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Isotopic tracers of the origin of Ca in a carbonate crust from the Middle Atlas, Morocco

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Abstract

Carbonate crusts developed on basalt were studied at Tazouta in the Moroccan Middle Atlas. The chosen representative weathering profile is 2.8 m thick and is composed from base to top of a fresh basalt overlain by a coherent saprolite, a friable saprolite and a surface soil. Carbonate crust genesis occurs by replacement of primary and secondary clay minerals by low Mg calcite. The ^{14}C dates of the calcite range from 15 to 14 ka in the coherent saprolite, and from 12 to 8.5 ka in the friable saprolite.

Smectitic weathering and replacement of Si-bearing minerals by carbonate are coupled processes leading to a strong calcium net gain (300 kg/m^3) within the friable saprolite. The low weathering rate of basalt compared to the calcrete genesis rate, and the high mobility of calcium in supergene weathering mantles, limit the basaltic Ca contribution to calcrete genesis. The contribution of the Triassic sediment is also limited by the mineralogical unavailability of Ca. The ^{87}Sr/^{86}Sr ratios confirm the low contribution of basalt and indicate an external origin of Ca. The Sr isotope ratios of calcrete are different from those of the adjacent Liassic carbonates and are close to rainfall values.

The carbon isotope compositions of carbonates (-8‰ to -9‰ vs. PDB) imply a significant contribution of C3-dominated organic carbon during carbonate precipitation. Oxygen isotopic compositions of carbonates (average -5.24‰ vs. PDB), show that carbonates are ^{18}O-enriched compared to meteoric waters (-4‰ to -3.5‰ vs. SMOW).

Keywords: Carbonate crust; Calcium; Isotope; Strontium; Carbon; Oxygen; Middle Atlas, Morocco

1. Introduction

Carbonate crusts are pedogenic formations developed under arid and semi-arid conditions (Nahon, 1976; Ruellan et al., 1979). Carbonate crusts, also called calcretes, cover 13% of the land surface (Yaalon, 1981) and may develop at the expense of various parent rocks. Numerous studies have examined the geochemical origin of calcites on the basis of morphological and petrographical data (Ruellan et al., 1979) or mineralogical observations (Coudé-Gaussen and Blanc, 1985; Coudé-Gaussen et al.,

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1987). The origin of calcium, however, remains difficult to trace and to quantify in most cases. Recently, carbonate crusts were considered as palaeoclimatological and paleoenvironmental indicators (Cerling, 1984; Mack et al., 1990; Cerling and Quade, 1993; Rossinsky and Swart, 1993; Pendall et al., 1994; Liu et al., 1996; Alam et al., 1997), and Sr, C and O isotopes are used to identify the sources of Ca (Capo and Chadwick, 1993, 1999; Stewart et al., 1993; Quade et al., 1995; Capo et al., 1998; Hamidi et al., 1999). In Morocco, only a few carbonate crusts developed over granitic rocks (Ducloux et al., 1990), schist and quartzite (Millot et al., 1977) and sedimentary rocks (Ruellan, 1970; Benabdallah, 1986; Badraoui et al., 1987) have been studied. In this work, we have investigated carbonate crusts developed upon Triassic basalts located in the Moroccan Middle Atlas, and identified the origins of Ca and C by measurement of Sr, O and C isotopes.

2. Geological setting and methods

The Moroccan Middle Atlas is composed of several plateaus of Liassic carbonate (Causses). These

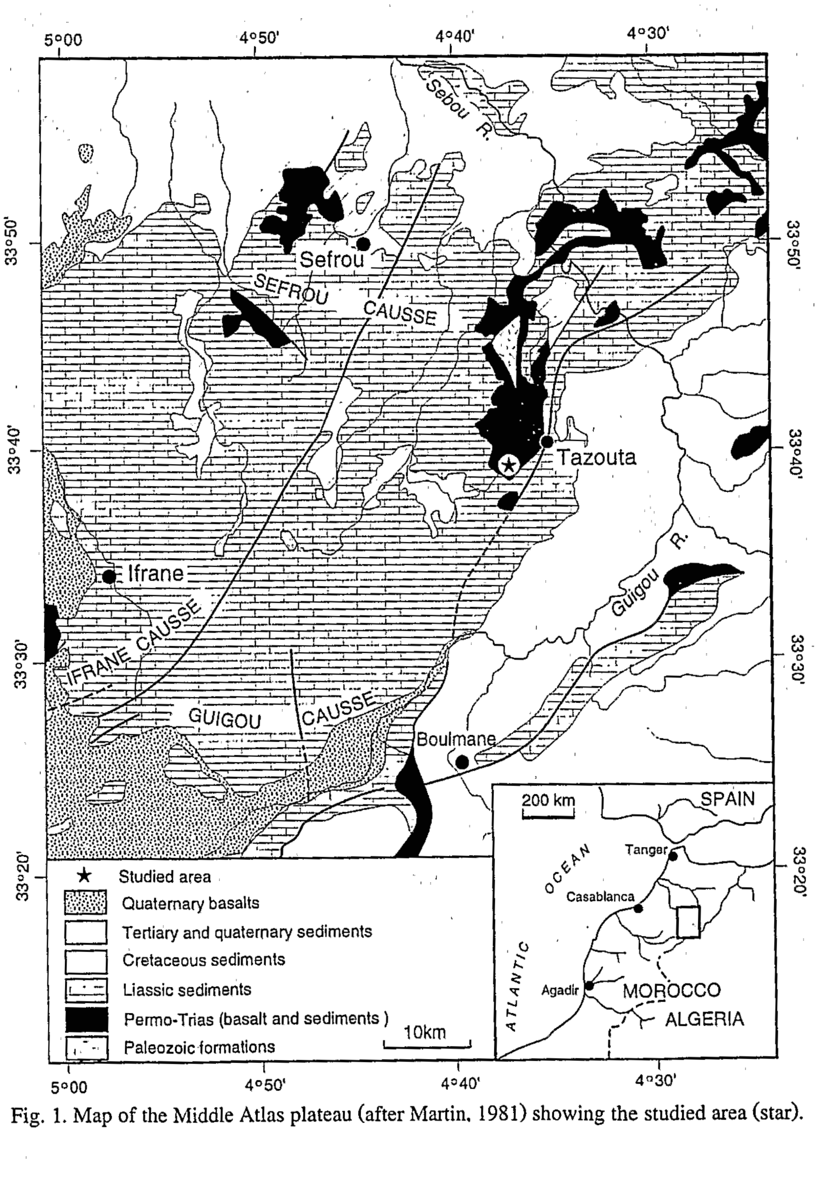


Fig. 1. Map of the Middle Atlas plateau (after Martin, 1981) showing the studied area (star).

plateaus are dissected by thalwegs and ravines in which Triassic age sediments and basalt outcrop. The Triassic basalt is a part of tholeitic series associated with the opening of the North Atlantic (Bertrand, 1991). In the Middle Atlas, pedogenic carbonate is commonly developed on the basalts.

The study area is located in the Tazouta region in the eastern part of the Sefrou Causses (Fig. 1). This area receives a mean rainfall of 516 mm/y, and has a mean annual temperature of 15.7°C (Bentayeb and Leclerc, 1977). Vegetation is of Mediterranean maquis type. The sampled profile is located in the Ain Lahjer area (Fig. 1). In addition to the soil profile samples, watershed bedrock (Triassic sediments and Liassic carbonates), groundwater and rainwater were sampled. Groundwater was sampled from wells and springs, while the rainwater sample was collected at a site 100 km southwest of the studied area.

Bulk rock samples were analyzed using X-ray diffraction (Philips P 1729), optical microscopy and scanning electron microscopy (Cambridge-Stereoscan 200). Calcium carbonate content was determined by selective dissolution (HCl) of samples. ICP and electrophoresis were used for chemical analysis.

Samples from each soil depth were split, and analysed for $^{87}Sr/^{86}Sr$. For the first split, the bulk sample (mixed carbonate and basalt) was leached with 0.27 N HCl and the leachate was analyzed. In the other split, $^{87}Sr/^{86}Sr$ was measured on pure carbonate pre-sorted from the bulk sample under a binocular microscope. Strontium isotopic ratios were determined using a VG SECTOR solid-source mass spectrometer in the CEREGE laboratory, Aix-en-Provence, France. The oxygen and carbon stable isotopes values were obtained only for pure carbonate. Fifteen milligrams of carbonate were reacted with 100% phosphoric acid (Craig, 1957) at 25°C for 12 h. The determination of the oxygen and carbon isotope ratios for the extracted CO_2 was carried out on a gas-source mass spectrometer (TRICARB 2260, 2560) at the IRD Laboratory (Bondy, France). The

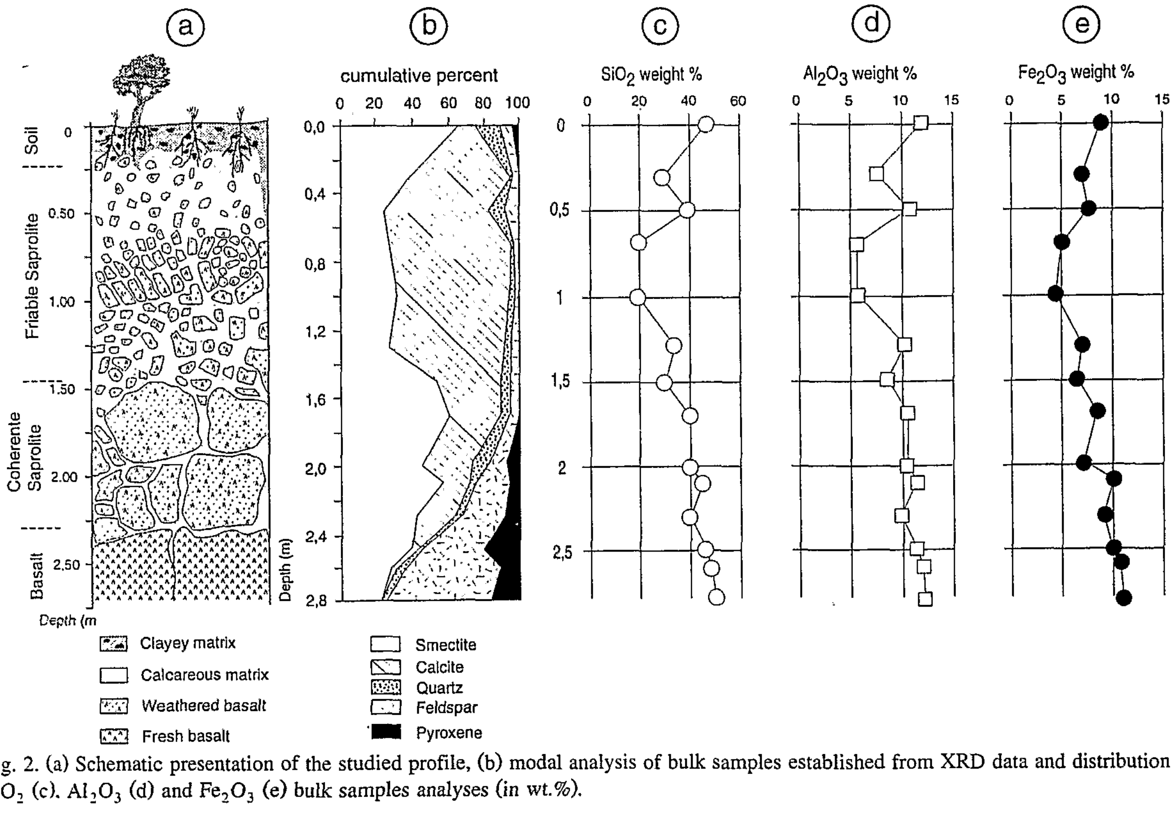


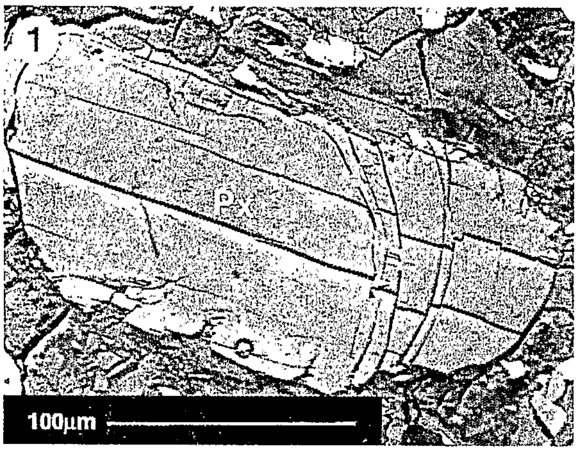
Fig. 2. (a) Schematic presentation of the studied profile, (b) modal analysis of bulk samples established from XRD data and distribution of SiO_2 (c), Al_2O_3 (d) and Fe_2O_3 (e) bulk samples analyses (in wt.%).

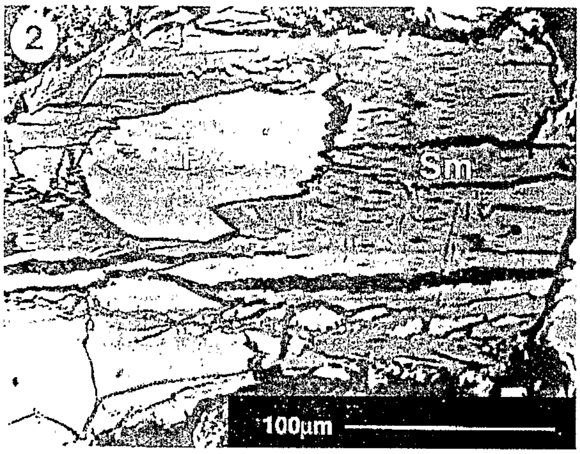
results are reported in the conventional δ notation with reference to the PDB standard.

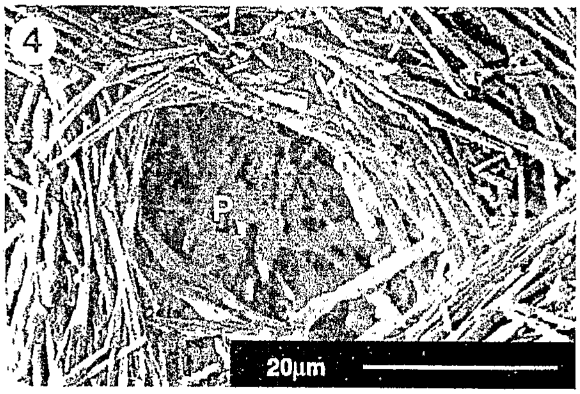
^{14}C analyses were measured on pure carbonate samples (five samples from the bottom to the top profile) at the IRD Laboratory. Forty grams of carbonate sample was reacted with 100% H_3PO_4 under vacuum to release CO_2. The CO_2 was purified and reduced to C_6H_6. The ^{14}C activity was counted by liquid scintillation spectrometry.

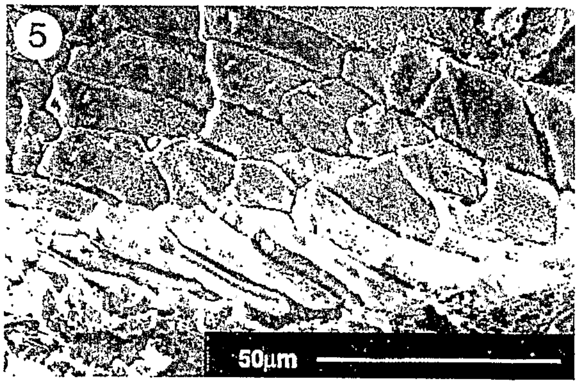
3. Weathering patterns

The weathering profile is 2.8 m thick and can be divided from bottom to top into four layers: a fresh









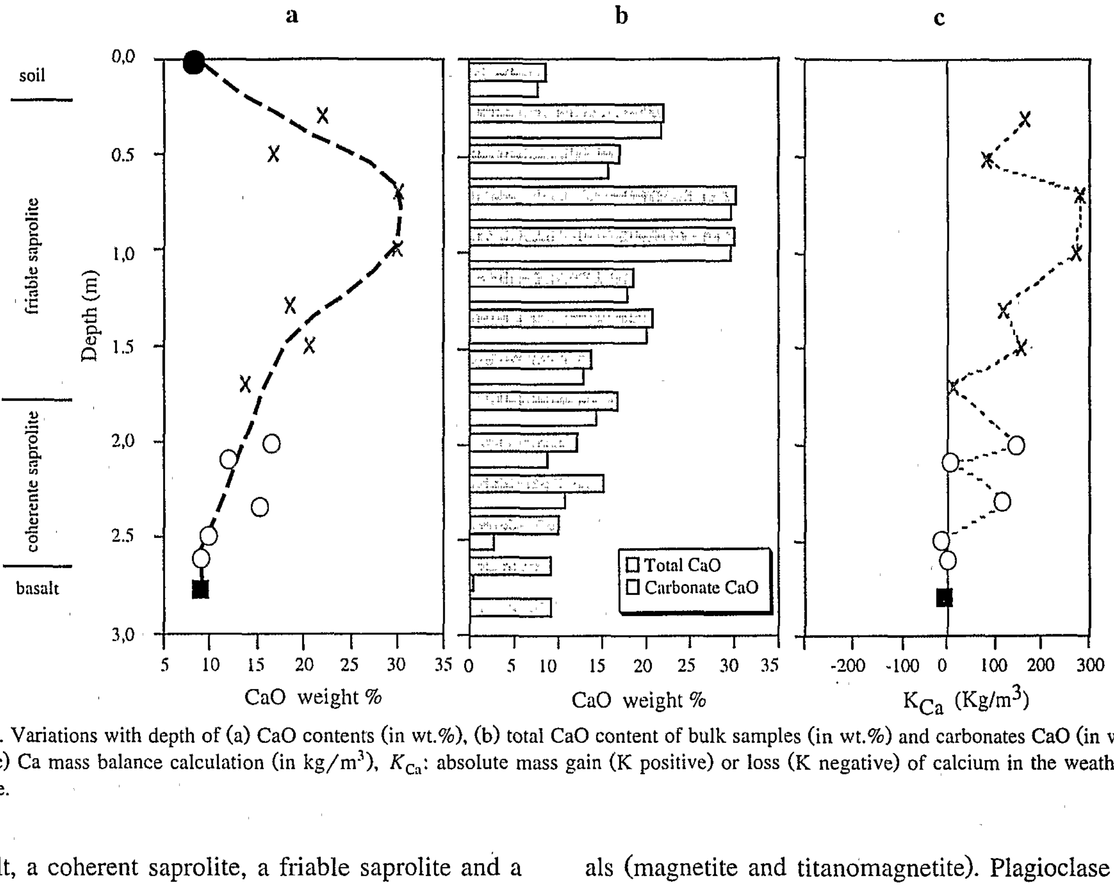


Fig. 3. Variations with depth of (a) CaO contents (in wt.%), (b) total CaO content of bulk samples (in wt.%) and carbonates CaO (in wt.%) and (c) Ca mass balance calculation (in kg/m^3), K_{Ca}: absolute mass gain (K positive) or loss (K negative) of calcium in the weathering profile.

basalt, a coherent saprolite, a friable saprolite and a surface soil (Fig. 2a). This profile displays upward increasing calcitization and decreasing size of basaltic blocks. The top soil is organic matter-rich including roots of various diameters. Weathering patterns were identified from the 14 soil bulk samples collected within the profile. The fresh basalt is composed of plagioclase, pyroxene (Scheme 1) and opaque minerals (magnetite and titanomagnetite). Plagioclase and pyroxene amounts decrease upwards in the profile (Fig. 2b) due, to their pseudomorphic transformation into smectite within the coherent saprolite (Scheme 2), and to epigenic replacement by carbonate in the friable saprolite (Scheme 3). Aggregated clay structure and strong biological activity characterize the surface soil. Weathering of primary minerals to

Scheme 1. Scanning electron image of unweathered pyroxene (Px) in the fresh basalt.

Scheme 2. Scanning electron image showing pyroxene (Px) weathering into smectite (Sm) in the coherent saprolite. The secondary product has replaced the pyroxene crystal implying conservation of primary mineral volume.

Scheme 3. Schememicrograph of plagioclase replacement (F) by micritic carbonates (C) in the friable saprolite. Note that the replacement begins at the crystal rims but also in the voids of plagioclase. Residual islands of plagioclase show optical continuity indicating conservation of primary texture.

Scheme 4. In the Tazouta profile, needle-fiber calcite usually occurs in pore environment with random or tangential fabrics. In this scheme, needles are oriented around a pore channel.

Scheme 5. Well-preserved calcified root cells observed by scanning electron microscope in the friable saprolite.

smectite and precipitation of calcite yield strong chemical variations: Si, Al and Fe amounts decrease from the fresh basalt to the top of the friable saprolite and increase in the soil (Fig. 2c,d and e). The lowest concentrations of each element are located in the maximum carbonation zone of the profile, i.e. the friable saprolite. Ca is the only element for which the concentration increases upward the saprolite (Fig. 3a).

4. Results

4.1. Carbonate types and calcium distribution in the profile

Chemical analysis and X-ray diffraction data show that carbonate is a low Mg calcite (Mg $< 4\%$). Microscopic study of thin sections display three calcite morphologies including: (1) rare sparry calcite, (2) micrite (< 4 μm) (Scheme 3), the most common form in and around residual basaltic minerals and (3) needle-fiber calcite randomly or oriented within pores (Scheme 4). Calcite crystals have been observed in preserved root cells (Scheme 5). In the Tazouta profile, carbonate (micrite) radiocarbon ages range from 15 to 14 ka BP in the coherent saprolite and from 12 to 8.5 ka BP in the friable saprolite (Fig. 4a).

The CaO content in the fresh basalt is 9%. The calcium is mostly incorporated into primary minerals, i.e. plagioclase and pyroxene. In the saprolite, CaO concentrations increase (Fig. 3a) and reach 30% at the top of the layer. Ca is mostly present in calcite rather than primary minerals (Fig. 3b). In the weathering patterns, we have observed that supergene processes do not appear to disturb the basaltic structures in the saprolite, implying no major volumetric changes. Assuming no volumetric changes, Ca mass balance calculations show progressive net gains (Fig. 3c), reaching 300 kg/m^3 in the friable saprolite.

4.2. Strontium isotopic data (^{87}Sr/^{86}Sr)

In the Tazouta profile, the strontium isotope ratio of leached fresh basalt is 0.706793. This value increases upward in bulk samples from the coherent and the friable saprolite horizons (Table 1) as does the carbonate content. The horizon with the highest carbonate content (sample Tz11) displays a ^{87}Sr/^{86}Sr ratio of 0.70917. Profile samples from pure carbonates show homogeneous values of ^{87}Sr/^{86}Sr of 0.709128 ± 0.00006 (four values) and one slightly lower ratio for T8 of 0.708805. There is no relationship between these values and carbonate concentrations in the studied profile (Table 1).

The ^{87}Sr/^{86}Sr Sr ratios are 0.707506 and 0.711308 (average of two analyses) for Liassic carbonate and

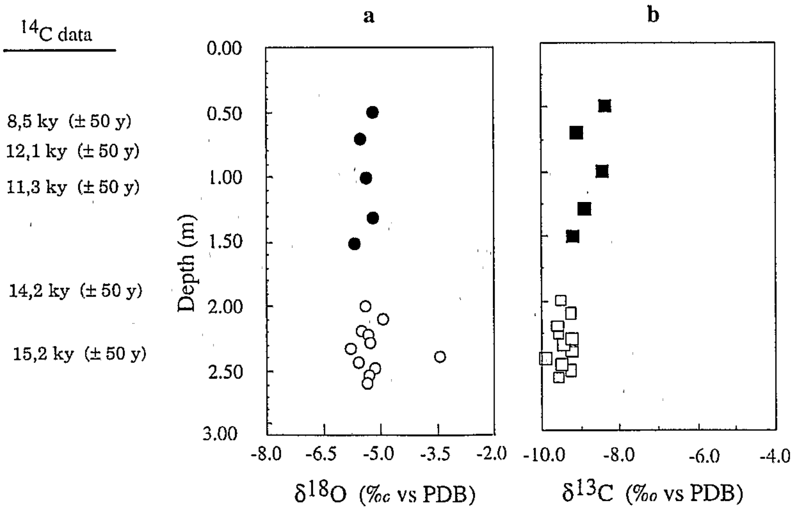


Fig. 4. Variations of δ^{18}O relative to PDB (a) and δ^{13}C relative to PDB (b) of carbonates with depth.

Table 1
Strontium isotopic compositions of sample profile and watershed formations

Samples	Depth (m)	Nature	Leaching $^{87}Sr/^{86}Sr$	Carbonate $^{87}Sr/^{86}Sr$
T1	2.80	fresh basalt	0.706793	–
T3	2.50	weathered basalt	0.707869	0.709145
T6	2.00	weathered basalt	0.708467	0.709160
T8 ($n=2$)	1.50	weathered basalt	0.708817	0.708805
T9 ($n=2$)	1.30	weathered basalt	–	0.709144
T11	0.70	weathered basalt	0.709170	0.709065
Lias	–	carbonates	–	0.707506
Trias ($n=2$)	–	clayey sediments	–	0.711308
Rainwater	–	–	–	0.709945

n = Number of analyses.

Triassic sediment, respectively (Table 1). The Liassic carbonate values are compatible with that of Jurassic seawater (Burk et al., 1982). The analyzed rainwater had a strontium isotope ratio (0.709945) (Table 1) slightly higher than the pedogenic carbonate value.

4.3. Oxygen and carbon isotopic data

The $\delta^{18}O$ values of carbonate are extensively uniform throughout the profile ($-5.8‰$ to $-5.1‰$ PDB) (Fig. 4a). The $\delta^{13}C$ values are more variable ($-9.8‰$ to $-8.3‰$ PDB), and display a slight increase upwards in the profile (Fig. 4b).

5. Discussion

The data relative to the Tazouta carbonate crust indicate the presence of two successive replacements of basaltic primary minerals, by smectite and then by carbonate. Attapulgite or sepiolite common in calcrete formation elsewhere (Millot et al., 1969, 1977; Paquet, 1983) were not observed in the Tazouta profile. This may be due to low activities of Mg and Si in the soil solution.

In the upper part of the profile, both residual primary phases and supergene clay minerals are replaced by carbonate. This incongruent dissolution enriches percolating soil solutions in Si, Al and Mg. Those solutions, reaching the fresh basalt at the oxidation front, induce the pseudomorphic replacement of feldspar and pyroxene by smectite. Both calcitization and smectitization are interpreted as coupled mechanisms leading to the development of the Tazouta weathering profile.

5.1. Calcium origins

The $^{87}Sr/^{86}Sr$ ratio of the basalt is lower than that of the pure carbonate, suggesting that the strontium signature of carbonate crust is not directly controlled by the basalt. In the saprolite, the soluble fraction and pure carbonates for the same sample have different strontium isotopic ratios. Those results imply that a part of the basaltic Sr was dissolved in the HCl leach and added to the Sr from the carbonate component in the bulk samples. Strontium derived from basalt weathering is low or absent in the carbonate crust. Several studies have demonstrated the high mobility of Sr and Ca during basalt weathering (Craig and Loughnan, 1964; Eggleton et al., 1987). In the Morrocan Middle Atlas, calcium has been depleted from the weathered profile derived from Triassic basalt (Hamidi et al., 1997, 1998). Smectitic weathering of this basalt from the Trias to the Quaternary produces a clayey saprolite. Basalt weathering rates are of about 40 mm/ka (Bendetti et al., 1994) under tropical climates. This value will be lower under Mediterranean conditions and in any case lower than the carbonate crust genesis rate at Tazouta, estimated from ^{14}C data as 205 mm/ka. Basaltic weathering could not have releases more calcium in the short time interval of Tazouta carbonate formation (since the late Pleistocene). Therefore, strontium as well as calcium has mostly been imported into the Tazouta soil. In addition, the lower weathering rate at the oxidation front compared to rate of carbonate formation above demonstrates clearly that the two coupled mechanisms are not in equilibrium and that ultimately the fresh basalt will be directly replaced by carbonate.

The Sr isotopic ratios of the profile bulk samples and the potential sources of Ca in the studied area (watershed formations and rainwater) are shown in Fig. 5. The pure carbonates display variable Ca/Sr ratios due to various calcite generations coexisting in the same sample, and the differing precipitation rates that may control the Sr incorporation in calcite (Lorens, 1981; Mucci and Morse, 1982). All the soil carbonate samples have a similar $^{87}Sr/^{86}Sr$ ratio very close to the value of present-day rainwater sampled at 100 km from the studied site. The Sr isotopic compositions of the pure carbonate plot inside a triangle defined by Triassic sediment, basalt, and Liassic carbonate. Mixtures of basalt–Triassic sediment or Triassic sediment–Liassic carbonate isotopes can explain the Sr isotopic compositions of pure carbonate. However, it seems unlikely that those sources were mixed in the same proportions to give an almost constant isotopic composition throughout the profile.

The high $^{87}Sr/^{86}Sr$ ratio of Triassic sediments would have a significant influence on a given mixture. Nevertheless, this material is the Ca poorest (9% of CaO). Ca is mostly incorporated in exchangeable minerals (smectite), which are the principal components of Triassic sediments (calcite < 4%). Therefore, the contribution of Ca from Triassic sediments to the carbonate crusts is limited by the lack of a mineral source of Ca. Rainwater and Liassic carbonates thus appear to be the major potential contributors to the calcrete formation. This suggestion is in contrast to the work of Sadiki (1991), who proposed the Liassic carbonate as the only possible external source of Ca in carbonate crust developed from Triassic basalt in the Boumia area (South Middle Atlas).

Strontium isotopic ratios of soil carbonates are closer to the value of present-day rainwater than to the Liassic carbonate values. This suggests either a major Ca contribution from rainwater, or an origin from both the Liassic carbonate and rainwater, which would require a high and constant water/rock ratio (about 20,000) to dilute the contribution of the Liassic carbonate Sr signature. The second hypothesis is the most probable because the studied area is at about 200 km from the Atlantic coast, and the marine contribution to Ca and Sr in soil carbonate drops with distance from coastline (Quade et al., 1995).

5.2. Rainwater Ca flux

In the Middle Atlas, the Ca concentration in the rainwater is about 5 ppm (Hamidi, 1996). Assuming

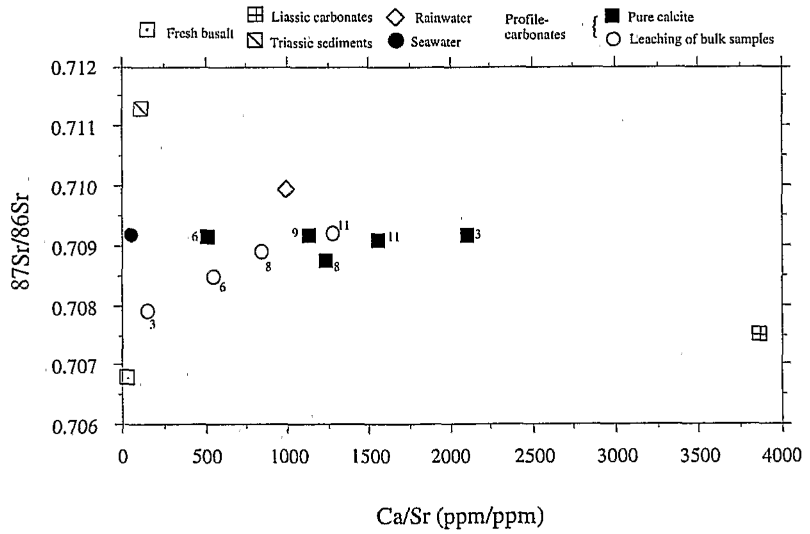


Fig. 5. $^{87}Sr/^{86}Sr$ ratios plotted against Ca/Sr: profile carbonate ratios are intermediate between basalt, Liassic carbonates, Triassic sediments and rainwater as an apparent mixture.

that Ca in rainwater is mostly in a dissolved state (no particles were retained on the filter), we estimate the Ca rainwater budget and its contribution to calcrete genesis over the proposal time scale. The calculated flux of Ca is of about 0.33 10^{-4} g/cm^2/year. This Ca input would produce a carbonate crust genesis rate of 0.0013 g/cm^2/ka if all rainwater Ca precipitates as calcite within the profile. Compared to the total carbonate content in the profile (170 g/cm^2), this rate value implies a continuous nourishment of the Tazouta carbonate crust by rainwater over 250 ka. The Tazouta profile is located in a quite steep land unit with a high run-off which exports a high proportion of rainwaters. This Ca loss makes the carbonate crust genesis rate lower and the time period longer than the above calculated value. Those considerations are in opposition with the apparent age of Tazouta calcrete given by ^{14}C dating (< 20 ka). However, the mean age ^{14}C of pedogenic carbonate can be affected greatly by dissolution–precipitation (Callen et al., 1983) which causes underestimation of the true ages particularly in soils older than Holocene (Amundson et al., 1994). For many reasons, the calculated value of carbonate precipitation rate is only approximate: (1) the value is calculated only from a few rainwater data (2) the rainwater samples were not collected exactly from the study area and (3) the contribution of dry deposition of Ca to the soil profile has not been quantified.

This discussion demonstrates that Ca in the carbonate crust has largely originated from rainwater and to a lesser extent from Liassic carbonate. The basaltic contribution is very small. This dominantly external Ca source implies that the Tazouta carbonate crusts are similar to those developed on Ca poorer rocks (granites, quartzites, ...).

5.3. Origins of carbon and mechanisms of carbonate precipitation

The carbon isotopic composition of pedogenic carbonates is determined by that of the soil CO_2, which represents a mix of plant-derived CO_2 (C3/C4), with atmospheric CO_2 (Cerling, 1984). The C3 and C4 plants use different photosynthetic pathways and have very different δ^{13}C values, averaging about −27‰ and −12‰, respectively. The atmospheric δ^{13}C is about −7‰ PDB (Rabenhorst et al., 1984; Rossinsky and Swart, 1993; Quade et al., 1995).

5.3.1. Carbon origins

In the Tazouta carbonate crust, δ^{13}C becomes less negative upward in the profile indicating a carbonate ^{13}C enrichment similar to that described by Quade et al. (1989) for surface horizons in desert soils near Las Vegas, NV, USA. This enrichment is due to mixing with atmospheric CO_2.

The large difference between Liassic carbonate δ^{13}C, which shows a marine signature (1.78‰) and that of profile carbonates implies that the carbonate in the soil was not derived from the Liassic sediments. In the profile, the carbonate carbon can have three origins: (1) via vegetation, (2) Liassic carbonates and (3) atmospheric CO_2. Dissolution of Liassic carbonates occurs by rainwater and atmospheric CO_2. In a simple case of a closed system, the δ^{13}C of the resulting solutions can be calculated as an average of the two end-members (rainwater and atmospheric CO_2) (Rabenhorst et al., 1984) and is 2.2‰ PDB (this value is more positive in an open system case calculation).

$$\underset{-7‰}{CO_2} + H_2O \Leftrightarrow \underset{-5.9‰}{H_2CO_{3(aq)}}$$

$$+ \underset{+1.78‰}{CaCO_3} \Leftrightarrow Ca^{2+} + \underset{+2.2‰}{2HCO_3^-}$$

with

$$\varepsilon_{CO_{2(g)}-HCO_3^-} = +9.02‰ \text{ at } 15°C$$

(mean annual temperature of Tazouta)

with

$$\varepsilon_{CaCO_3-HCO_3^-} = +0.41‰ \text{ at } 15°C$$

The soil carbonates are highly depleted in ^{13}C compared to the above calculation. If we take in to account the fractionation that occurs during calcite precipitation at 15°C, the isotopic composition of the solutions in equilibrium with the profile carbonates will be of about −9‰ to −10‰ PDB. These values are within the range of the δ^{13}C values (−10‰ to −18‰ PDB) estimated for soil solutions developed in arid regions (Salomons et al., 1978). So, Liassic carbonates are not a major source of C, which may correspond to the local vegetation dominated by C3 plants. Contribution of this vegetation was estimated at around 80% of the total carbon on the basis of the

Table 2
Oxygen and hydrogen isotopic compositions (‰ relative to SMOW) of groundwater in the Middle Atlas

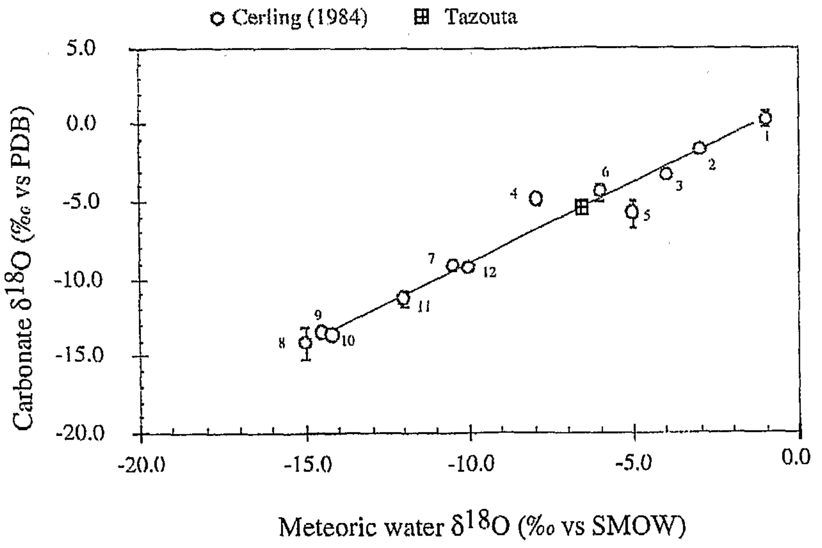
Samples	Nature	$\delta^{18}O$	δH
P1	well	−6.03	−39
P2	well	−5.41	−39
S1	spring	−6.07	−32
S2	spring	−5.78	−34.5

pedogenic carbonates $\delta^{13}C$ values. Carbonate dissolution–reprecipitation effects on carbon isotope composition of carbonate was not taken in to account in this estimation.

5.3.2. Mechanisms of carbonate precipitation

Pedogenic carbonate precipitation is generally considered to result from soil solution supersaturation due to evaporation/evapotranspiration and/or lowering of P_{CO_2} (Salomons et al., 1978). Oxygen and carbon isotope compositions of carbonates are sensitive to these processes.

The oxygen isotope composition of carbonates is determined by that of the rainfall and by local temperature. In the Middle Atlas, the $\delta^{18}O$ of rainfall is affected by elevation. In the highest Causse (Zad area 2200 m), rainfall $\delta^{18}O$ values average is −8.97‰ SMOW (Michelot et al., 1992). The altitudinal variation of 0.3‰/100 m given by Kabbaj et al. (1978) for the Middle Atlas was used to calculate the precipitation $\delta^{18}O$ within the Tazouta area (1400 m). The calculated value (−6.57‰ SMOW) is more negative than the value measured for the groundwater (Table 2). This difference can be attributed to the evaporation effect during infiltration. However, other factors such the seasonality of the rainwater composition must be analyzed in order to confirm this conclusion.



1 and 2 : Tanzania
3 : Kenya
4 : Holland
5 : Israel
6 : Iowa USA
7 : Dakota North USA
8 : Canada
9 : Alaska USA
10 : Utah USA
11 and 12 : Wyoming USA

Fig. 6. Position of Tazouta carbonate crust in a diagram of modern carbonates $\delta^{18}O$ vs. local meteoric water $\delta^{18}O$ (after Cerling, 1984).

In Tazouta carbonate crust, carbonates are essentially of the micrite type and precipitate by epigenesis of primary minerals. In the profile, carbonate $\delta^{18}O$ values are constant. This indicates that carbonate crust genesis occurs under stable environmental conditions. The average value of carbonate $\delta^{18}O$ is $-5.24‰$. If we assume that carbonate precipitation occurs at the beginning of summer at around 20–25°C, we can use the carbonate composition and the isotope fractionation factor water-calcite to calculate the meteoric water composition. The calculated value is around $-4‰$ to $-3.5‰$. The ^{18}O-enrichment in Tazouta carbonate crust is similar to that taking place in other carbonate crusts (Cerling, 1984; Cerling and Quade, 1993) as shown by the position of Tazouta site in the $\delta^{18}O_{\text{carbonate}}$ vs. $\delta^{18}O_{\text{meteoric water}}$ correlation diagram (Fig. 6).

6. Conclusion

In the Tazouta area, carbonate crusts are produced by replacement of basalt minerals and their weathering products by calcite. Smectitic weathering of basalt and carbonate accumulation occur as coupled mechanisms with strong and constant Ca enrichment within the profile.

Strontium isotope ratios and Ca flux calculations show that most Ca is of external origin originating from rainfall and from Liassic carbonate sources. Basaltic contribution to the carbonate crust genesis is negligible. The origin of carbonate crusts developed on these basalts is similar to that of those developed on Ca poor rocks such as granite and quartzite.

The Tazouta carbonate crust was developed under stable climatic conditions. ^{14}C data allow us to estimate an apparent rate (205 mm/ka) of carbonate accumulation. Carbon isotopes show that carbonate precipitation occurs in a system dominated by CO_2 derived from C3 vegetation.

The Ca rainwater budgets may include dissolved ions and solid dust particles. In this study, only dissolved Ca was determined, it will be interesting to establish the relative fluxes of dissolved Ca and carbonate particles and their relative contributions to calcrete genesis and isotope signatures. Also, other dating methods (i.e., U/Th desequilibrium) would be useful to constrain the real age of soil carbonates.

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