Role of porosity in rock weathering processes: a theoretical approach

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Abstract
Under surface and subsurface conditions, porosity is a major factor in rock weathering, for it controls not only the movement of the fluids throughout the rock mass but also the processes at work. Depending on the pore dimensions and pattern, mechanisms such as hydroxylation, diffusion or flow play their role in the weathering process.
Based mainly on theoretical arguments, three examples of silicate parent rocks replaced by carbonate, oxyhydroxides and silica are analysed, in terms of water activity, pF, specific surface, and molar volume.
In central Spain, Ca and Mg carbonates replace silicates and quartz in both calcretes and sandstones. Where the two cations are present, Mg mainly is associated with small pore spaces whereas Ca is dominant within larger pores, and there is a transition between the two extremes.
The replacement of the quartz grains in gravels and pebbles of quartzite by Fe oxyhydroxides is a typical feature of the old Rañas surfaces of central and western Spain. This replacement is the result of the alternating wet and dry seasons combined with poor drainage conditions that allow the xerolysis to be active over long periods.
In western Spain, remnants of a siderolithic sedimentary cover preserve a deeply weathered Hercynian basement. An upward enrichment in CT opal and in kaolin affects to both the weathered basement and the siderolithic cover. Recent studies show that these traits were caused by the weathering of an old land surface that was disrupted by Alpine tectonism. Weathering occurred under acid conditions which led to the release of most of the elements, Fe and Al included, but with the most of silica remaining as opal.

Key words: rock weathering, porosity, replacement, carbonates, oxyhydroxides, opal, kaolin.
**INTRODUCTION**

In 2004 Dr. M.J. WILSON of the Macaulay Institute of Aberdeen, Scotland, wrote: “Weathering is a fundamental process in the geological cycle that should be regarded as of equal importance as the processes of metamorphism, volcanism, diagenesis, erosion, etc., that are much more extensively studied in most departments of earth science”. Weathering processes are developed in the zone embracing the hydrosphere, lithosphere, atmosphere and biosphere.

A rock is a consolidated natural medium that is more-or-less heterogeneous. It consists of various minerals, each with distinct responses to external agencies. It is this heterogeneity that produces disequilibria within the rock, leading to its alteration.

Broadly speaking, weathering can be defined as the sum of processes that affect rocks and which give rise to new products and structures that are more stable under the surface environments. All weathering processes are controlled by three main factors: the rock (e.g. grain size, fabric, porosity, mineral and chemical composition); the nature of the solutions present (e.g. ions/molecules present, concentrations, ionic force, acidity, etc); and the environment (e.g. temperature, organic matter, drainage, etc). All these are interrelated so that variation in one of them leads to changes in the others.

In this paper an interpretation is offered of some regolithic profiles and the processes at work using examples from the Iberian Peninsula. Attention is drawn to the role of porosity.

**MICROSYSTEMS OF WEATHERING**

Porosity of a rock is one of the first factors that both controls and is affected by weathering. Changes in porosity give rise to changes in the pattern, distribution and size of pores. In addition, change in the pore/rock volume ratio alters the density (g/cc) and the “specific surface” (m²/g) of the rock. In general, increased weathering leads to a reduction in density (not always) and an increase in the specific surface. Some authors (PÉDRO and DELMAS, 1980; MEUNIER, 1983) have used these considerations to distinguish three systems of weathering, namely, contact microsystems (or microsites), with pore dimensions ranging from Amstrongs (Å) to nanometres (nm); plasmic microsystems, with pore dimensions of microns (mm); and fissure system, the dimensions of pores are from mm to mm or wider.

In contact microsystems many of the H₂O molecules are not stable and water occurs as OH⁻ ions attached to the hydroxylated minerals, such as serpentine, chloritised biotite, etc, in which crystal structure has been distorted. This water is not removed as long as the conditions of the microsystem remain unchanged. As weathering progresses, minerals dissolve and/or evolve to form clays which give rise to the plasmic microsystem, with high specific surface values (e.g. smectites > 200 m²/gram). Although water molecules are stable, they adhere tightly to the pore walls and display little or no motion, that is the “activity of water” (:\(a_w\))\(\rightarrow\)0. Under these conditions diffusion is the main mechanism of weathering (BRADY, 1990; PÉDRO, 1993; MEUNIER et al., 2007) leading to the development of particular microenvironments and features (e.g. nodules, pseudo-gley traits, etc).
When the pore diameter is wider than ca. 1-3 mm, flow becomes important, and drainage plays a role. Good drainage favours the release and leaching of solutes from the system, while poor drainage leads to stagnant conditions (e.g. generation of evaporites and/or gley traits).

pF concept

Once in a pore, water is subject to three main forces: force of gravity, force of osmosis, and force of retention by the pore walls. Retention force is the sum of adhesion and capillary forces. In order to quantify the force necessary to separate water and the mineral phases, scientists use the pF, a concept similar to that of pH: $pF = -\log_{10} \text{of the retention force}$. The negative symbol means a suction pressure: the drier a sample, the higher its pF. But two different samples with similar pF values can, however, have different water content depending on their texture and structure; for a fixed pF, a finely textured rock retains more water than a coarse textured one.

There is a relationship among pore diameter, pF values, water activity ($a_w$) and the main mechanisms of hydroxylation, diffusion and leaching. In practice, pF can be used to distinguish different types of pore waters: non-available capillary water, available capillary water and free water (figure 1).

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Fig. 1. Relationship among the pF values, water activity ($a_w$), pore diameter, mechanisms of weathering, and the "types" of water in a pore.
MINERAL REPLACEMENT: SOME EXAMPLES

One of the main processes of weathering occurring at, or close to, the earth surface is the replacement of the parent minerals of a rock by new minerals having a different structure and/or composition. When it is conservative in volume it is called an isovolume epigenetic replacement. This process is the sum of many different mechanisms giving rise to products of economic and/or scientific interest such as ferricretes, bauxites, silcretes, etc. Here, some of these processes are analysed.

Replacement of silicate by Ca/Mg carbonate

This process takes place under semiarid to subhumid climates (rainfall ca. 300-600 mm/m²) with a marked dry season and a source of carbonates. The result is the development of a calcrete (caliche, croute calcaire) profile regardless of the substratum. We present a calcrete profile on a silicate substratum (e.g. slates), a common situation in the western part of the Iberian Peninsula (figure 2). In these profiles, which can reach more than 2 m deep, it is possible to distinguish four levels or horizons from bottom to the top (figure 3): the parent rock (A), massive facies (B), laminated facies (C) and soil (D).

Fig. 2. Calcrete developed on Palaeozoic slates close to the village of Urda (Toledo). Calcrete is dissolved upwards by the soil processes and generated downwards by replacement.
In profiles of this type developed on siliceous basement, RUELLAN (1971) and MILLOT et al. (1977) pointed out that careful study of the profile (e.g. by hand lens) allowed the lower part (B level in figure 3, I), where carbonate and parent minerals are separated by newly generated clays, to be distinguished from an upper level (C level in figure 3, I) where carbonate and the relics of the parent minerals are in contact. Furthermore, corroded quartz grains and zones of precipitated silica (chert, silex) occur in close proximity; which is a geochemical contradiction. Also, higher in the profile, carbonates fill grooves within the corroded silicates and quartz, because most silicates are less soluble than Ca/Mg carbonates.

According to WANG et al. (1993,1994) the presence of Al and Mg ions play an important role in these processes, as they preferentially bond with silica to develop precursors of the clay minerals (e.g. palygorskite, smectites, sepiolite). If the \((\text{Al}_2\text{O}_3+\text{MgO})/\text{SiO}_2\) ratio in the solution is clearly $$<1$$ it is possible to find precipitated silica in the profile together with e.g. palygorskite; if the ratio is $$>1$$ there will no free silica to precipitate.

During the wet season solutions dissolve silica mainly from silicates in the slates, and to a lesser extent ($$<10$$ ppm) from quartz (corrosion), to give rise to new clays. These clays will not be well crystallised, and are easily dissolved. During the dry season both new clays and carbonate will crystallise and a set of reactive fronts appear in the pores (microsystem) (figure 3, II). In the lower part of the profile, genesis of the new clays is dominant at the expense of parent minerals. By contrast, in the laminated crust in the upper part of the profile, carbonate replaces clays (figure 4). At the top of the profile, soil forming processes dissolve the crust and all the systems move down, extending the weathered mantle at the expense of bedrock.
Replacement of quartz by oxyhydroxides

The replacement of silicates by oxyhydroxides is a common weathering process, leading to the micro accumulations (e.g. micronodules) to the development of ferricretes and lateritic soils. It has been studied by many authors (e.g. Nahon, 1976, 1991; Tardy and Nahon, 1985; Tardy, 1993). As a result, the role of porosity has been carefully analysed. In the Iberian Peninsula this process is apparent in many landscapes but here the weathering rind developed on the quartzitic pebbles and gravels of the Rañas cover is discussed.

Rañas are dissected piedmont alluvial fan deposits no more than 10-15 m thick, and common in the old Hercynian relief of the western half of the Iberian Peninsula (figure 5). They consist of pebbles and gravels, mainly of quartzite and some quartz, embedded in a clayey “matrix” with yellowish to reddish hues. The Rañas cover pediment platforms which stand ca. 150 m above the current river system. Their ages range from the Upper Neogene to the earliest Pleistocene.

The weathering processes affecting these sediments have been widely studied (ESPEJO, 1978, 1987; GALLARDO et al., 1987; MARTÍN SERRANO, 1988; MATÍNEZ LOPE et al., 1995; MOLINA BALLESTEROS and CANTANO MARTÍN, 2002). A typical profile of the Rañas has two parts (figure 6): the Hercynian basement below and the sedimentary cover above, the contact being sharp but irregular. Whatever the parent rock, the basement is consistently weathered to a depth of several metres beneath the cover. It is important to point out that this weathering process affects both the basement and the cover (VICENTE et al., 1997; CLAUSELL et al., 2001), and the weathering mantle attains a thickness of 30 m in some localities.

The weathered basement shows a progressive upwards reduction in mineral composition: on granite parent rock there is a reduction in feldspar content (mainly plagioclase) and inherited micas, an increase in vermiculites and smectites, and a release of oxy-hydroxides; on slates, there is a reduc-
Fig. 5. Typical Raña landscape during the wet season, when saturated profiles and pools of stagnant water are frequent. The Montes de Toledo appear in the distance.

Fig. 6. Sketch of a Raña profile. Mineralogy: A= quartz + hematites + goethite + micas + kaolinite; B= quartz + micas + kaolinite; C= quartz + hematites + goethite + kaolinite; D= quartz + hematites + kaolinite; E= quartz + hematites.
tion of chlorite and feldspar, the illite-mica content is constant, interstratified micas increase, and oxyhydroxides are released from the parent minerals.

Referring to the Raña cover, the main trait is the progressive transformation of the slate fragments once deposited, into the current clayey “matrix”. Therefore, instead of a matrix in a sedimentary sense, it would better be named as weathering “plasma” in the sense of NAHON (1991) as it has been generated in situ by weathering. Its clay fraction is rich in smectites, illite-micas and kaolinite with a variable content in Fe oxyhydroxides, depending on the hydromorphic conditions. While kaolinites are dominant upwards, illite-micas, smectites and remnants of some chlorites are present downwards in the profile.

Once generated, this clayey material is redistributed within both the profile and the landscape by progressive vertical and lateral leaching. This movement of matter within the sediment and through the landscape has led to the current morphology of the Rañas surfaces: open and flat surfaces slightly concave upwards.

According to MOLINA BALLESTEROS and CANTANO MARTIN (2002), three main types of pebbles and gravels can be distinguished, depending on their position within the profile and on the degree of weathering (figure 6):

- type I, with a pink interior (A) and some bleached and more or less friable external zones (C),
- type II, with a pink core (A), a bleached zone (C) and an intervening ochre and friable zone (B),
- type III, is restricted to all the Rañas surfaces and related to the soil in which there is an abrupt reduction in the clayey plasma content, and the cores of the pebbles and gravels are red (D) with an external dark rind (E).

Types I and II were, and are being, weathered in situ under more or less wet conditions. Quartzites release quartz grains and other components (mainly some micas and oxyhydroxides) to the clayey plasma where the microsystems play their role. This is shown by the changes in hue in both the plasma and the pebble: dark red hues of the cortex or rind are rich in goethite and hematites, ochre hues are rich in goethite while the white hues have lost both minerals.

Normally, size of pebbles and gravels of type III (figure 7, I) are smaller than the other two types, its dark cortex being ca. 3-10mm thick. In this cortex, quartz grains are replaced and/or corroded by hematite (figure 7, II). Type III occur where old and flat topographic surfaces have undergone alternating swampy and dry periods that promote the xerolysis process (CHAUVEL and PÉDRO, 1978; CHAUSSIDON and PÉDRO, 1979) over a very long period (probably more than 2 Ma.).

Silcretes

According to THIRY (1993, 1999) on an emerged land surface silica can be concentrated in three main landscape environments: soil, groundwater, and evaporitic sites. The pedogenic processes destroy the original bedrock structures, which are, however, preserved in silcretes developed in groundwater silcretes. The morphology of silcretes associated with evaporites varies according to the chemical changes that occur.

In the western limits of the Tertiary Duero and Tajo basins, western Spain, it is common to find remnants of a siderolithic sedimentary cover overlying the Hercynian
basement, the latter weathered to a depth of tens of metres (figure 8). The thickness of the cover increases eastwards and is formed by a set of gravel, sand and mud beds with interbedded palaeosols in which pedological features such as cutans, burrows and redistributed oxyhydroxides are common. During an Early Tertiary tectonic event, both basement and cover were tilted down to the east, leading to their progressively deeper burial beneath the younger Tertiary basin fill (SAAVEDRA and SANCHEZ CAMAZANO, 1981; MADRUGA REAL, 1991; MAS et al., 1989; RODAS et al., 1990). A sketch of the profiles developed on the Hercynian basement is shown in Figure 9.

Silicification has affected both the upper part of the siderolithic cover and, where the cover is < ca. 10-12m thick, the preserved basement. According to GARCÍA TALEGÓN (1995) and MOLINA BALL-ESTEROS et al. (1997a, 1997b), the silicification represents an alteration of the parent minerals that occurred under acid conditions and which led to: i) a relative concentration of resistant minerals (mainly quartz) and silica as CT opal, ii) the release of most other components, including Al and Fe, from the parent minerals, and iii) the local precipitation of acid sulphates of the alunites group in fractures and fissures. Phyllosilicates of the kaolinite group with the CT opal and

Fig. 7. I. Gravels and pebbles from the surface of the Raña of Navahermosa, Toledo province. In some of them is possible to distinguish the dark rind of weathering. II. Microphotograph (1 nicol) of thin section showing the relationships between quartz grains (Q) and Fe oxyhydroxides (Ox) in the dark rind of a pebble of quartzite.
quartz are the dominant minerals upward in profiles (GARCIA TALEGON et al., 1994). Age determination by the K-Ar method showed that the alunites have been formed ca. 58-67 Ma. (BLANCO et al., 1982).

The acid conditions were caused mainly by unbalanced SO$_4^{2-}$ radicals in solution which gave rise to the failure of the crystalline structures of many silicates, but which tend to preserve others. But a question remains: what was the origin of the sulphur that acidified the upper levels of the siderolithic cover and the weathered basement? The first isotopic data obtained from 7 samples of alunites were between 15 and 18 d$_{34}^{34}$S (MOLINA BALLESTEROS et al., 1997a). They confirm the evaporite origin of these minerals.

**DISCUSSION AND CONCLUSIONS**

In the three examples presented here, the replacement of parent minerals has been the main process. In the calcrete profiles and the ferruginous cortex of the Rañas pebbles, weathering involved new contributions of different composition to that of the parent material. In silcrete profiles, weathering involves the release of some components leading to a relative concentration of resistant minerals and silica.

One of the main factors controlling the replacement of silicates and quartz by Ca and/or Mg carbonates is the size of the space where the process is taking place. According to PÉDRO and DELMAS (1980), MEU-
NIER (1983), NAHON and BOCQUIER (1983), WANG et al. (1994), among many others, in the contact between silicate and quartz with carbonate, a microsystem of some nanometres wide is developed. In this space, diffusion is the mechanism of weathering: the silicate and quartz front retreats while the carbonate front advances (figure 3). In between, neoformed minerals (mainly clays) can develop. In this narrow space, the main variables are: i) the nature and size of the crystals generated and dissolved, ii) concentration of solutions, and iii) pressures (hydrostatic and crystallization) (DEWERS and ORTOLEVA, 1990; RIVAS BREA, 1997).

MALIVA and SIEVER (1988) suggest that one factor controlling the replacement of calcite by quartz or vice-versa is the rate of pressure change due to crystallization. Crystal pressures of calcite/quartz depend on their molar volumes (quartz ≈ 22cc/mol; calcite ≈ 38cc/mol). According to these authors a high concentration in carbonate is needed to replace quartz, and vice-versa, a low concentration in silica can replace the calcite. In the presence of both Ca and Mg, dolomite tends to crystallise in small pores and/or under pressure conditions, while calcite develops in wide and/or low pressure conditions, but all degrees of transition can occur (VARAS MURIEL and MOLINA BALLESTEROS, 2004). This observation may be explained by the molar volume of dolomite (=28cc/mol), which is smaller than that of calcite.

The replacement of pebbles and gravels of quartzite by Fe oxyhydroxides which takes place at the top of the Rañas profiles, is a consequences of xerolysis, a weathering process characterised by: (i) the dissolution of many of the primary minerals, mainly clays, (ii) the progressive enrichment in oxyhydroxides, and (iii) the development of an upper horizon, poor in clays and rich in sand and in black-red pebbles, the rest of the profile being rich in the clay fraction. Xerolysis takes place in acidic conditions with poor vertical and lateral drainage, long periods of drought and warm intervals interspersed with periods of flooding.

At the top of the Raña profile xerolysis proceeds in stages: During the wet season, pores of the pebbles are saturated by the solutions. At the beginning of the dry season a “dry front” subsides through the profile, not reaching more than 0.5-0.6 m in depth. By the end of the dry season (September-October), the surface of the profile can reach ca. pH~5 leading to the destruction of most of the clay minerals, and of some water molecules in the pores: the remaining solution is concentrated on the walls of the finest pores until totally evaporated.

In these acid environments, some of the solutes are Fe oxyhydroxides which can react with the surfaces of the pebbles and gravels of quartz and quartzite. According to MORRIS and FLETCHER (1987) and ABREU and ROBERT (1987) under wet-dry conditions with alternating redox potential, these oxyhydroxides react with the surface of the quartz grains giving rise to a silica-Fe complex some nm thick. This coating progresses or retreats depending on the conditions of the microsystem (mainly of the pH) where the process is taking place. The main mechanism working is diffusion.

Here the degree of dryness is important. In the very fine pores, or under very low water content, water activity is very low (w_a <<1) leading to the formation of the less hydrated forms of the Fe oxyhydroxides (TARDY and NAHON, 1985); that is hematites or maghemite rather than goethite. So, in the Rañas pebbles and gravels, the dark cortex is rich in hematites...
while goethite and amorphous phases appear mainly in the cores (figure 7).

In 1964 MILLOT explained that the different phases of silica depended on the conditions under which the tetrahedral of Si-O and Si-OH are polymerised. As a general rule, amorphous phases are more soluble than crystalline phases but, once in solution, the main factors controlling the precipitation of silica are pH, concentration, pollutant products (mainly ions and clays) and time. So: (i) acidity and salts (e.g. sulphates, nitrates and chlorines) lead to precipitation (MARSHALL and WARAKOMSKY, 1980); (ii) ions of Al and Mg reduce silica concentration because they take silica to generate clays; and (iii) an increase in silica concentration leads to poor crystallisation.

The other way to concentrate silica is to remove the rest of the components of the parent material, this being the process by which many silcretes have been developed (RAYOT, 1994).

Most surface and ground waters have silica concentrations of ca. 10-30 ppm, so they are saturated with respect to quartz but not in comparison with the amorphous phases (ca. 100-130 ppm). In this instance, the more-or-less acid processes of weathering gave rise to unstable and easily dissolved minerals which then released significant amounts of silica. This silica flowed through the pores and fissures of the siderolithic cover and of the upper part of the weathered basement generating new clays (e.g. newly formed kaolinites) or precipitating on pore

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Fig. 10. I. SEM photograph of CT opal lepispheres formed by fine micro blades of silica. Scale is 5 mm. II. Microphotograph (1 nicol) of a thin section from the silicified siderolithic cover in which an old void is filled by different phases of silica: Q, quartz grains; O, isotropic opal; CT, lepispheric opal; mq, neoformed micro-quartz.
walls and giving rise to different phases.

Under phreatic conditions (beneath or at the water table, where pF≤3) silica can give rise to a thin and homogeneous peel or carpet of small crystals on pore walls, or may completely fill the pore spaces. Different phases (small opal blades, fibrous phases, micro-quartz, etc.) will be present depending on the concentration, impurities and time (figure 10). High silica concentrations leads to amorphous phases (opal A), while low concentration and no impurities leads to pure quartz. With time, these phases evolve in the sense: A opal $\rightarrow$ CT opal $\rightarrow$ fibrous phases $\rightarrow$ micro-quartz $\rightarrow$ quartz.

Under vadose conditions, above the water table (pF >3), silica tends to precipitate in the meniscus and in the finest pores. In these zones, the water activity is clearly $a_w<1$, so they are attractive zones for the solutions (TARDY and MONNIN, 1983) leading to an inhomogeneous distribution of the precipitated silica.

In the profiles studied all phases of silica occur but the CT opal phase coating the pore walls is prevalent (figure 10, I). Fibrous and micro-quartz phases are present in-filling pores (figure 10, II) but they appear to be the result of a later process. All data indicate that once deposited, the sedimentary cover has experienced phreatic conditions where silica moved in solutions and precipitated upwards close to or at the old surface where acid conditions prevailed. At present, dissolution appears to be the main process.

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