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Dissolution and formation of quartz in soil environments: a review

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Abstract

The dissolution of quartz in soils is reviewed following brief consideration of the mineral's structure and chemistry, particularly emphasizing the effects of defects and dislocations at the crystal surface. Experimental dissolution investigations, usually under hydrothermal conditions, suggest that the principal factors controlling or inhibiting quartz dissolution are pH, and the concentrations of dissolved silica, alkali and alkaline earth cations, organic acids and aluminium and iron species in the external solution. The application of these factors to natural pedogenic environments is reviewed in the context of the orders of Soil Taxonomy, as revealed mainly by SEM observations of surface etching features in different horizons of the soil profile. For soils of a non-residual, alluvial nature it is possible that quartz grains will have been through several weathering cycles, leading to difficulties in interpretation, as both fresh and highly weathered quartz grains may occur in intimate admixture. However, where the soil is residual and directly related to the underlying parent rock, then it may be possible to relate the nature and extent of the dissolution features on quartz to the prevailing pedogenic regime and the principal chemical factors that have been explored experimentally. The formation of quartz in soils is controversial, although it is well-embedded in the soil science literature. In most soils, quartz dominates in the sand and silt fractions and is undoubtedly of inherited origin deriving ultimately from igneous and metamorphic rocks. Criteria that could be used to confirm the pedogenic formation of quartz in soils include separation of perfect unetched euhedral quartz crystals with an appropriate isotope composition confirming their low temperature origin. Experimental low temperature synthesis of quartz spans a time scale ranging from five years to millions of years and a critical analysis of the literature suggests that the latter is a more realistic assessment.

1. Introduction

Quartz is undoubtedly the most common mineral at the Earth's surface, whether in rocks, weathering profiles, sediments or soils, especially those of a sandy texture. Yet despite the universality of this mineral in surface environments, there are still certain aspects of its dissolution behaviour that are not yet fully understood, particularly with respect to the various physical and chemical conditions that may occur in different types of soils. It is the purpose of this review to consider the dissolution of quartz in the context of its structure and surface chemistry, taking account of the many experimental studies that have been made and considering how these may be applied to what has been observed in the natural soil environment.

With respect to the formation of quartz in soils as a secondary pedogenetic phase, this topic is critically reviewed, focusing on the empirical evidence that has been presented in the literature. It is concluded that such evidence is inconclusive or even negative, except in some exceptional cases.

2. Structure and chemistry of quartz

The essential building blocks of quartz consist of SiO_4 tetrahedra where every oxygen is linked to a silicon atom in a neighbouring tetrahedron, thus forming a framework or tectosilicate structure with an overall chemical formula of SiO_2. A *c* axis projection of this structure brings out its apparent hexagonal symmetry as well as the open channels that run parallel to the *c* axis. On the other hand, when the structural motifs are projected along the *a* axis, then a layer-like arrangement becomes apparent in which the silicon atoms are arranged in parallel horizontal planes (Achavan, 2013).

The compact structure of quartz suggests that there is limited opportunity for the incorporation of impurity elements, and these usually occur in trace to very minor amounts. However, as noted above the structure is characterized by the occurrence of channels running parallel to the *c* axis and these channels are wide enough to accommodate small cations such as Al^{3+} and Na^{+}. Aluminium is the most abundant impurity element in quartz (<

15–15,000 ppm), followed by Na (9–1420 ppm) and K (3–290 ppm (Heaney, 1994). Other less abundant elements include Ti, Fe, Li, Mg, Ca and H. If Al^{3+} occurs as a structural substituent for Si^{4+} then overall electrical neutrality may be maintained by the incorporation of univalent cations such as Li^+ or Na^+ within the *c* axis parallel channels.

Cathodoluminescence (CL) studies, combined with other investigative techniques, have shown that different luminescence colours and emission centres can be attributed to different kinds of structural defects in quartz, which in turn relate to the trace elements incorporated within the mineral (Götze et al., 2001). These authors listed several emission bands that could be related to incorporation of impurity elements including Li, Na, Al and Ti at various defects or vacancies.

Infrared spectroscopy has shown that the external surface of crystalline quartz is characterized by silanol (Si-OH) groups, which effectively replace siloxane groups in the more highly strained surface environment (Kronenberg, 1994 and references therein). At the fresh mineral surface, the silanols occur in isolated sites at first but later link through hydrogen bonding with other adjacent silanols or with adsorbed water molecules eventually to form clusters. According to Kronenberg (1994), the surfaces of crystalline quartz in nearly all geological environments may be expected to be silanol-saturated, which would eventually lead to a continuously bonded surface layer of water. In the more hydrous and less highly crystalline forms of silica, such as opal, adsorbed water may occur in continuous films, consisting of several ordered layers of molecular water that differ from liquid water in both their structure and properties. It is not certain to what extent this is true of quartz, but in any event the external surface of crystalline quartz particles in soils may be expected to participate, even if only to a very small extent, in adsorption and exchange reactions and in dissolution processes.

3. Defects and Dislocations

The three-dimensional framework configuration of the SiO_4 tetrahedra in quartz appears to have no obvious planes of weakness and indeed the mineral is characterized by lack of cleavage. It can be readily envisaged, therefore, that quartz is fundamentally resistant to decomposition through weathering. Nevertheless, nearly all naturally crystalline minerals exhibit imperfections in their structure to a greater or lesser extent and quartz is no exception to this generalization. The characterization of such defects is important because their intersection at the surface of a mineral creates points of high surface energy that are more susceptible to dissolution. This is usually manifested by the appearance of etch pits, as has been illustrated by many studies. For example, Yanina et al. (2006) reacted euhedral quartz with aqueous KOH solutions in a hydrothermal bomb at 400°K and found that the prismatic faces of the quartz crystal etched at nearly two orders of magnitude faster than the rhombohedral faces. This was attributed to differences in the densities of defects emerging at the different crystallographic faces.

In general, the defects in crystal structures have been classified as point defects, line defects and plane defects. Point defects can be associated with impurity ions which occur either as structural substituents or in interstitial sites. Structural vacancies, voids and fluid inclusions at a variety of scales can also be broadly considered as point defects. In addition, hydrogen in the form of H^+, OH^- and H_2O can be incorporated into the quartz structure in various forms, disrupting the Si–O bonds and leading to hydrolytic weakening (Griggs, 1967; McLaren et al., 1983; Stenina, 2004).

Line defects, or dislocations, involve lines in the crystal where the atoms are displaced with respect to their normal positions and where the inter-atomic bonds are so distorted as to represent a zone of weakness that enables selective dissolution to occur, or movement when stress is applied. Such defects have been implicated in the aqueous solubility and mechanical behaviour of quartz (Wintsch and Dunning, 1985; Doukhan, 1995). Finally, plane defects involve a mismatch of crystal structure across a surface, as represented, for example, by adjacent compositionally different domains, twin planes or even grain boundaries. Etching of quartz along twin boundaries was illustrated by Yanina et al (2006).

4. Experimental studies of quartz dissolution

The solubility of quartz in water at circum-neutral pH values ranges between 3 to 11 mg Si/L (Monger and Kelley, 2002). Morey et al. (1962) determined a probable solubility for quartz at 25°C of 6 mg Si/L, whereas Rimstidt (1997) determined a quartz solubility of about 11 mg Si/L. The lowest solubility of 3 mg Si/L at ambient temperature is based on the work of Siffert (1962). These determinations were generally made using bulk methods so that the dissolution mechanisms involved were deduced in an indirect way. Since the 1980's, however, the emphasis has been on the processes that occur at the grain surfaces and that control the overall dissolution kinetics of the mineral. Such surface features have been characterized by scanning electron microscopy (SEM) and later by atomic force microscopy (AFM).

Following recognition of the potential importance of specific active sites at grain surfaces in the weathering and dissolution of feldspar minerals, as revealed by etch pits relating to the emergence of structural dislocations and defects (Wilson, 1975; Berner and Holdren, 1977) – as opposed to dissolution through a more or less uniform leached layer – there has been much research directed at clarifying the details of the dissolution process in a quantitative way. Central to this research has been the identification of the factors that either inhibit or enhance the rate of mineral dissolution so that these factors can be applied to systems of geological interest such as the natural weathering that occurs in rocks and soils.

With regard to the rate of dissolution of quartz, one of the first aspects to be investigated was the influence of the pH of the aqueous solution (Brantley, 2005). At 25°C the minimum dissolution rate occurs at pH values close to the point of zero charge ($10^{-12.7}$ mol quartz m^{-2} s^{-1} in the pH range of 4–6). Dissolution rate increases linearly under both acid and alkaline conditions. At pH 2 the rate is $10^{-12.0}$ mol quartz m^{-2} s^{-1} while at pH 10 the rate is $10^{-11.0}$ mol quartz m^{-2} s^{-1}, indicating that quartz is more soluble under alkaline conditions.

The influence of the dissolved silica concentration under hydrothermal conditions (300°C) on the dissolution rate of quartz, as revealed by etch pit formation, was explored by Brantley et al. (1986). They established that there was a critical concentration (C_{crit}) of dissolved silica in the external solution, above which etch pits would not form, or formed at a much-reduced rate, and that under their experimental conditions the value of C_{crit} was about 0.75 of the equilibrium concentration (C_0) of quartz. The value C/C_0 was referred to as the "saturation index" and where the solution concentration C was low and far from equilibrium then the rate of etch pit formation was more rapid.

At this point, however, it was not clear to what extent etch pit dissolution contributed to the overall dissolution rate of quartz and to clarify this issue Gaultier et al. (2001) studied the dissolution of quartz at 200 to 250°C for a period of over a year under far from equilibrium conditions, at the same time observing the development of etch pits and other surface features. They showed that although the dissolution rates remained constant during the experiment, the surface area of the dissolving quartz increased by more than five times. As the surface area was determined by the adsorption of krypton gas molecules, it therefore included the contribution of etch pits and other surface roughness features. These findings were interpreted as indicating that most of the increase in surface area was due to relatively unreactive etch pit walls which did not therefore contribute significantly to the overall dissolution rate. It was also concluded that non-etch pit surfaces at edges and corners dissolved faster than the surfaces associated with etch pits. These findings have been supplemented by recent theoretical and experimental studies which view mineral dissolution surface processes as the exact reciprocal of mineral growth surface processes (Dove et al., 2005; Dove and Han, 2007). The basic elements of classical crystal growth theory were outlined by Cabrera et al. (1954) and Cabrera and Levine (1956) more than fifty years ago but were only applied to "reversed" mineral dissolution processes relatively recently. The concept views both growth and dissolution processes at crystal surfaces as proceeding by overcoming the same energy barriers that are controlled by parameters related to temperature, saturation, surface energy at step or dislocation features, and a kinetic coefficient related to these features (Dove and Han, 2007, Fig. 1a and b).

Dove and Han (2007) characterized the prismatic face of crystalline quartz by AFM images during aqueous dissolution at near neutral pH at 200°C with increasing levels of silica under-saturation, designated Ω, which essentially describes the chemical driving force of the dissolution process. Under near equilibrium conditions (Ω = 0.90) no etch pits were observed but at far from equilibrium conditions (Ω = 0.10) large etch pits with sloping sides became apparent. However, when electrolyte (0.0167 M $CaCl_2$) was added to the solution then dissolution rate was increased and showed the following features with increasing levels of under-saturation. At Ω = 0.90, no pits were observed, only straight edged steps, at Ω = 0.65 the surface was dominated by large and small flat-bottomed pits and at Ω = 0.10 there was a higher density of these pits with more steeply sloping sides. Dove and Han (2005) described the dissolution process of quartz at increasing levels of under-saturation in an electrolyte solution as progressing with increasing dissolution rate through the following consecutive steps: step retreat → etch pits at dislocations → nucleation of small pits at impurity defects → nucleation of a dense covering of small pits at 2D vacancy islands.

The enhancement of the dissolution rate of quartz in aqueous solutions containing weak concentrations of the commonly occurring alkali and alkaline-earth cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) has been known for some time but the mechanisms involved have remained obscure. The quartz dissolution experiments of Dove and Nix (1997) in weak solutions of alkali and alkaline-earth chlorides at 200°C yielded results that were consistent with their hypothesis that the enhancement of dissolution rates of quartz could be attributed to reactions at the mineral-solution interface involving increased rates of solvent exchange and rupture of Si–O bonds. Furthermore, their experiments showed convincingly that preferential dissolution was associated with various types of structural defect emerging at the crystal surface. Using a new spectroscopic technique to analyse surfaces and interfaces termed vibrational Sum Frequency Generation (vSFG), Dewan et al. (2017) obtained results on the effect of salt on the enhancement of silica dissolution over a range of pH values that fully support the concepts of Dove and her colleagues (Dove and Han, 2007; Dove and Rimstidt, 1994).

Other factors that may influence the dissolution rate of quartz include the presence of organic acids, as well as dissolved aluminium and iron species in the external solution (Dove and Rimstidt, 1994). Thus, Bennett and Siegel (1987) described a natural situation following an oil spill into a sandy aquifer where the etching of quartz grains appeared to be more intense wherever concentrations of dissolved organic carbon (DOC) were highest. They suggested that an enhanced dissolution of quartz was brought about by the effective complexation and mobilization of silica by organic acids, thus lowering the activity of dis-

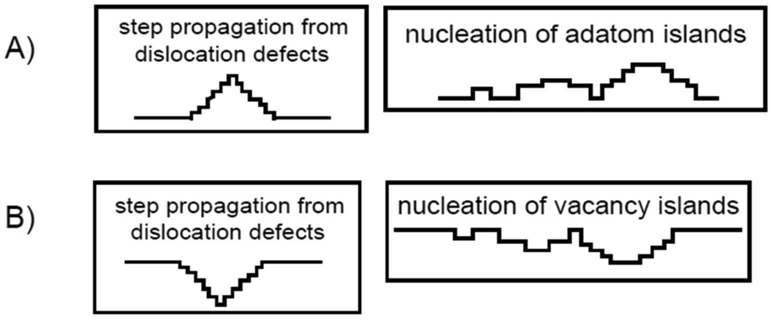

Fig. 1. Sketch showing the reciprocal relationship between (A) mineral growth processes and (B) mineral dissolution processes on the same crystal face. Reproduced from Dove and Han (2007), with the permission of AIP Publishing

solved silicic acid and leading to a far-from-equilibrium system. This reaction was thought to occur in waters close to neutral pH. Bennett et al. (1988) provided experimental evidence to show that dilute solutions of oxalic and citric acid significantly increased the solubility and dissolution rate of quartz at surface temperatures and near neutral pH conditions. The mechanism involved was thought to involve a surface complex between the organic acid anion and the silica surface, either directly through the framework Si–O–Si bonds or indirectly through the silicic acid adsorbed at the quartz surface. These mechanisms were considered only as hypotheses by Drever and Stillings (1997), as it seems that the oxalate anion does not adsorb to silica surfaces, although the enhancing effect of oxalate on the rate of quartz dissolution is real (Blake and Walter, 1999), provided that the concentration of oxalate is greater than about 1 mM. Although such concentrations are rarely encountered in bulk soil solutions (Drever and Stillings, 1997), the situation could be different in the rhizosphere and in other micro-environments within the pore structure of the soil.

The effect of dissolved Al in aqueous solutions in experiments aimed at understanding the dissolution behaviour of quartz has been long accepted as greatly decreasing its solubility and rate of dissolution (Dove and Rimstidt, 1994 and references therein). However, experiments by Dove and her colleagues (Dixit et al., 1995; Kumar and Dove, 1996; Kumar et al., 1996) indicated rather modest rate-inhibiting effects on quartz dissolution at acid and near neutral pH values (pH 4.0–6.5) which could be accounted for by the precipitation of amorphous aluminium compounds on the mineral surfaces, thus isolating them to a degree from the external solution. But at alkaline pH values, Bickmore et al. (2006) showed that the $Al(OH)_4^-$ anion had a much more inhibitive effect on the rate of quartz dissolution. Thus at pH 10–13 and at $Al(OH)_4^-$ concentrations below gibbsite solubility, quartz dissolution rate was decreased by up to 85% and the effect became even greater at lower pH values and higher $Al(OH)_4^-$ concentrations.

Regarding the effect of dissolved iron species on the aqueous solubility of quartz, Dove (1991) commented that they inhibit quartz dissolution at very low concentrations, although Morris and Fletcher (1987) found that quartz solubility increased over the pH range 4 to 8.6 in solutions containing ferrous iron and sodium. The effect became particularly marked after an initial period of oxidation, although it is presently uncertain as to whether these findings can be widely generalized to the soil environment.

5. Dissolution of quartz in different soil types

The preceding brief review of some experimental studies of quartz dissolution has highlighted the influence of several factors that may either inhibit or enhance the dissolution of the mineral in the earth surface environment. These factors include pH, and the concentrations of dissolved silica, alkali and alkaline-earth cations, organic acids, aluminium and iron species in the external solution. The question to be discussed here is to what extent these factors can be related to the dissolution features observed by SEM on quartz grain surfaces in the various horizons of different soils, particularly those of the Orders of Soil Taxonomy (Soil Survey Staff, 2014). It may be noted that this relationship may be anything but straightforward because many, probably most, soils are developed upon non-residual, alluvial-type material and here it is possible that many quartz grains will have been through a variety of weathering cycles. In these circumstances, it might be anticipated that completely fresh and highly weathered quartz grains may occur in intimate admixture. Where the soil is of a residual nature, however, and is directly related to the underlying parent rock then in principle this difficulty should not arise and it may be possible to relate the nature of the dissolution features on quartz grains to the physicochemical conditions that exist in the various horizons of the soil, although in such a case the age of the weathering profile would also have to be taken into account.

Brantley et al. (1986) studied the dissolution features on quartz grains in a residual Oxisol developed on granite in Venezuela. They observed a change from angular and etched surfaces at the top of the profile, where a substantial fraction of quartz was weathered out, to rounded quartz without etching at the base of the profile. This was related to probable changes in the Si concentration of the soil solution, with $C > C_{crit}$ at depth and $C << C_{crit}$ at the surface. Similarly, Schulz and White (1999) studied the weathering of quartz in a residual Ultisol in Puerto Rico that was developed on a deeply weathered granitoid rock with a saprolite extending to 8 metres. They found that the Si concentration in pore water increased with depth and that more abundant etch pitting of quartz occurred in the upper part of the saprolite compared with the lower part, again relating this to under-saturation and over-saturation of solute silica with respect to quartz solubility in the pore water in the upper and lower parts of the weathering profile respectively. These examples from the natural weathering environment are thus broadly consistent with the experimental and theoretical studies obtained under hydrothermal conditions on quartz solubility, particularly emphasizing the effect of Si concentration in the external solution (Brantley et al., 1986; Schulz and White, 1999).

This simple picture is not so obvious in other studies of dissolution features on quartz grains within deeply weathered residual profiles, suggesting the involvement of other factors such as the length of time during which weathering has been operative. Thus, Eswaran and Stoops (1979) observed that, in a weathering profile developed to a depth of 19 metres on granite in Malaysia, quartz grains became visibly etched at 18.5 metres depth and strongly etched at 9.5 metres depth, observations that accord well with those of the later findings of Brantley et al. (1986) and Schultz and White (1999). Eswaran and Stoops (1979) also observed that the quartz grains in Ultisols and Oxisols in Malaysia, Zaire (Democratic Republic of Kongo) and Angola were generally highly etched except where grain surfaces were coated with clay. Asumadu et al. (1987) studied the surfaces of quartz grains in sandy Oxisols on the lateritised Old Plateau surface in Western Australia and found that all were heavily etched.

For soils with a high level of base saturation, such as Alfisols and Mollisols, it is likely that the enhancing solubility effect on quartz grain surfaces of Ca^{2+} and Mg^{2+} cations in the soil solution will play a prominent role in influencing the extent of surface corrosion. White (1981) studied the extent of quartz weathering in Alfisols developed on a chronosequence of river terraces in California ranging in age from 22.7 ka to 63.3 ka BP. He found that dissolution features became more complex with depth, particularly in the C horizons of the soils on the oldest terraces, which would likely have the highest levels of base saturation in the soil profile. Douglas and Platt (1977) observed rounded surface irregularities and solution pits in quartz grains separated from an Alfisol developed on Illinoian till in Pennsylvania and concluded that although the quartz grains from the surface horizons of younger soils were somewhat more weathered than those from B and C horizons, in older soils developed on Kansan till there was little difference. Black and Dudas (1987) found that in prairie soils in Alberta, Canada, described as Chernozem, Luvisol and Solonetz, probably falling into the Mollisol and Alfisol orders of Soil Taxonomy, there was little significant difference in quartz weathering between the A and C horizons. It was suggested, however, that many of the dissolution features observed could be relicts of previous weathering cycles and were not related to current pedogenesis.

In general, Spodosols, when developed upon sandy parent material, are usually freely draining and acidic, with both soil and soil water pH values in the 4 to 5 range or even lower, and with a profile showing an accumulation of organic matter at the surface (O horizon), followed by a leached/eluviated, light coloured horizon (E), below which there is a distinct brown horizon (B_s) marked by an accumulation of sesquioxides (Al and Fe). Throughout the profile, the soil exchange complex is dominated by H^+ and protonated Al species and concentrations of exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ are extremely low. Ionic Al is usually low in the E horizon because most Al and Fe species enter into organic complexes which are then leached down the profile. These complexes are thought to be microbially degraded in the illuvial horizons leading to an accumulation of poorly ordered, inorganic Al and Fe compounds. Concentrations of ionic Al may therefore increase in soil water in the B and C horizons following degradation of the organic complexes. Bearing in mind the experimental factors identified above that are relevant to quartz dissolution, it is probable that in Podzol A horizons such dissolution is related to low pH, high concentrations of acidic organic anions and far from equilibrium Si concentrations, as the system may be a relatively open one. The enhancing dissolution effect of alkali and alkaline-earth cations would be likely to be negligible, as would the inhibiting effect of ionic Al, at least in E horizon.

Little et al. (1978) studied the dissolution features on quartz grains from dune sands of various ages (0, 145, 400 and >400 ka respectively) on which Spodosols had developed in eastern Australia. The influence of quartz microstructure was emphasized as a major factor influencing quartz dissolution, particularly where microcrystalline quartz had developed a saccharoidal structure. Asumadu et al. (1988) also studied quartz etching in sandy Spodosols developed on the Darling Plateau in South Australia. Etching was extensive at both surface and sub-surface levels of the soil profile, with an abundance of rectangular and triangular etch pits, probably representing pyramidal and rhombohedral facial planes as illustrated by Yanina (2006). Distinctive tessellated features were also observed, superficially resembling quartz overgrowths but probably forming at the intersections of parallel sets of planar microfractures and again highlighting the influence of microstructure on surface dissolution.

It is of interest, however, that in Spodosols in Scotland SEM observations of separated sand fractions often reveal extensive corrosion of quartz at all levels within the profile. Fig. 2 shows SEM images of surface features of quartz grains separated from a peaty gleyed Spodosol (Nethy No. 1) developed on fluvioglacial sands in north-east Scotland. Fig. 2a and b shows a quartz grain surface from the Eghorizon (pH_{H2O} 4.2) that is characterized by a series of distinctive steps, which could perhaps be interpreted as developing from microfractures as described above. However, the appearance of trenches and other irregularities in the grain surface (Fig. 2a) as well as the etch markings and shallow pits on all the individual steps (Fig. 2b) are clearly indicative of dissolution that is affecting the entire grain surface. This would be consistent with the intense weathering and leaching that is presumed to take place in the Spodosol A horizon. In the B2 horizon, the quartz grain surfaces are coated with amorphous aluminium and iron compounds (Fig. 2c and d) which extends into the upper part of the B/C horizon (pH 5.2). Remarkable dissolution features on quartz grain surfaces can be observed in this horizon, including individual deep etch pits and linear trenches which are made up of smaller but closely connected etch markings (Fig. 2e and f). Similar features were observed on quartz grains separated from the Cg horizon (pH 5.9) of an imperfectly drained iron Spodosol (Borrohill No. 2) developed on granitic material. Some of these grains appear to be almost completely unweathered, with clean surfaces and etching confined to rather small areas (Fig. 3a and b), but others are intensely corroded to such an extent that flaking of the grain surface can be readily envisaged (Fig. 3d and e). Even poorly drained non-podzolic soils in north-east Scotland contain quartz grains characterized by well-defined dissolution features. Thus Fig. 4 shows that the surface of quartz grains separated from the Bghorizon (pH 6.1) of a peaty gley soil (Drumlassie No. 3), developed on granitic parent material, is intensely corroded with deep etch markings.

The finding that highly corroded quartz grains commonly occur in gleyed subsoil horizons in the soils of north-east Scotland cannot easily be related to any of the factors that enhance quartz solubility as determined by laboratory experimentation. Soil pH values are not inordinately low, suggesting that high concentrations of acidic organic anions do not occur, and probably the imperfect drainage or gleyed nature of the soils suggests that concentrations of dissolved silica in the soil water will be at over-saturation levels with respect to quartz dissolution. It is possible, however, that the observed dissolution features have been inherited from the effects of former weathering cycles. It may be noted that there is abundant evidence of the influence of pre-glacial weathering on the clay mineralogy of soils in north-east Scotland (Wilson et al., 1984) and that the clay fractions of the gleyed horizons described above contain moderate amounts of kaolinite and halloysite, which are unlikely to have formed under the current poorly drained conditions.

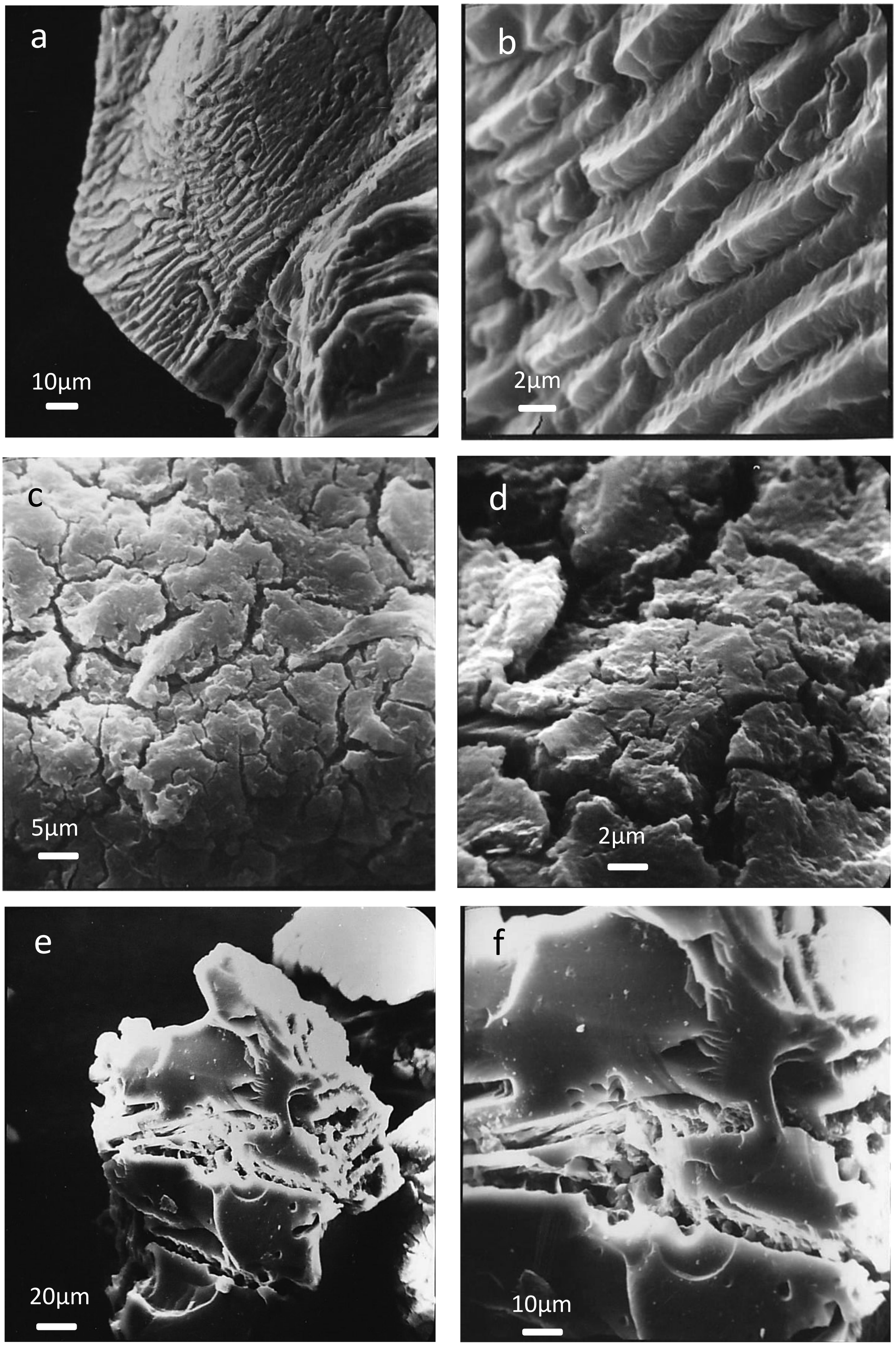

Fig. 2. SEM images of quartz grains from a peaty gleyed Spodosol (Nethy No. 1) showing (a–b) distinctive etched steps in the Eg horizon, (c–d) coatings of amorphous aluminium and iron compounds in the B2 horizon and (e–f) deep etch pits and linear trenches in the B/C horizon. Figure made by author

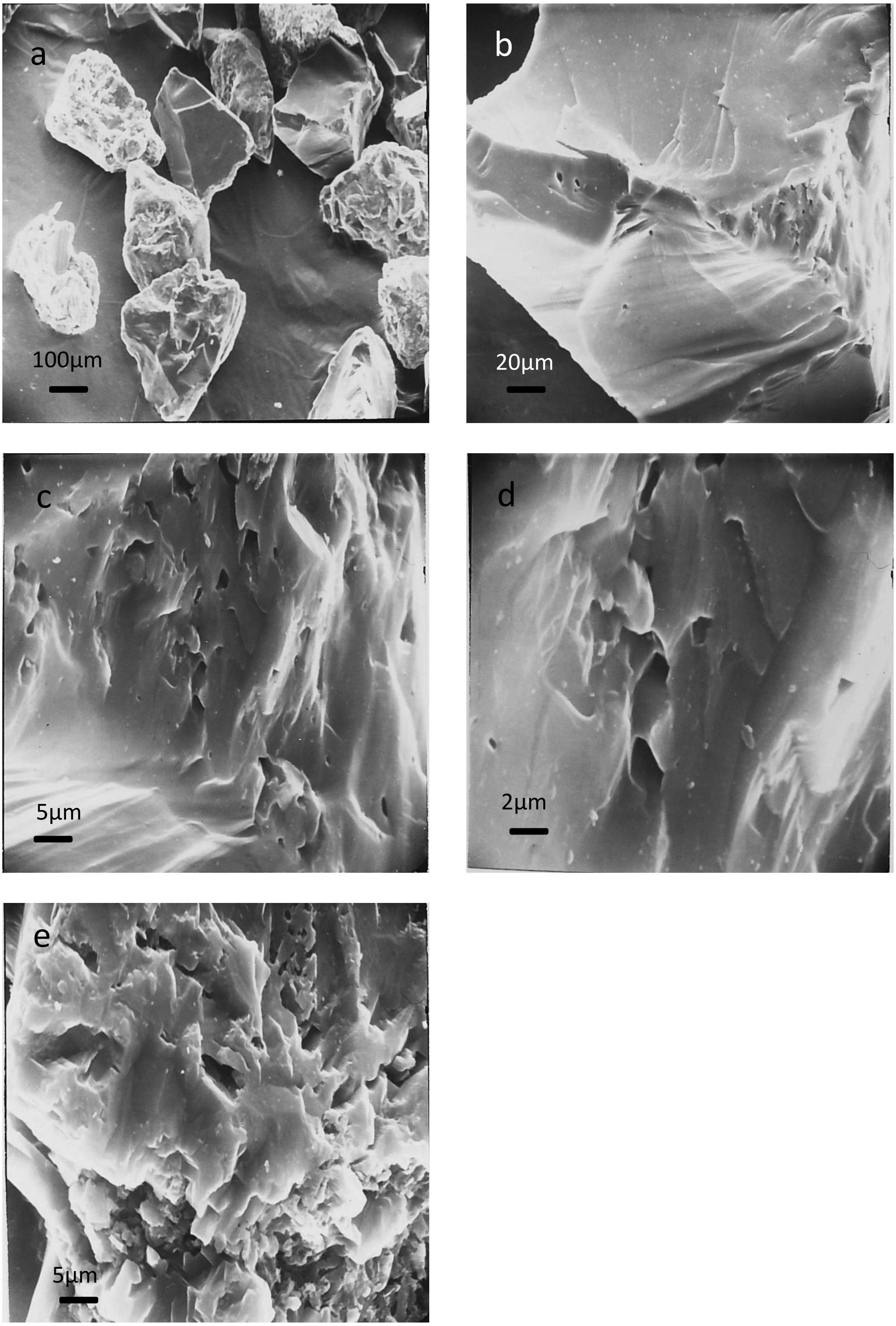

Fig. 3. SEM images of quartz grains from the Cg horizon of an imperfectly drained iron Spodosol showing (a–b) clean or slightly etched surfaces, (c–d) more intensive etching and (e) etched and disintegrating surface (Borrohill No 2). Figure made by author

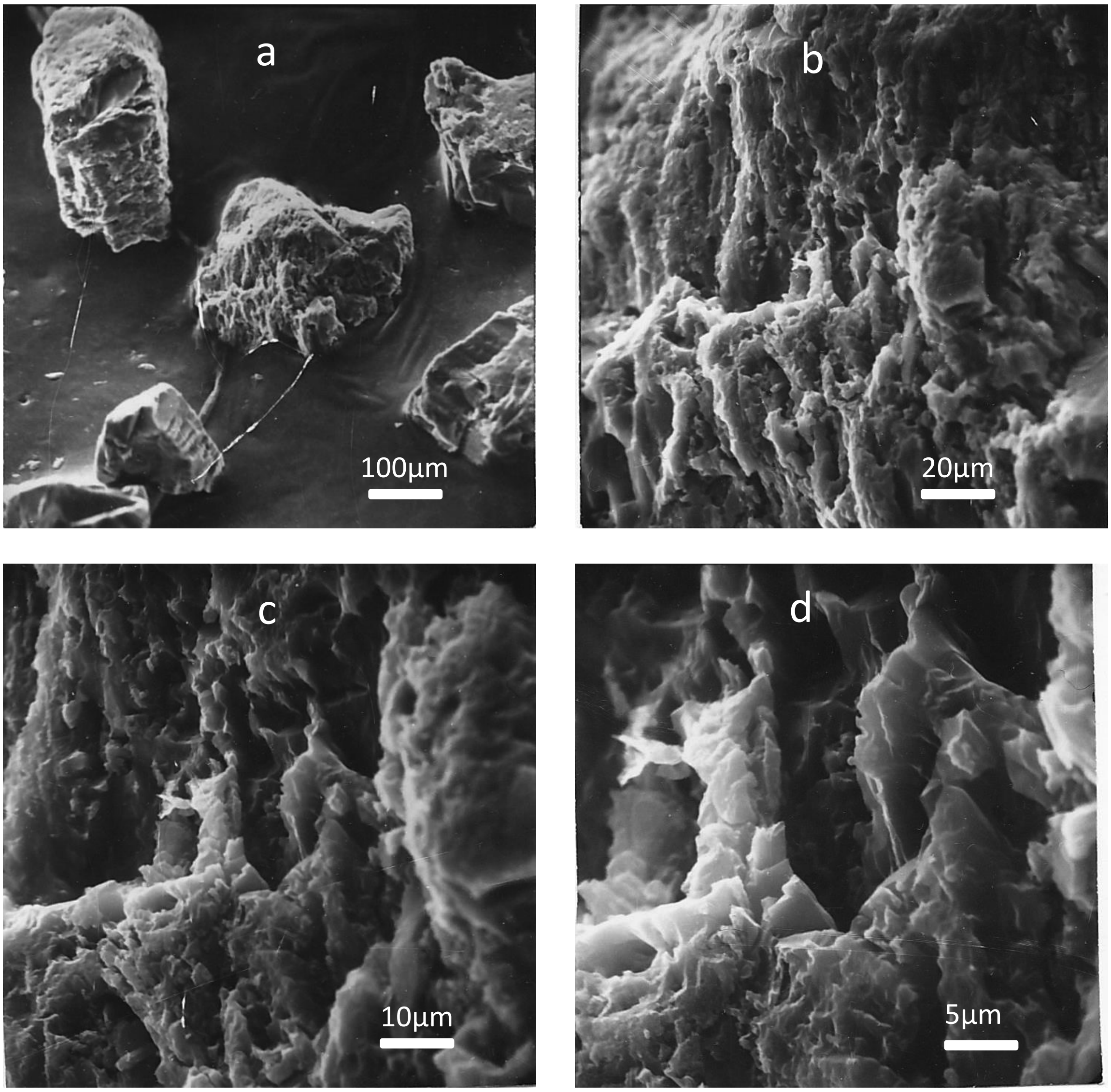

Fig. 4. SEM images of quartz grains separated from the Bg horizon of a peaty gley developed on granitic parent material showing their intense surface corrosion (Drumlassie No 3). Figure made by author

It may be concluded, therefore, that the application of experimental studies on quartz dissolution to the surface dissolution features observed on quartz grains in the soil should be undertaken with some caution, and must take into account the effects of previous weathering cycles, including the time factor, as well as the microstructure of the quartz grains themselves. However, even where the effects of previous weathering cycles can be excluded, as for example when poorly developed or incipient soils can be directly related to the underlying parent rock, it is surprising to find abundant evidence of quartz dissolution. Thus, Martín-García et al. (2004) found that quartz grains separated from the C horizons of Entisols (Orthents) directly derived from mica schists and quartzites in the Sierra Nevada, Spain, were characterized by well-defined dissolution features in the form of etch pits and so-called "corrosion gulfs" suggesting that these mountain soils had been subjected to a much higher degree of pedochemical activity than previously thought possible in the prevalent cryic temperature and xeric moisture regimes. These findings can possibly be related to the enhancing effects on quartz solubility of silica under-saturation in the soil solution consequent on the coarse texture and excessively well-drained nature of these soils. Etched quartz grains were found in a saline-sodic Entisol from Pakistan and a saline Entisol from Saudi Arabia (Shahid et al., 1992), possibly due to the enhancing solubility effect of Na^+ cations in the soil water and its high pH on quartz solubility. Strongly etched quartz grains were found in the petrocalcic horizon of an Aridisol in New Mexico, USA and in similar situations elsewhere, although this was attributed largely to pressure solution brought about by the force of crystallization of authigenic calcite (Monger and Daugherty, 1991).

Perhaps the most surprising evidence for quartz solubility in the natural environment is the occurrence of landforms developed on quartz sandstones that are directly analogous to the karstic landforms that develop on carbonate rocks (Wray, 1997). These include tower and pinnacle karst, caves (including stalactites), grikes, solution basins and notches etc., all clearly solutional in origin and are found not only in wet tropical climates but also in temperate and even sub-arctic regions (Wray, 1997). It can only be concluded that while quartz may be relatively resistant to weathering, in comparison with other rock-forming minerals like feldspar, it is by no means immune to this process and is solubilized in a wide variety of soil environments. Certainly, it cannot be used as a reference standard by which to gauge rates of weathering of other minerals in soil profiles as concluded by Little et al. (1978).

6. Occurrence and Origin of Quartz in Soils

Quartz occurs extensively in the sand and silt fractions of most soils and is nearly always considered to have an inherited origin, deriving directly from the parent material of the soil or indirectly from alluvial, colluvial, glacial, aeolian or other processes. In these circumstances, it usually has an initially anhedral form which may become well-rounded following subjection to erosive forces of considerable duration. The ultimate source of such quartz is from igneous or metamorphic rocks and as such should be characterized by an oxygen isotope ratio of ^{18}O relative to ^{16}O in both the sample and Standard Mean Ocean Water, that is appropriate to a high temperature of formation. So-called delta values (δ^{18}O) for quartz from such a provenance should be in the 8 to 17‰ bracket, whereas the oxygen isotopic composition of quartz formed at lower temperatures will range up to 35‰ (Allègre, 2008). Drees et al. (1989) show that the δ^{18}O value for quartz separated from soils can range up to 30‰, suggesting that some quartz may form in the soil as a secondary mineral. Ideally, the criteria that could be used to confirm this proposition should be the separation from the soil of perfect euhedral quartz crystals with no indication of etching on their crystallographic faces, as well as an appropriate isotope composition confirming low temperature formation as indicated above.

A possible example of quartz formation in a profile on deeply weathered granite is that described by Eswaran and Stoops (1979) in Malaysia showing an SEM image of small but perfectly formed euhedral quartz crystals with no indication of surface etching which were found at depths of 9.5 to 16 metres from the surface, which is also the zone of maximum halloysite formation. It is certainly conceivable that at this depth the Si concentration in the pore solution was well above the critical level, although it is also possible that this deeply weathered profile is of ancient origin. From the literature the question of the rate of formation of quartz under earth surface conditions is a rather confused one. On the one hand the experiments of Mackenzie and Gees (1971) suggest that quartz can be easily synthesized in a few weeks at normal temperatures and pressures, whereas extrapolation to surface conditions of the hydrothermal experiments of Ernst and Calvert (1969) on the recrystallization of cristobalitic porcelanite to quartz suggest that this is an extremely slow process, indicating a period of more than 100 million years.

The idea that quartz will form as a secondary mineral in soils subject to current pedogenic processes is certainly well-embedded in the soil science literature and has been since the early days of the subject. Thus, an early Russian textbook dating from 1933 states "We must distinguish between primary and secondary quartz. The latter forms by crystallization of silica gel, which precipitates in the weathering of silicates and aluminosilicates and occurs often in the shape of well-formed crystals" (Glinka, 1963). Other well-regarded Russian texts repeat the occurrence of secondary quartz in soils as a statement of fact. Thus, Rode (1955) observes "there is new formation of secondary quartz from silica separated from the weathering of minerals other than primary quartz" and Vilenskii (1957) also includes quartz as a secondary mineral encountered in soils. Gerasimov and Glazovskaya (1965) refer to "secondary quartz of non-biogenous origin" but add that "it has only been observed in a few soils". More recent authoritative reviews of silica in soils based upon the reviewers' own work as well as that published in the western literature agree with the idea that quartz can form as a secondary mineral in soils, presumably as a result of current pedogenesis. For example, Drees et al. (1989) state that "authigenic forms of quartz are relatively common in soils" and "direct neoformation of quartz (...) may occur in the complex soil environment". Again, Monger and Kelly (2002) include microcrystalline quartz as a secondary mineral forming in soils under certain conditions.

The evidence that supports the concept that quartz will form as a secondary mineral at ambient temperatures in soils that have developed *under current or fairly recent pedogenic conditions* will now be considered. The caveat in italics is necessary, as it is evident that secondary quartz does form in silcretes, but only after extended periods of geological time and under conditions that may not be pedogenic, as will be shown later. The necessary evidence showing that quartz can form as a secondary mineral in soils should at least consist of the observation by SEM of unetched, well-formed crystals that have been unequivocally identified as quartz by X-ray diffraction, preferably with an appropriate oxygen isotope composition confirming a low temperature origin. However, it is not often that these basic criteria have been fulfilled.

Drees et al. (1989) discuss the formation of quartz under near ambient conditions as a result of the pedogenic transformation of opaline silica and cite the published works of Flach et al. (1969), Brewer et al. (1972) and Dapples (1979) as supporting evidence. The first two works provide no convincing evidence of secondary quartz formation. Indeed, Flach et al. (1969) specifically describe opal as the siliceous cementing agent of the duricrusts and hardpans they studied in the USA. The hardpan soils investigated by Brewer et al. (1972) seem similarly to be cemented with amorphous silica and not secondary quartz. The work of Dapples (1979) is concerned mainly with silica transformations in rocks during burial diagenesis, so that none of the references cited actually support the concept of crystallization of secondary quartz during pedogenesis. Drees et al. (1989) also infer from the reported increase in oxygen isotope ratios with decreasing particle size of quartz separated from the surface horizons of some American soils (Sridhar et al., 1978; Clayton et al., 1978), that this is due to "a higher content of authigenic quartz", with the implication that this quartz formed in the soil. However, Sridhar et al. (1978) comment that the fine quartz fraction of the soils they studied probably comes from an extraneous chert source and Clayton et al. (1978) only found higher oxygen isotope ratios in the fine quartz separated from deeply buried Tertiary sediments. Quartz separated from the fine fraction of a deep weathering profile showed only a very marginal increase in oxygen isotope values.

Monger and Kelly (2002) state that microcrystalline quartz forms in the soil under certain conditions and refer to Wilding et al. (1977), Chadwick et al. (1975), Milnes and Thiry, (1991) and Alexander et al. (1994) as supporting work that is in the public domain. Wilding et al. (1977) provide little evidence for the formation of secondary quartz in soils other than to refer to the work of Flach et al. (1969) and Brewer et al. (1972) which have been commented on above. They do, however, mention that quartz may be of biogenic origin. The work of Chadwick et al. (1987), far from providing supporting evidence for secondary pedogenic quartz in their study of cemented duripans, is explicit that they were unable to find any supporting evidence for its existence. Thus, "we were unable to definitively identify any pedogenic microcrystalline quartz primarily because it has the same XRD pattern as allogenic quartz and it was impossible to physically isolate pedogenic quartz". They also concluded that "petrographic microscope studies did not indicate any pedogenic microcrystalline quartz". Again, the study of Alexander et al. (1994) on the chemistry and mineralogy of a hardpan in cemented ultramafic till beneath a Spodosol in Alaska provides no evidence of secondary quartz formation.

On the other hand, however, there is abundant evidence for the secondary quartz formation in the work of Milnes and Thiry (1991), but this refers to ancient weathering during the Cenozoic, mainly in the context of silcretes, which may be regarded as a special case. The term "silcrete" describes an accumulation of silica in soils, sediments or rocks such that the whole is converted to an indurated mass. Silcretes are generally agreed to have formed through near-surface processes and contain at least 85% SiO_2 and usually > 95% SiO_2 (Summerfield, 1983). There is no doubt that silcretes often contain neoformed microcrystalline quartz, as has been shown by many researchers, but the question here is whether they can be considered as soils. Nearly all silcretes have been formed from the prolonged and intensive weathering of stable landscapes dating from the distant geological past and although their origin is often described as "pedogenic", their relevance to the question of whether quartz can form as a secondary mineral in modern soils is highly dubious. In any event, the evidence of quartz formation in silcretes would seem to be in line with the conclusions of Ernst and Calvert (1969) that quartz formation in soils occurs over geological time, rather than those of Mackenzie and Gees (1972) that quartz could be easily formed in the laboratory.

7. Conclusions

The dissolution of quartz in soils in the context of the important factors identified experimentally, including pH, and the concentrations of dissolved silica, alkali and alkaline-earth cations, organic acids and aluminium and iron species in the external solution. The application of these factors is reviewed, as revealed by SEM observations of the etching features on quartz grains in the different pedogenic environments.

For residual soils, directly related to the underlying parent rock, these etching features may relate to the prevailing pedogenic regime and the important factors that have been experimentally identified. For soils of a non-residual including alluvial, glacial, aeolian, and colluvial, nature, however, the possibility that quartz grains will have been through several weathering cycles, resulting in mixtures of fresh and highly weathered grains, interpretation of which calls for a high degree of caution.

The pedogenic formation of quartz in soils is well-embedded in the soil science literature. However, a review of papers that are generally supportive of this claim shows that very few meet the basic criteria required to substantiate this concept.

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