olivina observa-se a lixiviação de Mg e Fe seguida de remoção mecânica do grão. Testou-se também a acção de água quente na rocha, usando o extractor de Soxhlet, observando-se alteração na cor da rocha e lixiviação de vários catiões dos seus componentes.

1. INTRODUCTION

Acid rains produced in polluted environments have accelerated the process of rock decay by weathering and have become a serious threat to old monuments, known through centuries, left by mankind as relict of their culture and habits in different places and at different times in the world. Urban and industrial areas are typical examples of these environments where the action of acid rains is increasingly felt, leaving behind unprecedented records of their effects.

The study of rock alteration requires a previous understanding of both the composition and the expected behaviour of the rock, whenever it is exposed to specific conditions. Experiments were carried out on anorthosite which is an ideal type of lithology to study alteration, due to its simple mineralogy, as already recognised by other authors (Fritz & Mohr, 1984). The samples are from the Kunene Complex, Angola, known as the "black granite", which due to its homogeneous black colour and texture has been widely used as dimension stone in Portugal and elsewhere.

After the rock had been characterized through physical tests, experiments were carried out involving the use of the Soxhlet extractor, in order to detect the alterations due to leaching produced by
rain water in tropical conditions. Simultaneously, polished fragments of the anorthosite were treated with acidified solutions of HCl, HNO₃ and H₂SO₄, simulating the composition of acid rain water in polluted environments. The purpose of this research is to follow the extent and the type of alteration in the rock, assuming that the action of the foreign agent is similar to the conditions which occur naturally in polluted atmospheres.

2. PETROGRAPHIC, MINERALOGIC AND CHEMICAL CHARACTERIZATION

The studied samples were collected in a quarry at Chicuatite, a locality in the Huila District (Angola), where a large anorthosite body which outcrops in southern Angola and Northern Namibia has been cut and explored as dimension stone in the Kunene Complex. The dominant lithologies are anorthosites and troctolites and both rock types have been commercially used for that purpose. These rocks are very dark, coarse grained and macroscopically are very similar. The whole Complex has been studied by Silva (1987, 1990 and 1992).

The anorthosite mineralogy is simple, having plagioclase and olivine as main components, pyroxene as common accessory and iron ore and biotite as minor accessories. Under the microscope the rocks have a cumulate texture, as defined by Irvine (1982), where plagioclase and olivine are cumulus and the pyroxene is usually the intercumulus. This homogeneity allows a close observation of the progressive alteration in each mineral, plagioclase and olivine, along the experiments. Figure 1 shows the polished surface of an anorthosite sample.

Petrographic analysis indicates the rock is a troctolite, according to Streckeisen classification (1976). Calcic plagioclase is the main component, followed by olivine and other ferromagnesian minerals, as shown in Table I. All minerals look fresh in appearance.

<table>
<thead>
<tr>
<th>Table I. Mineralogical composition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minerals</td>
</tr>
<tr>
<td>Plagioclase</td>
</tr>
<tr>
<td>Olivine</td>
</tr>
<tr>
<td>Pyroxene</td>
</tr>
<tr>
<td>Biotite</td>
</tr>
<tr>
<td>Opaque (oxides)</td>
</tr>
</tbody>
</table>

Figure 1. Photograph of polished anorthosite in hand specimen.
The rock was analyzed in the laboratories of the Geology Department of the University of Lisbon, Portugal. Wet chemistry was used in the determination of silica and atomic absorption (Varian Spectra, A-30), for the other oxides. Chemical and normative compositions are presented in Table II.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>(%)</th>
<th>Normative Minerals</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49,55</td>
<td>or</td>
<td>1,83</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21,70</td>
<td>ab</td>
<td>25,30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3,98</td>
<td>an</td>
<td>44,88</td>
</tr>
<tr>
<td>FeO</td>
<td>4,51</td>
<td>di</td>
<td>0,10</td>
</tr>
<tr>
<td>MgO</td>
<td>7,10</td>
<td>hy</td>
<td>18,06</td>
</tr>
<tr>
<td>CaO</td>
<td>9,07</td>
<td>ol</td>
<td>3,27</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2,99</td>
<td>mt</td>
<td>5,77</td>
</tr>
<tr>
<td>K₂O</td>
<td>0,31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>99,21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Chemical and normative composition.

#### 3. PHYSICAL CHARACTERIZATION

Physical tests (Table III) were performed at the Geotecnic Laboratory of F.C.T. (UNL), according to standard procedures specified by RILEM (1980), as such: porosity accessible to water, real and apparent volumic mass, coefficient of water saturation, water absorption at low pressure, expansibility by water absorption and salt crystallization test.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity accessible to water</td>
<td>0,1 %</td>
</tr>
<tr>
<td>Real volumic mass</td>
<td>2844 Kg/m³</td>
</tr>
<tr>
<td>Apparent volumic mass</td>
<td>2841 Kg/m³</td>
</tr>
<tr>
<td>Coefficient of water saturation</td>
<td>aprox. 0 %</td>
</tr>
<tr>
<td>Water absorption at low pressure (1 h)</td>
<td>0 cm³</td>
</tr>
<tr>
<td>Expansibility by water absorption (72 h)</td>
<td>aprox. 0 mm</td>
</tr>
<tr>
<td>Salt crystallization test (30 cycles)</td>
<td>0,18 %</td>
</tr>
</tbody>
</table>

These properties allow a classification of this anorthosite as "of good quality", suitable for the purpose it has been used in construction.

#### 4. EXPERIMENTAL ALTERATION OF THE ANORTHOSITE

Two types of experiments were performed on the anorthosite. Rock fragments were tested with the Soxhlet extractor and uncovered thin sections were wiped with acidified solutions of HCl, HNO₃, and H₂SO₄. The progressive alteration experienced by the rock was followed through microscopic observations and chemical analysis on the rock surface, by using the petrographic microscope and the SEM. Variations on the chemical composition of all liquids after leaching the rock samples were also determined through chemical analysis.

4.1. Experiments with the Soxhlet extractor

The Soxhlet extractor is used to simulate the effect of rain water on rocks through leaching.
during a specified period of time. Similar experiments have been performed in other rock types by Aires-Barros (1971, 1972 and 1991), in Aires-Barros & Mouraz-Miranda (1979) and Mouraz-Miranda (1984 and 1986), where the methodology is described.

The experiment was performed during six cycles of 1000 hours each, in a total of 6000 hours. At the beginning of each cycle the distilled water had a pH of 5.6, reaching 9.0 at the end; the percolated water was then collected and analyzed. Figure 2 shows the pH variation during the experiment and shows that although there is a substantial difference between the beginning and the end of each cycle, the range of variation is not significant among cycles. Estimation of the pH for the solutions was performed in a SOTEL WTW pH 350, at the Chemical Engineering Department of IST (Technical University of Lisbon).

Chemical analyses for major elements were performed in waters at the end of each cycle, by colorimetry and spectrophotometry, in a Varian SPECTRA A-30 at the GeoFCUL laboratories. The recorded data are presented in Fig. 3.

Solid residue left after filtering each solution was analyzed by X-ray diffraction (Phillips PW 1050/70), at the Geosciences Department of the University of Aveiro. Table IV reports the products which were identified at the end of each cycle (silica gel, feldspars, zeolites and kaolinite).

Table IV. Solid residues from the Soxhlet experiment after each 1000 hours cycle.

<table>
<thead>
<tr>
<th>Hours</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>silica gel; feldspar; zeolite?</td>
</tr>
<tr>
<td>2000</td>
<td>silica gel; kaolinite</td>
</tr>
<tr>
<td>3000</td>
<td>crystalline kaolinite</td>
</tr>
<tr>
<td>4000</td>
<td>crystalline kaolinite</td>
</tr>
<tr>
<td>5000</td>
<td>kaolinite</td>
</tr>
<tr>
<td>6000</td>
<td>poorly crystallized kaolinite</td>
</tr>
</tbody>
</table>

Fig. 3. Cumulative (——) and absolute (––) variations of $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{MgO}$, $\text{CaO}$ and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ during the Soxhlet experiment.
Most alterations in the anorthosite occur during the first two cycles, indicating a higher cation mobility during that stage. The increase in the oxides contents in water, shown in Fig. 3 illustrates this fact. After the 2000 hours stage, the variations in the concentrations are similar and all oxides register a decrease in their contents. The concentration in alumina though, after the two first cycles, of higher mobility, remains almost invariable, as registered by the presence of kaolinite as the only mineral present in the rock residue. Different behaviour is shown by iron, which exhibits a decrease in its content in the rock samples after the 6000 hours, contrasted to its absence in the solution after each 1000 hours cycle.

Change in colour of the rock is a striking feature observed while experiments were performed. From an initially dark, homogeneous black colour, the rock changed progressively to a brownish, spotted rock, suggesting to be residual iron oxide, due to the alteration of olivine.

4.2. Treatment with chemical solutions

The effect of chemical weathering activated by acid rain in the anorthosite was studied by promoting the treatment of rock samples with acidified solutions, simulating a natural situation. Polluted atmospheres carry sulphur, nitrogen and chlorine which are the common gases responsible for the production of acid rain, as they combine or are dissolved in water, lowering the pH of the natural rain water (around 5.6 in the presence of CO₂ and atmospheric pressure). Taking that into account, the experiments were performed with HCl, HNO₃ and H₂SO₄. The solutions were prepared by diluting (0.25% (v/v)) the concentrated acids as such: HCl (37%) and HNO₃ (65%) Prolab; H₂SO₄ (98%) Merck; the pH in the final solutions were 1.16, 1.41 and 1.40 for HCl, HNO₃ and H₂SO₄ respectively.

Three slabs of 4x4x0.7 cm (ref. 1, 2 & 3) and 18 others of 2x1.5x0.5 cm (1.1 to 3.6) were cut from the polished rock. Three sets of small six samples each were dumped in 80 ml of each acidified solution and every 15 days one of them was removed. At this point, the solution was analyzed as it was also the surface of the rock. The weight loss for each sample was then recorded; the total, cumulative loss is illustrated in Fig. 4. Major loss in weight occurred during the first two cycles and showed to be more effective in samples treated with H₂SO₄, as already recognized by Martin et al. (1992). Weight loss in smaller samples are similar during the four initial cycles when treated by HCl and H₂SO₄; from there on, this last acid is more effective; HNO₃ is the least effective of all three components.

Major element analysis by atomic absorption were performed in a PERKIN-ELMER spectrometer (model 2380) at the Earth Science Department of F.C.T. (UNL). Concentrations of Ca, Mg, Na, K, Al, Si and Fe were determined by spectrophotometer and the corresponding interferences were eliminated according to EAA (Perkin-Elmer, 1982). The evolution of the concentration of major elements in the solutions is illustrated in Fig. 5.

The action of different acids on the samples was slightly different, but in a general way, the mobility of all elements, as seen from the graphics, is higher during the first two cycles, regardless of the sample size.

As silica is concerned, the HNO₃ solution is the least effective of the three acids when used on smaller samples (Fig. 5.7); HCl displaces alumina...
more easily than other acids, and its action does not depend on the sample size.

Iron and magnesium seemed to be the most easily removed cations, due to the alteration and des-aggregation of olivine; the action of all acids was stronger in the larger samples. (Fig. 5.3 and 5.4).

Calcium was removed more effectively by HCl; however, gypsum crystals were left in the powdered dry residue from the $\text{H}_2\text{SO}_4$ solution, indicating that this cation did not remain in this solution. The atomic absorption low signal given by calcium in sulphuric medium could also be accounted for the low calcium content registered in that solution.

Sodium and potassium were recorded together due to their low concentrations in all solutions.

The action of different acids are illustrated in Fig. 5.6 and 5.12.

**Observation of hand specimens after treatment with acidified solutions**

Hand specimens observations indicate that the effect of all acidified solutions was similar; the rock, from initially black, turned to a whitish, rough material, exhibiting small cavities on its surface, corresponding to the location of the olivine grains; at first they were chemically altered, followed by a mechanical removal. Figure 6 illustrates the two stages, prior and after the use of $\text{H}_2\text{SO}_4$, (7-15 days cycles).

---

**Figure 5.** Cumulate variation of major elements on the solutions after treatment of anorthosite samples with HCl (---), $\text{H}_2\text{SO}_4$ (-----) and $\text{HNO}_3$ (-----). (Graphics 1 to 6: samples $4 \times 4 \times 0.7$ cm; Graphics 7 to 12: samples $2 \times 1.5 \times 0.5$ cm).
Observation of thin sections after the use of acidified solutions

As previously referred, three uncovered thin sections of the anorthosite were wiped with acidified solutions in order to allow a daily observation of the progressive alteration. The effect on the surface of the rock was recorded after every 15 days cycles and the changes were compared for each acid. Figures 7, 8 and 9 are illustrations of these changes.

The response of the anorthosite to the acid treatment was similar for the different solutions along the three cycles: progressive alteration of olivine until its complete removal and gradual sharpening of the fractures and cleavages of other minerals, particularly of the plagioclase grains.

Simão & Silva (1995), Silva & Simão (1995) and Simão (1996) have reported some particular features observed in the olivine grains under the microscope: gradual changes in the interference colour, reflecting the variations in chemical composition and variations in the appearance of the grain, up to its total removal after the second cycle. These grains were replaced by a yellowish, unidentified material, possibly limonite. Similar observations are reported by Fritz & Mohr (1984) in olivines of close composition to the ones studied presently. It should be mentioned that after the first cycle the olivine grains treated by HCl were gone, emphasising the severity of its action on that mineral (Fig. 7).

The other mineral components, namely pyroxene and plagioclase, showed to be more resistant; their alteration consisted mainly on the sharpening of their grain contours and on the cleavage traces and on the gradual darkening of the grains, similar to that observed in a saussuritized plagioclase.

Observation and chemical analysis of the surface of the rock samples

After the treatment with the acid solutions, the surfaces of all samples were analyzed using a scanning microscope so that the progressive alteration of all minerals could be detected.

The microscope was a JEOL 330A (0.6 A, 20 kv), connected to a TRACOR (EDS) Microprobe. Semiquantitative chemical analyses were restricted to the two main components of the anorthosite, plagioclase and olivine, and recalculated to 100%. Due to the fact that the analyses are referred to an area and not to a point, each one might include some traces of neighbouring minerals. The evolution of the analyses of samples 1.1 to 3.6 are registered in Figures 10 and 11.
Figure 7. Evolution of the anorthosite alteration observed in thin section after treatment with a 0.25% HCl solution (ol - olivine; pl - plagioclase; nicós X; ——|— = 0.1 mm).
Figure 8. Evolution of the anorthosite alteration observed in thin section after treatment with a 0.25% \( \text{H}_2\text{SO}_4 \) solution (ol - olivine; pl - plagioclase; nicós X; \( \text{——} \) = 0.1 mm).
Figure 9. Evolution of the anorthosite alteration observed in thin section after treatment with a $0.25\%$ HNO$_3$ solution (ol - olivine; pl - plagioclase; nicós $X$; $|=0.1\ mm$).
The response of plagioclase was similar in all samples, regardless of the nature of the acid solution. There is a relative increase in the silica content and decrease in the other components, observed on the grain surface. The apparent increase in MgO and FeO at the end of the first cycle is interpreted as due to the contribution of the neighbouring olivine. Olivine had a similar behaviour, exhibiting a superficial increase in the silica content and decrease in the other components, registering the lower reactivity of HNO₃ as compared to the HCl and H₂SO₄ solutions (Fig. 11).

Berner & Holdren (1979) have pointed out that the mechanism which rules the alteration and dissolution of plagioclase is a superficial reaction. In fact, Busemberg & Clemency (1976) have recognized that initially the dissolution is promoted by the exchange of the mineral cations and the hydrogen from the solution; this hydrogen from acid solutions is able to percolate through the plagioclase surface and infiltrate down to hundreds of angstroms (Casey et al., 1987, 1989a, 1989b).

Figure 12a illustrates the changes occurred on the surface of the plagioclase grains, as regular fractures developed after the thin layer of hydrated amorphous silica had dried out.

Casey et al. (1988, 1989a, 1989b) have described a similar feature developed in the plagioclase during experiments carried out with solutions having different pH; after the reaction
with solutions of pH lower than 4, the mineral surface is gradually enriched in silica, depleted in alumina, calcium and sodium, causing an increase in the porosity and widening the mineral structure; with a pH close to 1, after several hundreds of hours of experiment, a thin layer (nm thick) of repolimerized silica develops on the mineral surface, as already seen on Fig. 12a.

Some alteration develops near plagioclase cleavages and fractures, although the chemical composition of the mineral remains apparently unchanged. In Fig. 12b these altered areas correspond to the light zones. Gypsum crystals are additional features observed on the plagioclases treated with H$_2$SO$_4$, as illustrated in Fig. 12c.

Alteration of olivine is similar in all situations; the corrosive action over the grains surfaces is intense, after the treatment with the solutions. At the end of the complete cycles the grains were totally destroyed, except their framework and their fractures, presently filled with more resistant material (Fig. 12d). Olivines consume hydrogen from the acidified solutions and releases magnesium, iron and silica to the solutions (Nesbit & Wilson, 1992). Variations in the iron content shown in the curves of Fig. 11 are possibly due to retention of the hydrated iron oxide on the mineral surface during the alteration process. Concentrations of Al, Ca, Na e K as recorded in the olivine analysis can be accounted for the high mobility of these cations in the solutions and to the participation of the neighbouring minerals in the analyzed surface.
5. CONCLUSIONS

Within the silicate rocks, anorthosite represents a particularly good lithology to test alteration. Due to its simple mineralogy and texture, chemical and mineral modifications are readily identified, giving reasonable clues for their interpretation when faced with the action of acidified solutions simulating acid rain.

Anorthosite from the Kunene Complex of southern Angola was the rock chosen to be tested since it has a wide use as dimension stone in Portugal and elsewhere. The rock is homogeneous in texture and colour and has good physical characteristics such as low porosity and high saturation and absorption coefficients. The continuous action of warm water on the anorthosite produces progressive alteration while leaching silicium, aluminium, calcium, magnesium, sodium and potassium to the solution and causing the retention of iron in the altered olivine grains.

The effect of acid solutions on that rock is twofold: at first the rock changes its colour, becoming whitish and the mineral grains gradually exhibits different patterns of alteration. Plagioclase grains alter initially around cleavage surfaces and afterwards become covered by a thin layer of amorphous silica which acts as a protective layer to the mineral; under the action of sulphuric acid, gypsum crystals develop on its surface. Olivine has a similar response to the action of different acids but is particularly sensible to hydrochloric acid; initially the mineral is chemically altered, immediately followed by mechanical disruption. At a later stage, the grains are removed from the rock, a process which can compromise the use of this type of lithology in polluted environments, specially in case the olivine content is high.
These data give a useful clue to the changes of minerals in polluted environments and as such could be used as indicators of the behaviour of the silicate rocks in previously known polluted atmospheres.

REFERENCES