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# WEATHERING OF SEDIMENTARY STONE MATERIALS FORMED UNDER EARTH SURFACE CONDITIONS

Peter W. Mirwald[1], Anja Diekamp,[1] Michael Unterwurzacher[3] and Ulrich Obojes[2]

[1]*Institute of Mineralogy and Petrography, University of Innsbruck, Austria;*
[2]*Office of Geology and Building Material Testing, Bozen, Italy*
[3]*Institute of Geography and Geology, University of Salzburg, Austria*
e-mail: peter.mirwald@uibk.ac.at



## Abstract

Quaternary calcareous sediments, such as breccias and tufa play an important role as historic building materials – their use dates back far into historical times. These materials, although mostly of local occurrence only, are frequently found in areas where the regional geology is characterized by calcareous rock series, e.g. in the Alpine and in the Balkan realms. Compared to limestone of geologically older pre-quaternary provenance these quaternary calcareous materials show mostly an excellent weathering resistance.

Since stone deterioration in moderate climatic regions is closely related to water impact and hygric rock properties respectively, we analysed the relation of pore volume and the associated specific surface of quaternary sediments, lime mortars and pre-quaternary limestones. These properties are considered major petrophysical parameters in the decay processes. We compared data obtained on quaternary calcareous conglomerates, tufa-limestone and lime mortars as well as literature data of different limestones (Grimm 1990). We found a systematic correlation between the specific surface and its associated pore volume which are presented in diagrams of (spec. surface/pore vol.) versus pore volume. Surprisingly, the quaternary sediments and also mortars are characterized by the relatively largest quotient of specific surface to pore volume. This finding indicates that the weathering resistivity of these quaternary sediments is lastly not directly related to the pore properties in any case.

Considering that the quaternary materials have been formed and remained on the Earth surface till quarrying, they are in a distinct contrast to limestones. These materials experienced after sedimentation a diagenetic adaptation to higher pressure-temperature condition in some depth of the Earth crust before they returned on the Earth surface in the course of geological processes. This difference suggests that thermodynamic constraints play an important role: while the normal limestones which have been conditioned in the depth, have to re-equilibrate to the conditions on the Earth surface, the quaternary sediments have been formed there and have never left this regime and are therefore in a fair equilibrium with the environment.

**Keywords**: quaternary calcareous building materials, pore properties, weathering resistivity

## 1. Introduction

The stone materials of historical buildings usually reflect the specific rock spectrum of the regional geology, since transport facilities used to be limited and expensive. Good workable sedimentary rocks were given mostly preference to magmatic and metamorphic rock materials, despite their lower durability. Typical examples for this are the medieval cathedrals all over Europe.

As to the weathering behaviour quaternary calcareous materials like breccias, conglomerates and tufa–travertines are striking exceptions. These rocks are found locally, in geologically very young areas, e.g. in the Alpine realms and show an excellent performance over centuries as building materials. In contrast to other sedimentary rocks, which after sedimentation usually were subjected to the pressure-temperature conditions of the shallower Earth crust, quaternary sediments solidified under conditions very close to or on the Earth surface.

As materials of local importance quaternary sediments have not gained such a wide reputation and usage like, for example the Buntsandstone (red sandstone), the Muschelkalk (shell limestone), the Ammonitico Rosso, the Greek or Italian marbles etc. . Nevertheless, considerable parts of the built cultural heritage of Austria, Germany, Switzerland, Italy and the Balkan countries are constructed with these materials. Out of the enormous number of localities a few examples may be named, being of importance in our working area: the Hötting-breccia of Innsbruck, the Mönchsberg-conglomerate of Salzburg, the Munich and the Brannenburg Nagelfluh (conglomerates) and the tufa limestone ("tufa") of the Inn-valley – Vorarlberg region and the Bavarian-Austrian foreland of the Alps. The latter is the most prominent historic stone between Weilheim/Bavaria - Salzburg – Amstetten/both Austria.

With regard to the historic use, these materials were already employed in Roman times, particularly extensive during the medieval age and they are used also nowadays to a minor extent. Limiting constraint for their use is the exhaust of the quarries. This aspect represent in many regards the problems today, the more, since neither the properties of the used material nor that of the spare materials are well known which is a precondition for adequate maintenance or restoration of historical objects.

In recent work we concentrated on studying the properties of tufa and Hötting breccia which are typical such quaternary formations in our working area. These materials are easy to quarry and excel by a striking weathering resistance (Obojes et al. (2004), Mirwald (2007; Unterwurzacher & Mirwald (2006); Obojes et al. (2008); Unterwurzacher et al. 2010). In this communication we elucidate the petrophysical relations between two groups of calcareous materials, namely quaternary sediments such as tufa and Hötting breccia, and various limestones (Grimm, 1990).

## 2. Geological and petrographic background

Geologically, all these stones studied are quaternary calcareous sediments formed locally in the course of the erosion and elevation processes of the Alps. While most of these sediments remained in a low consolidation state, under the specific conditions of circulating groundwater these materials have been cemented to highly solidified calcareous stone.

Such a material is the Hötting breccia; it is an important stone in the Inn Valley around the cities of Innsbruck, Hall and Schwaz (Fig. 1). This breccia was extensively quarried until to the beginning of the $20^{th}$ century close to Innsbruck. It is interpreted as a Riss-Würm interglacial series of alluvial fans and talus slopes deposited above Innsbruck (Penck, 1921, Obojes 2003). Recent dating by Uranium/Thorium yielded ages between 100 000 and 70 000 years (Spötl & Mangini, 2006). Particular use of Hötting breccia was made in historic times in the valley region below Innsbruck because of a favourable transport of this material down the Inn river.

Tufa limestone occurs in many locations in West Austria and Bavaria. Extent of the deposits and material quality may differ considerably. Its geological setting is always related to (ground-spring)-water that is supersaturated in calcium carbonate. Tufa is found frequently on valley slopes or as a postglacial formation in the quaternary foreland sediments in positions on or very close to the surface. Tufa, often together with different kinds of conglomerates is quite common in the Bavarian-Austrian Alpine Foreland, in particular in the region between Inn and Salzach river. Indeed, they are there the most typical stone types for representative construction in historical times. The most prominent occurrence in Tirol is the tufa of Thiersee that served for the construction of the close-by Kufstein fortress (Fig. 2). We studied this material, and in addition tufa of Andelsbuch/Vorarlberg as a second sample material.

**Figure 1.** The cathedral of St. Jakob / Innsbruck/Tirol (left). Exterior wall and window embrasure of a medieval house /Hall/ Tirol (right). Both objects are built of Hötting breccia.

**Figure 2.** The fortress of Kufstein/Tirol (left); the outer fortification walls are constructed from Thiersee tufa. Remedial maintenance of the fortification wall (right).



While Hötting breccia is predominantly used for massive constructions, such as wall material, column material, and to a lesser extent for decorative purposes, the tufa were used in many respects, as building material, as well as for decorative purposes, e.g. portals of churches, embrasures of windows, for vault constructions (light porous material!). Due to its characteristic mega porosity it is also very apt for application of a lime cover that may serve as grounding for painting. With respect to the very open pore structure of that stone, it seems that this property was also the reason for selecting “soft” tufa as a material for the fortress walls of Kufstein instead of hard limestone because the large porosity may lower the impact of cannon shots.

Despite hundreds of years of exposure, it is a striking observation that the extent of damages on objects built from these two materials is low compared to other stone types, e.g. sandstone or limestone/marble.

## 3. Hötting breccia and spring tufa

The macroscopic inspection of the different stone materials (Fig. 3) shows that the fabric of the two materials discussed is significantly different from other stone materials e.g. marble and sandstone. The Hötting breccia is in principle of calcareous composition; it is characterized by different clastic components which comprise rock-material of the underlying Triassic substrate (mainly limestone) and rare crystalline components, remains of the preceding Riss-glaciation. The clasts are embedded in a fine grained carbonate matrix thus forming a well cemented compact rock. The ratio of clasts to matrix ranges widely between 30:70 and 70:30. Typically, the Hötting Breccia is red-coloured due to abundant Permo-Triassic Red sandstone clasts and fine debris in the matrix (Unterwurzacher & Obojes, 2011).

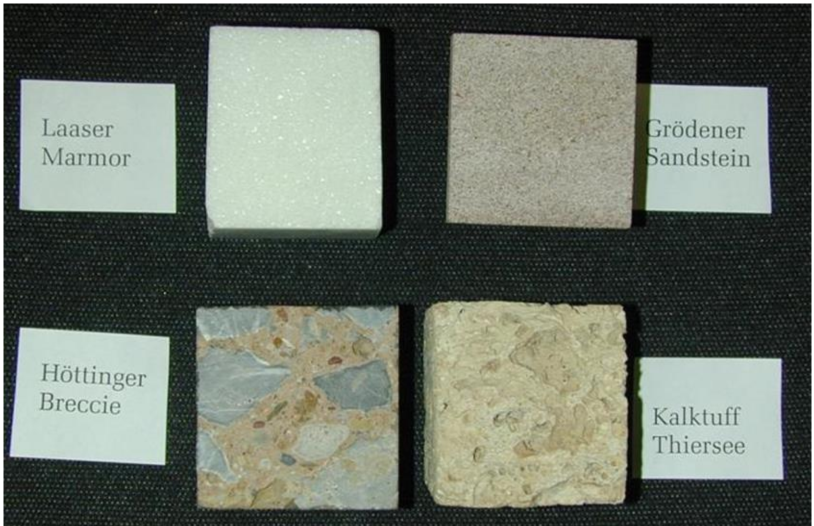


**Figure 3.** Specimens of Laas marble, Gröden sandstone, Hötting breccia and Thiersee tufa. They show the characteristic differences in fabric of the quaternary stone materials, Hötting breccia and the tufa, in comparison to the dense marble and the fine-middle grained sandstone. While the Hötting breccia is characterized by a colourful mix of calcareous clasts in a brownish, well-cemented matrix, the whitish to brownish tufa shows a very inhomogenous distribution of dense parts and pores of very varying size.



Similarly, tufa is a calcareous sediment, formed by precipitation processes of springs and ground waters which are supersaturated in calcium carbonate. Usually the rock is highly porous which implies a low raw density and it is therefore light in weight. Striking is that this light weighted material is of considerable strength. The microscopic analysis shows that they are mainly fossil phytoclastic waterfall tufa. Sometimes sub-spherical to ellipsoidical vadoids and cyanoids components of millimeter to centimeter size can also be observed. Incrustation structures of plants are frequent; in addition re-crystallisation phenomena may occur.

As indicated above, damages due to environmental impacts are strikingly small for these two materials. The very compact Hötting breccia may show dark surface depositions by particulate matter and algae; more severe are eventual matrix corrosion processes due to salt and humidity/water impact which may lead to material loss, in particular to break off of clasts.

The weathering behaviour of the tufa is characterized by certain dissolution phenomena by acid? rain and crumbling. In humid micro-environments tufa tend to be wet, what may lead to all sorts of biogenic activities.

## 4. Pore and hygric properties

Comparing the macroscopic appearance of the different rocks (cf. Fig. 3) the most striking feature of the Hötting breccia and the tufa is their heterogeneous fabric indicating a considerably large porosity.

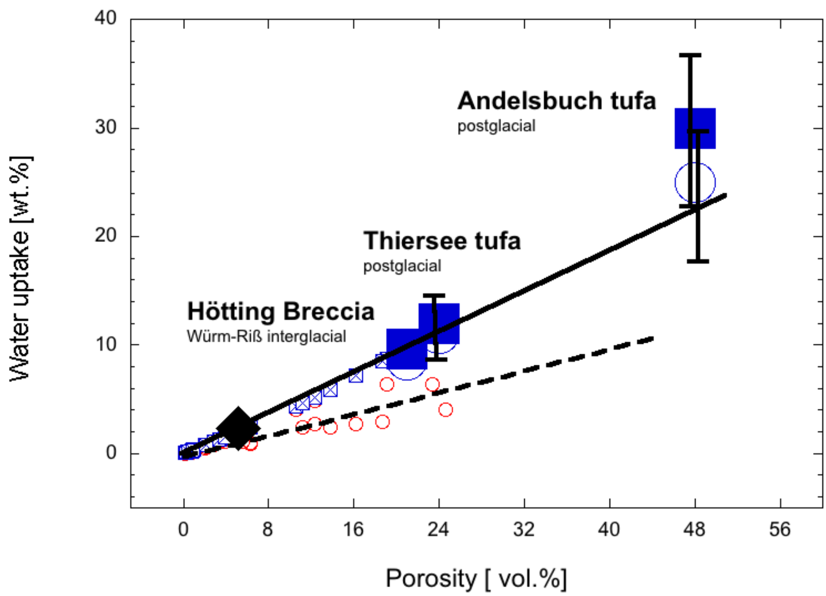


**Figure 4.** Plot of the water uptake (wt%) and pore volume (vol.%) of different limestones (Grimm, 1990) (small circles and squares), Gröden sandstone (closed diamond) and the studied quaternary sediments of Hötting breccia, Thiersee and Andelsbuch tufa (closed squares). While the open symbols represent water uptake at atmosphere condition, closed symbols give the uptake under vacuum. (Note: the data of the quaternary materials have been converted from vol.% to wt.%; cf. Table 1).



Fig. 4 shows a comparison of the water content of calcareous rocks (Grimm, 1990) and two local tufa limestones (Thiersee, Andelsbuch) and the Hötting breccia obtained by water uptake at atmosphere and vacuum conditions. As a reference material we choose the Gröden sandstone (Franzen, 2002) (s. Table 1). This material allows to demonstrate the principle contrast in petrophysical properties between the studied quaternary rocks and other sedimentary rocks which have been subjected to a considerable diagenesis due to pressure-temperature impact by subsidence into the upper Earth crust. Main reason for that choice of Gröden sandstone was that no other regional limestone is available of which the petrophysical properties are studied in such detail. The data in Fig. 4 show that the quaternary sediments tend to a considerably higher water content and pore volume respectively amounting up to about 2.5 times of that of limestone. While the $H_2O$ content data of the various limestones obtained at one atmosphere still show some deviation from linearity due to uneven water penetration into the pores, the data gained under vacuum conditions suggest a practically linear behaviour thus indicating complete filling. As to the quaternary stones the difference between the two uptake procedures is not really significant, which is due to the (very) high uptake coefficient "A" (cf. Table 1). See also there for a more detailed data comparison.

**Table 1.** Petrophysical data of the Hötting breccia, Thiersee and Andelsbuch tufa, and Gröden sandstone (Franzen 2002).

| Parameter | Hötting breccia | Thiersee tufa | Andelsbuch tufa | Gröden sandstone (Franzen, 2002) |
|---|---|---|---|---|
| Raw density<br>Theoret. density[g/cm$^3$] | 2.3 +/- 0.2<br>2.6 | 2.0 +/- 0.2<br>2.6 | 1.4 +/- 0.2<br>2.6 | 2.56+/- 0.02<br>2.7 |
| Porosity [vol.%] | 9.5 (matrix!)<br>(15–30 „bulk" porosity ! ) | 24 | 48 | 5.2+/- 1.5 |
| Estimated fraction of macropores of bulk. porosity [%] | ca. 60 | 15 – 30 <5mm plus ca. 30% >5mm | ca. 20 <5mm plus ca. 30% >5mm | ca. 20 |
| Av. pore radius (Hg.-porosimetry) [µm] | 0.6 | 10 | 30 | 5 - 10 |
| Shape of the pore radii spectrum | symmetric | asymmetric | asymmetric | asymmetric-bimodal |
| Spec. surface. (BET) [m$^2$/g] | 1.6 +/- 0.3( ? ) | 0.9 +/- 0.2 | 1.05 +/- 0.2 | 1.5 +/- 0.3 |
| A-coefficient [kg/m$^2$*h$^{1/2}$] | 1,9 +/- 0.2<br>(2.8 bis 6.3: „bulk"-value) | 26 +/- 5 | 355 +/- 20 | 0.7+/-0.2 |
| Water capacity (vol%) (bulk) | 4 +/- 3<br>3.5 h<br>(6 bis 13) | 19 +/- 7<br>0.5 h | 42 +/- 10<br>70 Sekunden! | 4 +/- 1 |
| Water uptake in 24h [vol.%] | 8 +/- 1<br>(12 bis 26) | 22 +/- 6 | 44 +/- 8 | 5 +/- 1 |
| Water uptake in vacuum [vol.%] (matrix) | 9.5 +/- 1<br>(15 bis 30) | 24 +/-69 | 48 +/- 9 | 5.2 +/- 1.5 |
| Drying [h] up to equilibrium und rel. humidity at room temperature | 36+/- 5<br>(50 bis 120) | 70 +/- 8 | 110 +/- 10 | 35 +/- 5 |
| Ratio: drying : water uptake | 1 : 2.7<br>(1 : (4 – 9) | 1 : 88 | 1 : 37 | 1 : 1.2 |



An intrinsic property of rocks is their specific surface representing mainly the wall surface of the pores, which may be roughly determined by BET measurements. One assumes that the specific surface of a material has the function of an internal reaction surface and, thus, it should be a characteristic parameter for the reactivity of a material in weathering processes. According to Table 1 this property does not vary much for the discussed materials, ranging between 1 to 1.5 $m^2/g$. However, with respect to the pore volume size, there are considerable differences.

Normalizing the specific surface by the corresponding pore volume, one obtains an interesting parameter, which shows how the pore volume or, indirectly the pore size is related to its pore wall surface. In Fig. 5 a plot of the (specific surface / pore volume) data of the two tufa and of the breccia is shown. Furthermore, these data are augmented by data of the Brannenburg conglomerate and the Cannstatt travertine both taken from Grimm (1990). In addition data of different limestones, also taken from Grimm, are compiled for comparison in that plot yielding an apparently irregular distribution on the low pore volume side (1-20 vol.%). The Gröden sandstone data (closed diamond) is found in the middle of this data field.

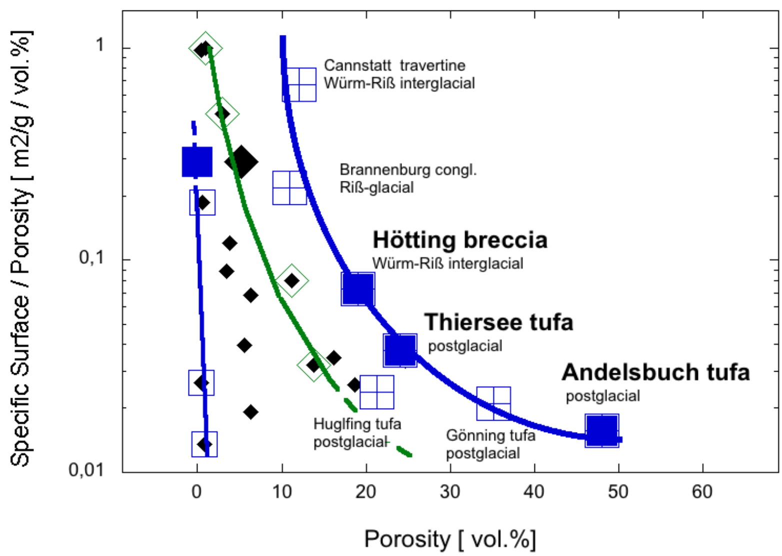


**Figure 5.** Comparison of the calcareous Hötting breccia and tufa (Thiersee, Andelbuch) with different limestones in a diagram of (specific surface/porosity) versus porosity. The normalized specific surface reveals a negatively sloped trend for the quaternary sediments (big closed squares: samples studied; open squares with cross: data from Grimm (1990). The limestone data (small closed diamonds) taken also from Grimm (1990) plot on the low porosity side of the diagram. Different Triassic shell limestones ("Muschelkalk"; large open diamonds centered by a small closed diamond) suggest a similar trend as observed for the quaternary sediments. Also very old Devonian limestones (open squares centered by a small closed diamond) follow possibly such a trend. Gröden sandstone: big closed diamond.

The inspection of the seven data of the quaternary sediments indicates an inverse relation: decreasing pore volume is correlated to an increasing specific surface. This means in principle that either smaller pore volumes are distinguished by a relatively larger specific surface or – more likely - that the original pore volume of a rock decreases due to diagenetic processes. whereby the surface of the pore walls is increased by cementation processes. This would be achieved e.g. by the formation of new fine, surface-rich crystals lining out the pore walls. This inverse relation between pore volume and specific surface observed for the quaternary sediments seems also of significance for the other calcareous rocks located on the low pore volume side in Fig. 5. At least the data available for four Triassic shell-limestones ("Muschelkalk"; Grimm 1990) suggest a similar correlation as for the quaternary materials. Possibly, also the data of three Devonian limestones (Grimm, 1990) plotting on the side of very low pore volume insinuate a comparable behaviour. Interestingly, the data pattern of this plot indicates also a sort of time dependence: there seems a systematic decrease of the pore volume of carbonates over geological times, ranging from the Quaternary to the Devonian period.

This finding of a systematic correlation between pore volume – specific surface – time(?) appears supported furthermore by recent data gained on medieval lime and magnesium-lime mortars. The mortars are distinguished by a striking weathering resistance, similarly to that of the quaternary sediments. So, for example, we still find romanic mortars characterized by smoothed out joints in almost perfect preservation on outside walls (Diekamp, Konzett (2007); Diekamp, Stalder, Konzett, Mirwald (2010)). In Fig. 6 we show three mortar data sets obtained from three sites ( i) Castle Landeck/Tirol; ii) archeological excavation at the Castle Landeck and iii) historic custom station of Finstermünz/Tirol). Although the data scatter is relatively large, the data show the essential features derived from above in Fig. 5: a) the data follow the specific inverse trend between pore volume and specific surface as do the data of the quaternary sediments, b) inferring the supposed time relation they are, as the youngest "calcareous sediments", located consequently on the side of the large pore volumes.

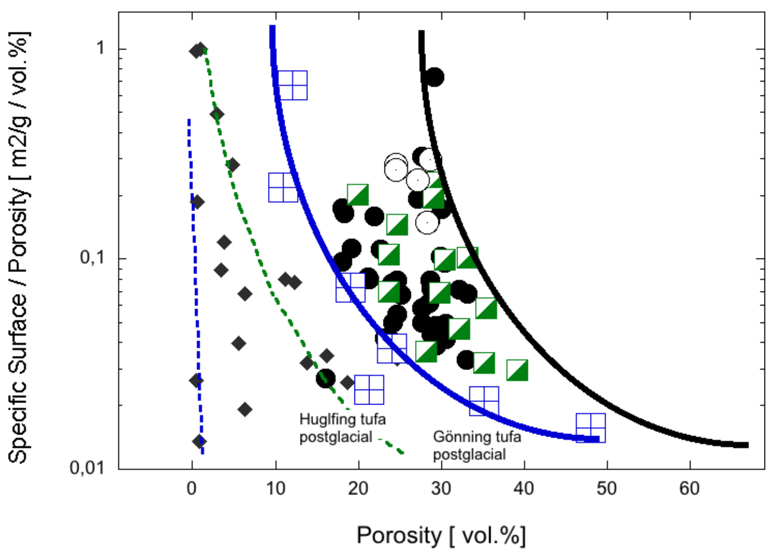


**Figure 6.** Plot of (specific surface/porosity) vs. porosity (cf. Fig. 5) with compilation of additional data of medieval lime mortars from three localities. The data of these "youngest sediments" plot on the high porosity side of the diagram indicating a similar trend as observed for the quaternary

sediment. Symbols: open circles: Castle Landeck/Tirol; closed circle: Archeological excavation at Castle Landeck; half closed squares: historic custom station of Finstermünz/Tirol). The other symbols: see Fig. 5.

## 5. Conclusions

Looking at the different calcareous sediments (including the lime mortars) from the point of weathering resistivity, we notice a very good behaviour for the geologically very young materials. As to the petrographic and petrophysical properties of these different calcareous materials, we find considerable variations in their parameters (Grimm (1990), Obojes, et al. (2008), Unterwurzacher et al. (2010).

With regard to the geological history, we know that most calcareous rocks when formed on the Earth surface were subjected subsequently to diagenetic processes by being buried in some depth of the Earth crust. There, they were adapted to the pressure-temperature and geochemical regime of that realm. The quaternary sediments and the mortar material as well are different in this respect: they were formed on the Earth surface and remained there. This implies no change in their geological environment, when used as building materials. For the quaternary materials the constraints of exposure as building stone are not significantly different from their conditions at formation. The same applies for the historic lime mortar. However, the other calcareous materials that have returned to the Earth surface are coined by their previous thermodynamic regime. In terms of thermodynamic constraints this means that all the calcareous stone returned from the depth are removed out of their previous stability field and are less stable under the condition of the Earth surface than the quaternary materials – including the historic, medieval lime mortars. So, it seems that thermodynamic constraints are largely responsible for the high weathering resistivity observed on these quaternary sediments including “equilibrated” historic lime mortars. The conditions of formation of these quaternary materials do not differ much from those prevailing at weathering, what implies a low decay potential.



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