

Research Paper 2

IRSL and Feldspar Weathering

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Abstract.

The effect of chemical weathering of the luminescence signal of feldspars has been recognised from the analysis of waterlain sediments from Britain and the Netherlands. The sediments fall into three groups based on their stratigraphic occurrence, mineralogy and luminescence signal characteristics.

The observed relationship between low signal intensities and weathered grains is tested by a simulated weathering experiment. The results support the proposal that chemical weathering selectively destroys the defects at which trapped charge is held; the resultant reduction and instability in the luminescence signal has severe implications for dating such sediments.

Introduction.

The work presented in this paper is part of an interdisciplinary project combining sedimentological analyses and luminescence dating in order to assess the effects of processes, such as transport, deposition and post-depositional changes in sediments, on the luminescence characteristics of the samples, and their potential for dating. The sediments are fine-grained (mainly 1- 60 μm), waterlain deposits of Holocene age, associated with archaeological material and sea-level changes, which, with ^{14}C , provide a chronological control for the samples.

This paper presents the results of a study of the effects of 'active' weathering of feldspars on the luminescence characteristics of a sample, and its significance for the dating of feldspar-rich deposits. 'Active' weathering in this case is defined as feldspars which are currently being broken down, as opposed to 'interrupted' weathering, where feldspars may have been weathered in the past, but in their present environment, they are in a stable state. Physical weathering processes in soils, such as decalcification and gleying, thought to be a possible zeroing mechanism (Wintle and Catt, 1985). The results in this paper indicate that chemical weathering is a cause of loss of signal and reduced potential for dating.

Luminescence Dating

Luminescence dating is based on the measurement of electric charge trapped in defects in crystals. The charge is derived from the effects of ionizing radiation from naturally occurring isotopes (Uranium, Thorium and Potassium). The defects in crystals act as traps in which this charge is held until evicted by heating or exposure to light. Sediment dating is based on the fact that exposure to sunlight empties the crystal of stored charge, thus 'resetting' the luminescence 'clocks'. The crystals, usually of quartz and feldspar, accumulate charge with time, according to the 'dose-rate' (or level of radioactivity) and time. The event dated is the last exposure to sunlight.

Measurement of the trapped charge in the laboratory, by the eviction of the charge as light can be by heating in the case of thermoluminescence (TL), or by exposure to light of specific wavelengths - optically-stimulated luminescence (OSL). The light sources normally used are a green laser for stimulation of quartz, or infra-red diodes for feldspars; the latter is called infra-red stimulated luminescence (IRSL).

The age of sediments is calculated by the equation: age = equivalent dose (ED) / annual dose-rate, where the ED is measured in the laboratory by giving a radiation dose of equivalent size to that emitted from the natural sample. The dose-rate is evaluated by measuring the alpha, beta, gamma and cosmic components of the bulk sediment.

Identification of the Problem.

The relationship between chemical weathering of feldspars and luminescence characteristics was first noted during the process of dating waterlain sediment samples for this project. Three types of sample were recognised, based on their combined sedimentological and luminescence characteristics. These are described below.

Group 1 comprised samples with clean grains of quartz and feldspars (mixed potassium and plagioclase), a low abundance of mixed-layer clay minerals (figure 1a), and other clay minerals dominated by kaolinite, which is the stable end-product of K-feldspar. The IRSL signal was strongly detected, with initial intensities over 160 counts in the first second. The signal exhibited a strong growth with added dose, and a low (< 5%) scatter in the normalized data. These samples were dated, with good agreement with expected ages, and errors of between 8.6% and 20.9% (The higher

values were primarily due to the saturated levels of water content in some of the sediments.)

Group 2 samples contained a proportion of weathered feldspar grains, but these were not as severely degraded as those of Group 3. The quartz grains tended to be unweathered. The clay content was dominated by kaolinite, with small amounts of illite and montmorillonite in some samples, but mixed-layer clays were rare. These sedimentological characteristics indicate that weathering of the grains has occurred, but that their present environment is relatively stable with respect to active degradation, illustrated by the preservation of fine laminations formed during deposition. The luminescence characteristics were similar to Group 1, and dates produced were in good agreement with expected ages, although there was a slightly increased scatter in the data for some samples, increasing the error to a maximum of 38.9%.

Group 3 samples were characterised by severely degraded grains, showing the etch pits and delineation of cleavage associated with weathering of feldspars (figures 1a, b). The clays were dominated by transitional clay products of weathering, illites and montmorillonites (from plagioclases), with only relatively small amounts of kaolinite (from K-feldspar). Mixed-layer clays were abundant. These characteristics suggest an actively weathering environment. The profiles of these sediment layers tended to be more mixed vertically, and no sedimentary structures were preserved. The luminescence characteristics of these samples comprised extremely weak signals, and a poor response to added dose. Several samples faded, even after storage at 50°C for 6 weeks. This instability was not removed by preheating at 160°C for 2 hours and 100°C for 3 days.

There are a number of causes of weak signals; mineralogy of the sample is a major factor. Pure quartz is not stimulated by IRSL, but all the samples in this study contained at least 40% feldspar, which is sufficient to emit substantial IRSL signals. However, the type of feldspar is also important, for example, albite has a low blue TL emission (Huntley et al, 1988), which is detected by the blue-biased equipment used for IRSL, but the dominant orange-red emission is not detected. If a sample contained large proportions of plagioclases, such as albite, the detected IRSL signal would be relatively weak.

This was tested on a weak sample by using CL to analyse the emission spectrum (although this is not directly comparable to TL, it indicates the dominant signal spectrum). This proved to contain larger proportions of blue than orange-red emissions, indicating that the feldspar

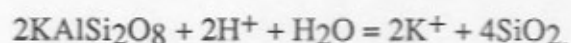
type was not primarily the cause of the weak signals. The correlation between weathered grains and indicators of active weathering processes *in situ*, together with the luminescence characteristics typical of Group 3 suggests that chemical weathering of feldspars selectively exploits the defects from which the luminescence signal arises, resulting in a loss of signal.

Chemical Weathering of Feldspars.

Chemical degradation of feldspars occurs by hydrolysis and the substitution of elements within the lattice, due to chemical disequilibrium between the surface of the solid and the surrounding soil solution. The soluble elements such as Ca^{2+} are replaced by lower valency cations, and Na^+ and K^+ by H^+ . This occurs primarily at 'centres of excess energy' (Berner and Holdren, 1977) such as cleavage and other planes of weakness, and at defects in the crystal lattice, resulting in the characteristic pitting of grains (figure 2a, b). These surface features are characteristic of those produced by the acid etching of quartz (Bell and Zimmerman, 1976).

The cations mentioned above are soluble at normal soil pH's (4.0 - 9.0), but Al^{3+} is not, and is a major structural element of feldspars. The solubility and mobility of Al is facilitated by the process of chelation, where the formation of complexes between metal and organic ions, renders the metals soluble at normal soil pH's. For this reason, the presence of organic acids (humic and fulvic) in a sediment or soil significantly increases the rate of feldspar dissolution. The high mobility of Ca^{2+} contributes to the fact that plagioclases tend to breakdown more rapidly than potassium feldspars, independent of climatic conditions (James et al, 1981).

Feldspars break down into clay minerals by hydrolysis and carbonation. Kaolinite is the stable end product for K-feldspars, which follows the formula:



The formation of particular clay minerals depends on the availability of ions free to crystallize out. If only part of the potassium is removed, K-feldspar may form illite ($\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$). Kaolinite is a 1:1 clay mineral, with a low cation-exchange capacity (CEC), indicating that it is more stable in soil environments, as it has a limited capacity to release ions from its structure. Illite and montmorillonite type clays are 2:1 expanding lattice clays which have weak bonds between cations which are easily substituted. Such minerals have higher cation exchange capacities, and are less stable in weathering environments, and represent intermediate stages in feldspar breakdown.

The clays often form adherent flakes on the surface of grains, which may be difficult to remove by sonication. These are hydrous, as they tend to curl up and flake off with drying. Such discontinuous coatings cannot therefore be responsible for reducing the emitted signal. Clay coatings are, however, a characteristic product of feldspar weathering.

The rate of weathering of feldspars depends on the abundance of defects and the structure of the grain, with respect to vulnerable cleavage planes, thus the rate is not directly affected by grain size or surface area (Holdren and Berner, 1979; Holdren and Speyer 1985, 1987). Weathering continues until an equilibrium state is established between the exposed grain surface and the surrounding solution, after which the grains will remain in a stable state, until further disequilibrium occurs. Groundwater is a major weathering agent, and removal of free cations by leaching maintains a state of disequilibrium.

The Weathering Experiment.

A fine-grained, feldspar-dominated sample from Group 1 was subjected to artificial weathering following the procedure used by Wollast (1967). The sample was gently broken up into individual grains. Buffer solutions of pH 6.0 and pH 8.0 (composition of buffers were made up as described in Wollast, 1967) were made up in a polythene bottle to 1 litre and 50 g of the sample was added. In addition a control sample was made with 50 g of sample in de-ionized water (pH 7.0). These were kept in a water bath at 20°C for 6 weeks, covered to prevent bleaching under the red light conditions of the laboratory, and agitated frequently.

Subsamples of c. 50 ml were abstracted at 10 day intervals from each bottle. Six discs were prepared from each subsample, using standard preparation techniques and settling onto abraded Al discs from acetone. The remainder of the dried sample was used for XRD analysis (using a Co-alpha tube and orientated samples). SEM was done on the surface of the prepared discs (gold coated, up to magnifications of up to x10 000 at a working distance of 6 - 7 mm).

TL and IRSL measurements were made of the natural signal (three discs for each) using a Risø automated system; for TL a Corning 7-51 filter and a heat rate of 10°C/sec were used, and for IRSL, 880 nm diodes and an exposure time of 160 sec. The three discs from each subsample per batch were normalised using a 1 second IR exposure. No preheating treatment was given, except in the case of the fading samples, discussed below. The natural signals, and mineralogy were compared to the characteristics of the original material, and the control sample.

Results.

The XRD analysis showed a significant change in the proportions of the identified minerals. There was a fall in the amount of feldspar and increase in the amount of clays, which were dominated by illite. This is shown in figure 3. The changes observed were similar for both acid and alkaline buffers, and no significant change was observed in the control.

Under SEM analysis, the grains of the control remained clearly defined, without significant abundance of clay flakes. After 40 days in the pH buffers, the grains exhibited some of the characteristic etch pits associated with weathering, and the development of flaky clay coatings associated with mineral breakdown. The change between the original material and that in a buffer after 40 days is shown in figures 4a, b.

The initial intensity of the natural IRSL signal fell dramatically with duration of exposure in the buffered samples, but not with the control (figure 5). The control therefore indicates that this reduction is not due to external effects, such as bleaching under laboratory light. This reduction reached levels as low as 27% of the original signal. These levels are typical of those samples in Group 3.

The natural TL signal was measured, and seen to suffer less reduction than the IRSL signal, but a significant change in the 280°C peak shape was observed, both for acid and alkaline buffers (figure 6). The flattening out of the peak indicates some charge transfer is taking place, which may result from changes in the surface distribution of luminescence centres associated with weathering (Bailliff, pers. comm.). This may also be a cause of the signal loss.

Another significant observation was the onset of fading of the sample (figure 7), which had previously shown no sign of instability. The control continued to remain stable, but the IRSL signal of the buffered samples shown to faded significantly, losing up to 45% of the signal. This fading component was not removed by the preheating treatment, similar to those samples in Group 3 which faded. The TL signal was also seen to fade.

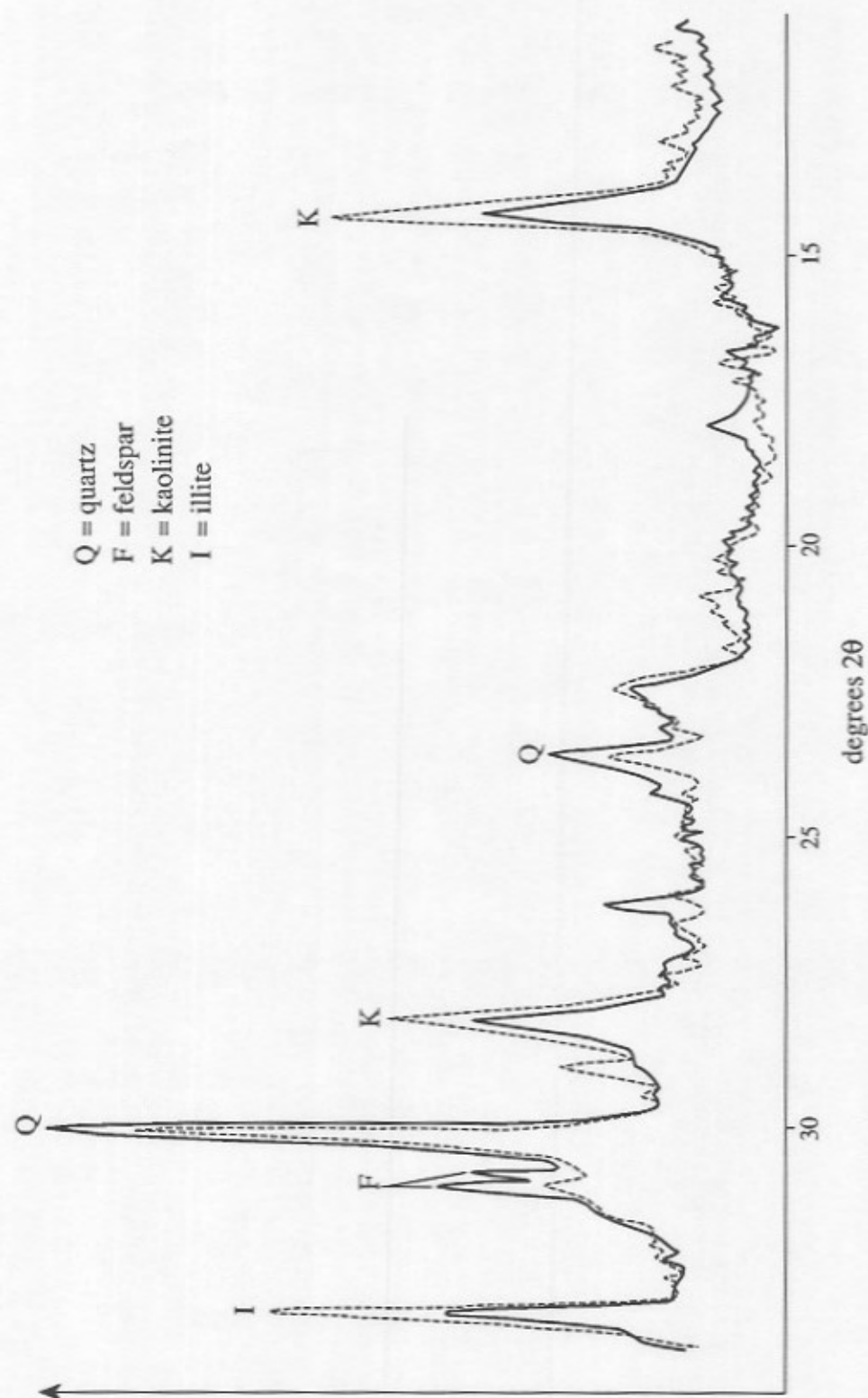


Figure 3. Effect of pH buffers on mineralogy; XRD analysis. The changes in mineralogy are similar for both acid and alkaline buffers; reduction in proportion of feldspar, and increase in clays, particularly illite. The control remains relatively unchanged.

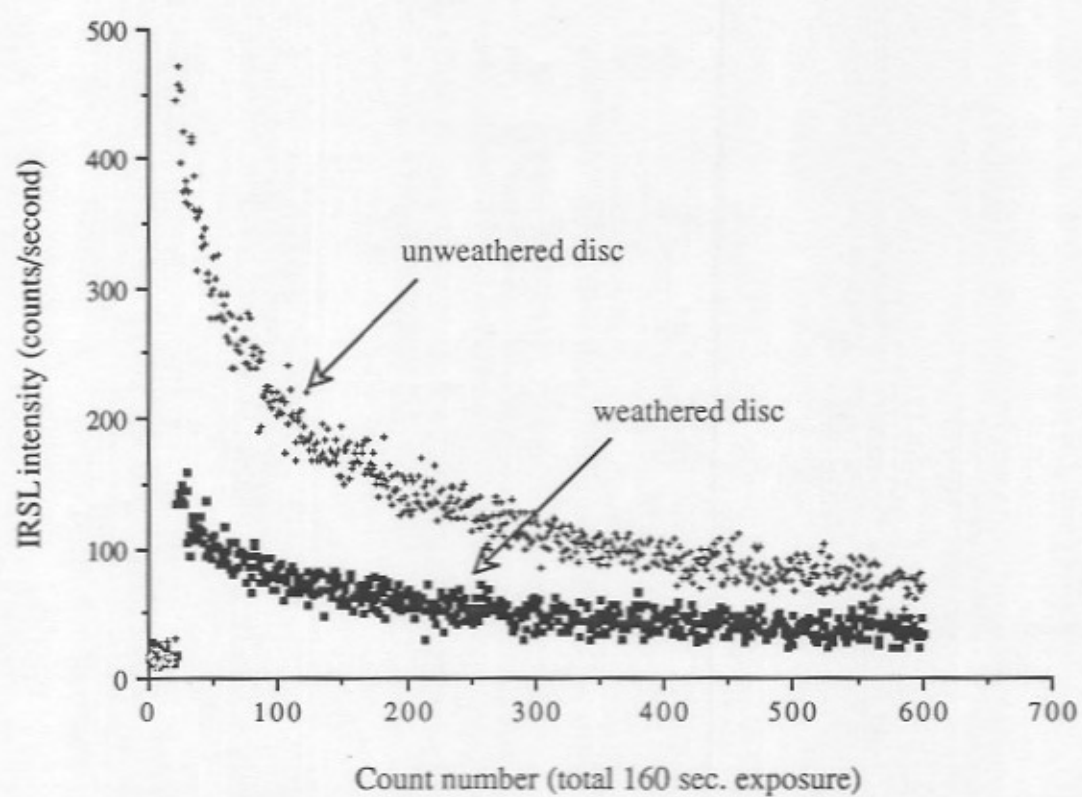


Figure 5. Reduction in IRSL intensity after weathering.

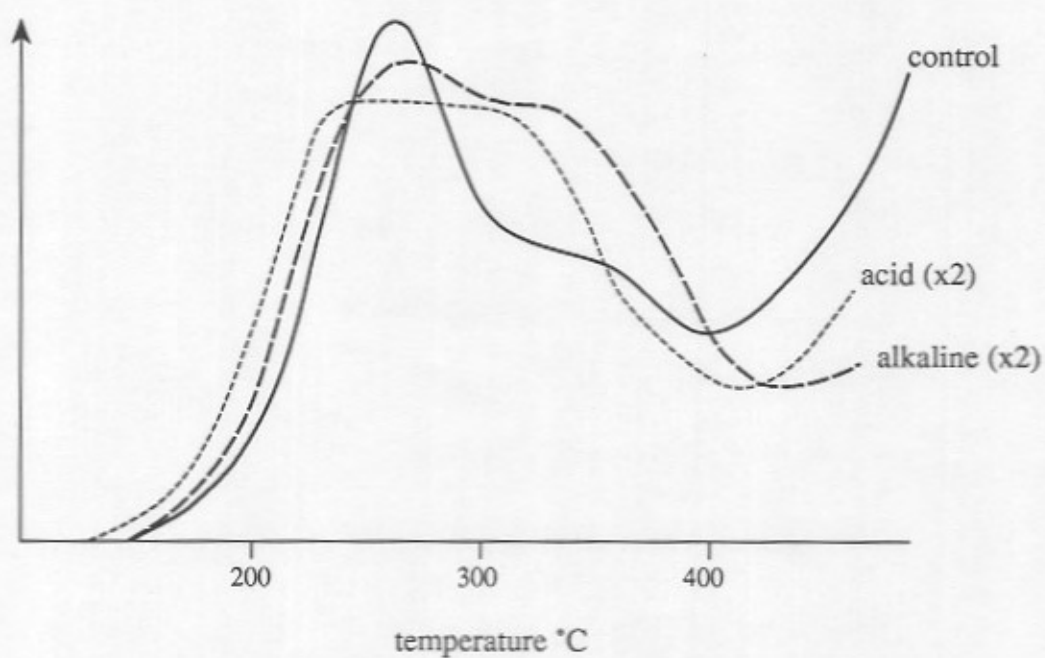


Figure 6. Changes in the shape of the 280°C TL peak after 40 days in the buffer solutions. The control was unchanged from the original sample (not shown). The acid and alkaline buffers have been scaled up by x2 to account for the loss of signal intensity.

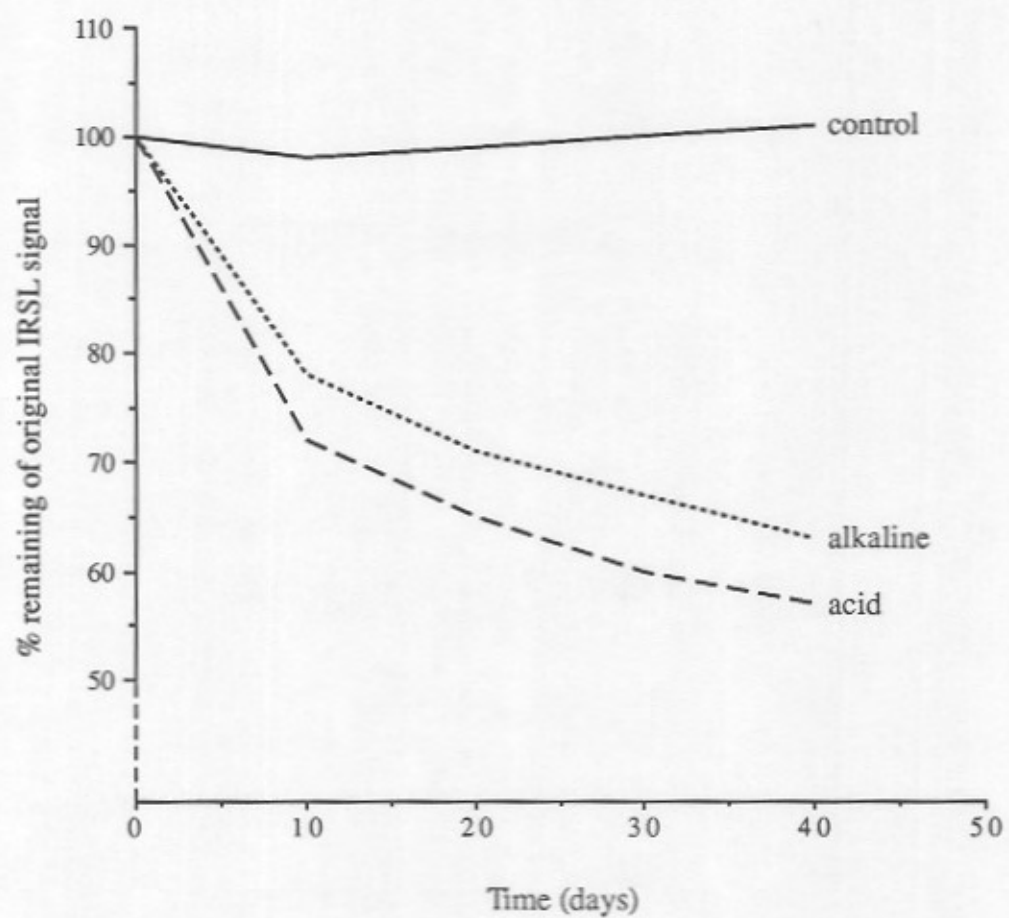


Figure 7. Loss of signal due to fading, after weathering.

Conclusions.

Chemical weathering selectively exploits the defects in feldspar crystals, and causes a loss of signal, and the onset of instability, manifest as fading and changes in the structure of the TL peak.

After 40 days exposure of a selected Group 1 sample to buffers of pH 6.0 and 8.0, the sample acquired the mineralogical and luminescence characteristics of a sample from Group 3. The control sample in de-ionized water remained unchanged, and thus retained the characteristics of the original material.

Artificial weathering, by inducing disequilibrium between solution and sample has been observed to cause a number of changes. Mineralogically, the indicators of active weathering develop, ie. the accumulation of mixed-layer clays and the etching of feldspar grains. With respect to the luminescence signal, a significant loss in intensity is observed, together with the onset of fading.

The observed correlation between weathering indicators and poor luminescence signals has been confirmed in this study, in that the same correlation has been induced by active weathering, as opposed to a stable-state of grains in equilibrium with their present environment.

Implications for Dating.

With respect to dating sediments, the importance of the identification of actively weathering environments must be stressed, and the dating of quartz from such layers may be more reliable. Detailed stratigraphic analyses, such as the examination of preserved microstructures can indicate that weathering is active. Microscopic examination of individual grains, for evidence of degradation and formation of weathering-related clay coatings (as opposed to those resulting from the translocation of fines within a profile) in support of the stratigraphic analysis is important.

In the case of sediments classified as Group 2 in this study, the grains may have been affected by weathering, but the sedimentary structures such as fine laminations have been preserved in the sedimentary section, indicating that leaching and mixing associated with active weathering has not occurred.

Other indicators of active weathering is in the clay mineralogy and the presence of mixed-layer clays. Clays dominated by kaolinite have a low CEC, and thus remain more stable in active weathering environments. Clays dominated by mixed-layer or expanding lattice types such as illite and montmorillonite are less stable, and more easily affected by cation exchange.

It is the combination of these characteristics that is most useful, rather than elements taken individually. It is the active weathering environment which appears to affect the dating potential of sediments; a stable environment containing either weathered or unweathered grains is not, in these samples, a cause for concern.

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Figure 1a. Grains from a Group 1 sample; clean faces, clearly defined grains. (x500; 1cm = 10 μ m)

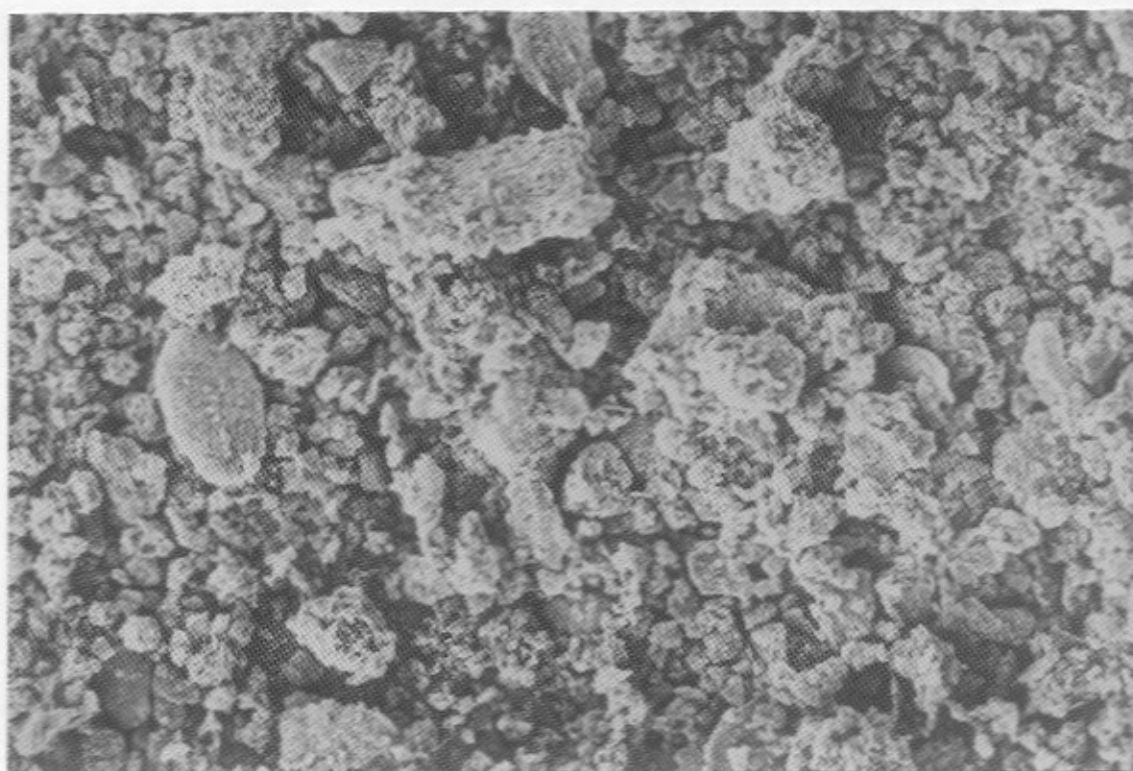


Figure 1b. Grains from a Group 3 sample; grains are clearly degraded, with abundant amorphous clay minerals. (x500; 1cm = 10 μ m)

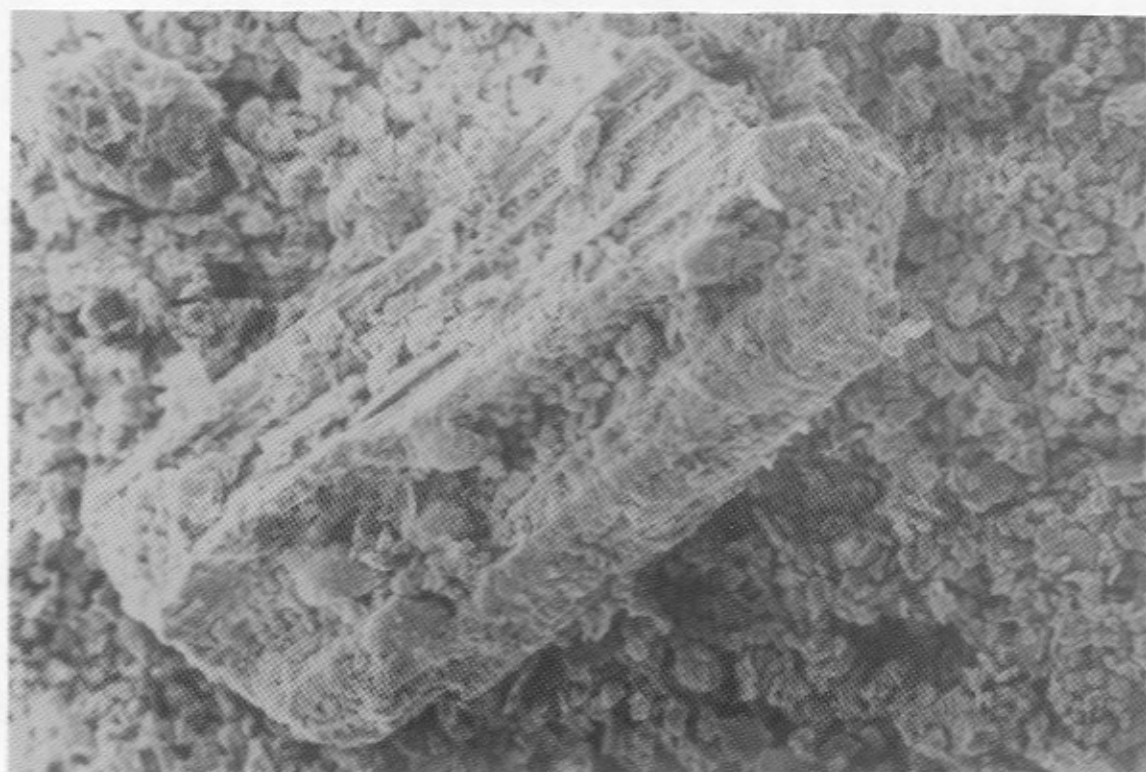


Figure 2a. K-feldspar grain severely degraded, showing the preferential exploitation of cleavage planes. (x10,000; 1cm = 0.5 μ m)

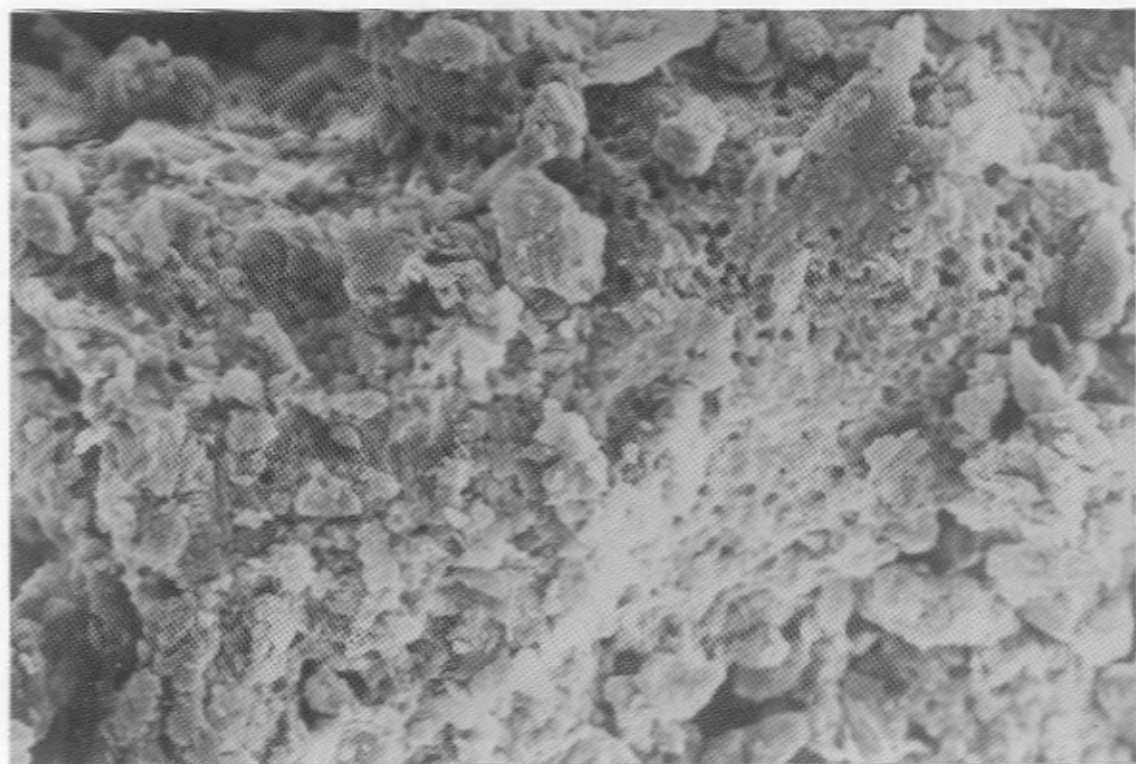
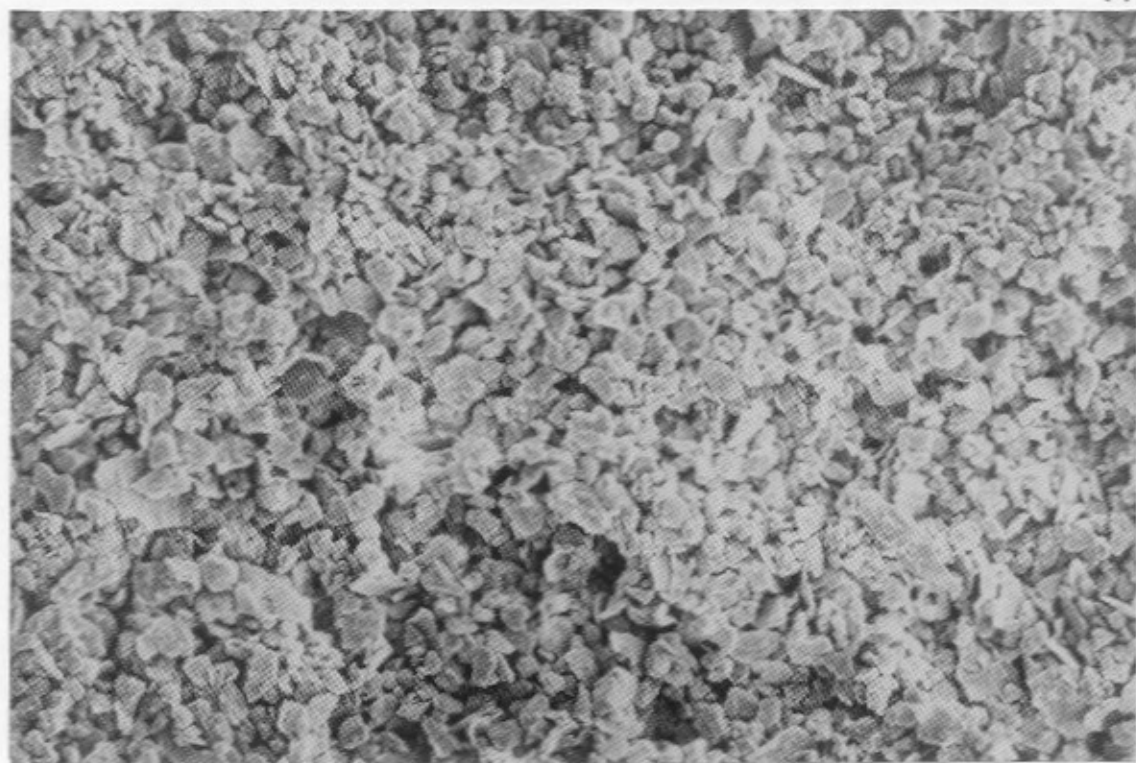


Figure 2b. A sub-rounded feldspar grain, showing distinct etch pits on the surface, formed by dissolution at 'sites of excess energy'. Notice the clay flakes adherent to the eroded surfaces. (x10,000; 1cm = 0.5 μ m)

(a)



(b)

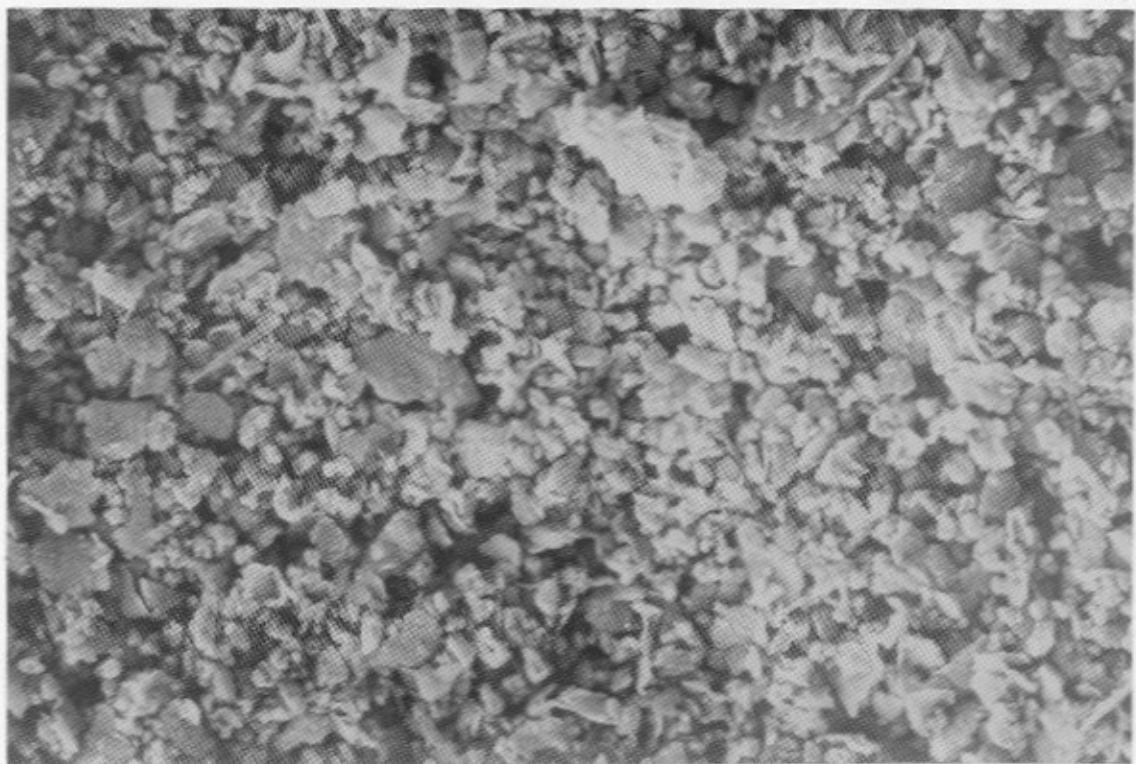


Figure 4. SEM photographs of the surfaces of discs prepared from the original material before weathering treatment (4a) and after 40 days in the acid buffer (4b). Note the change in surface texture and appearance of the grains, which are less clearly defined. The increase in clay minerals is also significant. The effect of the alkaline buffer was similar to that of the acid, and the control sample which was unchanged. (x500; 1cm = 10 μ m)