Heavy minerals in marine and fluvial sediments: provenance indicators and distributions in the tropical southeastern shelf of the Gulf of Carpentaria and its hinterland North Australia

Rabea A. Haredy
University of Wollongong

Haredy, Rabea A, Heavy minerals in marine and fluvial sediments: provenance indicators and distributions in the tropical southeastern shelf of the Gulf of Carpentaria and its hinterland North Australia, PhD thesis, School of Earth and Environmental Sciences, University of Wollongong, 2008. http://ro.uow.edu.au/theses/263

Chapter Two – Heavy minerals: A literature review

2. 1 – Overview and classification of heavy minerals

Heavy minerals are defined as high density minerals, which have specific gravities greater than 2.9 (Rothwell, 1989; Mange and Maurer 1992). They are deposited and sorted according to differences in size, shape and density (Padmalal *et al.*, 1998; Komar, 2007). These minerals not only occur in sedimentary rocks, but are also found in different types of unconsolidated sediment. According to Mange and Maurer (1992), heavy minerals are present in their original source rocks either as primary or accessory components (e.g. pyroxenes and zircon represent the former and latter components, respectively). Around 56 translucent detrital species of heavy minerals were described by Mange and Maurer (1992) and have been successfully used as sensitive indicators of sediment provenances (Morton, 1985; Morton and Hallsworth, 1999) and transport pathways in both modern and ancient units. The general classification of heavy minerals is based on the degree of transparency and, therefore, heavy minerals can be divided into two categories: opaque and non-opaque minerals. Both categories have optical and chemical properties that can be used to identify each mineral and to distinguish the different species of heavy minerals occurring in a sediment. Differences in resistance to mechanical erosion and chemical weathering have divided the non-opaque heavy mineral suite into two groups: ultrastable minerals (zircon, rutile and tourmaline) and metastable minerals (e.g. epidote, garnet, monazite, hornblende, olivine, etc; Rothwell, 1989).

2. 2 – Factors affecting heavy mineral assemblages and the hydraulic behaviour of heavy mineral grains

Various factors affect the assemblage of heavy minerals from their source to the depositional environments. These factors, according to Morton and Hallsworth (1994 and 1999), Morton *et al.* (2005) and Bateman and Catt (2007), include weathering at different stages between the original source rocks and the sedimentary environments, mechanical abrasion during transportation, physical sorting, and diagenetic processes during burial (Figure 2.1; Table 2.1). Moreover, laboratory errors caused by sample splitting and possible incomplete heavy mineral separation during sample preparation could affect the heavy mineral assemblages (Bateman and Catt, 2007).

Please see print copy for figure 2.1

Figure 2.1 – Factors affecting the heavy mineral assemblages in the sedimentary cycle between the source area and depositional basin, as defined by Morton and Hallsworth, 1999.

Please see print copy for table 2.1

Table 2.1 – Factors affecting the heavy mineral assemblages in the sedimentary cycle between the source area and depositional basin as defined by Bateman and Catt (2007).

The influence of the factors mentioned above on heavy mineral assemblages would vary significantly within different sedimentary environments in the same region (e.g. coast, shelf and basin). This significant variation is associated with the transportation distance between the source rocks and the sedimentary environments; the rate of elevation of the source rocks; weathering intensity; and the meteorological and hydrodynamical conditions of the area. For example, unstable heavy minerals could be destroyed by intensive weathering, and long transportation distance (Morton and Smale, 1990; Van Loon and Mange, 2007). Further, hydrodynamic conditions within coastal environments could redistribute the heavy mineral suites in sediments.

The differences in grain properties (density, size and shape) between heavy and light mineral grains result in different hydraulic properties, whereby a heavy mineral grain will be hydraulically equivalent to a light mineral grain of a larger size, based on the specific gravity of the heavy mineral grain (Table 2.2). The latter behaviour was explained by Rubey (1933) and is termed 'hydraulic equivalent size', which is defined as the difference in size between a given heavy mineral species and the size of a quartz sphere with the same settling velocity in water. In this case, heavy mineral grains are generally more difficult to entrain and transport by currents than other light mineral grains of the same shape and size, and, thus, heavy minerals are represented by smaller grains (Figure 2.2; Kudrass, 1987; Komar, 2007).

Please see print copy for figure 2.2

Figure 2.2 – Sorting of minerals in the surf zone based on the hydraulic equivalent concept (Kudrass, 1987).

Please see print copy for table 2.2

Table 2.2 – Density values of heavy minerals that occur in this study area (values are according to Mange and Maurer, 1992; Deer *et al.*, 1992; Jones, 2000).

Heavy mineral grains tend to accumulate on stream beds as a result of differences in the transportation rate of heavy minerals and other components of the sediments (Fletcher and Loh, 1996). Therefore, hydrodynamic conditions will partly govern the concentration of heavy mineral species between different sedimentary environments and sometimes within one environment. Slingerland and Smith (1986) described four hydraulic sorting mechanisms that could affect heavy mineral concentrations. These mechanisms are entrainment sorting, transport sorting, shear sorting and suspension sorting; the previous mechanisms take place during erosion, transportation and deposition, respectively (Slingerland and Smith, 1986; Hughes *et al.*, 2000; Komar, 2007). Fletcher *et al.* (1992) introduced a similar theory to Rubey (1933), but they concentrated on the behaviour of heavy mineral grains and their relation to transport velocity. They defined 'transport equivalence' as grains having the same average net transport velocities, despite their physical properties (Fletcher *et al.*, 1992). Examples of hydraulic sorting mechanisms and transport equivalence can be seen in the following studies. Fletcher and Loh (1996), who studied transport equivalence of cassiterite in a coarse sand and gravel stream bed in

Malaysia, revealed that fine cassiterite is transported at approximately the same rate as quartz grains three times larger.

Hughes *et al.* (2000) investigated the hydraulic sorting mechanisms of heavy minerals through standard petrographic examination, grain settling velocity and equivalent diameter, in the swash zone of Fishermans Beach sediments, east coast of Australia. They showed that beach types and wave breaking types produce different flow characteristics and have a key role in determining which sorting mechanism can operate in the swash zones. As Fishermans Beach is characterised by a steep slope and medium-grained sand, shear sorting dominates on this beach as a result of flow constraints, thus preventing suspension and entrainment sorting. The steep beach face and great water depth restrict wave action to a narrow area adjacent to the coastline whereby small waves surge up the beach face with minimal breaking, while large waves plunge onto the beach face or adjacent to it on the seaward side (Hughes *et al.*, 2000). They anticipated that flow velocity and turbulence strength are high in the swash zone of Fishermans Beach due to a great amount of water and turbulence entering the narrow swash zone as a result of breaking waves. Therefore, shear sorting was operated on this beach rather than entrainment sorting. However, entrainment sorting operates on gently sloping, fine sand beaches (Hughes *et al.*, 2000).

Another technique used to study the impact of hydrodynamic sorting is analysis of the whole geochemical composition of a sedimentary rock. This technique was used by Svendsen and Hartley (2002) on the Otter Sandstone Formation, southern England, and showed that the elements and oxides Zr, Ce, TiO_2, and P_2O_5 are enriched at the sides of a fluvial channel in comparison to the central part, as result of hydrodynamic sorting.

Further, Cascalho and Fradique (2007) studied the distribution of heavy minerals in the northern Portuguese shelf and adjacent rivers. They reported a high concentration of biotite in the middle shelf north of Douro River mouth. In addition to biotite-rich sources in the hinterland, the platy habit of biotite and the high energy conditions in winter allow suspension sorting processes to transport biotite and other platy minerals (e.g. hornblende) to deeper offshore areas that are less energetic. However, heavy minerals grains with lower mobility values such as zircon, tourmaline, coarse garnet and staurolite tend to remain relatively close to their input sources and thus these minerals are common in the inner-shelf zones near estuaries.

2. 3 – Zircon, tourmaline, and rutile proportions (ZTR index)

To assess the mineralogical maturity of sediments, it is important to calculate the percentages of zircon, tourmaline and rutile in the non-opaque heavy mineral suites. Hubert (1962) provided an index, which represents a combined percentage of the ultrastable heavy minerals (zircon, tourmaline and rutile; cf. Garzanti and Andò, 2007) in the non-opaque heavy mineral suite, excluding mica and authigenic minerals. This index is known as the ZTR index. Sediments with the highest concentrations of ultrastable heavy minerals reflect the most mature mineral composition. The sediments become immature as the proportion of unstable minerals increases.

2. 4 – Stability of heavy minerals and weathering

Detrital heavy minerals are derived from the weathering and erosion of pre-existing rocks. These minerals vary in their resistance to chemical weathering and physical erosion. As a result, heavy minerals were classified into two main groups: ultrastable (e.g. zircon, rutile, tourmaline) and metastable (e.g. epidote, augite, chlorite; Rothwell, 1989). Both the physical and chemical stability of heavy minerals have been studied by numerous researchers. The physical stability is related to grain properties, hydrodynamic conditions in the sedimentary environments, and distance from the source rock (section 2.2 in this chapter). Although mechanical abrasion during transportation of heavy minerals from their source may decrease the concentration of heavy minerals, there is no proof that heavy minerals are lost from assemblages during transportation (Morton and Hallsworth, 1999). Physical stability patterns of various heavy minerals (Table 2.3) were introduced by Freise (1931), Thiel (1945) and Dietz (1973) to rank heavy minerals according to their mechanical resistance during transportation. These patterns show some differences in the order of the mineral's stability. The major difference was found in Dietz's (1973) pattern in comparison to the Freise (1931) and Thiel (1945) patterns. This difference is most likely related to the experimental technique. Dietz (1973) used only shape and roundness as indictors to resistance to abrasion, whereas Freise (1931) and Thiel (1945) included weight loss in their experiment (Morton and Hallsworth, 1999).

Please see print copy for table 2.3

Table 2.3 – Order of physical stability of heavy minerals (cited in Morton and Hallsworth, 1999). Minerals are arranged in order of decreasing stability from top.

The chemical stability of heavy minerals is related to dissolution processes and intrastratal dissolution, which alter the original assemblage by removing soluble minerals and converting mineral species by chemical replacement (e.g. metastable minerals) in both the source rocks and/or the sedimentary environment. Thus, the interpretation of a source rock can be vague (Morton, 1985; Mange and Maurer, 1992; Morton and Hallsworth, 2007). Further, weathering at different stages has a great effect on the variation of a heavy mineral assemblage (Figure 2.1; Table 2.1). Differences in the mineral chemistry of individual species, the geochemical condition (pH and Eh values) of sedimentary environments, and the overall climate conditions yield a chemical stability pattern (Table 2.4; also see Table 3 in Bateman and Catt, 2007, p. 181) that divides heavy minerals from ultrastable to unstable according to their persistence to the weathering intensity.

Pettijohn (1941)	Pettijohn *et al.* (1973)	Acid leaching Morton (1985)	Deep burial saline or alkaline fluids Morton (1985)	Burial diagenesis Morton and Hallsworth (2007)
Rutile Tourmaline Zircon Garnet Apatite Xenotime Monazite Staurolite Kyanite Epidote Glaucophane-riebeckite series Ca-amphiboles Andalusite Sphene Pyroxene Sillimanite Olivine	Ultrastable Rutile Zircon Tourmaline Anatase Stable Apatite Garnet (iron-poor) Staurolite Monazite Moderately stable Epidote Kyanite Garnet (iron-rich) Sillimanite Sphene Zoisite Unstable Hornblende Actinolite Augite Diopside Hypersthene Andalusite Very unstable Olivine	Zircon, Rutile, Tourmaline Andalusite, Sillimanite Kyanite Staurolite Chloritoid, Spinel Epidote, Garnet Apatite Sphene Amphibole Olivine, Pyroxene	Zircon, Rutile, Tourmaline Apatite, Chloritoid, Spinel Garnet Staurolite Kyanite Sphene Epidote Amphibole Andalusite, Sillimanite Olivine, Pyroxene	Apatite Zircon Rutile, Anatase, Brookite Monazite Spinel Tourmaline Chloritoid Garnet Allanite Staurolite Sodic amphibole Kyanite Titanite (sphene) Epidote Sillimanite Andalusite Calcic amphibole Sodic pyroxene Clinopyroxene Orthopyroxene Olivine

Table 2.4 – Order of chemical stability pattern of heavy minerals (table modified from Mange and Maurer, 1992). Minerals are arranged in order of decreasing stability from top.

In terms of chemical weathering, Von Loon and Mange (2007) studied extremely weathered silver sands (sands that consist almost exclusively of quartz) in the Tertiary deposits in the border area between the Netherlands, Germany and Belgium. They reported very low proportions of heavy minerals, and also a limited number of species, resulting from dissolution of the less stable minerals (e.g. epidote hornblende). Further, Von Loon and Mange (2007) concluded that a low-diversity, stable-ultrastable species-dominated heavy mineral content should not be routinely accredited to the processes of deep-burial diagenesis. However, the reduction in heavy mineral diversity may reflect deep weathering of the source rocks and/or in situ weathering, especially in surficial sediments.

A study by Dill (1995) of the Parkstein Formation, southeast Germany, showed a high ZTR index and he referred that to a high degree of weathering of the parent rocks, where the unstable minerals were eliminated by dissolution. The intensive weathering also resulted in redeposition of rutile at the margin of the Parkstein fan, which led to a concentration of TiO_2 (Dill, 1995). Further, the increase of epidote and amphibole in the Hesserberg Formation is correlated to increasing pH values during the fan evolution (Dill, 1995). Another example of weathering was investigated by Poppe *et al.* (1995) in the rivers and insular shelf of north-central Puerto Rico. This study revealed that lateritic weathering has altered the mineralogy of the sediments and produced a remarkable amount of authigenic material in both the silt and sand fractions. The authigenic component was dominated by iron oxides, whereas some rutile grains were formed by chemical leaching of Fe from ilmenite (Poppe *et al.*, 1995).

2. 5 – Selected studies of heavy minerals: worldwide examples

The study of heavy minerals in sandstone and unconsolidated sediments of marine and coastal environments is considered to be the best guide to determine the provenance of the sediments and the transport pathways, as well as the morphology, weathering and erosional history of the parent rocks. The study of the heavy minerals is based on the differences in chemical composition, morphology, concentration, distribution and diversity of heavy minerals species in different sedimentary environments.

The provenance of sediments is usually one of the most important aims in heavy mineral investigations. For example, Damiani and Giorgetti (2008) identified the heavy mineral types and their chemical compositions in the glacial marine sediments under the McMurdo/Ross Ice shelf, Antarctica. They reported that heavy mineral assemblages in the above shelf area show high concentration of pyroxenes, olivines and glass grains associated with minor amounts of amphibole, epidote, garnet and apatite. Such metastable-dominated heavy mineral assemblage was derived from the adjacent lithologies, including the McMurdo Volcanics and the igneous and metamorphic rocks of the Transantarctic Mountains. All pyroxene grains were derived from volcanic, dolerite and tholeitic igneous rocks. However, amphibole grains indicate a mixture of detritus from metamorphic and igneous rocks of the Transantarctic Mountains associated with the McMurdo Volcanics. Finally, epidote and garnet point to metamorphic source rocks including the metasediments and orthogneisses of the Late Precambrian to Early Palaeozoic Koettlitz Group in the Transantarctic Mountains, while sub-rounded to rounded grains were recycled and could be derived from the Devonian to Triassic sedimentary rocks of the Beacon Supergroup of the Transantarctic Mountains (Ehrmann and Polozek; 1999; Damiani and Giorgetti, 2008).

Further, Morton *et al.* (2005) used a combination of heavy mineral data, including ratios, garnet and tourmaline chemistry, together with zircon chronology, to identify the provenance of the Late Cretaceous to Paleocene submarine fan sandstones in the Norwegian Sea. Their results show the occurrence of three sand types that derived from different areas. Sand type MN1, for example is characterised by the common occurrence of kyanite and staurolite, abundant low-Mg garnet and Al-poor metasedimentary tourmaline and small amount of granitic tourmaline. This assemblage was derived from a mixed metasedimentary–granitic terrain in northern mid-Norway. This terrain comprises the upper and uppermost Allochthon of the Caledonian nappe domain and basement windows that expose the westerly extension of the Fennoscandian Shield. However, according to tourmaline chemistry associated with zircon age data, sand type MN2 is predominantly of metasedimentary origin and was derived from northern East Greenland. High Ca and Mg garnet commonly appear in sand type MN3 that was derived from the adjacent gneisses in western Norway (Western Gneiss Region of the SW Scandinavian Domain; Morton *et al.*, 2004 and 2005).

Acquafredda *et al.* (1997) studied types and chemical compositions of heavy minerals as an indicator for the provenance and tectonic evolution of Pliocene-Pleistocene sedimentary strata that were deposited in piggy-back and foredeep basins, southern Apennines, Italy. They found that the occurrence of blue amphibole and staurolite in some of the Early Miocene sandstones (Tufiti di Tusa), Pliocene and Pleistocene strata, and their absence from the Tortonian siliciclastic strata indicate a provenance of basement detritus derived from part of the earlier Alpine chain due to the total similarities in petrofacies with the Corsica-Western Alps area. However, the closure of the Early Miocene basin and activation of Tortonian foredeep basins, as well as the rifting and sinking of some parts of the Tortonian chain, have resulted in the absence of blue amphibole and staurolite from the Tortonian siliciclastic strata. In addition, later after the closure of the Tortonian basins, the Tufiti di Tusa was exposed on the surface and supplied detritus to the Pliocene-Pleistocene basins as a result of the activation of thrusts close to the front of the Apennine chain (Acquafredda *et al.*, 1997).

Thamó-Bozso and Ó.Kovács (2007) evaluated the heavy mineral assemblages of the Quaternary fluvial successions in the central part of the Hungarian Plain using cluster and principal component analyses (PCA). These statistical analyses displayed appreciable similarities between the heavy mineral composition of modern river sediments and those from boreholes. As a result of grouping samples that have similar heavy mineral assemblages, both cluster analysis and PCA identified the sources of heavy minerals in the Hungarian Plain. Chlorite and garnet were mainly derived from metamorphic rocks, while hornblende and pyroxene were derived from volcanogenic sources (cf. Malone, 2007).

Heavy mineral distribution, diversity and occurrence in shelfal and coastal environments has varied significantly on a worldwide basis even in the same environment. This variation is a key issue in the understanding of the overall behaviour, characteristics and genesis of the entire sedimentary environment. Wong (2002) studied the spatial and temporal distributions of heavy minerals in relation to the sediment sources on the Palos Verdes margin, southern California, and found that heavy mineral assemblages could be represented by nine statistical factors. Two of the factors (1 and 2) represented more than 50% of the variance whereas the other factors were minor. For example, factor 1 includes apatite, green hornblende, epidote and sphene and occupies a coast-parallel band with high abundance in the outer part of the Palos Verdes shelf. These minerals decrease in abundance shoreward from the offshore Palos Verdes Point in the west (Wong, 2002). This trend is most likely related to a fluvial sediment supply to San Pedro Bay, whereas other sediment was transported northwestward to the Palos Verdes shelf, giving a clue that regional sedimentary processes influenced the distribution rather than the local processes. In addition, the Los Angeles County Sanitation District sewage system has influenced the distribution of heavy minerals by the effluent discharged to the shelf environment. Therefore, heavy minerals distributions on the Palos Verdes margin indicate that the sources of sediments are heterogeneous for the nearshore and onshore environments (Wong, 2002).

Furthermore, Mislankar and Gujar (1996) noticed a variation in the northern and southern heavy mineral assemblages on the eastern continental margin of India and referred that mainly to differences in the provenance associated with the sediment dispersion by rivers that drain the source rocks. In addition, the present coastal sorting processes, as well as selective chemical decomposition and hydraulic fractionation during the glacial regression and transgression, have shown effectiveness in the preferential concentration of heavy minerals according to their level of stability in the coastal and shelfal environments (Mislankar and Gujar, 1996).

In a comparative study of the heavy mineral suites between riverine and estuarine sediments on the southwest coast of India, Padmalal *et al.* (1998) found that the heavy minerals in the river environment occurred in three size intervals of sand fractions (medium, fine and very fine sand). However, only two size intervals of sand fractions (fine and very fine sand) contained heavy minerals in the estuarine environment. They referred this contrast in the heavy mineral suites to the density-based sorting associated with the higher content of coarse light minerals in the upper fluvial reaches of the Muvattupuzha River, affecting transport and entrainment of hydraulically equivalent smaller and heavier grains by shielding effects (Rubey, 1933; Fletcher *et al.*, 1992; Padmalal *et al.*, 1998). Also, the density-based sorting has differentiated the percentages of components within the heavy mineral suites in the Muvattupuzha River, where the proportion of denser heavy minerals (e.g. zircon, garnet) decreased downstream and the lighter heavy minerals increased (e.g. pyroxenes, amphiboles; Padmalal *et al.*, 1998).

In addition, selective grain transport has influenced the distribution of heavy mineral assemblages in the Nile Delta, Egypt, and yielded two factors or mineral groups (Frihy *et al.*, 1995; Frihy, 2007). Factor 1 includes heavy minerals of lower density and coarser size (augite, hornblende and epidote). Heavy minerals in this factor increase from west to east along the delta, as they are easily to entrained and transported by the wave currents. These waves are generated along the length of the Mediterranean Sea and arrive from the northwest, thus transporting the coastal sediments toward the east. In contrast, factor 2 includes heavy minerals of higher-density (opaques, garnet, zircon, rutile, tourmaline and monazite) and these minerals are difficult to entrain and transport by wave-current actions. Hence, minerals in this factor form a lag deposit within the delta and beach sand (Frihy *et al.*, 1995; Frihy, 2007).

Finally, provenance, stability level of minerals, sea level fluctuations during the Quaternary, offshore and the longshore drift currents, variations in fluvial and aeolian supplies to the marine systems have all influenced the nature, concentration and distribution of heavy minerals over the shelves and coastal environment sediments. Carriquiry *et al* (2001) found that a new sedimentary province, with a high concentration of zircon and garnet, appeared in the western part of the upper shallow shelf in the Gulf of California. This new province resulted from a diminution in the rate of fluvial supply from the Colorado River to the northern Gulf of California. This reduction in fluvial supply was caused by the anthropogenic effects of damming the Colorado River. Therefore, oceanic processes play a key role in the sediment dispersion pattern, in the absence of the fluvial processes associated with the promotion of alternate sediment source supply from the desert area in northwest of Mexico and the southwest of the USA (Carriquiry *et al.*, 2001).