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

Chapter Three – Methodology

3. 1 – Sampling

A total of 365 sediment samples were collected from the study area and analysed (Figure 1.1; see Appendix A for detail sample locations). In 1991, 25 surficial sediment samples were collected from the nearshore area between Accident Inlet and Gilbert River mouth by B. G. Jones using a Van Veen type grab sampler from a commercial fishing vessel. In 2003, another 291 sediment samples from the offshore area of the southeastern shelf of the Gulf of Carpentaria were collected by Geosciences Australia (103 surficial samples and 188 sub-surface samples from 40 vibracores; see Appendix A). These samples were collected in May-June, 2003 by P. T. Harris and his research team in Geosciences Australia (Survey No. 238; see Heap *et al.*, 2006 for details), using a Smith Macintyre grab sampler and a 6 m long electric-powered vibrocorer from the RV Southern Surveyor research vessel (Cruise No. SS04/2003). In 2004, the author collected a total of 49 fluvial surficial sediment samples using a polycarbonate sediment extractor barrel from 28 river systems and 5 creeks (Figure 1.3; Appendix A). These fluvial samples were grouped according to the geology of the drainage basins around the Gulf of Carpentaria (Figure 8.1; Tables 8.1, 8.2, 8.3, 8.4, 8.5 and 8.6).

3. 2 – Sample preparation

Each bulk sample was divided into three representative subsets for heavy mineral analysis, light mineral analysis, and textural analysis (grain size for the offshore shelf sediment samples were determined by Geosciences Australia; see Heap *et al.*, 2006). Selected sediment samples from the offshore shelf area were used to determine the bulk and clay

mineralogy using XRD analysis on the third subsets. Details of the sample preparation techniques for each analysis will be described in the following sections.

3. 2. 1 – Heavy minerals

Subsamples were treated with 10% HCl and 15% H_2O_2 to remove carbonate materials and organic matter (Mange and Maurer, 1992; p.11). Standard wet-sieving was performed on all treated sediment samples to extract the required very fine sand fraction (63-125μm) for the current study. The narrow grain size interval was chosen to reduce potential problems of selective sorting and to avoid bias by inherited grain size distributions from the source rocks. The very fine sand fraction is the one with the highest heavy mineral concentration and is unlikely to lack any key species (Morton, 1985; Morton and Hallsworth, 1994).

Heavy mineral separations from the very fine sand fraction (63-125μm) were carried out using a centrifuge with a sodium polytungstate solution (density = 2.85g/cm^3) as the heavy liquid (Mange and Maurer, 1992; Poppe *et al.*, 1995). Representative weighed (~1g) subsamples of the very fine sand fraction were placed individually in centrifuge tubes and then centrifuged for 10 min at a speed of 3000 rpm (Mange and Maurer, 1992). Two groups of funnels with filter papers were prepared to receive the heavy and light minerals. Both the heavy and light minerals were washed thoroughly with distilled water to recover the heavy liquid. The last wash was performed with alcohol to ensure that all the heavy liquid was cleaned from the heavy minerals and to accelerate the air drying process. As soon as the heavy minerals were completely dry, they were weighed to calculate the heavy mineral percentage in each sample (Appendix B). Representative splits of heavy mineral grains were mounted on glass slides using Canada balsam (RI = 1.52) for standard petrographic

examination. Other heavy mineral sets were prepared for microprobe analysis to identify the ambiguous and unknown grains through their chemistry, as well as to determine the chemical composition of minerals for provenance analysis.

3. 2. 1. 1 – Petrographic analysis of heavy minerals

Heavy mineral slides were examined using a polarising microscope in order to identify, characterise and calculate the percentages of the various types of opaque, weathered and translucent heavy mineral grains. Point counting was performed using the Ribbon counting technique, which is the most popular method for heavy minerals (Mange and Maurer, 1992; cf. Cascalho and Fradique, 2007). A total range of between 400-700 heavy minerals grains were counted per slide to achieve a high confidence estimation for the mineral proportions (Wong, 2002). Heavy mineral grains were counted in two steps: the first count involved grains of opaque and non-opaque minerals; the second count involved grains of non-opaque species only. The reason for counting the non-opaque species individually is to avoid an underestimation for the less common species. The counting results were then converted to numeric percentages for heavy mineral fractions (Appendix B). Also, some heavy mineral percentages were calculated in total sediments and total carbonate-free sediments (Chapter Five) as follows:

%Heavy mineral in total sediments = (%HM * %total translucent HM) / 100

%Total translucent HM = (%non-opaque * %total HM) / 100

%Heavy mineral in total carbonate-free sediments = (%Heavy mineral in total sediments * 100) / (100 - %carbonate).

3. 2. 1. 2 – Electron microprobe analysis of heavy minerals

Heavy mineral assemblages that represent 23 river systems, selected surficial and subsurface offshore assemblages were impregnated with epoxy resin, mounted on glass slides and ground to produce polished thin sections. The polished thin sections were then examined under a polarising microscope that integrated with a digitiser stage (Micro-GIS system; Figure 3.1) to register the coordinates of the heavy mineral grains for microprobe analysis. Mineral compositions of these pre-identified and located heavy mineral grains (≈ 600; Appendix C) were determined on the polished thin sections, which had been carbon coated, using a Cameca SX-100 electron microprobe (Figure 3.2) housed in the in the GEMOC ARC National Key Centre, Department of Earth and Planetary Sciences, Macquarie University. The Cameca SX-100 Electron Microprobe is fitted with 5 wavelength dispersive spectrometers (WDS) and an integrated Princeton Gamma-Tech (PGT) energy dispersive system (EDS). All quantitative analyses for Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na and K were obtained using WDS. The accelerating voltage used was 15 KeV, beam current 20 nanoamps, and a focussed beam (size 1-2 microns). Counting times for all elements was 20 seconds (10 seconds on peak and 10 seconds on background). End-members proportions for each mineral group were calculated and plotted on appropriate nomenclature diagrams, in order to classify the species of heavy minerals (see Chapter Six).

Figure 3.1 – Polarising microscope with Micro-GIS system to locate heavy mineral grains in the polished thin section.

Figure 3.2 – Cameca SX-100 electron microprobe.

3. 2. 2 – Light minerals (thin sections in the sand fraction)

Subsamples were wet sieved through a 63 μm cloth sieve in order to remove the mud fraction and prepare a thin section from the sand fraction in each sample. The dry mud-free sediment samples were impregnated in epoxy resin overnight in order to create solid sediment blocks (after Dobell and Day, 1966; Middleton and Kraus, 1980). These blocks were mounted on glass slides using the same epoxy resin on a 50 °C hot plate overnight. A diamond saw was adjusted to cut the mounted sediment blocks at approximate thickness of 100 μm. Each sample was ground down on a rotating carborundum plate to reduce the thickness to just before the standard thickness of a thin section (30 μm). The final stage of polishing was performed manually by hand on a glass plate to obtain the right thickness (30 μm; after Dobell and Day, 1966; Middleton and Kraus, 1980). Thickness was controlled optically on the basis of the quartz interference colours.

3. 2. 2. 1 – Petrographic analysis of light minerals in the thin sections

Thin sections were examined using a polarising microscope to identify and quantify the total light mineral compositions including quartz, feldspar, rock fragments, carbonate and collophane (fossilised bone and fish scales). Point counting was performed using the Ribbon counting technique (Mange and Maurer, 1992). A total range of between 300-500 light mineral grains were counted per thin section to estimate the light mineral proportions. The counting results were then converted to numeric percentages (Appendix D). Also, the feldspar weathering index (FWI) was estimated according to the degree of surficial alteration of the counted feldspar grains. They were assigned into four morphological classes that have specific weathering values (Table 3.1; Read *et al.*, 1996). The feldspar

weathering index was then calculated on the basis of these values using the following equation whereby letters represent the weathering classes and numbers represent the weathering values (Table 3.1; Appendix D).

$$\mathbf{FWI = [(L*1)+(Ml*2)+(Mh*4)+(H*8)] \div total\ number\ of\ grains}$$

Please see print copy for table 3.1

Table 3.1 – Feldspar weathering classes using the polarising microscope according to Read *et al.* (1996).

3. 2. 3 – Clay mineralogy – X-ray diffraction analysis

Selected core samples (Appendix E) were ground into a powder using an agate mortar and pestle in order to determine the clay mineralogy. X-ray Diffraction (XRD) of powdered samples utilising a Philips 1150 PW Bragg-Brentano diffractometer and CuK_{α} radiation between 4 and 70° 2θ. Diffraction peaks were selected by automatic and manual XRD trace processing operations using the computer program SIE122 and mineral identification was accomplished with the program μPDSM (micron Powder Diffraction Search Match) to identify the existing minerals. The quantification of crystalline minerals was performed using the program SIROQUANT. The main reason for using the XRD analysis is to

identify and quantify the clay minerals, which cannot be determined by means of petrographic examination since they are too finely crystalline.

Although this thesis focuses on the heavy mineralogy of the southeastern shelf of the Gulf of Carpentaria and its surrounding fluvial systems, light and clay mineral contents were determined in order to characterise the entire mineralogical components of sediments in the study area that never been investigated in previous studies. Detailed descriptions and distributions of the light and clay minerals are presented in Appendix F.

3. 2. 4 – Textural analyses

Textural analyses include visual description of the recovered vibrocores and grain-size analysis for the sediments (core logs described and prepared by Heap *et al.*, 2006; Appendices G and H). Grain-size distributions were measured with a Malvern Mastersizer 2000 instrument, which used laser diffraction particle size analysis. This diffraction analysis is based on measuring the angle of scattered light from a particle passing through the laser beam. The scattered light is collected by detectors that analysed particles ranging in size from 0.02 to 2000 μm. The Malvern Mastersizer 2000 instrument is attached to a computer with special software that compares the diffraction data with a database of a range of materials to identify the scattering signal and calculate the volumetric size distribution. The final data output after each experimental run are the various size percentiles, graphical mean grain size, standard deviation, skewness, kurtosis, and the percentage of sand, silt and clay.

3. 2. 4. 1 – Grain size of the offshore samples

The bulk samples of all surface and some subsurface sediments were split into two subsets for grain size analysis. The first sub-sample was sieved through a 2000 μm mesh to remove the gravel fraction. Organic matter in the fine fraction was then removed using dilute H_2O_2. The sample was thoroughly rinsed with distilled water and then placed in an ultrasonic bath for up to 2 mins to break up any remaining aggregates. The grain size distribution of the fine fraction was then measured using the Malvern Mastersizer 2000 instrument (see Heap *et al.*, 2006, for details).

The second sub-sample was wet-sieved through 2000 and 63 μm sieves in order to separate the main size fractions (mud-sand-gravel). The mud fraction was spun in a centrifuge at 3,500 rpm for 10 mins to separate out the sample. All of the fractions were oven-dried at 40° C for at least 24 hours to complete dryness. Each fraction was then weighed with an analytical balance to obtain the amount of gravel, sand and mud in the sample (see Heap *et al.*, 2006, for details; Appendix H).

3. 2. 4. 2 – Grain size of the nearshore and river samples

All the nearshore samples are less than 2000 μm and thus their grain sizes were measured directly with the laser particle size analyser (Appendix H). However, some of the river samples were very coarse sediments, as a result materials above 2000 μm were dry sieved using a nest of sieves (2000-2400-2800-3350-4000-4750-6700-8000-10000-16000 μm) and the resultant data were combined with the Malvern data according to the total weight of the

sample, weight of material < 2000 μm, weight of material > 2000 μm and the weight of each size in the gravel fraction.

3. 2. 5 – Radiocarbon age

A total of 77 samples collected from the vibrocores were prepared at Geosciences Australia and radiocarbon ages were determined using the Accelerator Mass Spectrometry at Rafter Radiocarbon Laboratories in New Zealand. Uncorrected ages were corrected by applying the marine reservoir correction of 450 years (see Heap *et al.*, 2006, for details).

3. 3 – Statistical analysis

The data sets acquired in this study are very large and difficult to interpret. Therefore, a large number of multivariate cluster analysis and descriptive statistical analysis (approximately 200 tests) were applied to all heavy and light mineral data using several cluster methods and different combinations of samples and variables in order to identify the mineralogical facies in the southeastern shelf of the Gulf of Carpentaria and its surrounding fluvial systems.

The heavy mineral facies of river, shelf surface and shelf sub-surface environments were identified through a Q-mode hierarchical cluster analysis for all sediment samples within each environment (excluding core catcher samples from the sub-surface sediments), using the volume percentages of zircon, rutile, tourmaline, hornblende, epidote, garnet and metamorphic aluminum silicate group (the total of sillimanite, andalusite, kyanite and staurolite) in SPSS statistical software. Between-group average-linkage method was applied to all sediment samples within each environment (cf. Damiani and Giorgetti, 2008), using

semi-metric distance measure (cosine), which is a compatible distance measure for the average-linkage clustering algorithms (Lance and Williams, 1967) and variables were standardised according to the Z score values. The above heavy minerals and their group were selected on the basis of mineral families, abundance, statistical relationships and correlations between minerals (R-mode clusters; see Appendix I).

Further, the mineral facies of river, shelf surface and shelf sub-surface environments were identified by the same cluster method mentioned above, using all heavy and light mineral data. Also, carbonate-free mineral facies (clastic facies) were identified by the same cluster technique, using the significant individual heavy minerals and their group (mentioned earlier), quartz and feldspar (see Appendix I). Descriptive statistics including mean, standard deviation, minimum and maximum were calculated for each variable within the identified mineralogical facies, in order to characterise the mineralogical facies and to determine the controlling variables for each facies. The statistical analyses showed that the spatial variability of the heavy minerals is the main factor influencing the formation of the mineralogical facies discussed in this thesis (see Chapter Seven and Appendix I).

3. 4 – ArcGIS and spatial distribution analysis

The spatial distribution of heavy minerals was extrapolated according to sample location and its heavy mineral content, using the universal Kriging algorithm method in ArcGIS software. The Kriging interpolation method in ArcGIS is based on a mathematical function associated with the distance between samples (ESRI, 1996) to create a spatial correlation between samples. Maps for each significant heavy mineral were produced to assess controls affecting the spatial distribution of these heavy minerals.