CARBONATE-SILICA CEMENTATION OF PLEISTOCENE FLUVIO-GLACIAL GRAVELS FROM DENMARK

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A carbonate cement of low-Mg calcite is described from Pleistocene fluvio-glacial gravels in sections of intermixed gravels and cross-stratified sands. The cement constists of a microcrystalline crust lining the pebbles and a drusy inward projecting crystal growth into the remaining pore volume. The cement is believed to have originated from ground water saturated with $CaCO_3$ deriving from dissolution of local Danian bryozoan limestone, Maastrichtian chalk and carbonate-rich moraines. The $CaCO_3$ was most likely precipitated by escape of CO_2 from solution favoured by the high permeability of the pebble beds close to the water table.

The extreme alkaline environment caused by the high carbonate content of the interstitial water resulted in partial replacement of quartz by calcite. Reprecipitation of the dissolved silica in the form of opal, partly as a rim around the remaining quartz grains, partly as a spongy mass interfingering with the calcite cement, may have been caused by fluctuations of pH. Associated with this precipitation of large quantities of silica there was also partial replacement by silica of limestone clasts.

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Carbonate cementation of Pleistocene fluvio-glacial gravels is a well known phenomenon. This sort of cementation has previously been reported from several localities in Denmark (Jessen, 1945; Nordmann, 1958). Outstanding localities are Åmølle, Grejs, Stentoft and Barsø in Jylland and Lille Dalby, Brorfelde and Sterkende on Sjælland (fig. 1). The consolidated gravels often have local names like "klipper", i.e. cliffs, caused by their prominent appearance in the landscape.

The locality particularly studied by the author is Åmølle situated 3 km south of Hadsund on the southern shore of Mariager Fjord. A section in fluvio-glacial sediments is here exposed in several small gravel pits as well as in a nearby road cut.

The cementation is best developed in the road cut. The section is about

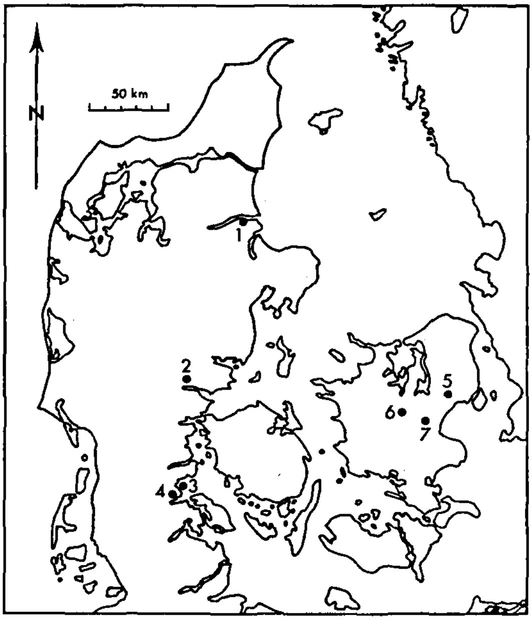

Fig. 1. Localities mentioned in the text. 1. Åmølle. 2. Grejs. 3. Barsø. 4. Stentoft. 5. Sterkende. 6. Brorfelde. 7. Lille Dalby.

10 m high and consists of a poorly sorted pebble bed situated between cross-stratified sands. The thickness varies from 1 to 5 m along a section of 100 m. The pebbles are a typical association of ice-transported rocks such as granites, gneisses, porphyrites, quartzites, chert, limestones etc., and they have all been extremely well rounded by the fluvio-glacial transport. The interstitial sands and silts which make up 40–50 wt % of the pebble bed are predominately composed of quartz grains.

The cementation has taken place exclusively in the pebble bed, which consequently is the most prominent horizon in the profile. The bed is consolidated but still so fragile that it can easily be broken into single pebbles. The carbonate cement consists of a microcrystalline calcite crust coating the pebbles and a drusy calcite cement in the remaining pore volume. In addition to the calcite cement a precipitate of silica is found interfingering the calcite crystals as a fragile spongy mass.

Material and methods

Samples were collected from the top, bottom and the central part of the pebble bed as well as from different locations along the sections.

Thin sections were examined under the light microscope between crossed nicols. The mineralogy and the chemistry of the cement were studied partly by staining (Feigl's solution and Alizarin Red S) and partly by use of atomic absorption spectrophotometry. The ultra- and microstructure were studied on fresh fractures as well as on polished and etched specimens with the scanning electron microscope (SEM). Etching was carried out by use of 10 % formic acid for 5 seconds. In some specimens the calcite cement was removed by 10 % HCl for 30 seconds for further examination of the silica precipitate.

The carbonate cement

The cement makes up 30–40 wt % of the total consolidated sediment mass of the pebble bed.

The calcite cement was identified by both staining and atomic absorption spectrophotometry to be low-Mg calcite throughout the section studied. According to atomic absorption spectrophotometry the Mg content is calculated to be approximately 0.1 wt % $MgCO_3$ whereas the Sr content is in the order of 0.02 wt % $SrCO_3$.

The fabric of the cement is composed of (a) a microcrystalline crust and (b) palisade calcite crystals.

The crust consists of optically non-oriented calcite crystals with a size range of 5–20 μm. The crust, which forms a coating on the non-carbonate clasts, may be up to 1 mm thick and causes the cohesion of the clasts and of the pebble bed as a whole.

The crust seldom occupies the entire primary pore volume. As a rule voids are partly filled in with a later cement formed by bunches of palisade calcite crystals projecting outwards with a preferred orientation of the longest axes normal to the crust (pl. 1, figs. 3, 5). The term palisade calcite cement is here used to describe elongate oriented crystals of sparry calcite cement. The most common crystal habits are trigonal prisms and steep positive and/or negative rhombohedrons. The longest diameter of the crystals ranges from 200 to 400 μm, whereas the shortest diameter varies from 50 to 100 μm. In the larger cavities, the crystals may obtain a length up to 1 mm. It is characteristic that the crystal size increases away from the crust.

A minor fraction of the clasts consists of Danian limestone and Maastrichtian chalk as well as bryozoan skeletons. In contrast to the non-carbonate clasts it is observed that the palisade calcite cement grows directly on the surface of the carbonate clasts without interjacent microcrystalline crust (pl. 3, figs. 3–4). The zooecia of the bryozoans are completely filled with sparry calcite cement (pl. 3, figs. 1–2). This cement most probably originated from diagenetic processes in the Danian and Maastrichtian sediments.

Quite commonly discontinuities in the cement are seen leading to second and third generations. The repetition always begins with a new microcrystalline crust followed by another palisade crystal growth (pl. 1, figs. 4, 6). The discontinuities are always parallel or sub-parallel to the surface of the clasts and perpendicular to the direction of growth. No more than three generations of cement have been observed in the material studied. The discontinuities can be followed over very short distances only, and are never seen lining all sides of a void. Serial sectioning also reveals that the discontinuities have a very restricted extension, usually only few mm^2. In order to reveal if periodical change in ion-composition of the ground water gave rise to the different generations, a rough estimation of the Fe^{2+} content was made by use of a staining solution of $K_3Fe(CN)_6$ in combination with Alizarin Red S (Evamy, 1963). The cement yielded a mauve stain indicating that the carbonate contains a relatively minor amount of Fe^{2+}, but no significant difference in Fe^{2+} concentration between the generations of microcrystalline cements and the palisade crystals was observed.

Replacement of quartz by calcite and precipitation of silica cement

Quite commonly a replacement of quartz by microcrystalline calcite cement is seen. This is indicated by extremely irregularly etched surfaces of the otherwise well rounded quartz grains in contact with the microcrystalline crust (pl. 1, fig. 2; pl. 2, fig. 3).

Silica occurs partly as a rim around some of the quartz grains (pl. 2, fig. 1), partly as a spongy mass filling fissures in the calcite crust (pl. 2, fig. 2) as well as in the open pore space interfingering the drusy calcite crystals (pl. 1, figs. 5–6). The silica also interfingers the sparry calcite cement in the bryozoan zooecia (pl. 3, figs. 1–2), and characteristically penetrates the porous limestone clasts (pl. 3, fig. 4).

This silica most likely originates from the dissolution of the etched quartz grains. The silica is believed to be opal because of the amorphous apperance in thin sections between crossed nicols, a refractive index as low as $n \sim 1.46$ and the low polishing relief compared to that of the quartz grains.

Removal of the calcite cement by HCl normally causes the pebbles to fall appart, showing that the silica cement plays only an insignificant part in the cohesion of the pebble bed.

Other localities

The localities mentioned in the introduction (Grejs, Stentoft, Barsø, Brorfelde, Lille Dalby and Sterkende) show the same phenomena of cementation as described from Åmølle (pl. 2, figs. 2, 5–6; pl. 3, figs. 2, 5–6). The cement is always restricted to the coarsest beds of the sediments. All the localities show replacement of quartz by calcite and reprecipitated silica, but the degree of replacement and the amount of silica and calcite cement varies considerably. Where large quantities of silica have been precipitated this occurs in a rigid framework in the pore space (pl. 2, fig. 6). Silicification may also result in partial replacement of limestone clasts by silica (pl. 3, figs. 5–6). Only skeletal calcite has resisted the replacement.

Discussion

The carbonate cement was precipitated from circulating ground water supersaturated with $CaCO_3$. However, the large quantity of $CaCO_3$ cement in the pebble bed rules out the possibility of leaching of the relatively thin superincumbent fluvio-glacial quartz sands as the only source of the carbonate. Carbonate in solution must consequently have been conveyed by lateral transport, and the possible carbonate sources are local Danian limestones, Maastrichtian chalks and carbonate-rich moraines. Danian limestone and Maastrichtian chalk form the substratum of the glacial sediments in this area and are exposed in several quarries in the neighbourhood.

Most probably the cementation has taken place in the phreatic zone where the pore space has been filled completely with water. The cement is evenly distributed in the pores and where the calcite cement does not occupy the entire pore volume the palisade crystals exhibit distinct euhedral crystal faces (pl. 1, figs 3–4). Moreover, the cement is distributed evenly from top to bottom of the pebble bed. There is no evidence of uneven style of cement, meniscus cement, which is characteristic for that formed in the vadose zone (Dunham, 1971; Schroeder, 1973). Neither has "gravitational" cement been observed as described by Müller (1971).

The consolidation is limited to the pebble bed, which is situated 2–4 m below the soil surface. The fluvio-glacial sands immediately below and above the bed are not affected by the cementation except at the contact zone. This feature shows that the high primary permeability has favoured the process of cementation of the pebble bed.

The different types of carbonate cements in relation to non-carbonate and carbonate clasts emphasize the importance of the substrate. The carbonate clasts act as nuclei for a growth of oriented palisade calcite cement. In the case of the non-carbonate clasts the first precipitated cement forms a microcrystalline crust lining the clasts. The oriented palisade crystals start to form upon the microcrystalline crust. The basal crust seems to be a necessity for the formation of the palisade cement, as no case of oriented crystal growth has been observed in direct contact with the surfaces of the non-carbonate clasts.

The presence of two or three generations of cement may be due to local insufficiency in nucleation. The restricted extension of the secondary microcrystalline crusts excludes the possibility of an overall insuffiency in supply of carbonate in solution or fluctuations in the ground water level. Neither do the contacts between the secondary microcrystalline crusts and the palisade cement show any signs of dissolution. The methods applied here do not reveal any chemical or mineralogical changes between the different fabrics. It is not probable that the secondary microcrystalline crusts are the result of recrystallization since the cement, i.e. the crusts as well as the palisade crystals, were precipitated from meteoric water. The fact that the surfaces of the secondary crusts always are situated perpendicular to the direction of growth emphasizes that the discontinuities are related to growth and not to filling of cracks or recrystallization along planes of stress. The interruptions in nucleation must have taken place under such physical and chemical circumstances that it was impossible to continue the growth on the already existing crystal faces. The processes which prevent such a continuous crystal growth are not understood.

The replacement of quartz by calcite can be caused by extreme alkaline conditions in the interstitial water. It is a well known phenomenon that precipitation of calcite is associated with instability of silica. Laboratory data (Krauskopf, 1959) indicate that the solubility of silica at normal temperatures increases rapidly at pH values 9 and higher. The solubility of $CaCO_3$, however, decreases with increase in pH. Moreover, rising temperature increases the solubility of silica whereas the opposite is the case for $CaCO_3$. This inverse relationship in solubility of silica and $CaCO_3$ with change in pH and temperature as the most important factors was demonstrated by Correns (1950) and Okamoto et al. (1957) (compare Fairbridge, 1967; Dapples, 1967 a, b; Gavish & Friedman, 1969).

Alimen (1958) described from the Pliocene and Pleistocene of Sahara a sediment type, the "meuliéres", the fabric and mineralogy of which seems to be in principle similar to that of the consolidated gravels here studied. The basic material is an eolian sediment predominately composed of quartz, which partially is dissolved and replaced by calcite cement and secondary silica (identified as chalcedony). An intergrowth between calcite and silica was demonstrated as well. Alimen (1958) suggests rapid evaporation of the interstitial fluid owing to intense insolation as the reason for the alkaline environment necessary for calcite-silica replacement. This cannot be a valid explanation for the genesis of the sediment here studied as the cemented gravel is covered by several meters of glacial sand.

Theoretical and experimental data of Garrels (1960) show that a system containing $CaCO_3$ in water in equilibrium with the CO_2 pressure of the atmosphere has a pH of 8.4. Of special interest is that pure deaerated water in equilibrium with $CaCO_3$ has a pH in the range of 9.8–10.0. Most pH analyses of water in nature never reach values so high even in carbonate-rich environments. But this may well reflect insufficient methods of pH measurements of interstitial water permitting the sample to attain CO_2 equilibrium with the atmosphere (Garrels, 1960; Walker, 1962).

The silicification-desilicification and carbonate cementation here described in fluvio-glacial gravels indicate that high alkaline conditions may occur in epidiagenetic processes in a temperate humid climate. Composition and fabric of the void filling minerals (intergrowth between silica and carbonate) would indicate that the interstitial water has been saturated with $CaCO_3$ and the acidity has fluctuated around pH 9.

Silica-carbonate replacement reversals as described by Walker (1962) have not been observed although such reactions would be possible under the chemical conditions inferred. The silica seems to be present in the voids between the crystals of the calcite cement only, and it is observed that the interface between the palisade calcite crystals and the silica are smooth without any sign of dissolution or replacement. Where the spongy mass of silica is in contact with the microcrystalline crust it has not been possible to reveal if any replacement has taken place. The replacement of the carbonate clasts by silica indicates, however, the probability of replacement reversals in the interplay between silica and microcrystalline crust.

Dansk sammendrag

Forekomsten af kalkcementerede pleistocæne fluvio-glaciale grusaflejringer er forholdsvis hyppige i Danmark. Kalkcementen består af lav-magnesium kalcit. Der kan skelnes mellem to strukturelle typer. Den primære cement består af en mikrokrystallinsk skorpe, der omgiver og sammenbinder de enkelte klaster. I det øvrige porevolumen ses en delvis udfyldning af en sekundær euhedral krystalvækst hovedsagelig bestående af trigonale kalcitprismer. Kalkcementen formodes afsat af cirkulerende grundvand mættet med $CaCO_3$.

Den mikrokrystallinske kalcit ses delvis at replacere kvartskornene i det sammenkittede sediment. Den opløste kisel genafsættes som opal omkring kvartskorn og som

en svampet masse i revner og hulrum i kalcitcementen. Denne sammenvoksning af kisel- og kalcitcement i porevolumenet skyldes formodentlig extremt basiske forhold i porevandet med pH værdier svingende omkring 9.

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Plate 1

Fig. 1. Quartz grains cemented by microcrystalline calcite crust. Fracture surface. Åmølle (SEM) × 45.

Fig. 2. Supposed replacement of quartz by microcrystalline calcite (arrows). Polished and etched section. Åmølle. (SEM) × 200.

Fig. 3. Palisade calcite cement showing trigonal prisms. Åmølle. (SEM) × 60.

Fig. 4. Repeated calcite cementation. Palisade calcite crystals separated by a microcrystalline calcite crust (arrows). Fracture surface. Åmølle (SEM) × 45.

Fig. 5. Microcrystalline calcite and palisade calcite crystals in intergrowth with silica. The microcrystalline crust (c) lines the quartz grains (q). Note the palisade calcite crystals partially filling the remaining pore space. The silica (s) is seen to envelope the calcite crystals. Polished and etched section. Åmølle. (SEM) × 400.

Fig. 6. Repeated calcite cementation. Palisade calcite cement (pc). Microcrystalline crust (c). The direction of growth is toward the left in the picture. Polished and etched section. Åmølle. (SEM) × 200.

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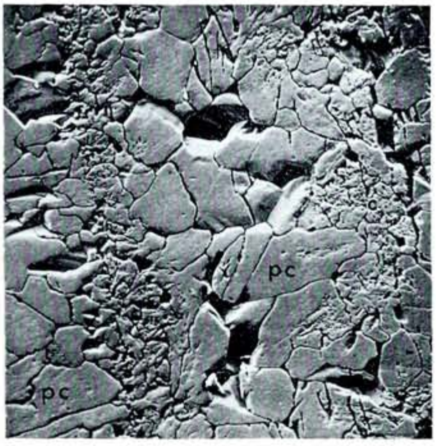

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Plate 2

Fig. 1. A silica rim (s) which has enclosed a lost quartz grain. The silica shows irregular contact with the microcrystalline calcite crust (c). Polished and etched section. Åmølle. (SEM) × 50.

Fig. 2. Spongy mass of precipitated silica between two quartz grains (q). Polished section where the calcite has been removed by HCl. Lille Dalby. (SEM) × 200.

Fig. 3. Polished section where the calcite has been removed by HCl showing the deeply corroded surface of a quartz grain. Åmølle. (SEM) × 100.

Fig. 4. Intergrowth of silica (s) and microcrystalline calcite (c) between two quartz grains (q). The silica has a low relief compared to the detrital quartz. Polished and etched section. Åmølle. (SEM) × 1000.

Fig. 5. The spongy mass of silica (s) in contact with the etched surface of a quartz grain (q). The calcite cement has been removed by HCl. Fracture surface. Lille Dalby. (SEM) × 850.

Fig. 6. Example of large scale precipitation of silica. The silica (s) forms solid continuous framework in between the quartz grains (q). Polished and deeply etched section. Brorfelde. (SEM) × 50.

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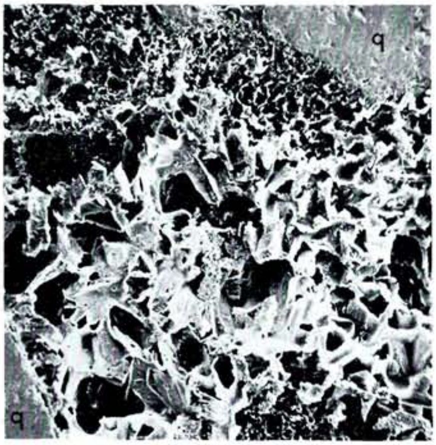

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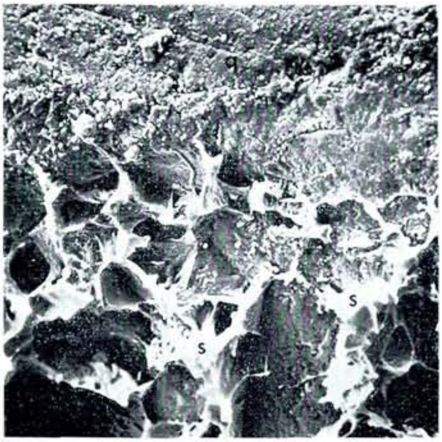

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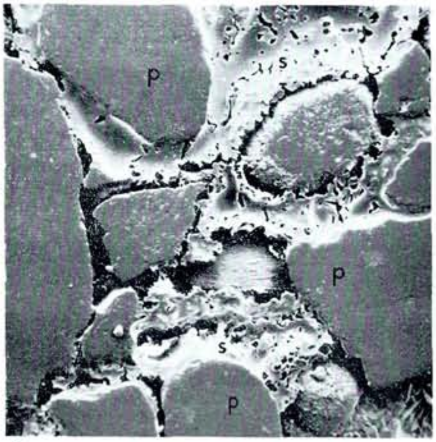

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Plate 3

Fig. 1. Bryozoan skeleton fragment as clast in glacial gravel. The zooecia are filled with sparry calcite cement (sc) which is penetrated by silica (s). Polished and deeply etched section. Åmølle. (SEM) × 100.

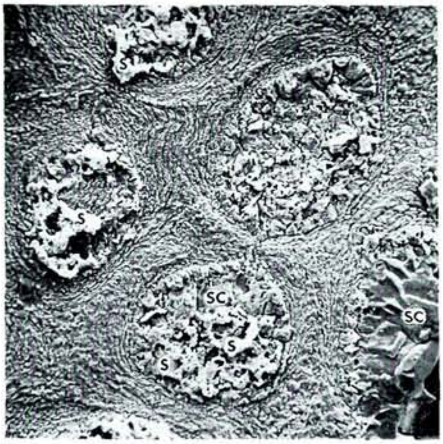
Fig. 2. Bryozoan skeleton fragment as clast in glacial gravel. The zooecia are filled with sparry calcite cement (sc) which is penetrated by silica (s). Note the casts of the trigonal calcite prisms formed by the silica (arrows). Polished and deeply etched section. Lille Dalby. (SEM) × 290.

Fig. 3. Interface between bryozoan skeleton fragment (b) and palisade calcite cement (pc). Note the sharp boundary without interjacent microcrystalline crust. Polished and deeply etched section. Åmølle. (SEM) × 500.

Fig. 4. Interface between limestone clast (lc) and calcite cement (pc). The boundary is sharp without interjacent microcrystalline crust. Note the silica (s) in the porous limestone clast. Polished and deeply etched section. Åmølle. (SEM) × 420.

Fig. 5. Example of large scale silification. The major part of the limestone clast (lc) is replaced by silica. The skeletons only have resisted the silicification. The limestone clast is surrounded by calcite cement (c) in intergrowth with silica (s). Polished and deeply etched section. Lille Dalby. (SEM) × 200.

Fig. 6. Detail of fig 5. The almost silicified limestone clast contains a foraminifera test and a skeleton fragment, which have resisted the replacement. Polished and deeply etched section. Lille Dalby. (SEM) × 1000.



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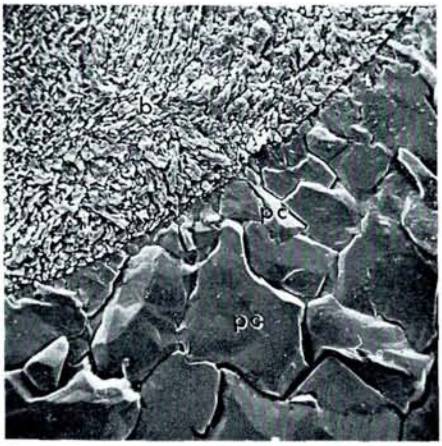

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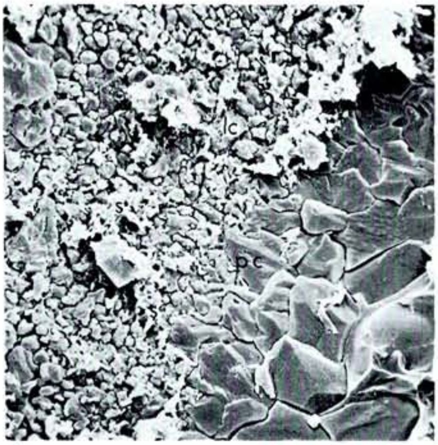

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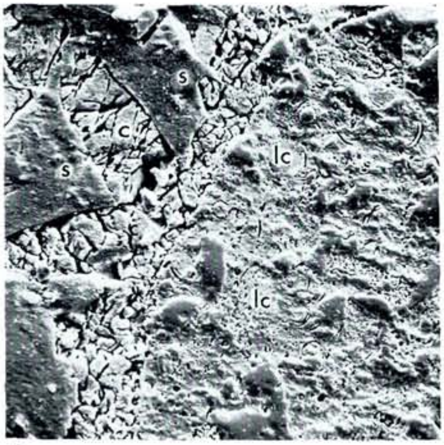

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