Chapter 6

'IN SITU' DISSOLUTION OF HEAVY MINERALS THROUGH EXTREME WEATHERING, AND THE APPLICATION OF THE SURVIVING ASSEMBLAGES AND THEIR DISSOLUTION CHARACTERISTICS TO CORRELATION OF DUTCH AND GERMAN SILVER SANDS

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ABSTRACT

Diverse processes during the sedimentary cycle may generate heavy mineral associations that are devoid of clear signatures of the source region, especially in sediments that experienced unusually severe environmental conditions, and thus their provenance reconstruction becomes problematical. This study provides a new insight into the impact of 'in situ' weathering on heavy mineral assemblages, rarely dealt with in recent years, by evaluating the effects of extreme weathering that imparted an unusual bulk and heavy mineral composition to the Tertiary Dutch and German 'silver sands' (sands that consist almost exclusively of quartz).

Specific findings of our heavy mineral study of these silver sands include: (1) tourmaline can be strongly weathered; (2) the chemical weathering of tourmaline is colour-related and therefore depends probably on its particular chemistry; (3) staurolite is a reliable indicator of the degree of chemical weathering; (4) the effects of extreme chemical weathering on a heavy mineral assemblage differ fundamentally from those of burial diagenesis as, for example, in the total disappearance of apatite; (5) the joint occurrence of fresh and strongly weathered grains (with the same chemical composition) of one heavy mineral species indicates that the degree of chemical weathering is a statistical rather than a fixed parameter; (6) no heavy mineral analysis is reliable if the degree and the effects of in situ weathering are not taken into account; (7) a reliable analysis of extremely weathered sediments requires sand samples of several kilograms.

Although regional or local differences in weathering may obscure original heavy mineral compositions and thus impede subdivision of, and correlation between, sedimentary units, understanding the end-products of in situ weathering may also be helpful in drawing stratigraphic boundaries between units with originally comparable heavy mineral compositions, as is proven for the silver sands.

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1. INTRODUCTION AND GENERAL CONSIDERATIONS

It is widely documented that heavy mineral assemblages do not necessarily reflect the original assemblages that were deposited at the sampling site: some of the heavy mineral species may have disappeared completely, while the ratios of others may have changed as a result of differential dissolution (Morton and Hallsworth, 2007, this volume). Mange and Maurer (1992) state in this context, 'The importance of post-depositional dissolution cannot be overemphasised.' Changes of heavy mineral compositions with time in outcrop and shallow subsurface are commonly the result of weathering (particularly if a soil was formed not far above a particular deposit) but other processes (almost always related to groundwater movements) may also play a role; corrosive pore fluids may affect—or even completely dissolve—unstable minerals (Morton, 1985; Morton and Hallsworth, 2007, this volume). Diagenetic processes, in addition to the progressive dissolution of the labile grains, cause changes in heavy mineral compositions of a different kind by the formation of new heavy minerals. Another important point also needs consideration: during disaggregation fine lithic fragments, present in some sandstones, especially lithic arenites in low-permeability intervals, may release fresh mineral grains. These, being protected from pore fluids, preserve important clues to the history of the sediment. To the authors' knowledge, no such occurrences have, apart from concretions and early carbonate cement-sealed sediments, ever been evaluated. Although diagenesis is, in the mineralogical context, commonly considered as a process that leads to authigenesis (the formation of new minerals, with or without grains of the same mineral as a nucleus), it should be realised that most of the authigenic minerals owe their origin to the entire or partial dissolution of previously present minerals (which may be either the same or other species). In soil horizons, and in the underlying sediments, both light and heavy mineral assemblages may become severely depleted, and many species may even disappear entirely. Under such conditions, heavy mineral composition in a specific unit progressively changes with depth in accordance with the decreasing influence of the zone of pedogenesis (Grimm, 1973; Friis, 1976; Milliken and Mack, 1990). Because the chemically highly stable species are most likely to survive, relatively high concentrations of ultrastable minerals such as zircon, rutile and tourmaline are commonly found in superficial deposits. Surprisingly, however, the presence of high concentrations of ultrastable minerals is often ascribed to another factor, viz. their resistance to attrition during prolonged transport and/or several depositional cycles of repeated erosion and transport.

One of the main reasons why early, pre-burial chemical weathering of heavy minerals is considered relatively rarely in geology, as opposed to burial diagenesis, is because not all heavy minerals react in the same way to specific conditions. The result is that some minerals are relatively easily dissolved under conditions that hardly affect others, whereas the situation may be the reverse under different conditions (e.g., Morton et al., 2003; Morton and Hallsworth, 2007, this volume). The behaviour of particular species during weathering is contrasted with its response to burial and acid versus alkaline conditions. Climate also influences the dissolution response of heavy minerals during soil formation (Busacca and Cremaschi, 1998; Lång, 2000; Xiubin et al., 2002, 2004). It is important to recognise and evaluate the effects of climate, because understanding the response of heavy mineral assemblages to weathering in different climatic regimes may allow inferences to be drawn about particular ancient climatic conditions (Amireh, 1991).

Heavy mineral assemblages in modern sediments mirror primarily the effects of a single phase of post-depositional weathering that commonly involves a number of simultaneous and/or progressive processes affecting the individual grains (Hubert, 1971; Nickel, 1973; Morton, 1984, 1985, 2003). The nature of various factors controlling the weathering process may change overtime, giving rise to stepwise weathering of the same particular grains (Grimm, 1973). Stages of weathering may be diverse because minerals may undergo weathering during temporary alluvial storage or weathering may already start in the source area (Friis, 1978; Dill, 1995, 1998; Xiubin et al., 1997; Singh and Rajamani, 2001) marked by conditions that differ from those during transport (Morton and Smale, 1990; Weibel, 2003), or at the final depositional site. Other studies emphasise the influence of organic matter on chemical weathering (e.g., Olivia et al., 1999).

Recognition and understanding of the wide variety of processes that are encoded in the heavy mineral composition of a sediment sample help to reconstruct its history. The early literature on heavy mineral research, published in the middle of the twentieth century (Edelman and Doeglas, 1934; Bramlette, 1941; Dryden and Dryden, 1946; Blatt and Sutherland, 1969; Nickel, 1973), reflects this well. However, the results of experimental weathering (and comparisons with field data) were found strongly contradictory (Velbel, 2007, this volume and references therein). It is one of the reasons why assessment of weathering has often been neglected in heavy mineral studies, although this is particularly relevant when exploring for economically valuable ores (Peuraniemi and Heinänen, 1985). The heavy mineral composition of a given sediment may be so different from that of the parent rocks that the omission of weathering analysis may prevent recognition of the relationship between the sediment and its source area (Friis, 1974; Milliken, 1988; Lacassie et al., 2004).

A primary parent rock may be affected by strong subaerial weathering, or a pre-existing sedimentary source rock may have undergone advanced diagenesis (Sawyer, 1986; Morton et al., 1996, 2002). The consequences of intensive weathering of a parent rock are commonly overlooked. This aspect is, nevertheless, of utmost importance because detritus eroded from a source rock (or regolith) that has undergone deep weathering and, hence, comprises a low diversity heavy mineral suite, will produce sediments with an equally low-diversity heavy mineral composition (and an equally low or even lower heavy mineral content). This could erroneously be interpreted as a consequence of strong in situ weathering of the resulting sediments (or the effect of deep burial diagenesis). Advanced diagenesis in a pre-existing sedimentary source rock may also generate authigenic heavy minerals that will be transferred to the sediments derived from it. These 'detrital' diagenetic minerals may be erroneously interpreted as being authigenic, perhaps leading to false proof of deep burial of the derived sediment.

Although there are, obviously, important relationships between the heavy mineral assemblages of the parent and daughter sediments, a resemblance of the heavy mineral assemblages of a given sediment to those of a lithified potential source rock does not, by definition, imply that the two units have a mother/daughter relationship. On the other hand, parent rocks whose heavy mineral suites include species that become easily weathered and eliminated may result in daughter sediments with a strongly diverging heavy mineral assemblage (Yang et al., 2003). This is an extremely important issue because there is an increasing tendency to reconstruct sediment provenance from rare-earth elements in the daughter sediments (Bhatia, 1985; Mongelli, 1993; Yang et al., 2002). The rare-earth signatures of a given sediment are generally provided by its heavy mineral composition, because a relatively large part of the rare-earth contents (commonly tens of percents) are found in the accessory heavy mineral fraction of a sediment (e.g., Yang et al., 2001; Totten and Hanan, 2007, this volume).

This does not imply that weathering has only negative consequences for establishing relationships between mother and daughter sediments, or for reconstructing provenance and palaeotransport. On the contrary, analyses of the extent of weathering may help to establish lithostratigraphic correlations (see also Mange-Rajetzky, 1995; Mange et al., 1999; Morton et al., 2002) and to define stratigraphic boundaries at locations where other techniques are not available, too expensive, or otherwise impracticable (Van Loon, 1972/1973).

2. HEAVY MINERALS IN EXTREMELY WEATHERED SEDIMENTS

The most intensive chemical weathering of source rocks and derived sediments occurs in the tropics. Pedogenesis in the tropics can, depending on the type of sediment, affect the surficial sediments to a considerable depth (tens of metres), with leaching of the labile components. A specific type of sediment may result, particularly if the parent material is a pre-existing sediment that yields already well sorted detritus. Examples are the white sands that, in many countries in Europe, are called 'silver sands' (the bright white colour is caused by the virtual leaching of nearly all mineral species—including iron oxide and iron hydroxide coatings—leaving a residue containing predominantly quartz). Their remaining heavy mineral percentages (in the 50–500 μm size fraction) may be as low as 0.003% (De Jong and Van der Waals, 1971).

2.1. Sampling Problems

The above-mentioned very low heavy mineral percentages present a problem, because relatively large bulk samples need to be prepared to obtain sufficient amounts of grains for a statistically acceptable grain counting. A further problem is that the high weathering rate generally results in the relative enrichment of opaque minerals (predominantly leucoxene, ilmenite and virtually opaque rutile); these constitute up to 80% of the heavy mineral fraction in the silver sands under study. In addition, the transparent to translucent suite comprises varying amounts of unidentifiable, strongly weathered grains. These are generally grouped into a category, termed 'alterites', which often make up 5–10% of the non-opaque grains. Statistically reliable heavy mineral data, i.e., an analysis with a 95% chance of a maximum deviation of 10%, if a particular species makes up exactly 50% of the identifiable grains, requires that at least 100 identifiable grains are counted (Kalsbeek, 1969). Therefore, the size of a sample, collected at an outcrop, should be large enough to meet the prerequisite of a reliable heavy mineral analysis. The following principles need to be considered:

(1) A heavy mineral content of 0.003%, as sometimes found in the silver sands under study (De Jong and Van der Waals, 1971), implies that only 3 out of 100,000 grains are heavy mineral grains. To encounter 1 heavy mineral grain, a field sample containing approximately 33,000 grains is therefore needed.
(2) As mentioned above, up to 80% of the heavy mineral fraction is made up by opaque grains. To find 1 non-opaque grain, one thus needs a field sample of $5 \times 33{,}000 =$ (approximately) 165,000 grains.
(3) Up to some 10% of the non-opaque heavy mineral grains are alterites. Therefore, to find 1 non-opaque, non-alterite heavy mineral grain a field sample of $1.1 \times 165{,}000$ grains = (approximately) 183,000 grains need to be available.
(4) If 100 identifiable grains have to be counted per sample, one thus needs a field sample of $100 \times 183{,}000 = 18{,}300{,}000$ grains (roughly 20×10^6 grains).
(5) If these grains have average dimensions of $0.25 \times 0.25 \times 0.1$ mm ($= 0.00625\,\text{mm}^3$) and an average mass of $0.003\,\text{g/mm}^3$, one grain weights on the average 0.0000187 g ($\sim 20 \times 10^{-6}$ g).
(6) This implies that one reliable count needs a field sample of at least some $(20 \times 10^6) \times (20 \times 10^{-6})\,\text{g} = 400\,\text{g}$.
(7) It is generally necessary to have a sufficient amount of material available for a possible control; thus, taking into account 'laboratory losses', a sample should be at least 1 kg.

In general, a heavy mineral analysis should be based on the counting of more grains than described above. Reliable results need approximately 300 identifiable non-opaque grains. Consequently, the weight of each field sample should be at least 3 kg in the case of extremely weathered sediments. If the routine heavy mineral analysis is to be complemented by the investigation of particular mineral species, for instance for a weathering analysis (see below), a statistically reliable result requires the additional counting of approximately 100 grains of the selected specific mineral. If such a mineral makes up some 10% of the non-opaque, non-alterite heavy mineral fraction, the sample weight should be 10 times larger than the weight calculated above (3 kg), i.e., some 30 kg (10 kg if 'only' 100 specimens of the selected mineral type have to be analysed). Such unusually large samples are difficult to process, and this may explain why commonly insufficient grains of a specific mineral are available for weathering analysis. This also occurred in the present study but only in a few samples (indicated in the text or the figure captions).

3. METHODS

Material for the study was taken from two shafts (II and IV) of the previous Dutch coal mine Hendrik, from sandpit Beaujean, approximately 2–3 km north of the town of Heerlen (The Netherlands), and from sandpit Nievelstein (Germany), approximately 7 km east of Heerlen (Fig. 1). From the Hendrik-shaft II section, 56,

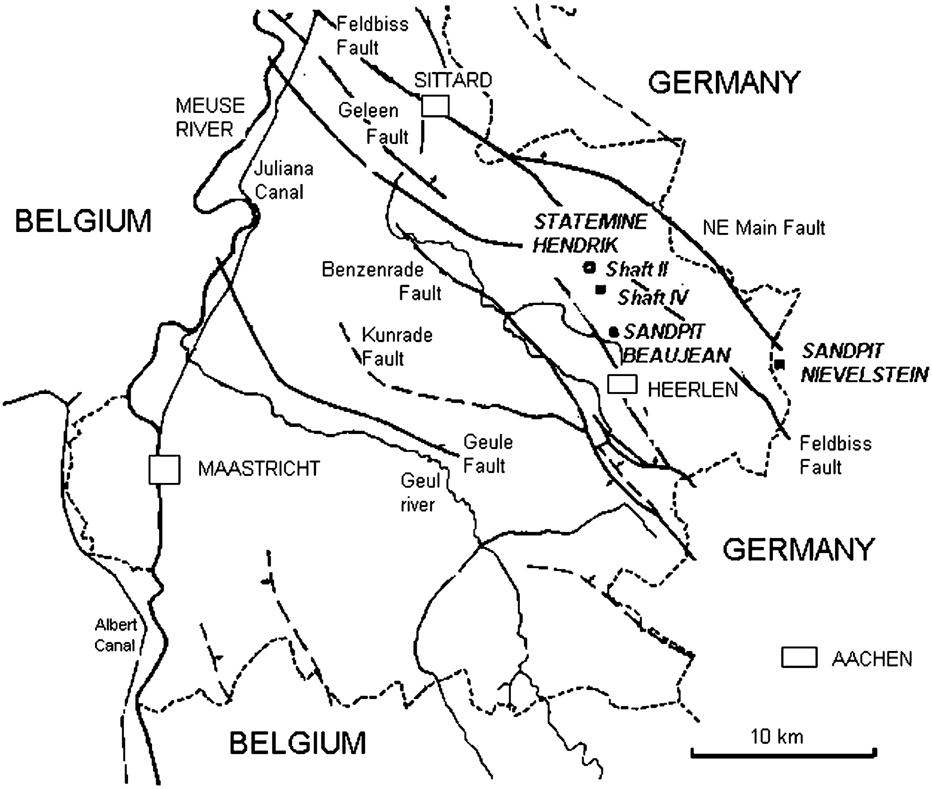


Fig. 1. Location map with the four sample areas (shafts II and IV of the Hendrik State Mine, Beaujean pit, Nievelstein pit).

and from shaft IV, 35 samples were collected. From the Beaujean surface profile 16 and from the Nievelstein pit 10 samples were taken. No material was sampled from the nearby silver sands at a possibly similar stratigraphic position in Belgium. Sample preparation for heavy mineral analyses focused on the 50–500 μm size range. For statistical reliability, explained above, 100 transparent heavy mineral grains were counted in each sample, except in sample L20 where, due to small sample size, only 65 identifiable heavy mineral grains were found. When specific heavy mineral species were investigated for their properties (shape, weathering and—in the case of tourmaline—colour), wherever possible, 100 grains of the particular species were counted in each sample, though this sum could not always be reached.

4. THE DUTCH/GERMAN SILVER SANDS

Characteristic examples of extremely weathered silver sands are represented by Tertiary deposits in the border area of The Netherlands, Germany and Belgium ('Dutch/German/Belgian silver sands') (Fig. 1). They are typically fine-grained, with well-rounded mineral grains, and are economically significant because they are often

Fig. 2. Browncoal seam (approximately 30 cm thick) of the Ville Formation overlying the silver sands (Heksenberg Member of the Breda Formation) in the Beaujean pit.

exploited for glass manufacturing or, as in the case of Southern Limburg (The Netherlands), for the production of fine-grained abrasives.

The origin and the age of these sands still remain enigmatic. In The Netherlands, they form the 5–50 m thick Heksenberg Member of the Breda Formation (De Mulder and Ritsema, 2003), previously known as the Heksenberg Formation (Kuyl, 1975). This is overlain by the Ville Formation (previously considered part of the then Heksenberg Formation; Kuyl, 1975), a browncoal unit (Fig. 2) of up to 300 m thick (although, in places, this brown coal has been entirely eroded).

4.1. Palaeogeography

The Heksenberg silver sands are considered as possibly beach sands by De Mulder and Ritsema (2003). Others argue that the occurrence of specific shell fragments points to tidal-flat conditions (Laban, 2004). One of the main problems in the interpretation of the depositional environment is that only a relatively thin part (some 20 m) of the Heksenberg Member is exposed. The original type section of the former Heksenberg Formation (now Heksenberg Member of the Breda Formation) was represented by a section in the Beaujean pit (which has disappeared through ongoing exploitation), combined with underlying strata, known only from a borehole (Kuyl, 1975). A further problem is that the scattered exposures (there are five isolated silver sand quarries in this area of The Netherlands) prevent an accurate palaeogeographical interpretation. The overall uniform grain size makes it, as a rule, difficult to recognise sedimentary structures and to analyse facies transitions. Schematic sketches of the palaeogeography during the Oligocene and Miocene are provided by Westerhoff et al. (2003), indicating that the area was roughly at the seashore at that time. The 'reference section' referred to in this contribution (shaft II of the Hendrik State Mine) contains by far the longest vertical section through the silver sands, however, a follow-up study of palaeogeographic developments and sedimentological characteristics is prevented by the lack of surface exposures and the fact that the shaft is no longer accessible because the mine has been closed several decades ago.

4.2. Dating and Stratigraphic Correlations

Originally, the silver sands were probably 'normal' sediments, containing clay (typical of almost all shallow marine and coastal deposits), plant debris and iron components (which occur in almost all sands); this hypothesis is supported by such characteristics in the lateral, eastward, continuation of this unit. The sands in the Dutch/German border area, however, have lost all these components, and are strongly depleted in both labile light and heavy minerals. Their extreme weathering (a form of eogenesis) is attributed to a combination of tropical pedogenesis and subsequent long-lasting leaching caused by large volumes of percolating humic acids from the overlying—originally locally up to 300 m thick—browncoal seams of the Ville Formation.

The lack of any suitable component in the silver sands has prevented thus far a reliable dating. Muller (1943), on the basis of their heavy mineral content, which he compared with similar assemblages from dated stratigraphic units, considered them as possibly ranging from Early Oligocene to Middle Miocene. However, Muller did not take account of the significant post-depositional changes in the heavy mineral assemblages of the silver sands. The age of the overlying browncoal seams is not precisely known either, but is now assumed to be Oligocene and/or Miocene (De Mulder and Ritsema, 2003; Laban, 2004). This would imply that Muller's dating was probably—at least in part—incorrect. It is hoped that, as new techniques become available, exact dating of these sands may be achieved.

All silver sands in the Dutch/German/Belgian border region (Fig. 3) look macroscopically exactly the same, commonly without any traceable sedimentary structures, which makes it practically impossible to distinguish and subdivide them in the field. The former Netherlands State Geological Survey, nevertheless, considered it important to identify any characteristics that might help to establish their stratigraphic position for correlation purposes. This was one of the objectives of Muller's (1943) heavy

Fig. 3. Silver sands in the Nievelstein sandpit (Germany), closely resembling those in the nearby Beaujean pit (Netherlands). Height of the sand wall approximately 15 m.

mineral study. Later heavy mineral analysis by Van Loon (1972/1973) resulted in a more relevant approach, which facilitated recognition of either differences in sediment supply or non-deposition when pedogenesis and post-depositional weathering prevailed. As a result, units with different geological histories could be distinguished, and boundaries between them delineated. It is beyond the scope of this contribution to discuss the precise stratigraphy yielded by heavy mineral analysis. Instead, attention will be focused on the approach used and observations that resulted in the successful analysis of these extremely weathered sands.

4.3. Heavy Mineral Content

Following identification and point counting, the number-percentages of the identified detrital heavy mineral species were calculated. Samples from all four analysed sites (Fig. 1) show low-diversity assemblages, consisting mainly of tourmaline, zircon, rutile and minor quantities of anatase; high-grade metamorphic minerals such as andalusite, staurolite and kyanite occur in very low number, and sillimanite was found only in trace amounts. The metamorphic minerals showed similar physical appearance and identical optical properties in all samples, and were interpreted as having been derived from one single metamorphic source. Garnet was found only in the two mineshafts in almost each sample (commonly in relatively high abundance: 10–30%) (Fig. 4). Epidote occurs throughout the samples from both mineshafts but is rare in the Beaujean pit, and absent in the Nievelstein pit. Accessory minerals (brookite, hornblende, corundum, monazite, sphene, zoisite, spinel and topaz) were encountered only in samples from the mineshafts. Apatite is completely absent, which is interpreted by its sensitivity to tropical weathering and/or leaching by humic acids.

Similarities of the heav mineral associations and the presence/absence of epidote, garnet and accessories allowed us to reach the tentative conclusion that all four sites represent a similar—or at least partly similar—stratigraphic interval, and that the sands in the two sandpits had undergone a more intensive and continued weathering than those in the shafts.

4.4. Stratigraphic Subdivision Based on Heavy Mineral Assemblages

Based on changes in the ratios of the main heavy mineral components the 'reference section' can be subdivided into five units (Fig. 4A). Muller (1943) tentatively allocated them as Early Oligocene, Middle Oligocene, Middle Miocene + reworked Oligocene, distinguishing also a Middle Miocene garnet-bearing assemblage and a Middle Miocene, Limburg assemblage, respectively. The current study found similar changes in heavy mineral compositions but—because Muller's dating had no precise constraints—in this study the five units are indicated by letter codes (A through E, from bottom to top) rather than by chronostratigraphic terms. The boundaries between the five units are based on the following changes in heavy mineral composition (Fig. 4A):

- A/B boundary: distinct increase in ultrastable minerals (zircon, rutile, anatase), decrease in epidote and garnet;
- B/C boundary: almost complete disappearance of epidote, increase in garnet; some increase in tourmaline. Muller (1943) considered this unit, which he called 'Middle

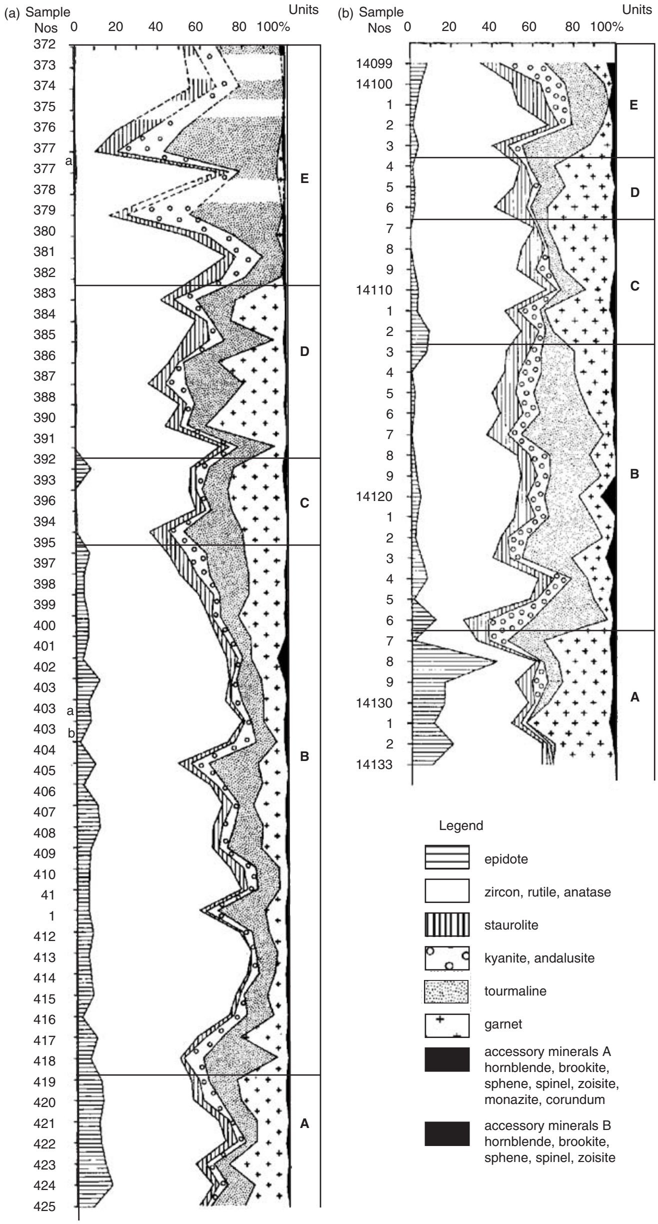


Fig. 4. Composition of the 50–500 μm heavy mineral fraction from the shafts of the Hendrik State Mine (based on 100 translucent grain counts per sample). Adapted after Van Loon (1972/1973). a (left): Shaft II. Stratigraphic interpretation according to Muller (1943). b (right): Shaft IV. Counting by the then Geological Survey of The Netherlands.

Miocene + reworked Oligocene' as a unit composed of newly supplied sediment, intermixed with reworked material from the top of the underlying unit. The present authors fully agree with this interpretation;

- C/D boundary: strong increase in garnet, mainly at the expense of the ultrastable species; further increase in tourmaline;
- D/E boundary (marks the most obvious change in composition): a sudden, almost complete, disappearance of garnet, accompanied by an increase of staurolite and a marked increase in tourmaline.

Garnet has not been encountered in any of the samples from the Beaujean pit, and was found only as a very minor component in the lowermost sample from the Nievelstein pit. The overall heavy mineral content gives the clear indication that the lower section (80%) of the Beaujean samples should be attributed to unit E (Fig. 5A). The upper part (20%) is marked by a sharp increase in the abundance of zircon, rutile and anatase from ~10 to ~30–50%, accompanied by a distinct decrease in tourmaline from ~50 to ~35%. The upper part of the Beaujean Pit is, therefore, tentatively allocated to a level above unit E, although no boundary between these two units can be observed in the field. The situation is less clear for the

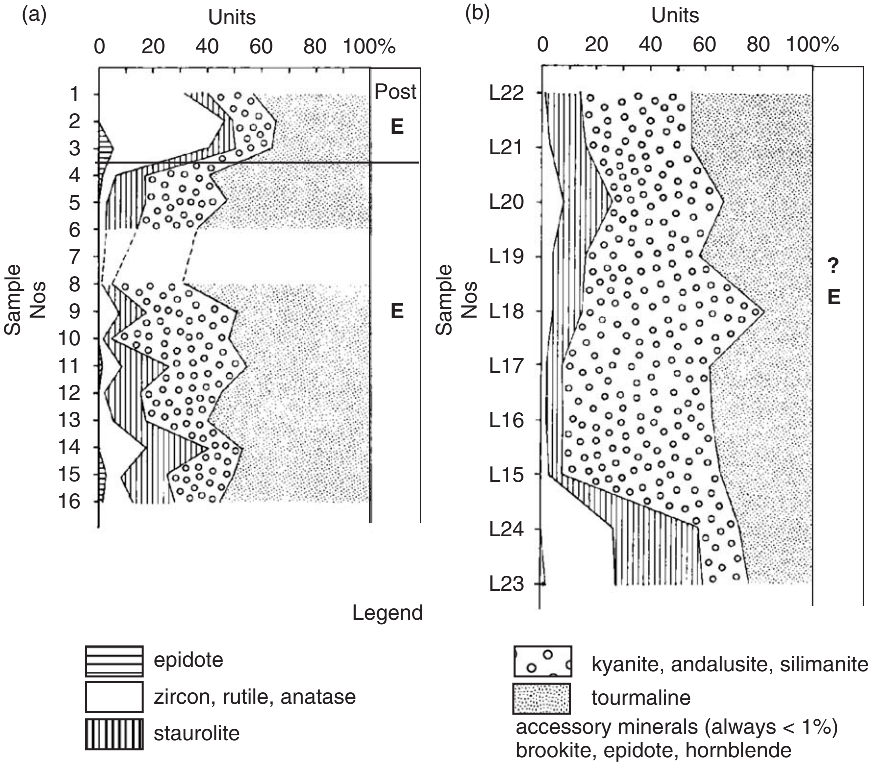


Fig. 5. Composition of the 50–500 μm heavy mineral fraction from the two investigated sandpits (based on 100 translucent grains counts per sample). Slightly modified after Van Loon (1972/1973). a (left): Sandpit Beaujean (The Netherlands). b (right): Nievelstein sandpit (only 65 translucent grains were found in sample L20).

Nievelstein pit (Fig. 5B), although the ratios between the various heavy minerals suggest that this section is correlatable with the lower part of unit D.

4.5. Tourmaline Colour Varieties

Tourmaline, overall the most abundant mineral, comprises a number of colour varieties, which were distinguished in eight groups:

1. Grains are pleochroic from dirty grey to entirely black. Sometimes a slight pink tint may glimmer through the grey colour.
2. Grains are mainly brown. The following pleochroism may be found: (a) colourless to brown; (b) light brown to dark brown; (c) brown to almost black; (d) faintly pleochroic, fairly dark brown; (e) brown to greenish; (f) yellow to brown.
3. Grains show both brown and greenish blue colours. This may be due to pleochroism when the grain is rotated over 90° but these colours may also exist simultaneously, usually showing brown streaks in a greenish blue field. Greenish blue, non-pleochroic grains are also considered to belong to this colour variety.
4. Grains are mainly green, sometimes with a brownish tint. Pleochroism may be: (a) from light to dark green; (b) from green to almost black; (c) almost absent in dark green grains.
5. Grains are blue, usually with a very bright hue, changing from light to darker, rarely from dark blue to almost black.
6. Grains have a typical wine red to brownish red colour, turning into very dark green (sometimes nearly black) when rotating them over 90°.
7. Grains show pleochroism from dirty pink to greenish blue.
8. Grains show pleochroism from light red to bright green.

None of these groups showed more than a vague relationship with the total mineralogical compositions and indicated no relationship at all with the total tourmaline percentage in a sample. However, some trends were detectable between the various colour varieties and one colour variety showed a distinct relationship with the staurolite percentage. This is noteworthy because, as will be shown later, staurolite abundance reflects the degree of weathering. This implies that the response of the various tourmaline colour varieties to the intensity of weathering may not be uniform, and this might explain the differences reported in the literature on the resistance of tourmaline to chemical weathering (see, amongst others, Makarov and Kondrateva, 1965; Varadachari et al., 1994; Morton and Hallsworth, 2007, this volume).

4.6. Grain Shapes

The original grain shape of minerals is affected primarily by weathering and attrition during transport/recycling and by weathering in situ. To augment information, the morphology of zircon (idiomorphic, rounded prisms, rounded) and tourmaline (idiomorphic, irregular, rounded) was also recorded. This revealed that the tourmaline colour varieties responded similarly to attrition. The effects of chemical weathering on tourmaline colour varieties will be evaluated in the next section.

5. CHEMICAL WEATHERING OF HEAVY MINERALS IN THE SILVER SANDS

Studies on weathering processes aim to assess the rate of weathering, to identify the chemical milieu and to reconstruct the time span over which grains were exposed to particular weathering conditions (Velbel, 2007, this volume). If the rate of weathering is not excessive many mineral species can be investigated. The highly weathered silver sands contain only three species (in sufficient quantities) that are suitable for a weathering analysis: garnet, staurolite and tourmaline. All three display clearly the different stages of weathering. This is remarkable because garnet is commonly considered as relatively prone to chemical weathering, while tourmaline is generally defined as an ultrastable, highly resistant species. However, unusual conditions in the silver sands (tropical pedogenesis, followed by the percolation of humic acids, probably in large amounts, during a prolonged period) indicate that weathering under extremely aggressive conditions differs considerably from common chemical weathering, even if it continues for a long time.

Garnet is present in suitable quantities in shaft IV (100 grains per sample) and shaft II (50 grains) of the Hendrik mine but is virtually absent in the two sandpits. Staurolite was successfully investigated from all four localities and its relative abundance allowed inspecting 50 grains per sample. Tourmaline was found in sufficient quantities in both the mineshafts and the Nievelstein pit sands, enabling inspection of 100 grains per slide.

5.1. *Weathering of Garnet*

It has been proved that garnet disappears at a geologically rapid rate in acidic soils (e.g., Velbel, 1984), which explains the paucity of garnet in the analysed samples. Where garnet was present, the grains could be subdivided into four dissolution stages (Fig. 6), ranging from fresh (no dissolution can be detected under the light microscope) to strongly corroded (either at one or several points, or the entire grain). Differing garnet chemical compositions and internal structure, such as zoning, can

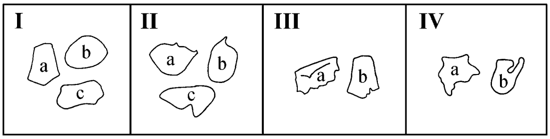
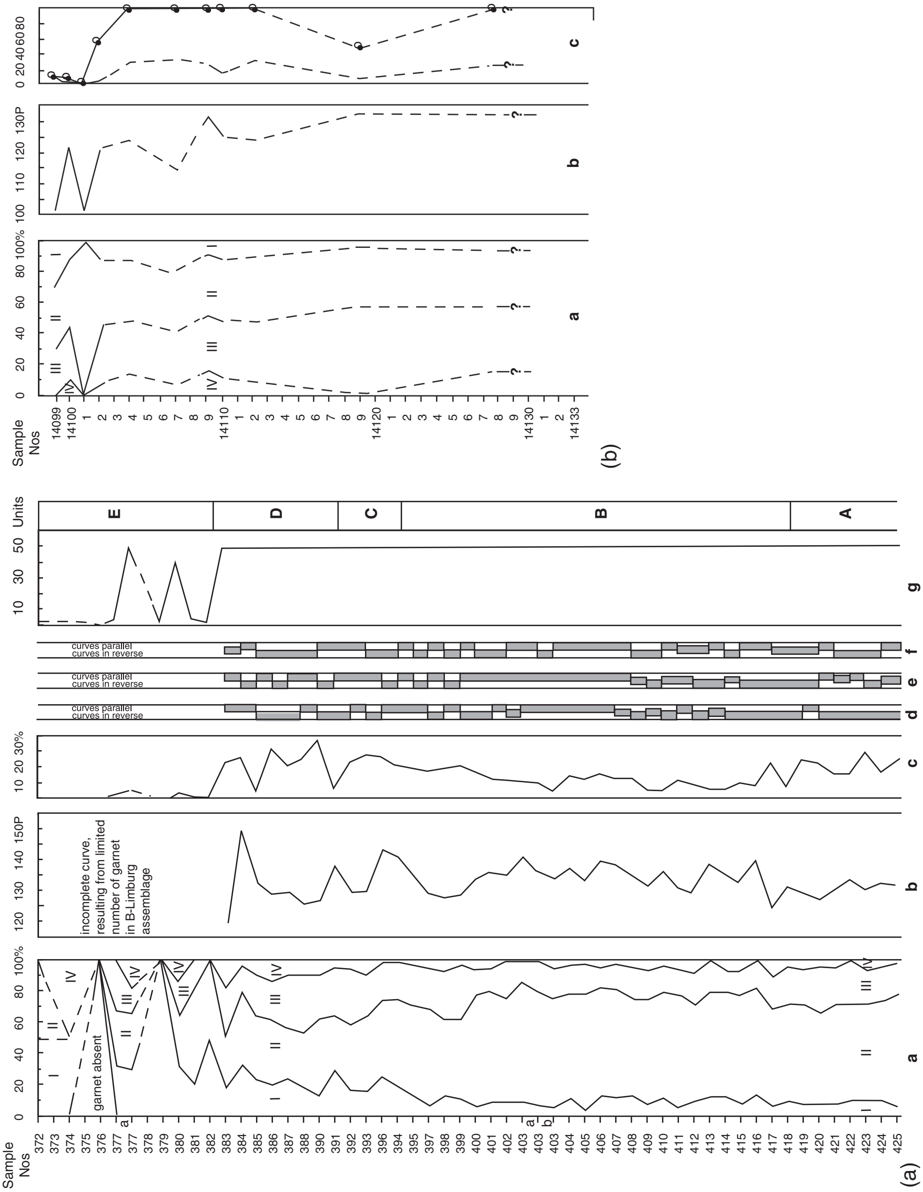


Fig. 6. Schematic representation of corrosion classes (dissolution stages) of garnet. I: The contours of the grains show no irregularities as a result of corrosion, but some etching may be found. Usually, the grains are angular (a), possibly due to frequent breakage; sometimes they are well rounded (b) or sub-rounded (c). II: The shape of the grain is difficult to explain by transport only. The grains may be rounded, but initial corrosion seems to have taken place (a). Selective corrosion may result in ‘spines’ at resistant parts (b) or in cavities at less resistant areas (c). III: The grains show distinct corrosion, usually only locally (b). One fresh surface (a) may originate from breakage shortly before deposition. IV: The grains indicate highly advanced dissolution. They may be entirely corroded (a), or dissolution occurs only in one particular area (b).


Sample Nos
(a)
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I
II
III
IV
garnet absent
a
120 130 140 150P
incomplete curve, resulting from limited number of garnet in B-Limburg assemblage
b
10 20 30%
c
curves parallel
curves in reverse
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f
10 30 50
g
Units
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D
C
B
A
(b)
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a
100 110 120 130P
b
0 20 40 60 80
c

cause differences in garnet behaviour during chemical weathering. It is therefore important to note that all garnets observed during these analyses had similar optical characteristics (colour, isotropism, inclusions, relief), even though their weathering degrees showed differences. It is, from a chemical/petrological/pedological point of view, interesting that all four dissolution stages (Fig. 6) were detected in almost all samples from the two mineshafts, presenting an association of strongly corroded and completely fresh grains in a single sample. Because all grains were extracted from relatively small size samples, this enigmatic behaviour cannot be explained with spatially different corrosive conditions.

The fragile form of the heavily corroded garnet grains indicates that they are not inherited because these would have been destroyed by the prolonged rigorous action of waves and currents in their depositional environment; therefore, dissolution must have taken place in situ (after deposition). Considering the fact that all garnet grains in these sands have similar properties, the logical conclusion is that chemical weathering affects minerals in a statistical way, with the implication that—if a realistic insight into the degree of post-depositional weathering is to be achieved—a statistically significant number of grains of a particular mineral species needs to be analysed. The sample size of extremely weathered sediments should therefore be larger than the 10 kg mentioned above, even if garnet is present in quantities of over 10% in the non-opaque suite.

Fig. 7 shows that no relationship exists between the degree of garnet weathering and garnet percentage in the samples. This may be due to the fact that extreme weathering causes the complete dissolution of many of the garnet grains, resulting in an unrealistic picture caused by the relative enrichment of the less affected grains. Concluding from the above, garnet is—in general—less suitable for the study of mineral weathering in highly weathered sediments; on the other hand, it can be used as a very good signature for the relative degree of weathering in less intensely weathered sediments.

5.2. *Weathering of Staurolite*

In the silver sands, staurolite appears to be resistant to acidic leaching, as indicated by an increase in its percentage in samples containing a relatively high number of weathered grains (Fig. 8) but, similarly to garnet, 'fresh' specimens coexist with strongly corroded ones. This finding is consistent with that of Ollier (1969), who

Fig. 7. Corrosion of the garnet in the shafts of the Hendrik State Mine. Adapted after Van Loon (1972/1973). a (left): Shaft II. (a) Relative proportions of corrosion classes (see Fig. 6 for details). (b) Simplified curve, constructed on the basis of weighed percentages of the corrosion classes. (c) Percentage of garnet in the 50–500 μm heavy mineral fraction. (d) Relationship between simplified corrosion curve (b) and percentage curve (c). (e) Relationship between simplified corrosion curve (b) and the corrosion of staurolite. (f) Relationship between simplified corrosion curve (b) and the corrosion of tourmaline. (g) Number of classified garnet grains. b (right): Shaft IV. (a) Relative proportions of corrosion classes (see Fig. 6 for details). (b) Simplified curve, constructed on the basis of weighed percentages of the corrosion classes. (c) Percentage of garnet in the 50–500 μm heavy mineral fraction (left) and number of classified garnet grains (right).

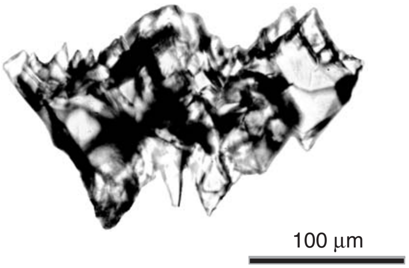

Fig. 8. Strongly corroded staurolite grain (plane polars).

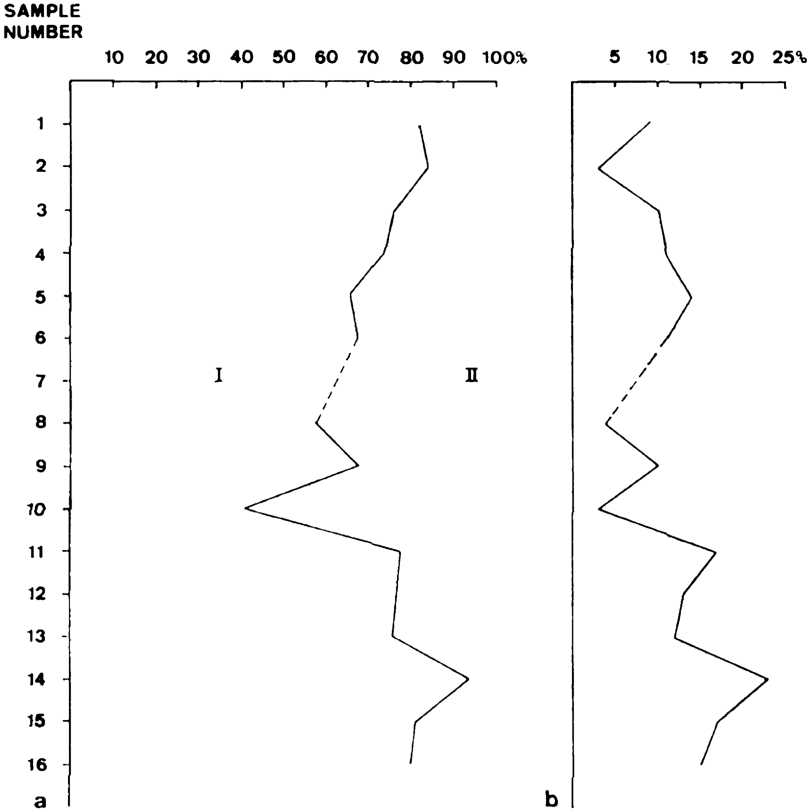

Fig. 9. Corrosion of the staurolite in the Beaujean sandpit. In each sample 50 grains were classified, except in samples 10 (34 grains) and 12 (30 grains). From Van Loon (1972/1973). (a, left) Corrosion curve, dividing type I grains (the grains are not or only slightly weathered) from those of type II (strongly corroded grains). (b, right) Percentage of staurolite in the heavy mineral fraction.

called staurolite a useful indicator mineral of weathering. There are some horizons, particularly in the upper part ('younger than unit E') in the Beaujean pit, however, where the weathering/corrosion curves and the percentage curves show distinctly opposite trends, contrasting with the 'normal', parallel, curves in the lower part of the section (Fig. 9). The only explanation for this trend is that the quantity of staurolite was initially different in beds in the upper level. This observation is significant, because it indicates that, even in extremely weathered sediments, staurolite—if present—may be used for detecting changes in sediment supply.

5.3. Weathering of Tourmaline

A high number of tourmaline grains shows appreciable signs of corrosion in the reference section (Fig. 10). Although tourmaline is generally considered both mechanically and chemically resistant and has been shown that it is able to survive several deposition/erosion/transport cycles (e.g., Ollier, 1969; Nickel, 1973; Friis, 1974, 1976; Morton and Hallsworth, 1999), in most samples of the reference section some 10–20% of tourmaline grains show a certain extent of corrosion (Fig. 11), commonly in the form of etch pits, but sometimes as thin, fragile 'wings'. Idiomorphic grains appear to be corroded slightly more frequently than rounded ones (Fig. 12). The various colour varieties also display slight differences in their weathering susceptibility. The influences of both shape and, concluding from their colour, chemical composition make tourmaline less suitable for studies of weathering under extreme conditions. This is amplified by the fact that tourmaline cannot be

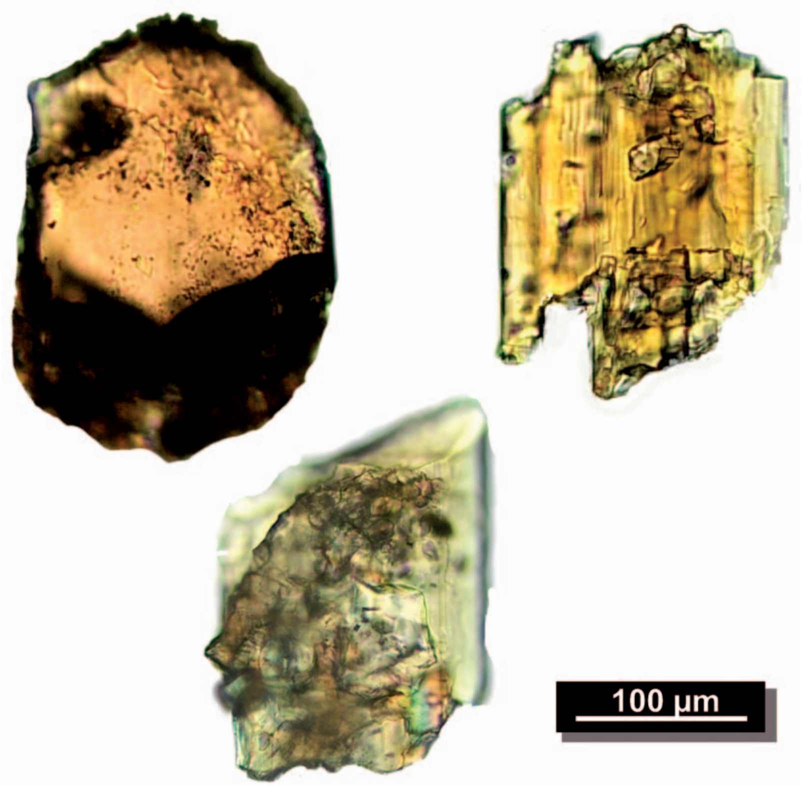

Fig. 10. Strongly corroded tourmaline grains.

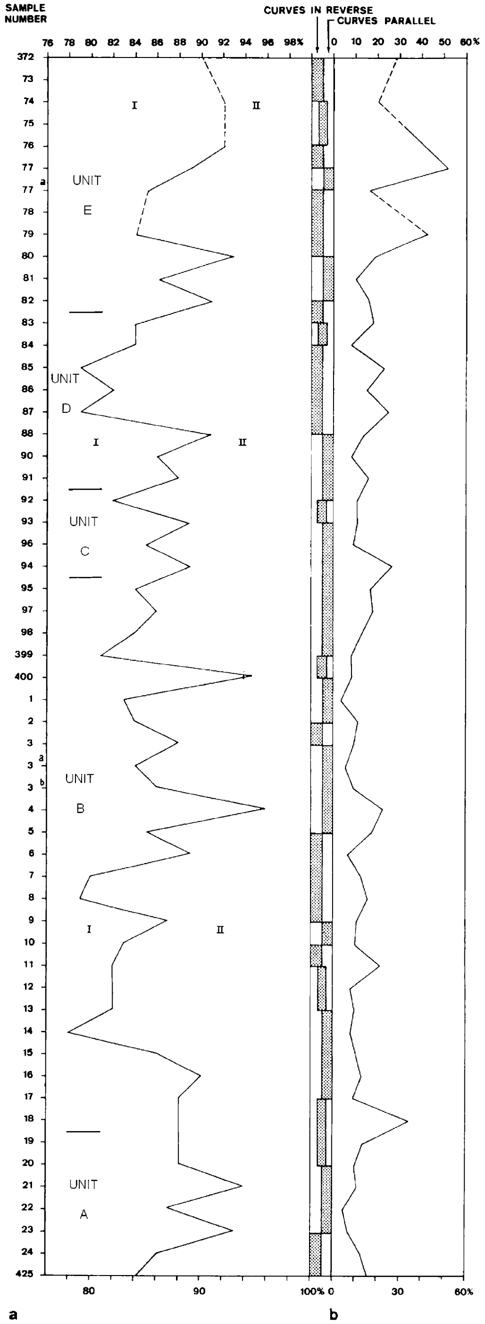
SAMPLE NUMBER
CURVES IN REVERSE
CURVES PARALLEL
76 78 80 82 84 86 88 90 92 94 96 98%
0 10 20 30 40 50 60%
372 73 74 75 76 77 a 77 78 79 80 81 82 83 84 85 86 87 88 90 91 92 93 96 94 95 97 98 399 400 1 2 3 a 3 b 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 425
I
II
UNIT E
UNIT D
UNIT C
UNIT B
UNIT A
80
90
100% 0
30
60%
a
b

Fig.11

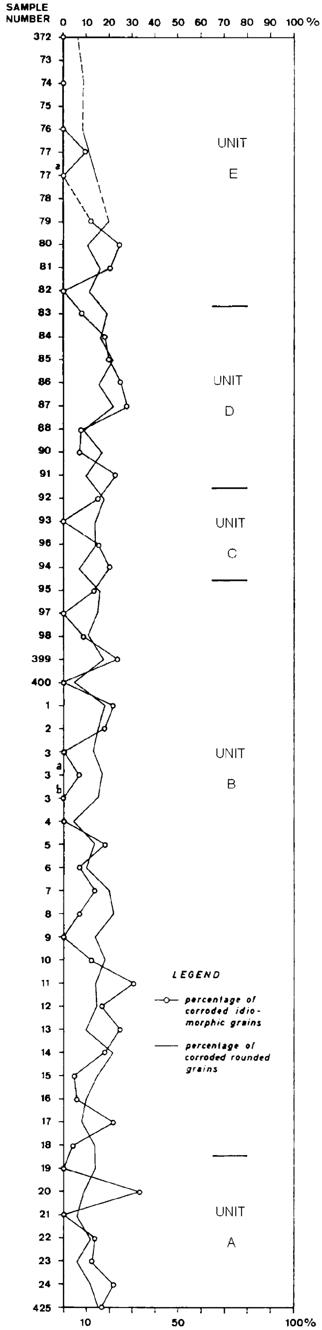
SAMPLE NUMBER
0 10 20 30 40 50 60 70 80 90 100%
372 73 74 75 76 77 a 77 78 79 80 81 82 83 84 85 86 87 88 90 91 92 93 96 94 95 97 98 399 400 1 2 3 a 3 b 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 425
UNIT E
UNIT D
UNIT C
UNIT B
UNIT A
LEGEND
percentage of corroded idiomorphic grains
percentage of corroded rounded grains
10
50
100%

Fig.12

selectively enriched as a result of weathering but, as shown by this study, it can also become relatively impoverished with highly advanced weathering (see also Morton and Hallsworth, 2007, this volume). Our observations may contradict most findings thus far, including the well-established ZTR (zircon, tourmaline, rutile) maturity index (Hubert, 1962) but such extreme conditions that produced the silver sands are far less frequent than common chemical weathering.

6. CONCLUSIONS

Extremely weathered sands, exemplified by the Dutch/German silver sands, contain not only very low proportions of heavy minerals but, resulting from dissolution of the less stable minerals, also a limited number of species. The present-day heavy mineral content differs considerably from their original composition. On the basis of the remaining specific minerals, the degree of weathering can be estimated. Staurolite, when present, appears to be most suitable for assessing the intensity of weathering in extremely weathered sediments. This, in turn, may allow an assessment of the other minerals that may have been present initially. For instance, strongly weathered staurolite in a sample indicates that minerals that are more susceptible to weathering were eliminated. Moreover, the presence of staurolite, often associated with andalusite and kyanite in regionally metamorphosed rocks, suggests that they were probably present at the time of sedimentation, and provides information on sand provenance.

The Dutch/German silver sands present a prime example of dual episodes of intensive weathering that were presumably common in the geological past. This study also conveys a warning, and demonstrates that a low-diversity, stable-ultrastable species-dominated heavy mineral content should not be routinely ascribed to the causes of deep-burial diagenesis. Therefore, a low-diversity heavy mineral assemblage in surficial sediments may reflect in situ weathering, or deep weathering of the source rocks. The location (either source rock or derived sediment) of the weathering can be reconstructed from grain morphology. Because fragile grains cannot survive—at least not in large quantities—long transport or processes like wave action, their presence in a given sediment indicates that weathering has taken place in situ. On the other hand, if there are no signs of in situ corrosion in highly depleted assemblages, it is most likely that the dissolution took place in the sediment source area. Distinguishing between these possible sites of weathering is important for accurate provenance determination using heavy minerals, and for correlating sand units in reservoir successions.

Fig. 11. Corrosion of the tourmaline from shaft II of the Hendrik State Mine. In each sample 100 grains were classified, except in samples 372 (55 grains), 381 (59 grains) and 413 (69 grains). Slightly modified after Van Loon (1972/1973). (a) Corrosion curve, dividing type I grains (the grains are not or only slightly weathered) from those of type II (strongly corroded grains). (b) Percentage of tourmaline in the heavy mineral fraction.

Fig. 12. Corrosion curves for idiomorphic and rounded tourmaline grains from shaft II of the Hendrik State Mine. Slightly modified after Van Loon (1972/1973).

Grain shape also influences the susceptibility to post-depositional weathering, and should be taken into account, especially if a species is represented by different or contrasting morphologies, such as idiomorphic and rounded. This is especially applicable to mechanically highly resistant minerals such as zircon, rutile and tourmaline.

The simultaneous occurrence of highly corroded and apparently fresh grains of the same mineral species within one single sample indicates that corrosion has statistical significance; therefore, the degree of weathering cannot be determined on the basis of a few corroded grains alone. Weathered grains with fragile 'spines' cannot be transported far by running water without losing most of the fragile parts, as grains in the 50–500 μm size range are most commonly transported by saltation and as bedload; in both cases strain is exerted on the grains. This study shows that the combined presence of fresh and strongly weathered grains does not necessarily signal supply from dual or multiple sources.

It is essential to analyse a sufficient number of grains (at least 50–100 grains per species) to enable comparison and evaluation of the degree of weathering in different samples from a sediment package. Our study of the silver sands reveals that whereas slow, prolonged weathering produces grains with (for one mineral species) approximately similar degrees of weathering, aggressive weathering, even during a shorter time span (such as pedogenesis under tropical conditions; Horbe et al., 2004), may result in variably corroded grains. Such aggressive conditions were probably responsible for the extreme corrosion of the mineral components of the silver sands.

The response of minerals of a solid solution series between two (or more) chemical end members, such as tourmaline, to chemical weathering appears to be partly controlled by the chemistry of the individual members. In contrast to what is commonly stated in the literature, tourmaline content, though generally becoming higher with increasing degree of weathering, can also become relatively impoverished at some intervals. The relative proportions of tourmaline colour varieties (see Hawthorne and Henry, 1999 for an overview of minerals of the tourmaline group) in the current study most probably reflect their different chemistry-controlled reactions to the weathering agents. Unravelling the geological history of a sediment on the basis of varying grain shape and composition of the tourmaline colour varieties is a novel approach. For example, Willner (1987) and Jiang et al. (1999) demonstrated that a detailed analysis of changes in the ratios between the various colour varieties could provide information on different sediment source areas.

The greater is the diversity of a heavy mineral assemblage, especially if rare but diagnostic species are present, the more accurately the provenance of the sediments can be reconstructed. In cases of low-diversity assemblages high-resolution heavy mineral analysis (as demonstrated by Lihou and Mange-Rajetzky, 1996) may help with provenance reconstruction and correlation by focusing on the characteristic varieties of ultrastable minerals. The silver sands under study are poor in heavy mineral species and no provenance-diagnostic minerals occur. Their highly depleted heavy mineral assemblages have presented a particular challenge. However, distinguishing and combining corrosion and attrition signatures of the suitable heavy mineral species enabled, with great reliability, the correlation of the sample set from shaft IV of the Hendrik State Mine with a large part of the reference section (i.e., shaft II the Hendrik State Mine) (compare Fig. 4). Similarly, the silver sands from the Nievelstein sandpit in Germany could also be correlated with the reference section, though with somewhat less certainty because the extreme weathering in the Nievelstein sandpit had progressed so far that almost all heavy mineral species have disappeared. Nevertheless, its lower profile seems to be comparable with the upper part of the reference section (compare Fig. 4).

Weathering signatures also proved useful in the case of the Beaujean silver sandpit. Sudden changes, both in heavy mineral composition (Fig. 5A) and in grain characteristics, permitted delineation of a distinct boundary, even though no boundary could be detected in the field. Concluding from differences in the degree of corrosion, the lower interval of the Beaujean section can be correlated with the top part of the reference section (compare Figs. 4A and 5A). This also indicates that the upper part of the Beaujean pit is younger (post-unit E) than the upper part of the reference section (units D and E).

Surficial sediments may show heavy mineral assemblages that have been modified in the course of time by dissolution during intensive weathering. They thus obscure the original heavy mineral composition and may also give misleading (or at least incomplete) information on sediment provenance. No heavy mineral study is therefore complete without a systematic analysis of the degree of weathering. This study introduces the environment of advanced weathering in surficial sediments, contrasting with that of deep burial (Morton and Hallsworth, 2007, this volume). Although both processes result in depleted heavy mineral suites that comprise the common ultrastable 'heavy mineral end-members', their geochemical environments (e.g., temperature, pressure, pore fluids, compaction) differ considerably. When analysing diagenetically affected, low-diversity assemblages (especially where a systematic analysis of progressive changes/depletion of heavy mineral suites is not possible), it is most important to consider whether all dissolution occurred during burial diagenesis, or whether the sediments experienced a longer period of surface weathering and mineral dissolution prior to burial, which then may have imparted little modification to the already depleted assemblages.

Finally, it is important to note that detailed analysis of the dissolution stages of specific heavy minerals in extremely weathered sands (such as the silver sands studied here) requires unusually large field samples (at least a few kg and for specific purposes even 10 kg). The difficulty of dealing with such large sample volumes may be one of the reasons why so few studies of this type have been carried out on sediments with very low heavy mineral content.

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REFERENCES

Amireh, B.S., 1991. Mineral composition of the Cambrian-Cretaceous Nubian series of Jordan: provenance, tectonic setting and climatological implications. Sedimentary Geology 71, 99–119.

Bhatia, M.R., 1985. Rare earth element geochemistry of Australian Paleozoic graywackes and mudrocks: provenance and tectonic control. Sedimentary Geology 45, 97–113.

Blatt, H., Sutherland, B., 1969. Intrastratal solution and non-opaque heavy minerals in shales. Journal of Sedimentary Petrology 39, 591–600.

Bramlette, M.N., 1941. The stability of minerals in sandstone. Journal of Sedimentary Petrology 11, 32–36.

Busacca, A., Cremaschi, M., 1998. The role of time versus climate in the formation of deep soils of the Apennine fringe of the Po valley, Italy. Quaternary International 51/52, 95–107.

De Jong, J.D., Van der Waals, L., 1971. Depositional environment and weathering phenomena of the white Miocene sands of Southern Limburg (The Netherlands). Geologie en Mijnbouw 50, 417–424.

De Mulder, F.J., Ritsema, I., 2003. Duurzaam gebruik en beheer van de ondergrond. In: De Mulder, F.J., Geluk, M.C., Ritsema, I., Westerhoff, W.E., Wong, Th.E. (Eds.), De Ondergrond van Nederland (Geologie van Nederland 7). Nederlands Instituut voor Toegepaste Geowetenschappen, Utrecht, pp. 11–64.

Dill, H.G., 1995. Heavy mineral response to the progradation of an alluvial fan: implications concerning unroofing of source area, chemical weathering and palaeo-relief (Upper Cretaceous Parkstein fan complex, SE Germany). Sedimentary Geology 95, 39–56.

Dill, H.G., 1998. A review of heavy minerals in clastic sediments with case studies from the alluvial-fan through the near-shore environments. Earth-Science Reviews 45, 103–132.

Dryden, A.L., Dryden, C., 1946. Comparative rates of weathering of some common heavy minerals. Journal of Sedimentary Petrology 16, 91–96.

Edelman, C.H., Doeglas, J.D., 1934. Über Umwandlungserscheinungen an detritischem Staurolith und anderen Mineralien. Tschermaks Mineralogische und Petrologische Mitteilungen 45, 225–234.

Friis, H., 1974. Weathered heavy mineral associations from the young-Tertiary deposits of Jutland, Denmark. Sedimentary Geology 12, 199–213.

Friis, H., 1976. Weathering of a Neogene fluviatile fining-upwards sequence at Voervadsbro, Denmark. Bulletin of the Geological Society of Denmark 25, 99–105.

Friis, H., 1978. Heavy mineral variability in Miocene marine sediments in Denmark: a combined effect of weathering and reworking. Sedimentary Geology 21, 169–188.

Grimm, W.-D., 1973. Stepwise heavy mineral weathering in the residual quartz gravel, Bavarian Molasse (Germany). Contributions to Sedimentology 1, 103–125.

Hawthorne, F.C., Henry, D.J., 1999. Classification of the minerals of the tourmaline group. Journal of Mineralogy 11, 201–215.

Horbe, A.M.C., Horbe, M.A., Seguio, K., 2004. Tropical spodosols in northeastern Amazonas State, Brazil. Geoderma 119, 55–68.

Hubert, J.F., 1962. A zircon-tourmaline-rutile maturity index and the interdependence of the composition of heavy mineral assemblages with the gross composition and texture of sandstones. Journal of Sedimentary Petrology 32, 440–450.

Hubert, J.F., 1971. Analysis of heavy mineral assemblages. In: Carver, R.E. (Ed.), Procedures in Sedimentary Petrology. Wiley, New York, pp. 453–478.

Jiang, S.Y., Yang, J.H., Palmer, M.R., 1999. Chemical compositions of tourmaline from the Inch Conglomerate Formation, Dingle Peninsula, SW Ireland, and their implications in provenance analysis. Chemie der Erde 59, 123–133.

Kalsbeek, F., 1969. Note on the reliability of point counter analyses. Neues Jahrbuch für Mineralogie, Monatshefte, Jahrgang, pp. 1–6.

Kuyl, O.A., 1975. Lithostratigrafie van de Mio-Oligocene afzettingen in Zuid-Limburg. In: Zagwijn, W.H., Van Staalduinen, C.J. (Eds.), Toelichting bij geologische overzichtskaarten van Nederland. Rijks Geologische Dienst, Haarlem, pp. 56–63.

Lacassie, J.P., Roser, B., Del Solar, J.R., Hervé, F., 2004. Discovering geochemical patterns using self-organizing neural networks: a new perspective for sedimentary provenance analysis. Sedimentary Geology 165, 175–191.

Laban, C., 2004. Wandelen over kanariezand. Mens & Wetenschap 31, 62–65.

Lång, L.-O., 2000. Heavy mineral weathering under acidic soil conditions. Applied Geochemistry 15, 415–423.

Lihou, J.C., Mange-Rajetzky, M.A., 1996. Provenance of the Sardona Flysch, eastern Swiss Alps: example of high-resolution heavy mineral analysis applied to an ultrastable assemblage. Sedimentary Geology 105, 141–157.

Makarov, V.N., Kondrateva, D.M., 1965. Alterations of tourmaline in weathering profile of the Yakovlev iron-ore deposits in the Kursk magnetic anomaly area. Akademiya Nauk Ukrainskoi SRS (Kiev) Dopovdi 1, 84–87.

Mange, M.A., Maurer, H.F.W., 1992. Heavy Minerals in Colour. Chapman and Hall, London, 147.

Mange, M.A., Turner, P., Ince, D., Pugh, J., Wright, D., 1999. A new perspective on the zonation and correlation of barren strata: an integrated heavy mineral and palaeomagnetic study of the Sherwood Sandstone Group, East Irish Sea Basin and surrounding areas. Journal of Petroleum Geology 22, 325–348.

Mange-Rajetzky, M.A., 1995. Subdivision and correlation of monotonous sandstone sequences using high-resolution heavy mineral analysis, a case study: the Triassic of the Central Graben. In: Dunay, R.E., Hailwood, E. (Eds.), Dating and Correlating Biostratigraphically-Barren Strata, 89. Geological Society of London Special Publication, pp. 23–30.

Milliken, K.L., 1988. Loss of provenance information through subsurface diagenesis in Plio-Pleistocene sandstones, northern Gulf of Mexico. Journal of Sedimentary Petrology 58, 992–1002.

Milliken, K.L., Mack, L.E., 1990. Subsurface dissolution of heavy minerals, Frio Formation sandstones of the ancestral Rio Grande Province, South Texas. Sedimentary Geology 68, 187–199.

Mongelli, G., 1993. REE and other trace elements in a granitic weathering profile from "Serre", southern Italy. Chemical Geology 103, 17–25.

Morton, A.C., 1984. Stability of detrital heavy minerals in Tertiary sandstones from the North Sea Basin. Clay Minerals 19, 287–308.

Morton, A.C., 1985. Heavy minerals in provenance studies. In: Zuffa, G.G. (Ed.), Provenance of Arenites. Reidel, Dordrecht, pp. 249–277.

Morton, A.C., 2003. Heavy minerals. In: Middleton, G.V. (Ed.), Encyclopedia of Sediments and Sedimentary Rocks. Kluwer, Deventer, pp. 356–358.

Morton, A.C., Allen, M., Simmons, M., Spathopoulos, F., Still, J., Hinds, D., Ismail-Zadeh, A., Kroonenberg, S., 2003. Provenance patterns in a neotectonic basin: Pliocene and Quaternary sediment supply to the South Caspian. Basin Research 15, 321–337.

Morton, A.C., Claoué-Long, Berge, C., 1996. SHRIMP constraints on sediment provenance and transport history in the Mesozoic Statfjord Formation, North Sea. Journal of the Geological Society 153, 915–929.

Morton, A.C., Hallsworth, C.R., 1999. Processes controlling the composition of heavy mineral assemblages in sandstones. Sedimentary Geology 124, 3–29.

Morton, A.C., Hallsworth, C.R., 2007. Stability of detrital heavy minerals during burial diagenesis. In: Mange, M.A., Wright, D.T. (Eds.), Heavy Minerals In Use. Developments in Sedimentology (this volume).

Morton, A., Knox, R.W.O.-B., Hallsworth, C., 2002. Correlation of reservoir sandstones using quantitative mineral analysis. Petroleum Geoscience 8, 251–262.

Morton, A.C., Smale, D., 1990. The effects of transport and weathering on heavy minerals from the Cascade River, New Zealand. Sedimentary Geology 68, 117–123.

Muller, J.E., 1943. Uitkomsten van nieuwe geologisch-paleontologische onderzoekingen van den ondergrond van Nederland. Sedimentpetrologie van het dekgebergte in Limburg. Mededelingen Geologische Stichting Serie C-II 2 (2), 1–78.

Nickel, E., 1973. Experimental dissolution of light and heavy minerals in comparison with weathering and intrastratal solutions. Contributions to Sedimentology 1, 1–68.

Olivia, P., Viers, J., Dupré, B., Fortuné, J.P., Martin, F., Braun, J.J., Nahon, D., Robain, H., 1999. The effect of organic matter on chemical weathering: study of a small tropical watershed: Nsimi–Zoétélé site, Cameroon. Geochimica et Cosmochimica Acta 63, 4013–4035.

Ollier, C.D., 1969. Weathering. Oliver & Boyd, Edinburgh, 304pp.

Peuraniemi, V., Heinänen, K., 1985. Mineralogical investigations in the interpretation of heavy mineral geochemical results of till. Journal of Geochemical Exploration 23, 315–328.

Sawyer, E.W., 1986. The influence of source rock type, chemical weathering and sorting on the geochemistry of clastic sediments from the Quetico metasedimentary belt, Superior Province, Canada. Chemical Geology 55, 77–95.

Singh, P., Rajamani, V., 2001. REE geochemistry of recent clastic sediments from the Kaveri floodplain, southern India: implication to source area weathering and sedimentary processes. Geochimica et Cosmochimica Acta 65, 3093–3108.

Totten, M.W., Hanan, M.A., 2007. Heavy minerals in shales. In: Mange, M.A., Wright, D.T. (Eds.), Heavy Minerals In Use. Developments in Sedimentology (this volume).

Varadachari, C., Barman, A.K., Ghosh, K., 1994. Weathering of silicate minerals by organic acids. 2. Nature of residual products. Geoderma 61, 251–258.

Van Loon, A.J., 1972/1973. "Habitus" of some heavy minerals from the Tertiary of Southern Limburg (The Netherlands). Mededelingen Rijks Geologische Dienst, Nieuwe Serie 23, 39–67.

Velbel, M.A., 1984. Natural weathering mechanisms of almandine garnet. Geology 12, 631–634.

Velbel, M.A., 2007. Surface textures and dissolution processes of heavy minerals in the sedimentary cycle: Examples from pyroxenes and amphiboles. In: Mange, M.A., Wright, D.T. (Eds.), Heavy Minerals In Use. Developments in Sedimentology (this volume).

Weibel, R., 2003. Alteration of detrital Fe-Ti oxides in Miocene fluvial deposits, central Jutland, Denmark. Bulletin of the Geological Society of Denmark 50, 171–183.

Westerhoff, W.E., Wong, Th.E., De Mulder, E.F.J., 2003. Geschiedenis van de ondergrond. In: De Mulder, F.J., Geluk, M.C., Ritsema, I., Westerhoff, W.E., Wong, Th.E. (Eds.), De Ondergrond van Nederland (Geologie van Nederland 7). Nederlands Instituut voor Toegepaste Geowetenschappen, Utrecht, pp. 119–246.

Willner, A.P., 1987. Detrital tourmalines as indicators for the source rocks of Late Precambrian—Lower Cambrian greywackes (Puncoviscana Formation) in NW Argentina. Zentralblatt für Geologie und Paläontologie 1987, 885–891.

Xiubin, H., Junliang, T., Keli, T., Jianzhong, S., Matthews, J.A., 2004. Bio-climatic imprints on a Holocene loess palaeosol from China. Journal of Asian Earth Sciences 22, 455–464.

Xiubin, H., Keli, T., Juanliang, T., Matthews, J.A., 2002. Paleopedological investigation of three agricultural loess soils on the Loess Plateau in China. Soil Science 167, 478–491.

Xiubin, H., Keli, T., Xiangyi, L., 1997. Heavy mineral record of the Holocene environment on the Loess Plateau in China and its pedogenetic significance. Catena 29, 323–332.

Yang, S.Y., Jung, H.S., Choi, M.S., Li, C.X., 2001. The rare earth element compositions of the Changjiang (Yangtze) and Huanghe (Yellow) river sediments. Earth and Planetary Science Letters 210, 407–419.

Yang, S.Y., Jung, H.S., Lim, D.I., Li, C.X., 2003. A review on the provenance discrimination of sediments in the Yellow Sea. Earth-Science Reviews 63, 93–120.

Yang, S.Y., Li, C.X., Jung, H.S., Lee, H.J., 2002. Discrimination of geochemical compositions between the Changjiang and the Huanghe sediments and its application for the identification of sediment source in the Juangsu coastal plain, China. Marine Geology 186, 229–241.