Chapter 7

STABILITY OF DETRITAL HEAVY MINERALS DURING BURIAL DIAGENESIS

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ABSTRACT

Detrital heavy-mineral assemblages respond to increasing burial diagenesis by progressive dissolution of unstable components. Case studies from sedimentary basins worldwide show a uniform pattern of relative stability. The order of stability during burial diagenesis is olivine (least stable) < orthopyroxene, clinopyroxene < sodic pyroxene < calcic amphibole, andalusite, sillimanite < epidote < titanite < kyanite < sodic amphibole < staurolite < allanite < garnet, chloritoid < tourmaline, monazite, spinel < rutile, anatase, brookite, zircon, apatite (most stable). Mineral dissolution can be recognised by corrosion textures on grain surfaces and by preservation of unstable minerals in low-porosity zones adjacent to friable sandstones with less diverse assemblages. Increasing pore fluid temperatures, accompanied by changes in pore fluid composition, are responsible for progressive mineral dissolution. There is, therefore, an indirect relationship between mineral diversity and burial depth in sedimentary basins worldwide. However, the depths at which individual minerals disappear vary markedly between basins, largely due to differences in pore fluid temperature gradients. Geological time is another significant factor in mineral depletion.

Interpretation of provenance using heavy-mineral data from sandstones likely to have suffered burial diagenesis must carefully consider the possibility that some heavy-mineral species have been eliminated through dissolution. Evaluation of provenance under such circumstances must rely on parameters that are demonstrably unaffected by diagenesis. A combined approach, integrating provenance-sensitive ratio measurements with varietal data, either petrographic, geochemical or isotopic, is recommended.

Keywords: heavy minerals; diagenesis; stability; corrosion; provenance

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Developments in Sedimentology, Vol. 58, 215–245

ISSN: 0070-4571/doi:10.1016/S0070-4571(07)58007-6

1. INTRODUCTION

Heavy-mineral analysis is one of the most widely used techniques in the determination of sandstone provenance. A large number of detrital heavy-mineral species have been identified in sandstones: over 50 translucent detrital minerals were described by Mange and Maurer (1992), many of which have specific and restricted parageneses, thereby providing crucial provenance information that cannot be acquired by any other means.

One of the problems encountered while using heavy-mineral data to interpret provenance is that heavy-mineral assemblages in sandstones do not solely reflect the composition of the parent rocks. This is because the original provenance signal is modified by a number of processes that operate at different stages during the sedimentation cycle (see review by Morton and Hallsworth, 1999, and references therein). Assemblages are modified by weathering at source, prior to sediment entering the transport system; by processes that operate during transport and deposition (hydrodynamic fractionation, mechanical abrasion and weathering during alluvial storage); and post-depositionally by diagenesis during burial. These processes can cause sandstones derived from a single source, possessing a common mineralogical signature at the time of origin, to now contain markedly heterogeneous heavy-mineral assemblages. Similarly, sandstones from different sources, with different suites at the time of origin, may now possess superficially similar assemblages. Therefore, it is crucial that the potential effects of these modifying factors are considered when using heavy-mineral data to characterise and differentiate provenance.

Arguably, the most profound modification of heavy-mineral assemblages takes place in the subsurface, during burial diagenesis. Heavy-mineral suites react to burial diagenesis by dissolution of unstable phases (a process known as intrastratal dissolution) and growth of secondary minerals, as documented in the accompanying chapters by Turner and Morton (2007, this volume) and Milliken (2007, this volume). Burial diagenesis has the potential to dramatically alter heavy-mineral assemblages, causing detrital suites that have high diversity at the time of deposition to become highly restricted at great burial depths. In this chapter, we (1) discuss the features that are diagnostic of dissolution in the subsurface, (2) consider, by means of case studies, the effects of burial diagenesis on heavy-mineral suites and (3) work towards the establishment of a comprehensive stability series for heavy minerals during burial. Finally, we briefly describe the heavy-mineral parameters that can be used to evaluate provenance in sandstones that have undergone extensive diagenetic modification.

2. DIAGNOSTIC CRITERIA FOR HEAVY-MINERAL DISSOLUTION

Mineral dissolution in the subsurface can be recognised in three ways: (1) by the presence of corroded surfaces on mineral grains, (2) by the co-existence of high-diversity and low-diversity assemblages in adjacent high- and low-permeability sandstones, and (3) by a decrease in mineral diversity with increasing burial depth within the sedimentary basin. The presence of all three lines of evidence may be taken as proof of intrastratal dissolution, but caution is required if some of the evidence is missing. For instance, decreasing diversity with increasing depth might be a provenance effect, and the presence of corrosion textures on mineral grains may be the result of localised weathering processes (for example, in a non-marine depositional setting or below a subaerial unconformity).

2.1. Surface Textures

The most direct indication of heavy-mineral dissolution is the presence of corrosion textures on grain surfaces. Corrosion textures, which were first documented by Edelman and Doeglas (1932, 1934), include etch pits, surface mamillae, facets, ragged edges, hacksaw terminations and skeletal structures (Rahmani, 1973; Hemingway and Tamar-Agha, 1975; Morton, 1979; Milliken, 2007, this volume; Turner and Morton, 2007, this volume; Van Loon and Mange, 2007, this volume; Velbel, 2007, this volume). Differences in mineral composition and crystal structure yield different surface corrosion textures. It is also possible that differences in fluid composition may lead to variations in surface textures. Hubert (1971) urged caution in interpreting all corrosion textures as indicative of ongoing dissolution, arguing that they can be inherited from precursor diagenetically modified sandstones. For example, Palaeozoic sandstones of the Clair Field, west of Shetland (UK), contain etched staurolite and garnet in conjunction with unetched grains of epidote (Allen and Mange-Rajetzky, 1992). Since epidote is less stable than staurolite and garnet, the surface textures of these co-existing minerals indicate that the staurolite and garnet were recycled from pre-existing sandstones. However, such situations are comparatively rare, and we believe that grain surface corrosion should be regarded as indicative of in situ intrastratal dissolution unless it can be argued otherwise.

Corrosion textures similar to those observed on natural grain surfaces have been produced in laboratory experiments. Nickel (1973) used a variety of acids and alkalis to leach heavy minerals, Berner et al. (1980) simulated natural hacksaw terminations on clinopyroxene and amphibole by acid leaching at room temperature, and Hansley (1987) generated faceted surfaces on garnet using warm acids. There has been a debate over the origin of some surface textures, most notably facets on garnet grains, which have been attributed to both corrosion and overgrowth. Morton et al. (1989) and Salvino and Velbel (1989) used thermodynamic considerations, experimental studies, distribution of faceted garnets in the subsurface, textural relationships and compositional variations within faceted grains, to examine this question in detail, and concluded that the overgrowth hypothesis cannot be sustained.

Although the presence of corrosion textures on grain surfaces is strong evidence for the operation of dissolution processes, it has been argued that intrastratal dissolution is a local, rather than a widespread, phenomenon (Van Andel, 1959; Weissbrod and Nachmias, 1986). However, as Turner and Morton (2007, this volume) show, corrosion textures are commonplace in sedimentary basins worldwide. It is therefore becoming evident that heavy-mineral corrosion is a global feature, implying that intrastratal dissolution is likely to have operated in all deep sedimentary basins to some extent.

2.2. *Preservation of High-Diversity Assemblages*

Direct evidence for mineral dissolution in the subsurface is provided by the occurrence of high-diversity detrital heavy-mineral zones within sandstone successions otherwise typified by low-diversity assemblages. Examples include: higher-diversity assemblages in early calcite concretions compared with enclosing friable sandstones, as first identified by Bramlette (1941); higher-diversity assemblages in mudstones compared with interbedded sandstones (Blatt and Sutherland, 1966); and higher-diversity assemblages in oil-bearing sandstones compared with adjacent water-wet sandstones (Yurkova, 1970). Similar examples have been described in Palaeocene sandstones of the UK continental shelf (Morton, 1984; Morton et al., 2002), with higher-diversity heavy-mineral assemblages occurring in calcite concretions, in analcite-cemented zones, in mudstones, in sandstones with limited pore-fluid connectivity and in oil-bearing intervals, compared with adjacent sandstones with low-diversity assemblages (Fig. 1).

In such cases, it is unreasonable to argue for a difference in provenance between the high-diversity and adjacent low-diversity zones. Therefore, at the time of deposition, there was no significant difference between heavy-mineral assemblages in zones that now show marked differences in diversity. This implies that the high-diversity zones were protected from the corrosive action of pore waters that caused depletion of unstable heavy minerals in the adjacent low-diversity sandstones. Protection has been afforded by (1) poor initial permeability (as in the case of the mudstones), (2) early cementation, destroying initially good permeability and sealing the sandstone from circulating pore waters, (3) poor fluid connectivity, restricting the circulation of pore waters and (4) displacement of pore waters by oil during hydrocarbon emplacement. Identification of adjacent high- and low-diversity heavy-mineral zones is important not only because it proves that intrastratal dissolution has taken place, but also because the preserved assemblages give important provenance information, since they provide a record of the composition of the detrital assemblage prior to dissolution.

2.3. *Relationships Between Burial Depth and Diversity*

Patterns of decreasing mineral diversity with increasing burial depth are common in sedimentary basins worldwide. The most likely cause of such patterns is intrastratal dissolution during burial diagenesis. However, such patterns could also arise through an evolution in provenance, and this possibility should always be eliminated before diagnosing burial-related diagenesis as the cause. Evaluation of potential provenance variations can be achieved using parameters that are insensitive to diagenetic processes, as discussed by Morton and Hallsworth (1994, 1999) and summarised later in this contribution. The case studies described below come from sandstones known to have a common provenance, so that depth/diversity relationships can be confidently ascribed to intrastratal dissolution.

2.3.1. *Palaeocene-Eocene, North Sea.*

Palaeocene-Eocene sandstones of the Dornoch and Forties Formations in the central North Sea provide a well-constrained study of the effects of burial diagenesis on

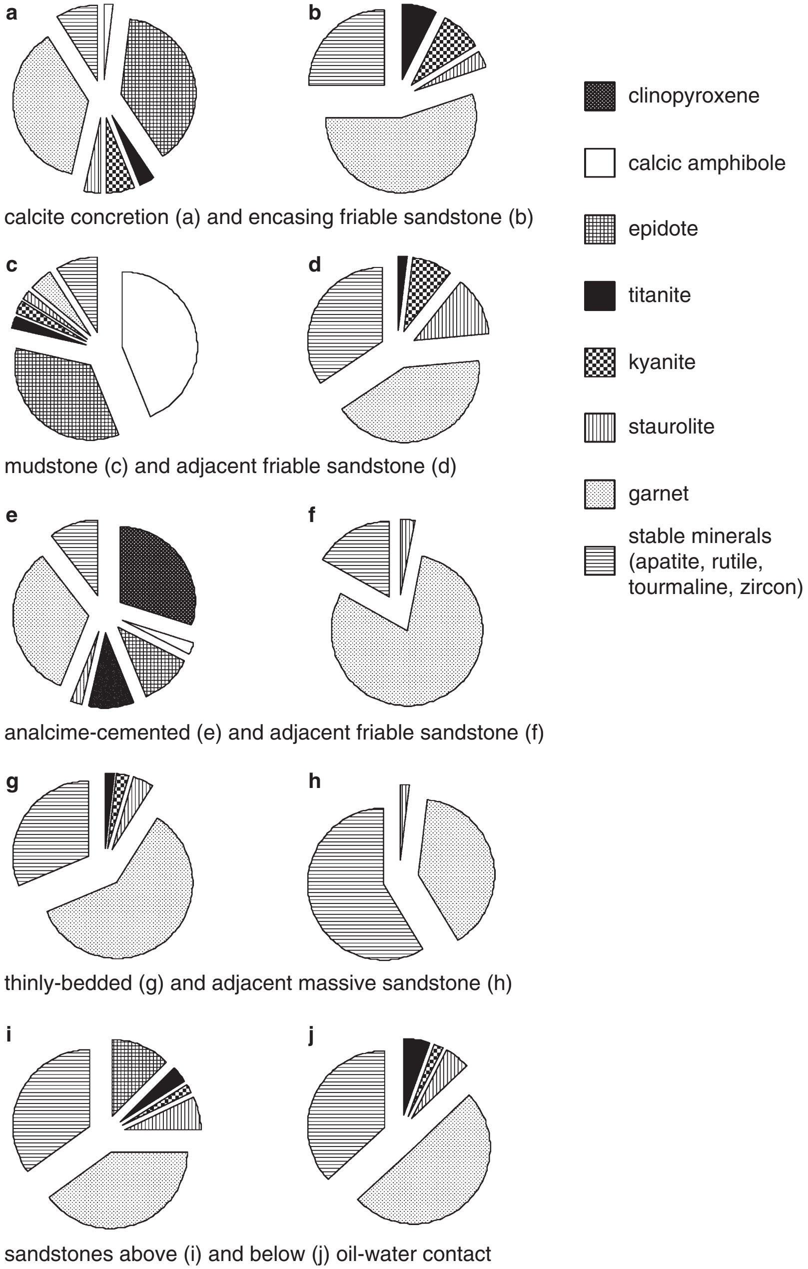

Fig. 1. Examples of preservation of heavy minerals from North Sea Palaeocene-Eocene successions. (a) Well 2/10-4, 1652 m; (b) Well 2/10-4, 1645 m; (c) Well 9/13-1, 1459 m; (d) Well 9/13-1, 1460 m; (e) Well 15/26-2, 1914 m; (f) Well 15/26-2, 1978 m; (g) Well 21/30-1, 2003 m; (h) Well 21/30-2, 1996 m; (i) Well 16/26-6, 1936 m; (j) Well 16/26-6, 1973 m.

heavy-mineral assemblages (Morton, 1984). The Dornoch Formation represents a prograding coastal-deltaic complex, shown, on the basis of seismic data, to be derived from a source area in the Scottish landmass to the northwest (Rochow, 1981; Bowman, 1998). The Forties sandstones were deposited in a submarine fan complex at the foot of a delta slope, basinward of the area where the Dornoch sandstones were deposited. The top of the succession is less than 200 m below seabed at the basin margin, but is nearly 3 km at the basin centre, and the thermal history is one of continued subsidence throughout the Tertiary. The Palaeocene-Eocene of the central North Sea thus forms an ideal case study of the effects of increased pore-fluid temperature on heavy-mineral suites.

Within this succession, suites become steadily less diverse as burial increases due to elimination of heavy-mineral species through dissolution (Fig. 2). Calcic amphibole is the first to disappear, at around 600 m below seabed. This is followed successively by epidote (~1100 m), titanite (~1400 m), kyanite (~1800 m) and staurolite (~2400 m). Each phase becomes more corroded as burial depth increases (Fig. 2). Although garnet declines markedly in abundance relative to the stable mineral zircon, in conjunction with increasing severity of surface corrosion textures, it does not disappear entirely. However, in the underlying Jurassic of the central North Sea, garnet is rarely present at burial depths in excess of 3500 m (Fig. 3). Other minerals present in the North Sea Palaeocene-Eocene (anatase, apatite, chrome spinel, monazite, rutile, tourmaline and zircon) rarely display signs of etching, and are apparently stable (Morton, 1979).

2.3.2. Palaeocene, Faeroe-Shetland Basin.

Palaeocene sandstones in the Foinaven Sub-basin (Faeroe-Shetland Basin) cover a wide range in burial depth, from approximately 1300 to 2400 m below seabed. Provenance variations within these sandstones are relatively muted, with all sandstones having a similar range of minerals in the shallow subsurface. However, there is evidence for differences in relative contributions from metamorphic basement and Palaeozoic-Mesozoic sediment, and also in the degree of weathering prior to sediment entering the transport system (Morton et al., 2002).

Burial depth/abundance plots for a number of minerals in Palaeocene sandstones from the Foinaven Sub-basin are shown in Fig. 4. Amphibole is the first mineral to disappear, being absent from virtually all samples over 1500 m below seabed. Epidote disappears at ~1620 m, titanite at ~1700 m and kyanite at ~1760 m. Staurolite and garnet are present throughout. Relative abundances of garnet become greater with increased burial between ~1400 and 1800 m burial, compensating for the disappearance of amphibole, epidote and titanite. Some samples below 2200 m have relatively low garnet abundances, but this is considered to be a provenance effect related to deep weathering of the Cretaceous land surface (Morton et al., 2002), rather than depletion during burial diagenesis. Other minerals in the Palaeocene of the Foinaven Sub-basin (apatite, chrome spinel, monazite, rutile, tourmaline and zircon) show no evidence for depletion with increasing burial depth, and are considered stable.

2.3.3. Plio-Pleistocene, US Gulf Coast.

Milliken (1988, 2007, this volume) examined dissolution of heavy minerals in the Plio-Pleistocene of the US Gulf Coast, using a combination of thin section

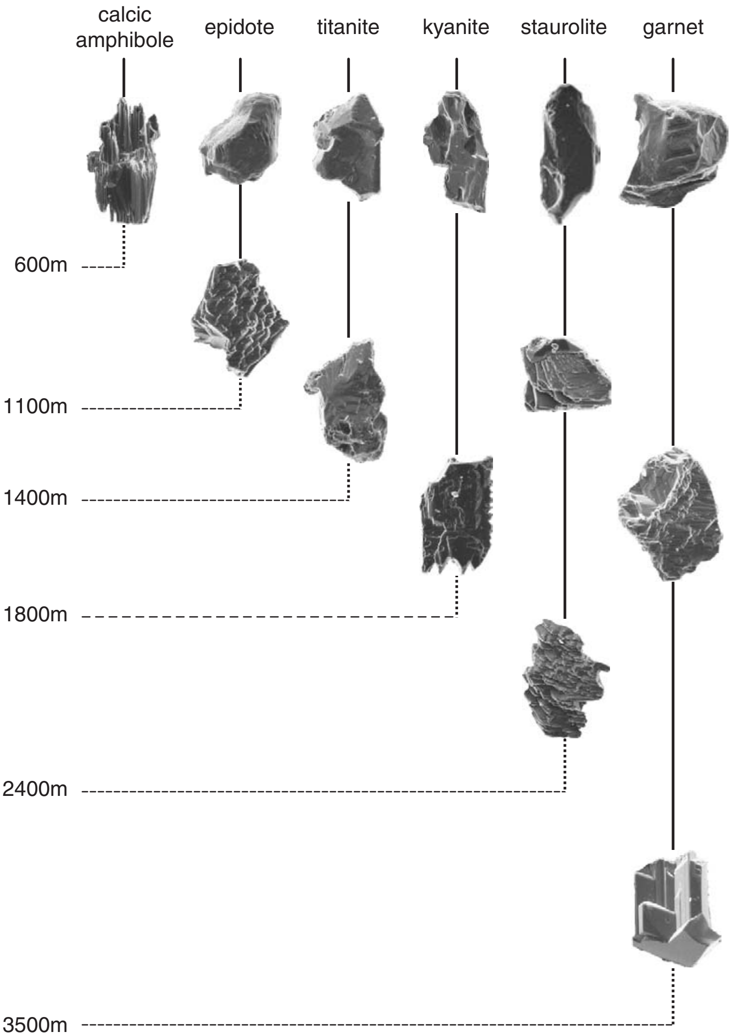

Fig. 2. Burial depth distribution of heavy minerals in Palaeocene-Eocene sandstones of the central North Sea, showing the decrease in mineral diversity with increasing burial caused by dissolution of unstable minerals (adapted from Morton, 1984, and Morton and Hallsworth, 1999).

petrography coupled with SEM examination to identify grain surface corrosion. These sediments were all transported by the Mississippi River system, and—because of extremely high sedimentation rates—are buried between ~450 m and 5 km. In these sandstones, pyroxene is least stable, followed by amphibole, kyanite, epidote, titanite and garnet. Oligocene sediments in the US Gulf Coast show a similar pattern (Milliken and Mack, 1990; Milliken, 2007, this volume). Stable heavy-mineral phases in the US Gulf Coast are considered to be apatite, chrome spinel, TiO_2 minerals, monazite, tourmaline and zircon. The pattern of mineral depletion in the US Gulf Coast is similar to that seen in the North Sea and Faeroe-Shetland Basins, except for

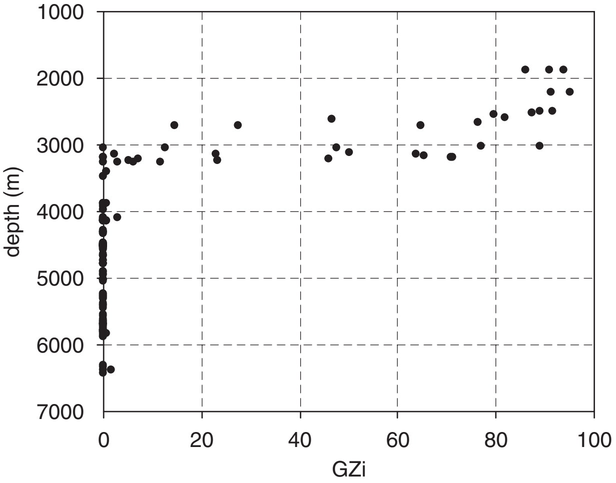

Fig. 3. Relationship between GZi and depth in Late Jurassic sandstones of the central North Sea, showing that complete garnet dissolution is commonplace in sandstones buried in excess of 3.5 km. GZi = % garnet in total garnet plus zircon (see Morton and Hallsworth, 1994, for definition).

kyanite, which disappears at shallower depths than epidote and titanite. However, the burial depths at which the heavy minerals disappear in the Gulf Coast succession are considerably greater than in the offshore UK area. For example, titanite persists to 3–4 km in the Plio-Pleistocene of the Gulf Coast, compared with just over 1 km in the North Sea.

2.3.4. Pliocene, Kura Basin, Azerbaijan.

Pliocene sediments from the Kura Basin of Azerbaijan were sourced from Mesozoic metamorphic, ophiolitic and volcanic rocks of the Lesser Caucasus and transported by the paleo-Kura River (Morton et al., 2003). Provenance-sensitive ratio and garnet geochemical data from paleo-Kura sandstones are closely comparable to those of the modern Kura, indicating little difference in source area characteristics between the Pliocene and the present day. Despite the uniform provenance, there are marked variations in the relative abundance of amphibole, epidote and clinopyroxene within the group of samples sourced from the Lesser Caucasus. Amphibole contents range from 3 to 40%, clinopyroxene from 0 to 70%, and epidote from 1 to 75%. A ternary plot of the relative abundances of the three minerals (Fig. 5) shows that the modern Kura River and Pliocene sandstones from the Aktapa Bridge outcrop have the highest clinopyroxene abundances. By contrast, sandstones from depths in excess of 4000 m from the Kursanga and Karabagli oilfields are epidote dominated, with scarce amphibole and clinopyroxene. Sandstones from relatively shallow burial depths (<3500 m) in the Kursanga and Karabagli oilfields, together with outcrop material from the Babazanan site, show a trend away from the clinopyroxene pole.

Sandstones from intermediate burial depths in Kursanga and Karabagli (3500–4000 m) show a second trend towards the epidote pole. Morton et al. (2003) explained this pattern as the result of progressive mineral dissolution, initially of

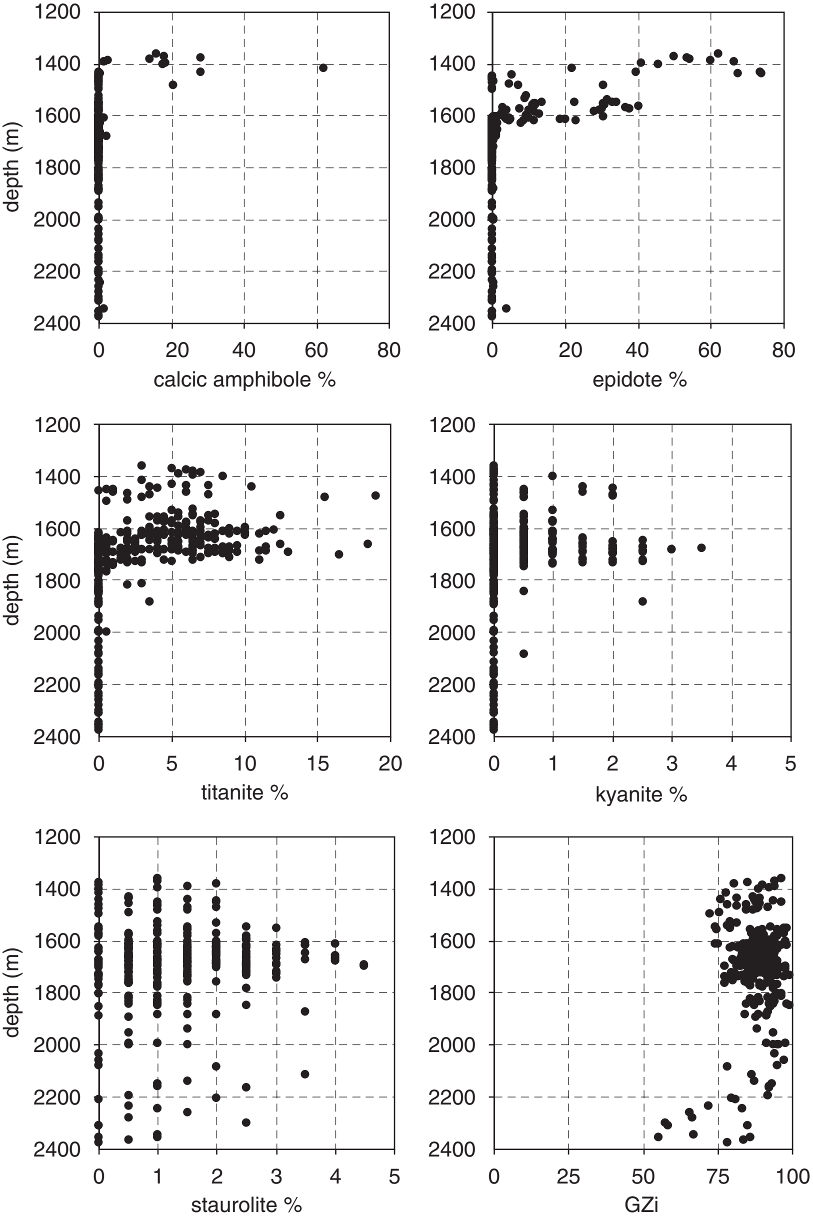

Fig. 4. Distribution of heavy minerals in subsurface Palaeocene sandstones of the Foinaven Sub-basin, Faeroe-Shetland Basin (adapted from Morton et al., 2002).

clinopyroxene and then of amphibole. The dissolution concept is supported by the presence of etched surfaces on clinopyroxene and amphibole grains, which diagnose ongoing corrosion in the subsurface (Turner and Morton, 2007, this volume). Other minerals in the sandstones (apatite, chrome spinel, garnet, rutile, titanite, tourmaline and zircon) show no evidence of corrosion, and are present at all burial depths.

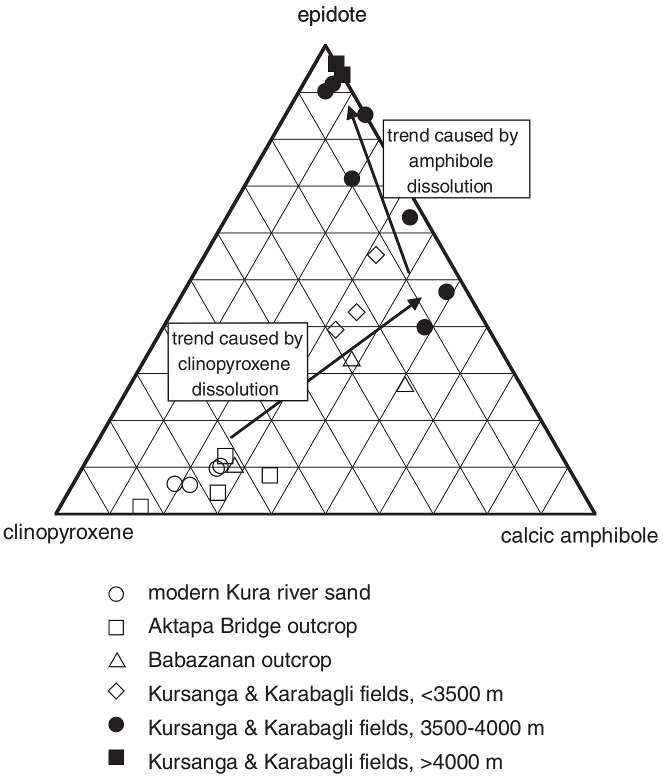

Fig. 5. Relative abundance of amphibole, clinopyroxene and epidote contents in sandstones deposited by the Kura River, Azerbaijan, and its late Miocene-Pliocene precursor, showing the modification to mineral assemblages caused by burial diagenesis (adapted from Morton et al., 2003).

These phases therefore appear to be stable in the Kura Basin over the investigated depth range.

2.3.5. *Miocene, Bengal Basin.*

Miocene sandstones of the Bengal Basin, Bangladesh, were deposited by a paleo-Brahmaputra river system that drained the nascent Himalayan mountain belt during uplift (Uddin and Lundberg, 1998a, 1999). Variations in provenance characteristics within the Miocene succession are comparatively limited, with an orogenic source identified throughout, although continued unroofing led to the exposure of granitic rocks in the Late Miocene and Pliocene (Uddin and Lundberg, 1998b).

Heavy-mineral assemblages in a 3000 m thick Miocene sandstone succession in the Bengal Basin show a marked decline in mineral diversity with depth. Calcic amphibole disappears at approximately 2 km depth, epidote (excepting the rare-earth epidote mineral allanite) at about 3 km depth, and kyanite and titanite at some 3.3 km depth (Fig. 6). Increasingly intense surface corrosion features accompany the downhole decrease in abundance of these minerals. Staurolite also shows a decline in abundance, and displays surface corrosion textures (Turner and Morton, 2007, this

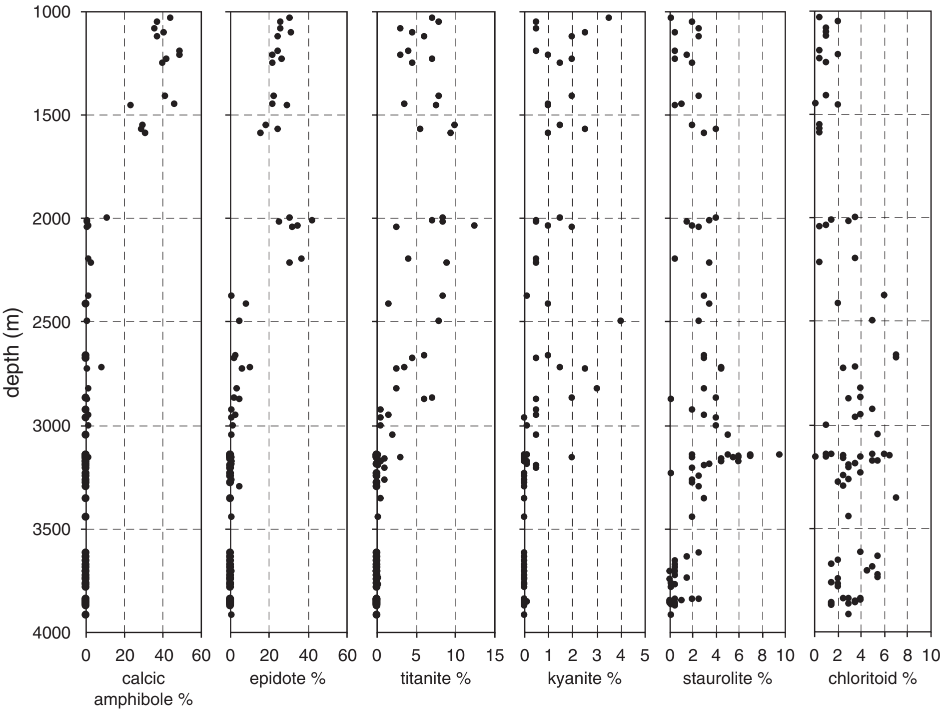

Fig. 6. Relationship between abundance of selected minerals and burial depth in Miocene sandstones of the Bengal Basin.

volume), but does not disappear entirely from the assemblages. The relationship between the decline in mineral abundance and increased surface corrosion texture indicates that the decreasing diversity is the result of intrastratal dissolution, rather than provenance. Other minerals (allanite, apatite, chloritoid, chrome spinel, garnet, monazite, rutile, tourmaline and zircon) do not decline in abundance with increasing depth, lack well-developed surface corrosion textures, and are considered stable in the analysed sandstones.

2.3.6. Eastern India.

Miocene sandstones derived from the Eastern Ghats of India have diverse heavy-mineral assemblages, including andalusite, anatase, apatite, calcic amphibole, chrome spinel, chloritoid, epidote, garnet, kyanite, monazite, rutile, sillimanite, staurolite, titanite, tourmaline, zinc spinel and zircon. Nevertheless, there is a well-defined pattern of decreasing calcic amphibole and sillimanite abundances with depth (Fig. 7), in both cases accompanied by an increase in severity of surface corrosion textures (Turner and Morton, 2007, this volume). None of the other heavy minerals show depletion with increasing depth, but this is because data are available only over a comparatively limited burial depth range (~1100–1600 m), precluding a comprehensive assessment of the diversity/depth relationship in this case study.

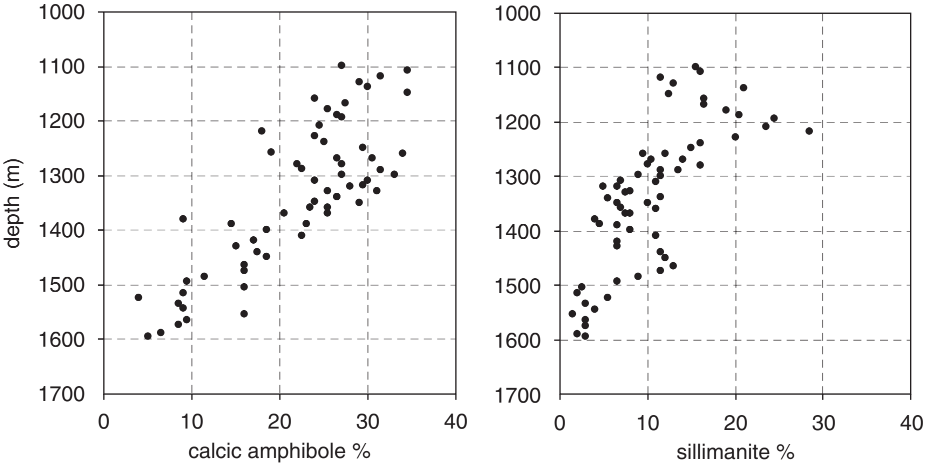

Fig. 7. Abundance of calcic amphibole and sillimanite with respect to burial depth in Miocene sandstones from eastern India, showing that the two minerals have very similar rates of depletion.

2.3.7. Eocene-Oligocene, New Zealand.

Heavy-mineral dissolution patterns in the Eocene-Oligocene McKee sandstones of New Zealand were discussed by Smale and Morton (1987) and Smale (2007, this volume). The McKee sandstones had a uniform provenance, comprising basement schists and granites, and have been subjected to burial depths in the range 2100–4100 m. However, the maximum burial depth is not known in all cases, since some of the area has been subject to uplift. All the suites in the McKee sandstones contain a relatively limited number of detrital heavy minerals, but they show a clear decrease in diversity with depth, staurolite disappearing at ~3100 m and garnet at ~3600 m. Both species show evidence of surface corrosion prior to their ultimate disappearance. Zircon, rutile, tourmaline, apatite, chloritoid and spinel are apparently stable.

2.3.8. Neogene, Yugoslavia.

Miocene and Pliocene sandstones of the Sava River Basin (Yugoslavia) show a decline in heavy-mineral diversity with depth (Scavnicar, 1979), interpreted as resulting from intrastratal dissolution. Kyanite disappears first, followed by epidote group minerals, titanite and finally staurolite. Garnet, chloritoid, rutile, tourmaline, zircon and apatite are present throughout. Apart from the disappearance of kyanite at comparatively shallow depths, the pattern of mineral disappearance matches those described elsewhere. The possibility that provenance variations may have been a factor in controlling some of the changes in mineralogy, notably the shallow disappearance of kyanite, cannot be entirely eliminated in this case study.

2.3.9. Contessa Megabed, Italy.

Cavazza and Gandolfi (1992) demonstrated that a sandstone unit with an essentially uniform provenance (the Contessa megabed in the northern Apennines of Italy) shows mineralogical variations related to burial depth. Of the heavy minerals, zircon, monazite, rutile, spinel, garnet and chloritoid are ubiquitous over the area, and are considered to be stable under the conditions experienced by the megabed, but staurolite and titanite show variable distribution attributed to dissolution during burial. This study is particularly significant because it demonstrates that other mineralogical parameters also vary because of burial depth, notably the abundance of smectite and interstratified illite/smectite and the abundance of intrabasinal carbonate clasts.

3. RELATIVE MINERAL STABILITY

In addition to the case studies described above, there are a number of other areas where burial-related dissolution is interpreted to have taken place. These include the Northern Apennines of Italy (Gazzi, 1965), the Vienna Basin in Austria (Wieseneder and Maurer, 1958), the Cleveland Basin of Yorkshire, UK (Smithson, 1941), the Cretaceous-Tertiary of Alberta, Canada (Rahmani, 1973) and the North Sumatra Basin of Indonesia (Morton et al., 1994). There is, therefore, overwhelming evidence to show that there is a consistent pattern of declining mineral diversity with increasing burial depth in sedimentary basins worldwide.

The case studies described above have not established diversity/depth relationships for all detrital heavy minerals. This is partly due to the relative scarcity of some heavy-mineral species, such as corundum, lawsonite, pumpellyite and topaz, which precludes acquisition of meaningful abundance data across the range of burial depths in any individual sedimentary basin. Certain other minerals, such as andalusite or olivine, are relatively common in sediments derived from specific lithologies, but diversity/depth data are not presently available from sediments derived from such sources. The relative stability of such minerals can be judged only by the extent to which corrosion textures develop on their grain surfaces compared with minerals that have known stability relationships. The present status of knowledge on relative mineral stability is summarised below.

3.1. *Olivine*

Olivine is an exceptionally scarce detrital phase in sandstones, despite its abundance in certain source rocks (for example, basic and ultrabasic igneous rocks). The reason for its scarcity is almost certainly its instability. Olivines in a sand sample from the seabed on the west coast of Scotland show well-developed corrosion textures on their grain surfaces (Turner and Morton, 2007, this volume), indicating ongoing dissolution at ambient temperatures without any burial. Clinopyroxenes in the same sample show no evidence for dissolution, indicating that olivine is less stable than clinopyroxene. This supports previously published relative stability patterns, such as those of Pettijohn (1941, 1975) and Morton (1984), which also show olivine to be the least stable of all detrital heavy minerals.

3.2. Pyroxene

Clinopyroxene is known to be highly unstable in sandstones, being more stable only than olivine (Pettijohn, 1941, 1975; Morton, 1984). The instability of clinopyroxene is further verified by the Kura Basin data described above, where it becomes depleted more rapidly than calcic amphibole and epidote during burial, and by the advanced development of grain surface corrosion textures in the shallow subsurface (Turner and Morton, 2007, this volume). The relative stability of other pyroxenes is less well known, due to their general scarcity in sediments. Orthopyroxene is generally held to be as unstable as clinopyroxene (Pettijohn, 1941, 1975; Morton, 1984). Aegirine, by contrast, appears to be more stable than clinopyroxene, given that highly etched clinopyroxene co-exists with unetched or slightly etched aegirine in the same sample from the shallow subsurface in the Rockall Trough (Turner and Morton, 2007, this volume). The same sample also contains highly etched aenigmatite, a pyroxenoid mineral, indicating that aenigmatite and clinopyroxene have similar stabilities. At present, there is no information on the stability of other pyroxene or pyroxenoid minerals, such as jadeite or wollastonite, which are virtually unrecorded as detrital phases.

3.3. Amphibole

Calcic amphibole is highly unstable in the subsurface, being more stable only than olivine and pyroxene. Its instability is verified by its relatively early disappearance from heavy-mineral assemblages during burial in the central North Sea Basin, Faeroe-Shetland Basin, Bengal Basin, Kura Basin and US Gulf Coast, and by the widespread occurrence of well-developed grain surface corrosion textures in amphibole-bearing sandstones (Rahmani, 1973; Morton, 1979; Milliken, 2007, this volume; Turner and Morton, 2007, this volume). Calcic amphiboles have a wide range of compositions (Deer et al., 1997a), and it is likely that different varieties have different stabilities; however, to date there has been no systematic study on the relative stability of the calcic amphibole group.

There is much less information on the stability of the other amphibole group minerals. The iron-magnesium amphiboles (such as grunerite and cummingtonite) and the sodic-calcic amphiboles (such as kataphorite) are scarce as detrital phases. Sodic amphiboles (such as glaucophane and riebeckite) are more common, but despite their wider distribution their relative stability remains poorly known. The little available data suggest that they are considerably more stable than calcic amphiboles. In Miocene sandstones of the Mahakam delta area, offshore Borneo, highly etched sodic amphibole (glaucophane) co-exists with etched staurolite and slightly etched garnet (Turner and Morton, 2007, this volume); kyanite and titanite are scarce or absent. In this basin, therefore, sodic amphibole appears to be more stable than kyanite and titanite, and marginally less stable than staurolite.

3.4. Epidote

Case studies from the central North Sea Basin, Faeroe-Shetland Basin, Bengal Basin, Sava River Basin and US Gulf Coast demonstrate that epidote group minerals are unstable during burial, although they are more stable than pyroxene and calcic amphibole. The instability of epidote is further demonstrated by increasingly intense surface corrosion textures with increasing burial depth (Morton, 1984; Turner and Morton, 2007, this volume). Epidote group minerals show a range of compositions (Deer et al., 1997b; Spiegel et al., 2002), with variations in both major elements (notably Ca, Fe, Mg, Mn and rare-earth elements) and trace elements. There is, however, little information on the effects of varying composition on epidote stability. The only piece of available evidence is from the rare-earth epidote mineral allanite, which appears to be significantly more stable than other epidote minerals. This is shown by the persistence of allanite to greater depths than the other epidote group minerals in the Bengal Basin, and by the minor development of corrosion textures on allanite grains in association with etched staurolite (Turner and Morton, 2007, this volume). Therefore, allanite appears to be more stable not only than the other epidote group minerals, but also than titanite, kyanite and staurolite.

3.5. *Titanite*

The relatively stability of titanite can be judged on the basis of several case studies, including the central North Sea Basin, Faeroe-Shetland Basin, Bengal Basin, Sava River Basin, US Gulf Coast and Contessa megabed. In most of these examples, titanite appears to be less stable than kyanite, staurolite and garnet, but more stable than epidote. However, in the Bengal Basin, titanite and kyanite disappear at similar depths, and in the US Gulf Coast and the Sava River Basin, kyanite depletion appears to take place before that of titanite. The reason for this inconsistency is unclear. It may be partly a provenance effect, rather than a diagenetic effect. However, it could also be due to differences in titanite composition, since the mineral shows compositional ranges in a number of elements, including Al, Fe and rare earths (Deer et al., 1997c).

3.6. *Al_2SiO_5 Minerals (Kyanite, Sillimanite, Andalusite)*

The three Al_2SiO_5 polymorphs (kyanite, sillimanite and andalusite) have markedly different stabilities during burial. Kyanite is the most common of the three minerals in detrital heavy-mineral assemblages, and therefore its relative stability is comparatively well known. The instability of kyanite in the subsurface is demonstrated by the widespread development of intense surface corrosion textures (Morton, 1984; Turner and Morton, 2007, this volume). In most case studies, kyanite depletion occurs after that of titanite and before that of staurolite. However, in the Faeroe-Shetland Basin, kyanite depletion appears to occur at depths similar to that in the case of titanite, and in the US Gulf Coast and the Sava River Basin, kyanite apparently disappears before titanite.

The only well-constrained data set on sillimanite stability is from eastern India, where sillimanite depletion occurs at a rate similar to that of calcic amphibole (Fig. 7). Grain surface corrosion textures are well developed on both minerals (Turner and Morton, 2007, this volume), indicating that the depletion trend is due to burial diagenesis. It therefore appears that sillimanite has a stability similar to that of calcic amphibole.

The only available evidence for the relative stability of andalusite is from surface textural information, because andalusite is comparatively rare in heavy-mineral suites from sandstones in the subsurface. Where present, andalusite is generally corroded (Turner and Morton, 2007, this volume) and therefore appears to be highly unstable, confirming conclusions reached by previous workers (Pettijohn, 1941, 1975; Morton, 1984).

3.7. Staurolite

Staurolite shows burial-related diagenetic depletion in many of the cases studies described above. In all cases, staurolite survives to greater depths than kyanite, titanite, epidote, calcic amphibole and pyroxene, and is therefore considered more stable than these species. However, it is less stable than garnet. Staurolite shows limited geochemical variation, mainly expressed in terms of Fe, Mg, Mn and Zn contents (Deer et al., 1997c); there is no information available on the effects of staurolite composition on its stability. The instability of staurolite in the subsurface is further demonstrated by the widespread development of spectacular grain surface corrosion textures (Morton, 1984; Turner and Morton, 2007, this volume).

3.8. Garnet

Garnet dissolution has been recognised in many deep basins, including the central North Sea (Morton, 1984), offshore New Zealand (Smale and Morton, 1987), the Cleveland Basin of Yorkshire (Smithson, 1941) and the Vøring Basin, offshore Norway (Morton et al., 2005a, b). In all cases, garnet survives at depths greater than those shown by staurolite, and is therefore considered more stable.

Compared with other heavy minerals, a comparatively large amount of data on detrital garnet compositions is available because garnet geochemistry is a highly sensitive guide to the discrimination and identification of provenance (Morton et al., 2004). The garnet compositional dataset can be used to examine the relationships between garnet composition and stability. Cretaceous-Palaeocene sandstones in the Vøring Basin, offshore Norway, can be categorised into a number of sandstone types based on heavy-mineral criteria (provenance-sensitive ratios, mineral chemistry and detrital zircon age data), each representing input from a different source region (Morton et al., 2005a, b). The effects of increasing burial diagenesis on garnet compositions in two of the sand types, MN1 (derived from northern mid-Norway) and MN2a (derived from northern East Greenland), are evaluated in Fig. 8. In both sandstone types, there is a clear relationship between Ca content and burial depth, with a marked decrease in Ca content of garnet with increasing burial. In compensation, there is a distinct increase in Fe content, with little perceptible effect on Mg or Mn. The data from the Vøring Basin are therefore entirely consistent with data from Palaeocene-Eocene sandstones of the central North Sea (Morton, 1987), Late Cretaceous sandstones of offshore Taranaki, New Zealand (Smale and Van der Lingen, 1989) and Oligocene sandstones of the US Gulf Coast (Milliken and Mack, 1990), which also suggested that Ca contents control garnet stability. Since Ca-rich garnets are less stable than Ca-poor garnets, increasing burial causes detrital garnet

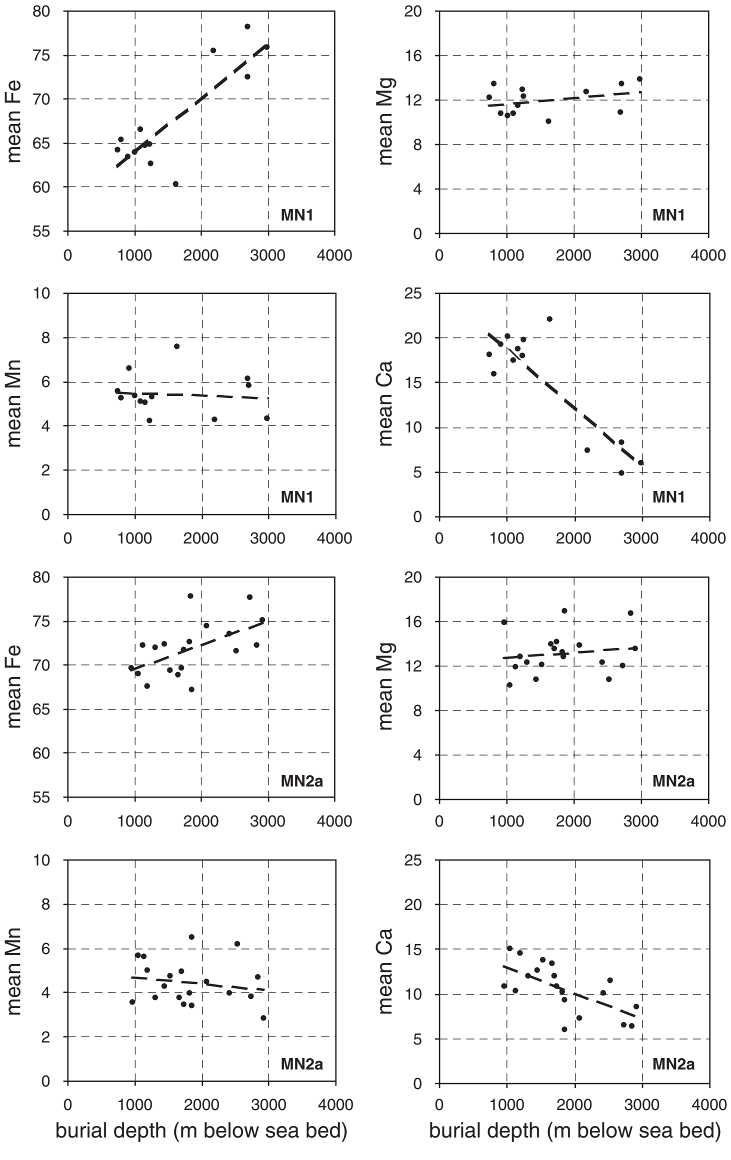

Fig. 8. Effects of burial depth on garnet compositions in Cretaceous-Palaeocene sandstones of the Vøring Basin, offshore Norway. Two examples are shown, relating to two different sand types (MN1 and MN2a, as defined by Morton et al., 2005a, b).

populations to decrease in diversity and become dominated by low-Ca types, prior to complete garnet dissolution.

Garnet also undergoes dissolution by acidic groundwater during weathering, and this process should always be considered as a possible cause of low garnet abundances, especially if low-garnet zones are found in association with high-garnet zones. For example, garnet depletion in specific zones within the

Rhaetian-Hettangian Statfjord Formation of the northern North Sea has been attributed to phases of intense surface weathering (Morton and Berge, 1995; Morton et al., 1996). Since garnet is more stable than apatite under weathering conditions (Morton, 1984), garnet depletion through weathering is likely to have taken place only if apatite depletion has also occurred.

3.9. Chloritoid

Chloritoid is a relatively stable heavy mineral, but is nevertheless susceptible to dissolution in very deeply buried sandstones, where it shows surface corrosion textures (Morton and Hallsworth, 1999; Turner and Morton, 2007, this volume). The data from the Bengal Basin (Fig. 6) show that chloritoid is more stable than staurolite, but provide no evidence for the relative stability of garnet and chloritoid. In Cretaceous sandstones in the Vøring Basin (offshore Norway), chloritoid depletion apparently occurs at similar depths to garnet, indicating that chloritoid has stability similar to that of Ca-poor garnet. Chloritoid shows variations in composition, mainly expressed by Fe, Mg and Mn but there is no information on the effects of compositional variations on chloritoid stability.

3.10. Tourmaline

Tourmaline is regarded as one of the most stable detrital minerals in sandstones (Hubert, 1962; Pettijohn, 1975). This is borne out by the various case studies described above, in which tourmaline contents show no relationship with burial depth. However, there is some evidence to suggest that tourmaline is unstable under some circumstances. Morton and Hallsworth (1999) figured an etched tourmaline from Jurassic sandstones in the Outer Moray Firth, North Sea, and suggested that one possible explanation is that tourmaline may be unstable in reservoirs where the hydrocarbons contain high H_2S contents. Since this first record of etched tourmaline, further instances have been noted, including Jurassic sandstones from the Norwegian Sea (Turner and Morton, 2007, this volume), and Palaeocene sandstones of the Faeroe-Shetland Basin. In all cases where tourmaline etching has been noted, burial depths are very high, close to or in excess of 4 km, and it therefore appears that tourmaline does become unstable in very deeply buried sandstones. However, tourmaline etching does not appear to be ubiquitous at great depth, and it may be that tourmaline dissolution requires the combination of depth and unusual fluid compositions, one possibility being high H_2S contents. Tourmaline etching has also been observed in silver sands (The Netherlands, Belgium and Germany), which have been subjected to extreme weathering (Van Loon and Mange, 2007, this volume).

Authigenic tourmaline has been observed to occur in evaporites, ironstones and carbonates (e.g., Henry et al., 1993, 1999). Although secondary tourmaline has been identified in sandstones (e.g., Stow, 1932), it is relatively uncommon, and does not appear to be specifically related to burial diagenesis. As with tourmaline dissolution, tourmaline growth probably requires special geochemical conditions to proceed.

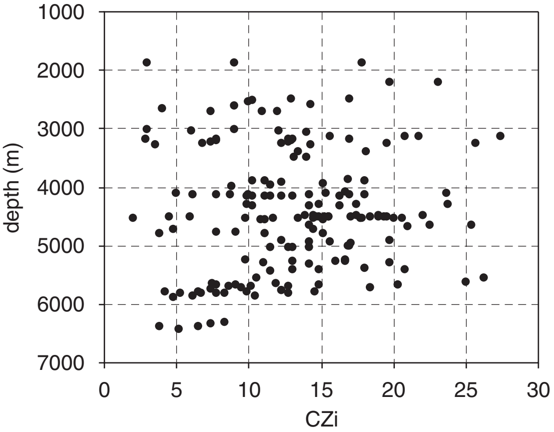

Fig. 9. Plot of chrome-spinel/zircon ratio (CZi) and burial depth in Late Jurassic sandstones of the central North Sea, showing that there is no evidence for loss of chrome spinel even at burial depths in excess of 6000 m.

3.11. *Spinel*

A wide range of natural spinel compositions are known, but comparatively few are commonly found as detrital heavy minerals. The most common translucent detrital spinels belong to the chromite series (chromite and magnesiochromite), collectively termed chrome spinel. Detrital chrome spinels are sufficiently common to enable an assessment of its stability during burial diagenesis. In the Upper Jurassic of the central North Sea, which is variably buried to depths from approximately 2000 m to in excess of 6000 m (Fig. 9), there is no evidence for a relationship between depth and the chrome–spinel/zircon index (CZi). In the same sandstones, complete garnet depletion occurs at ~3500 m (Fig. 3). In the most deeply buried North Sea Late Jurassic sandstones, there is some evidence for incipient grain surface corrosion (Turner and Morton, 2007, this volume), but this is of limited extent, and chrome spinel is therefore considered to be an exceptionally stable detrital phase.

The only other translucent spinel commonly found in sandstones is the zinc spinel, gahnite. However, it is much less common than chrome spinel, rarely forming more than 0.5% of heavy-mineral residues. It is therefore difficult to reliably ascertain depth/abundance relationships, and surface textural evidence provides the only basis for determining its stability. As Turner and Morton (2007, this volume) show, gahnite shows no evidence of corrosion textures as a result of burial diagenesis, and the phase is, therefore, considered stable.

3.12. *Monazite*

Monazite is also considered to be a stable phase during burial diagenesis, with no evidence for depletion with increasing depth in the case studies described above. Its stability is supported by surface texture data, with little or no evidence for corrosion at depth. Monazites in deeply buried (> 4400 m) Triassic sandstones from the central

North Sea are unetched (Morton and Hallsworth, 1999). Most monazites in Jurassic sandstones from the Norwegian Sea, buried to depths in excess of 5100 m are unetched, although minor incipient etch pitting was observed on a small number of grains (Turner and Morton, 2007, this volume). Monazite is therefore considered to be stable during burial. However, monazite frequently shows mechanically induced pitting owing to its relatively low hardness. Mechanical pitting, which is unoriented, is readily distinguished from etch pitting, which is crystallographically controlled (see Turner and Morton, 2007, this volume).

3.13. Rutile, Anatase and Brookite

Rutile is considered to be amongst the most stable detrital minerals in sandstones (Hubert, 1962; Pettijohn, 1975). In all the case studies described above, there is no evidence for depletion of rutile with increasing burial depth. Furthermore, there is no surface textural evidence to suggest that rutile grains become corroded in the subsurface (Morton, 1979; Turner and Morton, 2007, this volume). Detrital anatase and brookite are less common components of heavy-mineral assemblages, and consequently data on the relationship between abundance and burial depth are lacking. However, both minerals are common as authigenic phases, implying that they are stable under burial diagenetic conditions.

3.14. Zircon

Zircon is another member of the group of minerals considered to be stable in sandstones (Hubert, 1962; Pettijohn, 1975). It shows no evidence for depletion with increasing burial, and grains lack surface corrosion textures even under advanced diagenetic conditions (Morton, 1979; Turner and Morton, 2007, this volume). Therefore, although dissolution of zircon has been observed in isolated cases of specific weathering environments (Carroll, 1953; Oliva et al., 1999), zircon is considered to be an exceptionally stable phase during burial.

Metamict zircons (those that have suffered radiation damage to their crystal lattice) are known to be more soluble in weathering environments than crystalline zircons (Balan et al., 2001). It is reasonable to assume that they are also more susceptible to dissolution by high-temperature pore fluids during burial diagenesis, although direct evidence from the subsurface is presently lacking.

3.15. Xenotime

Since xenotime is generally scarce in detrital heavy-mineral assemblages, direct evidence for its stability during burial is scarce. However, sandstones that have been subjected to advanced burial diagenesis commonly contain zircons with xenotime ‘outgrowths’, described initially by Butterfield (1936) and Smithson (1937), and illustrated by Turner and Morton (2007, this volume). Development of xenotime outgrowths on zircon marks an advanced stage of burial diagenesis, since it generally occurs in sandstones that have undergone garnet depletion, an observation made originally by Smithson (1937). Xenotime is therefore considered to be stable during burial diagenesis. As discussed by Vallini et al. (2005), overgrowths on xenotime offer possibilities for U-Pb radiometric dating of diagenetic events by the sensitive high-resolution ion microprobe (SHRIMP).

3.16. Apatite

In the 'order of persistence of heavy minerals' formulated by Pettijohn (1941), apatite appears to be less stable than zircon, rutile, tourmaline and garnet. However, apatite shows no evidence for dissolution during deep burial, either in the case studies discussed above or in the North Sea Jurassic as described by Morton (1986). Indeed, apatite grains commonly develop overgrowths during advanced stages of burial diagenesis (Morton and Hallsworth, 1999; Turner and Morton, 2007, this volume). Apatite is therefore considered to be exceptionally stable under burial diagenetic conditions. The extent to which apatite develops overgrowths in the subsurface presumably depends on the availability of phosphate, and is therefore more likely to take place in marine sediments rich in biogenic phosphate. Secondary apatite growth is believed to have important implications for the validity of whole-rock Sm-Nd model ages in sediments (Ehrenberg and Nadeau, 2002), and the widespread occurrence of apatite overgrowths therefore indicates that caution is required during interpretation of Sm-Nd isotopic data in diagenetically modified sandstones.

Nevertheless, apatite grains frequently show evidence of corrosion, indicating that they have been partially dissolved. An example of etched apatite is shown by Turner and Morton (2007, this volume). This etched apatite co-exists with pristine apatite grains that show no sign of corrosion, evidently indicating that the etching did not take place in situ. Apatite is known to be unstable under surficial weathering conditions, especially in humid environments (Morton, 1986), and the presence of etched apatite grains in subsurface sandstones therefore indicates that the sediment has undergone a phase of weathering under subaerial conditions. Apatite is less stable than garnet in surficial weathering environments, explaining why it appears below garnet in the 'order of persistence of heavy minerals' (Pettijohn, 1941), despite being more stable during burial diagenesis.

4. FACTORS INFLUENCING HEAVY-MINERAL DISSOLUTION IN THE SUBSURFACE

The order of stability of detrital heavy minerals gleaned from case studies and surface textural data is shown in Table 1. Several unknowns still remain, the main ones being the stability of generally scarce minerals such as cassiterite, corundum, pumpellyite and topaz, and variations in stability within complex mineral groups such as the amphiboles. However, it is unlikely that major alterations to the pattern shown in Table 1 will be necessary as further data from deep sedimentary basins will become available.

Although the order in which heavy minerals disappear during deep burial remains essentially uniform in sedimentary basins worldwide, there are major differences in the burial depths at which specific minerals become depleted. For example, amphibole depletion takes place at ca. 4000 m in the Kura Basin Pliocene, but only 600 m in the central North Sea Eocene. Garnet dissolution is complete at ~3500 m in the central

North Sea Jurassic, but shows only incipient signs of dissolution at the same depth in the Bengal Basin. Clearly, therefore, burial depth itself is not the only control, with other factors also playing an important role. The most important of these other factors are pore-fluid temperature and composition, rate of pore fluid movement, and time (Morton and Hallsworth, 1999).

4.1. Pore Fluid Temperature and Composition

Increasing pore fluid temperatures are an inevitable consequence of increased burial, and it would therefore appear that pore fluid temperature is the main driving mechanism behind heavy-mineral dissolution. The importance of elevated pore fluid temperatures, as opposed to increased burial depth, is illustrated by Karroo (Permian) sandstones in Zimbabwe. Bond (1943) noted that staurolite, present throughout the Karroo in the area of study, was etched only in a sandstone immediately below a basaltic lava flow, and he therefore considered that the etching was caused by flushing of the sandstones by high-temperature pore fluids introduced at the time of basalt emplacement. A similar situation occurs in the Pleistocene of the Escanaba Trough (Juan de Fuca Plate, NW Pacific), where dissolution of pyroxene and amphibole has taken place in sandstones affected by hydrothermal alteration (Zuffa et al., 2002; Zuffa and Serra, 2007, this volume).

As sandstones are buried and pore fluid temperatures rise, reactions take place to alter the composition of the pore waters, such as the transformation of smectite to illite (Hower et al., 1976) and the decarboxylation of organic matter to generate hydrocarbons (Tissot et al., 1974). The rising pore fluid temperatures and consequent changes in pore water composition cause heavy minerals to become unstable and start dissolving. The relative stability of the heavy minerals remains the same, but the

Table 1. Relative stability of detrital heavy minerals in deep burial conditions

Least stable
Olivine
Orthopyroxene, Clinopyroxene
Sodic pyroxene
Calcic amphibole, Andalusite, Sillimanite
Epidote
Titanite
Kyanite
Sodic amphibole
Staurolite
Allanite
Garnet, Chloritoid
Tourmaline, Monazite, Spinel
Rutile, Anatase, Brookite, Zircon, Apatite
Most stable

absolute depths at which they become unstable vary from basin to basin, dependent on the pore fluid temperature gradient, which is ultimately controlled by heat flow. One of the main reasons why heavy minerals are preserved to anomalously great depths in the Kura Basin is the suppressed thermal regime of the South Caspian Basin (Abrams and Narimanov, 1997), caused by low heat flow and rapid Mesozoic-Cenozoic sedimentation (Morton et al., 2003).

Comparatively little is known about the precise conditions under which burial-related mineral dissolution occurs, with only garnet having been studied in detail. Hansley (1987) documented the generation of etch facets on garnets by the action of warm dicarboxylic acid, and concluded that organic acids at temperatures exceeding 80 °C, generated through alteration of organic matter, cause garnet dissolution. In the Cleveland Basin of Yorkshire, sandstones showing intense garnet dissolution (Smithson, 1941) are associated with secondary sphalerite, which contain fluid inclusions that indicate crystal growth took place at temperatures of 79–82 °C (Shepherd, quoted in Hemingway and Riddler, 1982). In the same succession, vitrinite reflectance and spore colouration measurements indicate a maximum temperature of 95 °C (Cooper and Barnard, quoted in Hemingway and Riddler, 1982). In a series of mineral dissolution experiments using fluids with pHs of 3.6, 5.6 and 10.6 at room temperature, Nickel (1973) failed to simulate the pattern of relative mineral stability identified during burial. However, a limited series of experiments using a near-neutral fluid (pH of 8) simulated the relative stability of apatite, kyanite and garnet as seen in deep burial, with kyanite < garnet < apatite (Nickel, 1973). This suggests that near-neutral fluids best describe the conditions responsible for the subsurface dissolution patterns.

The only mineral to show significant differences in relative stability in sedimentary basins worldwide is kyanite. For example, kyanite is more stable than titanite in the central North Sea, but disappears at depths similar to that for titanite in the Faeroe-Shetland Basin, and is reported to be less stable than titanite in the US Gulf Coast. It is unclear why kyanite behaves more erratically than the other heavy minerals, but differences in pore fluid composition between the various basins discussed in this contribution are considered to be the most likely cause.

4.2. Rate of Pore Fluid Movement

The rate at which pore fluid moves through sandstones is another important factor in governing mineral distribution in the subsurface. Poor porosity and low permeability inhibit pore fluid movement, thereby decreasing the rate of mineral dissolution. Mineralogically immature sandstones may degrade rapidly during early burial, as in the case of the Kura Basin, where the sandstones have a predominantly volcanic provenance (Morton et al., 2003). Siltstones and mudstones also have poor porosity and permeability, and thus tend to preserve more diverse heavy-mineral assemblages than adjacent sandstones (Blatt and Sutherland, 1966). Early cementation, for example by carbonate minerals, causes a reduction in porosity and permeability, thereby preserving unstable heavy minerals compared with adjacent less cemented sandstones (Bramlette, 1941).

4.3. Geological Time

Pettijohn (1941) showed that, in general, older sandstones have less diverse heavy-mineral assemblages compared with younger sandstones, and proposed that the principal cause of heavy mineral loss was geological age. Turnau-Morawska (1984), however, presented an alternative relationship between heavy mineral diversity and age, in which only Quaternary sediments have significantly more heavy minerals than the remainder of the geological column. There are many examples of ancient sandstones with rich and diverse heavy-mineral assemblages: the Permo-Triassic of the pre-Urals foredeep (Ukraine) contains abundant amphibole and pyroxene (Sarksiyan, 1958), the upper Devonian of the Pyrenees (France and Spain) contains abundant amphibole and epidote (Stattegger, 1976), the Ordovician of the Southern Uplands (Scotland) contains abundant amphibole and pyroxene (Kelling, 1962; Styles et al., 1989), and the Ordovician of the South Mayo Trough contains abundant amphibole, pyroxene and sillimanite (Dewey and Mange, 1999). These ancient successions with anomalously diverse assemblages tend to be poorly sorted and contain high proportions of labile lithic material, which limited permeability prior to burial and underwent further rapid degradation of reservoir quality during diagenesis. Under such circumstances, the preservation of unstable heavy minerals is regarded as a consequence of the low permeabilities, which sealed the sediment from circulating pore fluids and thus protected the heavy-mineral grains from dissolution.

Therefore, although older sandstones tend to have low-diversity heavy-mineral assemblages, the presence of ancient sandstones with diverse heavy-mineral assemblages proves that geological age is not the main factor controlling intrastratal dissolution. Nevertheless, inevitably, the longer sandstones are subjected to circulating high-temperature pore fluids, the more depleted the assemblages will become. Geological age is therefore an important factor, albeit indirectly. A comparison of the Upper Jurassic and Palaeocene-Eocene of the central North Sea illustrates the effects of increasing age. In the Palaeocene-Eocene, as described above, staurolite is a common component of assemblages until burial depths of approximately 2400 m. However, staurolite is extremely scarce in the underlying Jurassic, even in the shallowest sandstones at less than 2000 m burial.

5. ASSESSMENT OF PROVENANCE IN DIAGENETICALLY MODIFIED SANDSTONES

Dissolution of unstable heavy minerals during diagenesis causes loss of valuable provenance information (Morton, 1984; Milliken, 1988), and the role of burial-related diagenetic processes on heavy-mineral assemblages must therefore be considered when assessing provenance. Nevertheless, despite the possibly profound impact of burial diagenesis on the detrital mineralogy, assemblages still retain fundamental information on provenance. It is therefore critical that the parameters used for interpretation of provenance reflect source area characteristics, rather than subsequent diagenetic processes. Two complementary approaches were recommended to assess provenance under such circumstances (Morton and Hallsworth, 1994, 1999), one that uses the entire heavy-mineral suite (conventional heavy-mineral analysis) and one that concentrates on the attributes of individual mineral species (varietal heavy-mineral analysis).

5.1. Conventional Heavy-Mineral Analysis

Ratios of stable minerals with similar hydrodynamic behaviour reflect source area characteristics, since they cannot be fractionated either by burial diagenesis or by hydraulic processes that operate during transport and sedimentation (Morton and Hallsworth, 1994, 1999) Of the provenance-sensitive parameters proposed by Morton and Hallsworth (1994), rutile/zircon (RuZi), monazite/zircon (MZi), chrome-spinel/zircon (CZi) and apatite/tourmaline (ATi) ratios are unaffected by burial diagenetic processes, since apatite, chrome spinel, monazite rutile, tourmaline and zircon are all stable. The garnet/zircon index (GZi) is, however, likely to be modified in sandstones that have suffered garnet dissolution, and care is therefore required in interpreting GZi values under such circumstances. Although ATi is a useful provenance-sensitive parameter, it may also be affected by loss of apatite during weathering at several stages in the sedimentation cycle, and therefore may provide information on sediment transport history. Prolonged or intense weathering may also result in lowered GZi, as in the Statfjord Formation of the northern North Sea (Morton and Berge, 1995).

5.2. Varietal Heavy-Mineral Analysis

The effects of diagenesis on heavy-mineral assemblages can be minimised by concentrating on properties displayed by a single stable mineral group. Varietal heavy-mineral methods fall into three main categories, petrographic, geochemical, and isotopic. Petrographic varietal data relate to optical properties such as colour, habit or zoning pattern. For example, zircon morphology has been used as a petrogenetic indicator (Pupin, 1976), and colour varieties of zircon (Mackie, 1923) and tourmaline (Krynine, 1946; Mange-Rajetzky, 1995) may be diagnostic of provenance. Textural data may also yield important information on sedimentation history. For example, changes in apatite morphology within the Devonian-Carboniferous succession of the Clair Field, UK continental shelf, are attributable to variable interplay between fluvial and aeolian transport processes (Allen and Mange-Rajetzky, 1992).

Mineral chemistry, as determined by electron microprobe methods, is a powerful tool in provenance reconstruction from diagenetically modified suites. The two most useful minerals are garnet and tourmaline, since both are relatively stable and show a wide range in compositions that can be related to specific source lithologies (Henry and Guidotti, 1985; Morton et al., 2004). The applicability of garnet geochemical analysis is restricted, since garnet undergoes dissolution in very deep burial conditions. The method can be used in sandstones in which garnet dissolution has been active, but caution is required in interpretation since Ca-rich garnets are less stable than Ca-poor varieties. Chrome spinel has variations in major element composition that have been used to infer provenance (Pober and Faupl, 1988; Cookenboo et al., 1997), although Power et al. (2000) suggest that characterisation of provenance using chrome spinel compositions may be unreliable. The other stable phases (apatite, monazite, rutile, zircon) lack significant major element variation, but trace element data may prove useful in provenance reconstruction. For example, rare earth element variations in apatite (Fleischer and Altschuler, 1986; Morton and Yaxley, in press) and trace element abundances in rutile (Zack et al., 2004) appear to be dependent on their source rock composition.

Single-grain isotopic methods provide powerful constraints on provenance, since they give geochronological data that can be used to complement the mineralogical constraints provided by conventional heavy mineral and mineral chemical data. Single-grain U-Pb dating of zircon (Rainbird et al., 1992) and monazite (Evans et al., 2001), both of which are stable phases during diagenesis, is now relatively commonplace, and provides crucial information on the ages of major crust-forming events in the source area. Alternatively, ^{40}Ar$-$ ^{39}Ar laser probe dating of mica (Sherlock et al., 2000) and fission-track dating of minerals such as apatite or zircon (e.g., Carter, 1999) provide information on the metamorphic history and unroofing of the source terrain.

ACKNOWLEDGMENTS

We are grateful to Andrew Hurst, Maria Mange and Peter Mozley for their constructive comments on an earlier draft on this manuscript.

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