

SUPPLEMENTARY MATERIAL TO

The Heavy Mineral Map of Australia: vision and pilot project

Patrice de Caritat ^{1,*}, Brent I.A. McInnes ², Alexander T. Walker ², Evgeniy Bastrakov ¹, Stephen M. Rowins ² and Alexander M. Prent ²

¹ Geoscience Australia, GPO Box 378, Canberra ACT 2601, Australia; Patrice.deCaritat@ga.gov.au

² John de Laeter Centre, Curtin University, Bentley WA 6102, Australia

* Correspondence: Patrice.deCaritat@ga.gov.au

S1. Materials

In 2019 Geoscience Australia and Curtin University conducted a pilot study to determine the potential use and application of the National Geochemical Survey of Australia (NGSA) samples to quantify, characterize, map and statistically analyze the distribution of heavy minerals (HMs) in the surficial regolith of Australia. The NGSA samples cover over 80% of Australia (Figure 1 in the main paper) and originate from both top (0-10 cm) and deeper (~60-80 cm) sediments accumulating near the outlet of large (~5000 km²) terrestrial catchments (www.ga.gov.au/ngsa, accessed on 28 July 2022; Caritat & Cooper, 2011 [1]). These sediments are mostly similar to floodplain sediments, with an aeolian input in places. Floodplain sediments have been shown to provide a good representation of the major soils, sediments and rocks in the catchment they originate from [2] and are a common low-density geochemical survey sampling medium. NGSA samples have to-date been analyzed comprehensively for bulk properties (pH, electrical conductivity, color, grain-size distribution), geochemistry (by various methods ranging from total to partial analyses), and spectral mineralogy [3]. In addition, a subset of samples have been the subject of isotopic system investigations (e.g., U-Pb Sensitive High Resolution Ion Micro Probe [SHRIMP], Sm-Nd isotopes, Sr isotopes [4], and Pb isotopes [5]). Their HMs, however, have not been systematically investigated yet. As analyses to-date have concentrated on the fine (<75 µm) and coarse (<2 mm) fractions, the intermediate grainsize fraction (75-2000 µm) is available for additional analyses and is ideal for a HM study (i.e., ease of mineral identification).

Ten NGSA sites were selected to represent a range of geological environments and hence a range of HM concentrations and diversity by selecting samples ranging from low to high Zr content as well as representing geological regions [6] ranging in age from Proterozoic to Meso-Cenozoic. As shown on Figure 1 in the main paper, two of those sites are from Western Australia (Pinjarra and Yilgarn geological regions); two from the Northern Territory (Birrindudu and Arafura); one from South Australia (Adelaide); two from Queensland (Carpentaria and Paleozoic-Qld); two from New South Wales (both Paleozoic-SE); and one from Victoria (Murray). Ten NGSA Top Outlet Sediment (TOS; 0-10 cm) samples were sent to Curtin University in March 2019 to develop, test and cost a fit-for-purpose analytical workflow, culminating in production of mineral mount images (and associated data) using a TESCAN® Integrated Mineral Analyzer (TIMA) operated by the John de Laeter Centre (JdLC) at Curtin University. Although the formal NGSA site IDs are in the format '200719xxxx', the last four digits ('xxxx') are used herein as unique identifiers.

S2. Methods

S2.1. Sample Preparation

The ten NGSA 75-2000 µm TOS fractions (200-400 g each) supplied to the JdLC were prepared for automated mineralogical analysis using specialized techniques. Due to the large volume of original material supplied relative to the high spatial resolution (~5 µm)

of the microscopy technique utilized, a sample preparation methodology was designed that would maximize the number of individual grains analyzed by considering only a finer grain sub-fraction (75-430 μm). A secondary factor taken into consideration was the probability that the NGSa samples would be rich in quartz, a mineral with limited petro-genetic or exploration application. Accordingly, an aliquot of the original sample was sub-jected to density separation techniques in order to concentrate the HM fraction. Finally, in anticipation that certain minerals would need to be re-located for in-situ LA-ICP-MS or other microanalysis, two or three large pyrite grains were added to the epoxy mounts to serve as navigational markers.

The sample processing workflow is listed below:

1. Separate sample into two aliquots
 - a. Sieve and isolate sample to 75-430 μm fraction. The 75-430 μm fraction is homogenized then riffle split into two aliquots: 'Group A' (WR, whole rock) and 'Group B' (HM, heavy mineral concentrate)
 - b. Residue >430 μm is bagged and stored
 - c. Residue <75 μm (if any) is bagged and stored
2. 'Group A' mount
 - a. Prepare acrylic TIMA 'dump mounts' by pouring 'Group A' minerals into a 25 mm diameter round mould and add liquid epoxy. When epoxy is fully hardened, the dump mount is polished and carbon coated for TIMA im-aging
3. 'Group B' mount
 - a. Weigh 'Group B' starting aliquot
 - b. Process 'Group B' aliquot using Jasper Canyon Research® (JCR) table (Fig-ure S1) as described below in order to separate heavy and light mineral fractions
 - The sample is poured into feeder pot ('A' in Figure S1 left), water is added from faucet ('B') and stirrer ('C') started. Stirrer will mix sam-ple and water together into a suspension
 - Microprocessor is started, which controls water flow rates from fau-cets 'B' and 'E'
 - Faucet B will slowly add water into pot 'A', causing sample + water suspension to slowly overflow and exit out of outlet ('J') and onto slab ('F')
 - A low voltage motor (inside waterproof box 'G') vibrates the slab
 - Four small arms and hangers ('H') support the corners of the light-weight slab and pivot to accommodate the vibration motion
 - Sample + water suspension spills out of outlet 'J' and drops inside curved dam ('K') on slab. Faucet E adds water to dilute the suspen-sion
 - A network of branching grooves ('L') spreads out the sample + water so they are evenly distributed in a thin layer when they flow across reference line 'M'
 - About 90% of HMs will be captured and will stay inside the first two collector grooves; most of remaining HMs will be captured by the next two grooves (Figure S1 right)
 - 'Group B' light grains are deposited in plastic tray ('O')
 - After run is completed, a disposable plastic pipette ('Q') is used to vacuum 'Group B' heavy fraction out of grooves for collection in a beaker
 - c. 'Group B' heavy and light fractions are air-dried in oven at 50°C. 'Group B' light fraction is bagged and stored
 - d. Dried 'Group B' heavy fraction subjected to heavy liquid separation using lithium heteropolytungstate solution (2.9 g/cm³)

- 'Group B' minerals that float in sodium polytungstate solution are rinsed, dried, bagged and stored
 - 'Group B' minerals that sink in sodium polytungstate solution are the final heavy mineral concentrate (HMC) product for analysis. These are rinsed and air-dried at 50°C then weighed
- e. Calculate %HMC yield ($100 \times \text{mass Step 3d2} / \text{mass Step 3a}$)
 - f. Prepare acrylic TIMA dump mounts by pouring 'Group B' HMC into a 25 mm diameter round mould to which liquid epoxy is added. Where more HMC has been produced for a sample than is required for the mount, the HMC is split using the 'cone and quarter' method to ensure that only a quantity of HMC sufficient to cover the mount surface is used; the excess HMC material is archived. When epoxy is fully hardened, the dump mount is polished and carbon coated for TIMA analysis.
4. TIMA analysis of acrylic 'Group A' (Step 2a) and 'Group B' (Step 3f) dump mounts (see Section S5)

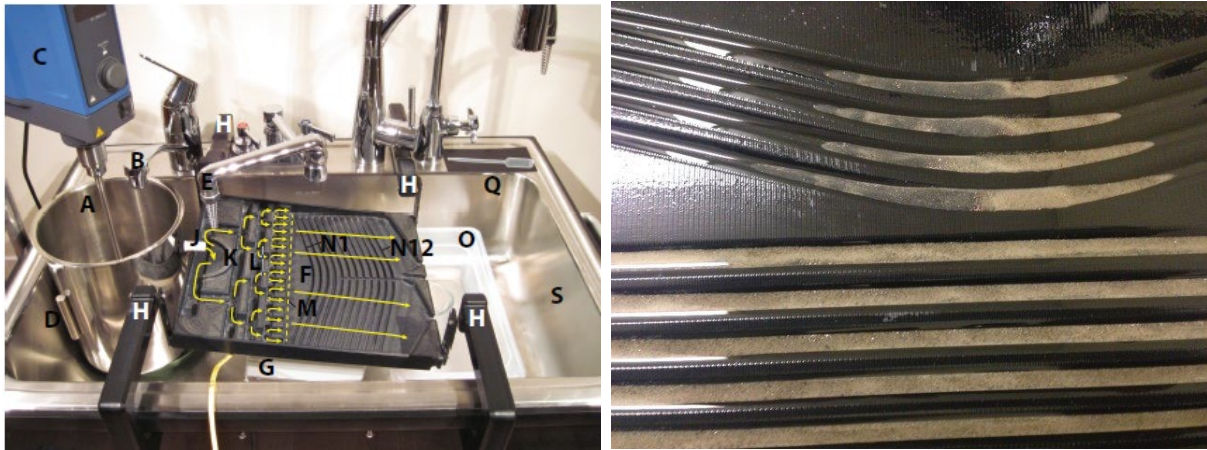


Figure S1. JCR® table used at the JdLC (left; letters label items discussed in text). Detail (right) shows the heavy minerals (dark grains) accumulated in the top four grooves.

S2.2. Automated Mineralogy

Petrologists use scanning electron microscopy (SEM) techniques to determine the chemical composition and morphology of samples at the microscopic scale. Compositional data is obtained using energy dispersive X-ray spectrometers (EDSs), which measure the spectrum of X-rays generated during the interaction between the electron beam and the analyzed mineral. The mineral's spectral signature is characteristic of the atoms making up its crystallographic structure. The spectrum of an unknown mineral can be compared to a library of known mineral spectra, and where there is a match the unknown mineral can be positively identified. The robotic automation of this analytical process allows for the rapid and accurate identification of rock samples at the microscopic scale, and is termed automated mineralogy [7].

The automated mineralogy system at the JdLC, TIMA, was manufactured by TESCAN® and purchased by Curtin University in 2015. The TIMA is comprised of an SEM equipped with four silicon drift EDSs (Figure S2). TIMA analyses were conducted at operating conditions of 25 keV using a spot size of 73 nm, a working distance of 15 mm and a field size set at 1500 μm . The samples were analyzed in high-resolution mapping mode with an analytical stepping distance of 3 μm . At each analytical location, an EDS spectrum was acquired along with a back scattered electron (BSE) signal, used to automatically determine the boundaries between mineral grains. The technique is capable of classifying 200,000 unknown grains per hour.



Figure S2. TESCAN® Integrated Mineral Analyzer (SEM-EDS) at the JdLC.

The mineral data are collected in the rawest form as ‘observations’ or counts, where an observation is defined as a closed monomineralic phase either found as a single ‘grain’ under the SEM/BSE, or part of a multimineralic grain, e.g., an inclusion or a composite rock fragment. The TIMA software also computes mineral abundances in volume percent (vol%) and/or weight percent (wt%) relative to the HMC by measuring the area of a given grain in pixels, calculating the radius of a circle of equivalent area, and then finally calculating the volume of a sphere of that radius. A high-resolution mineral ‘mount image’ is recorded for each sample mount (see Section S5 below).

In addition to identified minerals, the classification software reports on three other possible outputs:

1. ‘Holes’ refers to parts of the mount where there is an absence of an X-ray spectrum, usually caused by a void in the mount that may reflect mineral loss due to plucking during polishing, bubbles in the epoxy or (pore) space between minerals
2. ‘The Rest’ refers to minerals that have been positively identified but are only present in minor amounts (<0.2 wt%)
3. ‘Unclassified’ refers to analyses where the measured X-ray spectrum did not match any of the spectra in the mineral library. This typically occurs where minerals contain ultrafine assemblages of secondary minerals resulting from exsolution (e.g., ilmenite exsolution from titanomagnetite) or alteration (e.g., saussurite within plagioclase). These secondary minerals often have grain dimensions (<2 µm) that are smaller than the electron beam interaction volume. Consequently, the X-ray spectrum generated from ultrafine-grained secondary minerals is that of a mixture of minerals that cannot be matched to a single mineral by the classification algorithm

The acrylic mounts are suitable for archival purposes and should remain intact over decadal timescales, such that they can serve as mineral libraries for subsequent studies utilizing microanalytical techniques.

S3. References

1. Caritat, P. de; Cooper, M. National Geochemical Survey of Australia: The Geochemical Atlas of Australia. *Geosci Austral Rec*, **2011**, 2011/20, 557 p. [[CrossRef](#)]
2. Ottesen, R.T.; Bogen, J.; Bølviken, B.; Volden, T. Overbank sediment: a representative sample medium for regional geochemical sampling. *J Geoch Explor*, **1989**, 32, 257–277. [[CrossRef](#)]
3. Caritat, P. de; Cooper, M. A continental-scale geochemical atlas for resource exploration and environmental management: the National Geochemical Survey of Australia. *Geoch Explor Env Anal*, **2016**, 16, 3–13. [[CrossRef](#)]
4. Caritat, P. de; Dosseto, A.; Dux, F. A strontium isoscape of inland southeastern Australia. *Earth Syst. Sci. Data Discuss*, preprint, in review, **2022**. [[CrossRef](#)]

5. Desem, C.U.; Maas, R.; Woodhead, J.; Carr, G.; Caritat, P. de. Towards a Pb isotope regolith map of the Australian continent: a Northern Territory perspective. In *Exploring for the Future: Extended Abstracts*, Czarnota, K., Roach, I., Abbott, S., Haynes, M., Kositsin, N., Ray, A., Slatter, E., Eds., Geosci Austral, Canberra, **2020**. [[CrossRef](#)]
6. Blake D.; Kilgour B. *Geological Regions of Australia 1:5 000 000 Scale*. Geosci Austral, Canberra, **1998**. Available at: <http://pid.geoscience.gov.au/dataset/ga/32366>
7. Schulz, B.; Sandmann, D.; Gilbricht, S. SEM-based automated mineralogy and its application in geo- and material sciences. *Minerals*, **2020**, *10*, 1004. [[CrossRef](#)]

S4. Data Tables

Table S1. Names (sorted alphabetically), formulas, average specific gravity (Ave SG) and common environments of occurrence/host rocks of selected heavy minerals (Source: www.webmineral.com, accessed on 28 July 2022).

[See Excel table Supplementary TableS1.xlsx]

Table S2. Quantitative mineralogy data (vol%) for the whole-rock (WR) mounts of the ten NGSA pilot project samples.

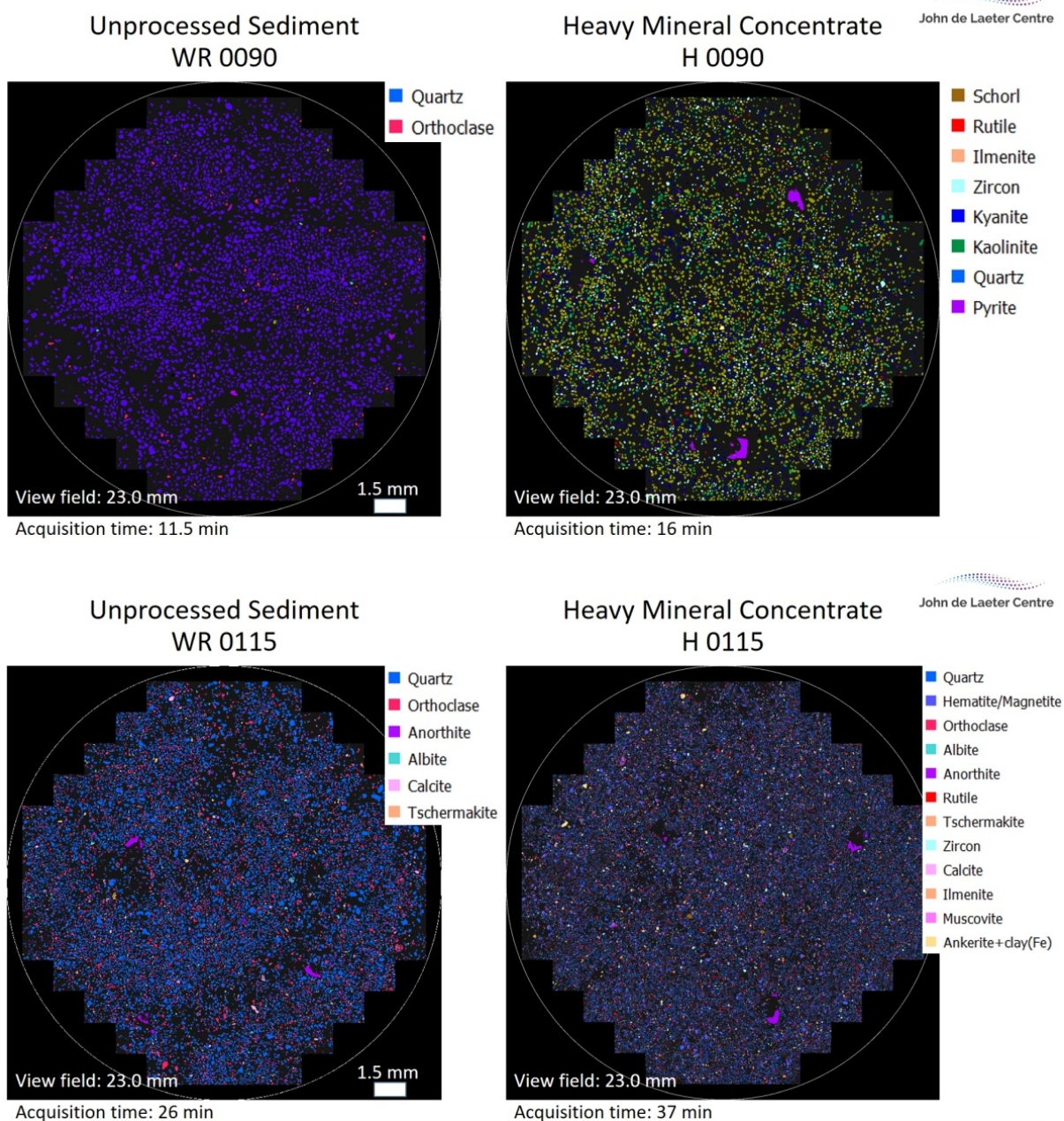
[See Excel table Supplementary TableS2.xlsx]

Table S3. Quantitative mineralogy data (vol%) for the heavy mineral (H) mounts of the ten NGSA pilot project samples.

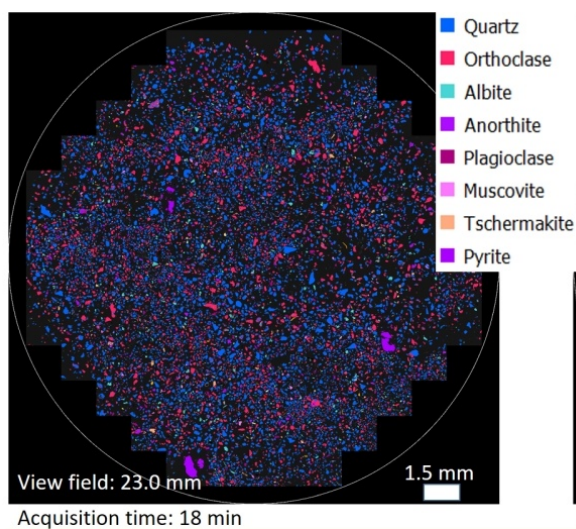
[See Excel table Supplementary TableS3.xlsx]

S5. Mineral Mount Images

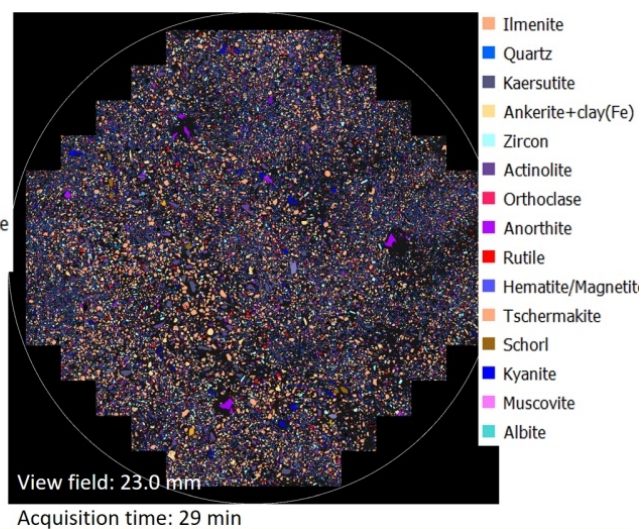
Grain mount images of 10 NGSA samples showing mineral identification produced by TIMA as a bulk 75-430 μm fraction sample (WR, left) and HM concentrate (H, right). The large pyrite grains (purple) are artefacts placed for positioning.



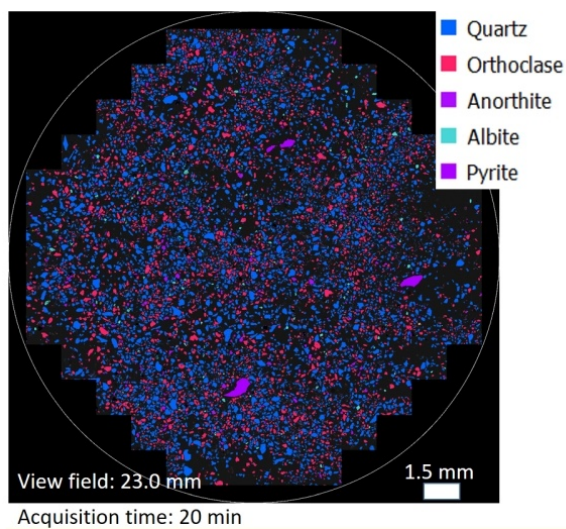
Unprocessed Sediment
WR 0453



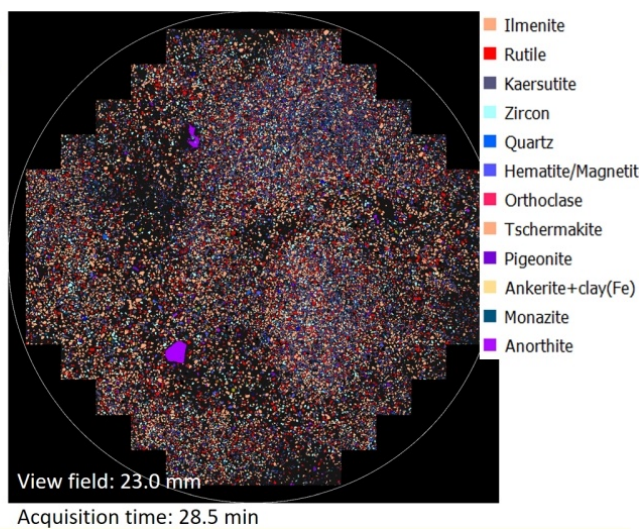
Heavy Mineral Concentrate
H 0453



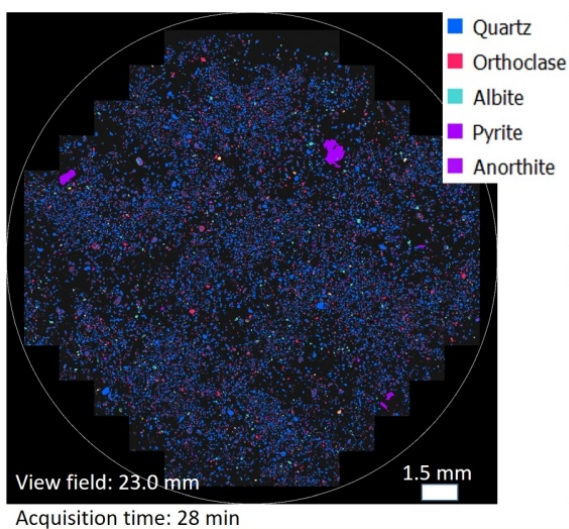
Unprocessed Sediment
WR 0602



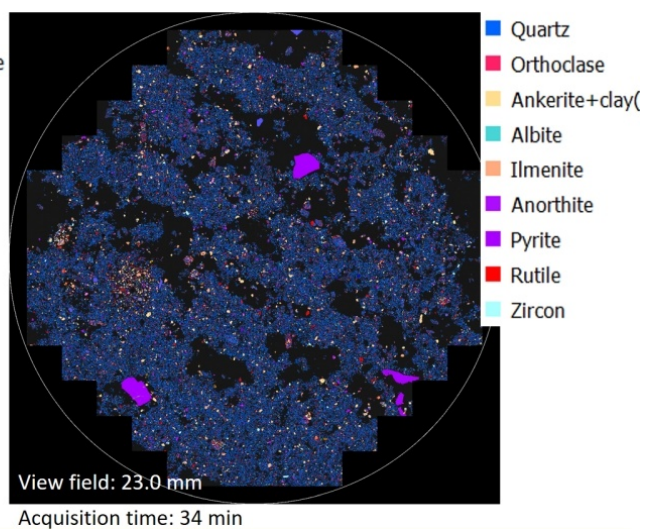
Heavy Mineral Concentrate
H 0602



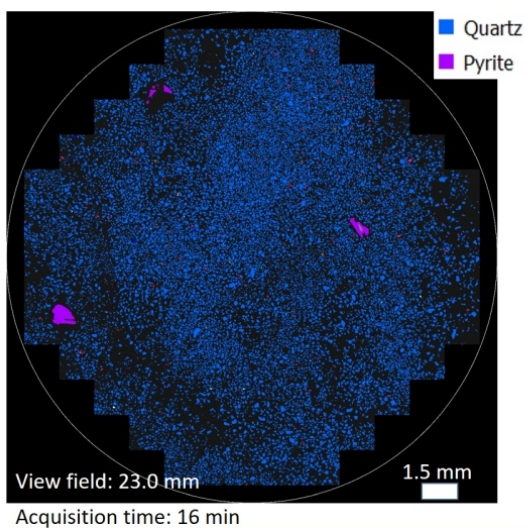
Unprocessed Sediment
WR 0755



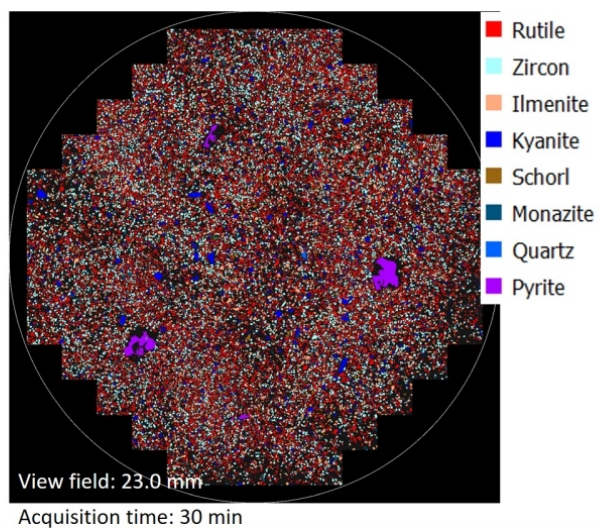
Heavy Mineral Concentrate
H 0755



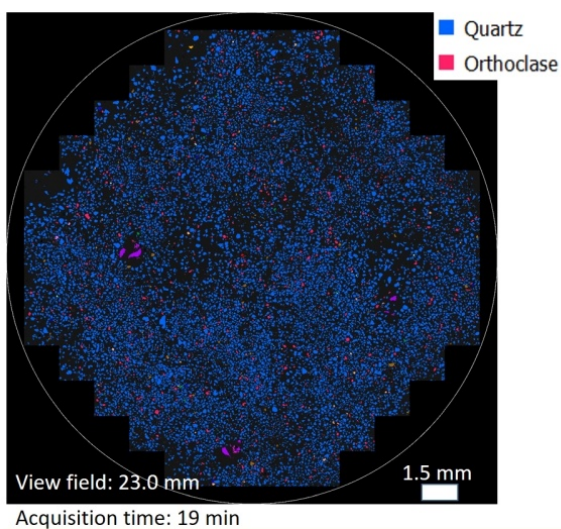
Unprocessed Sediment
WR 1046



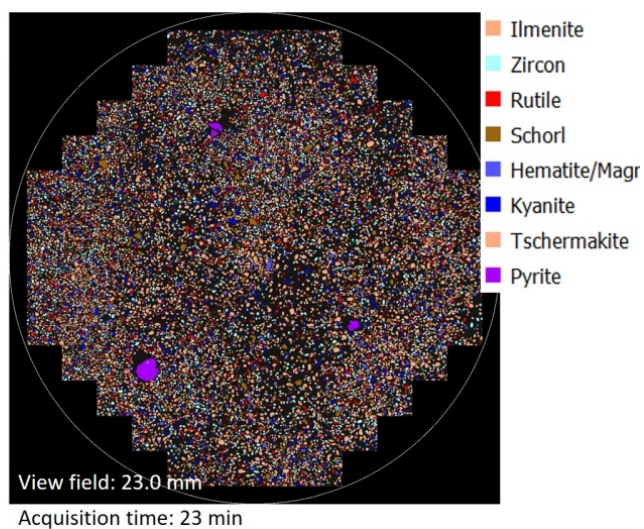
Heavy Mineral Concentrate
H 1046



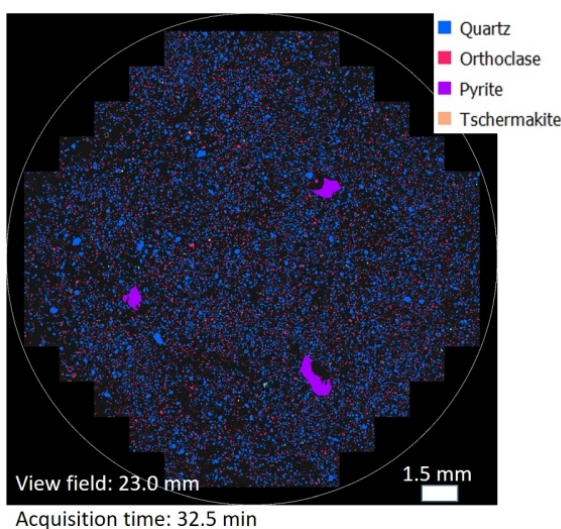
Unprocessed Sediment
WR 1052



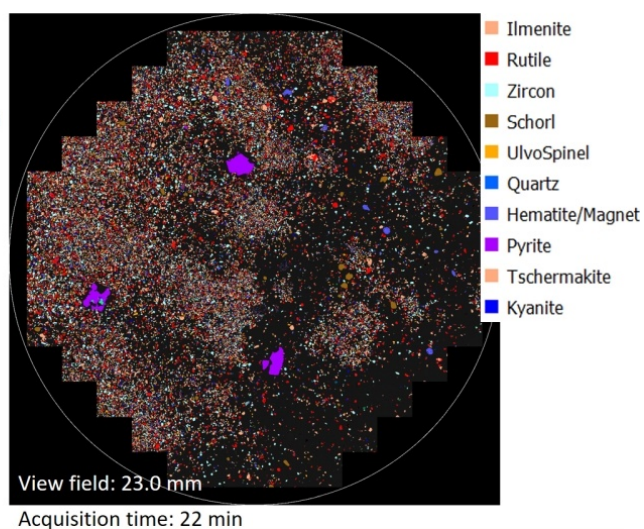
Heavy Mineral Concentrate
H 1052



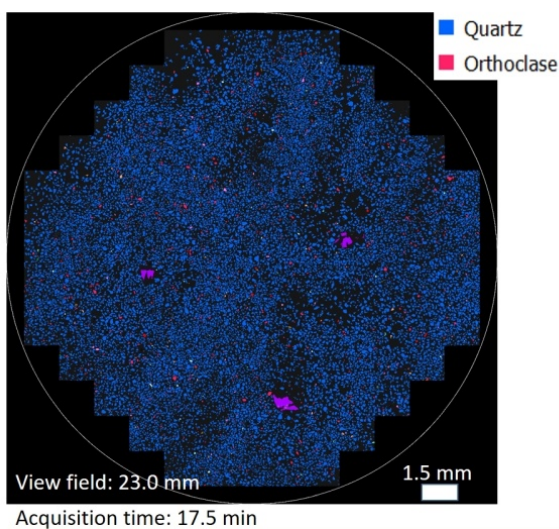
Unprocessed Sediment
WR 1067



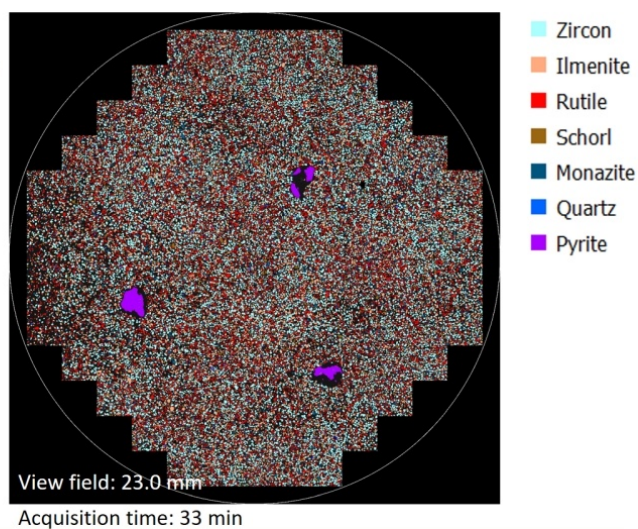
Heavy Mineral Concentrate
H 1067



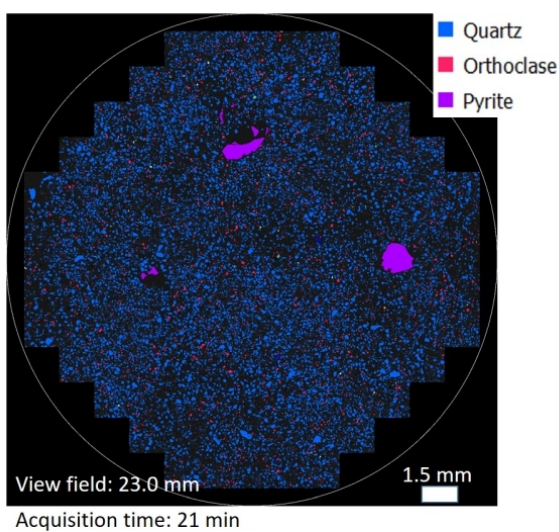
Unprocessed Sediment
WR 1337



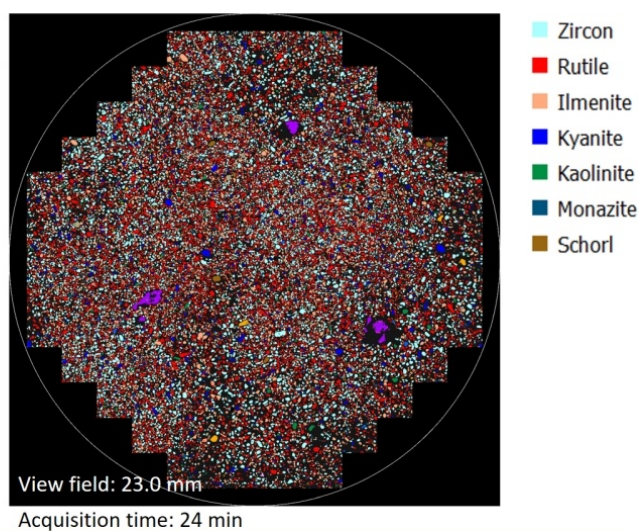
Heavy Mineral Concentrate
H 1337



Unprocessed Sediment
WR 1353

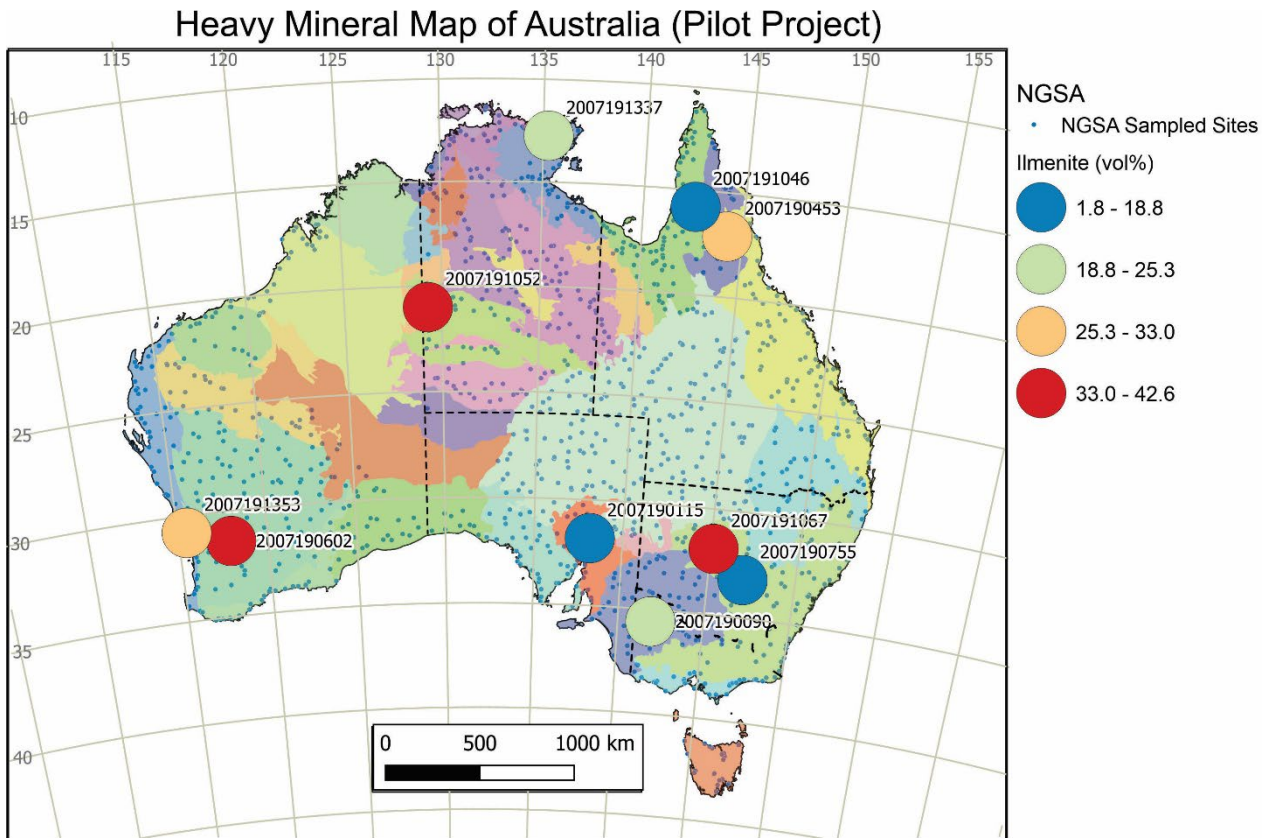


Heavy Mineral Concentrate
H 1353

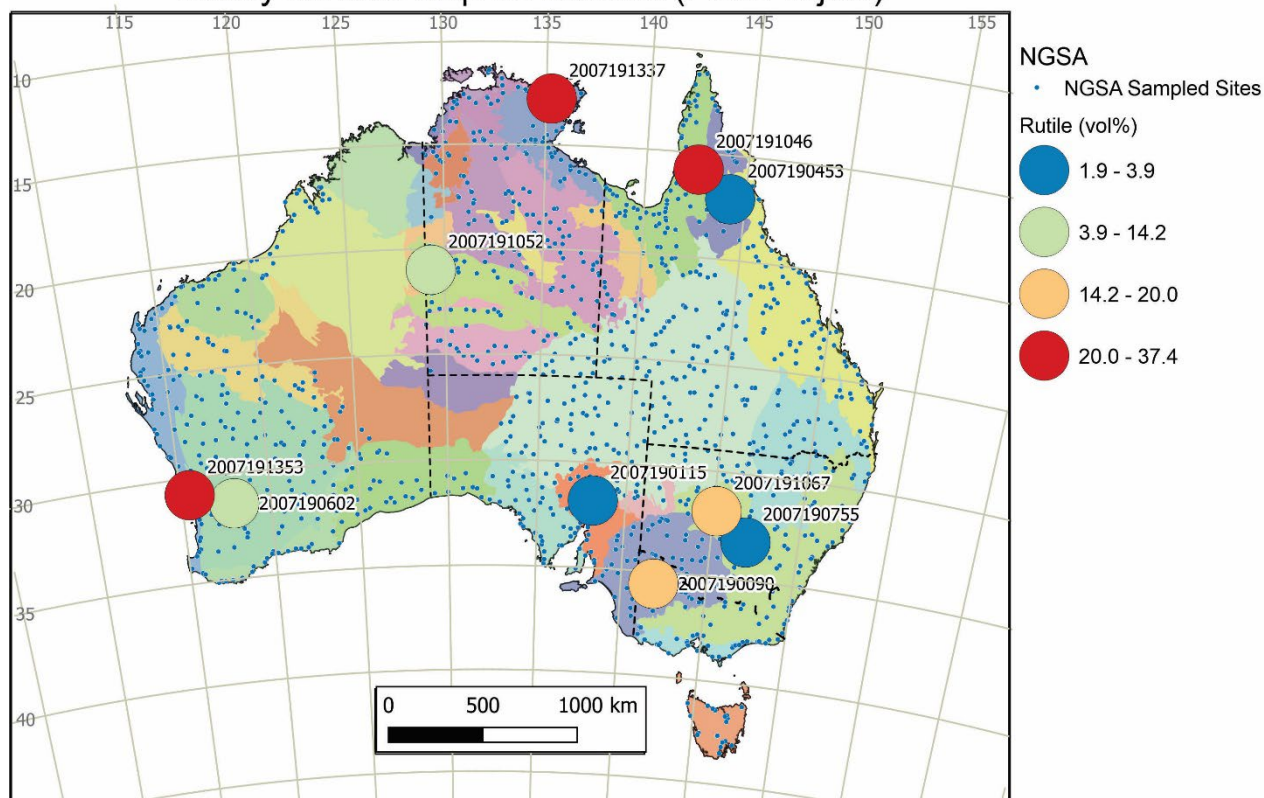


S6. Heavy Mineral Maps

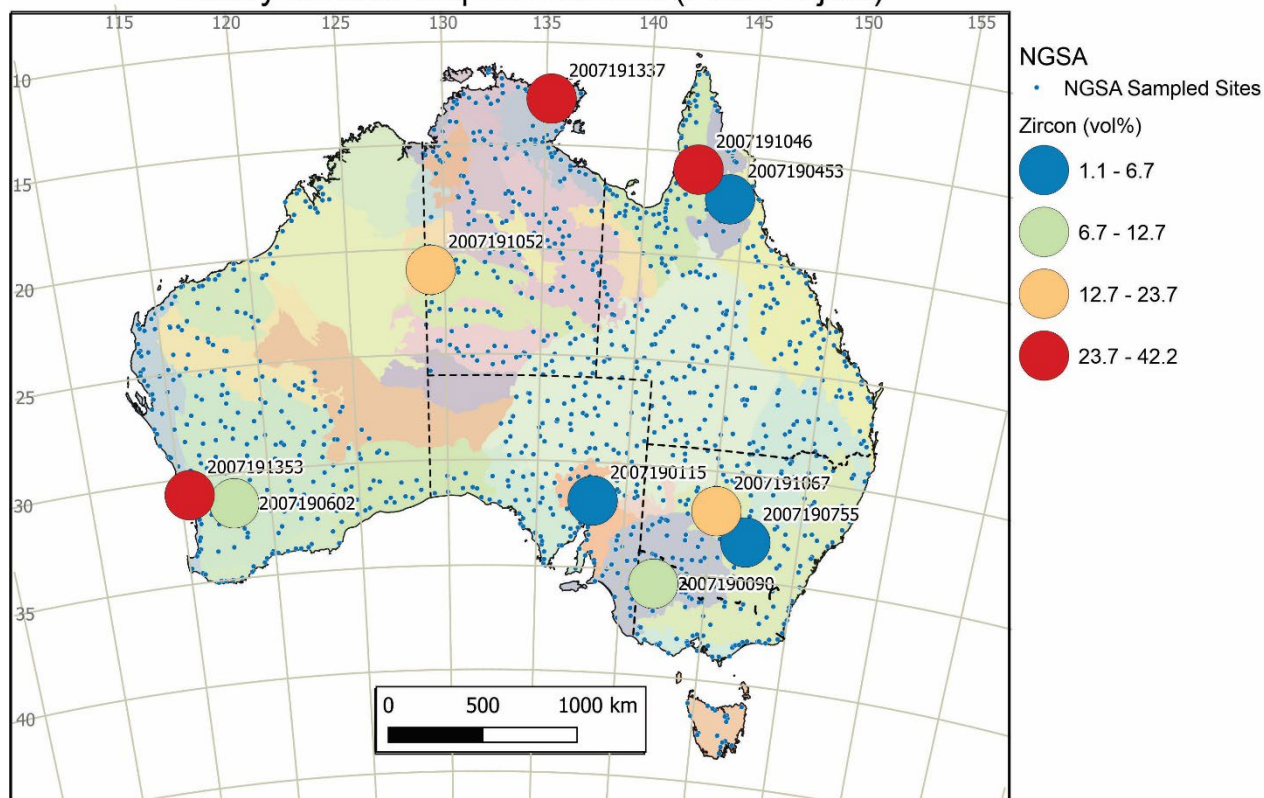
Distribution maps of selected heavy mineral proportions (ilmenite, rutile, zircon, tourmaline (schorl-dravite), hematite/magnetite, pseudorutile/leucoxene, tourmaline (uvite-feruvite), pumpellyite, and monazite) in the HM concentrates of the 10 NGSA sample used in the present pilot project (quartile classes), overlain on Australia's geological regions (variable colors; [6]). Other NGSA sampled sites shown as blue dots. Map projection: Albers equal area.



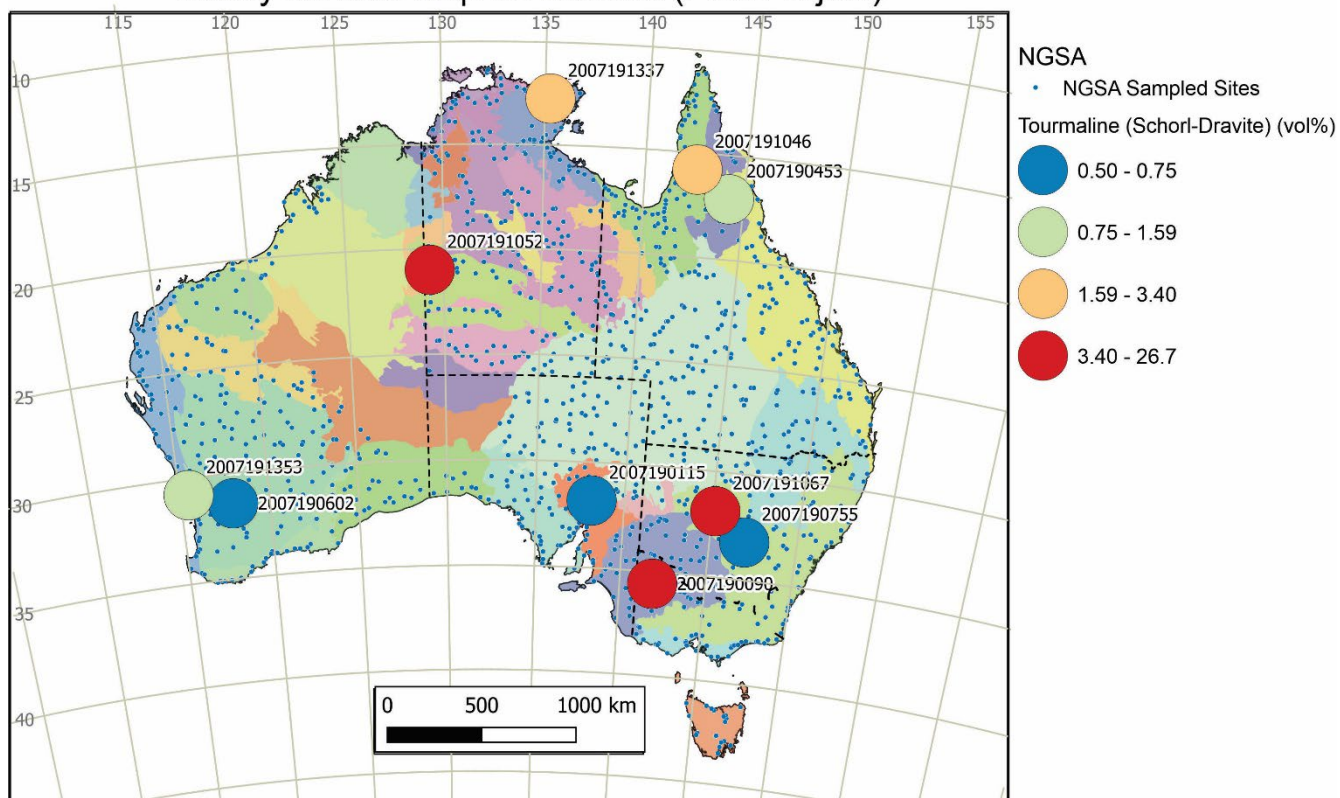
Heavy Mineral Map of Australia (Pilot Project)



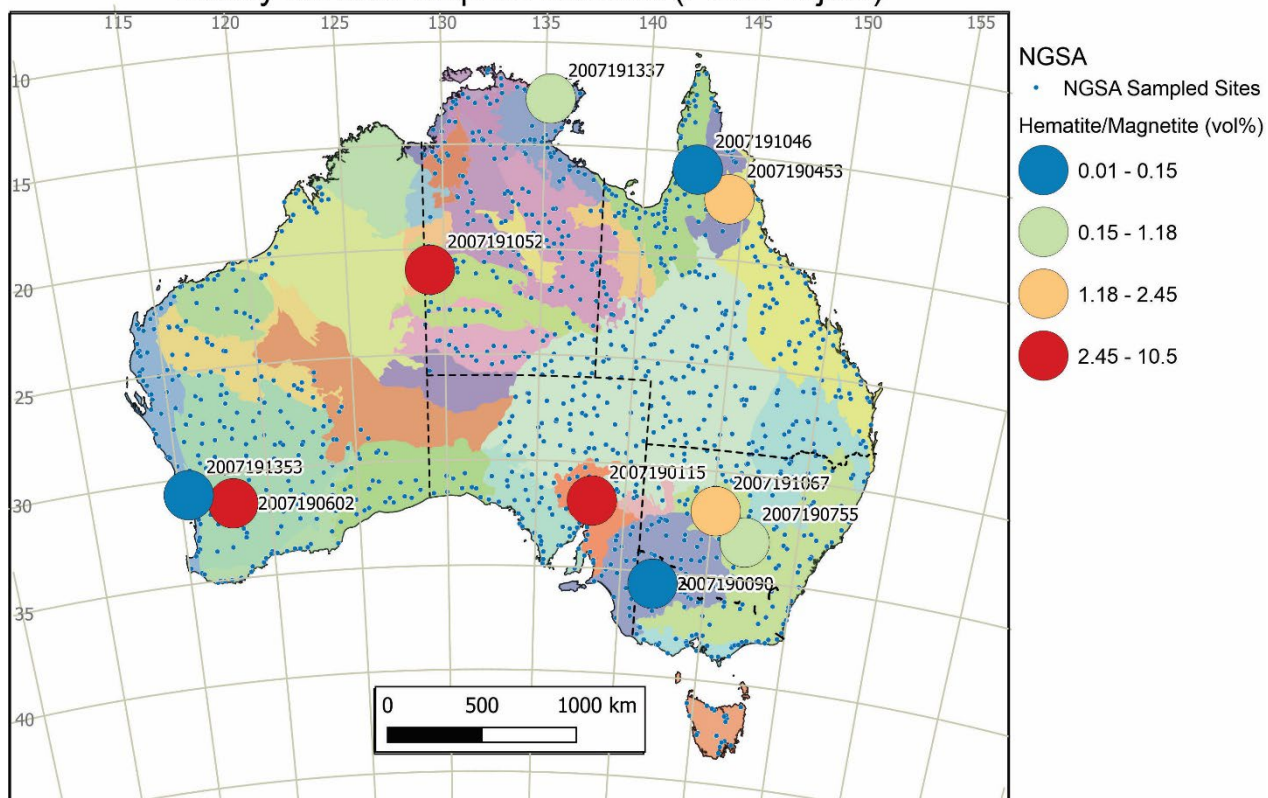
Heavy Mineral Map of Australia (Pilot Project)



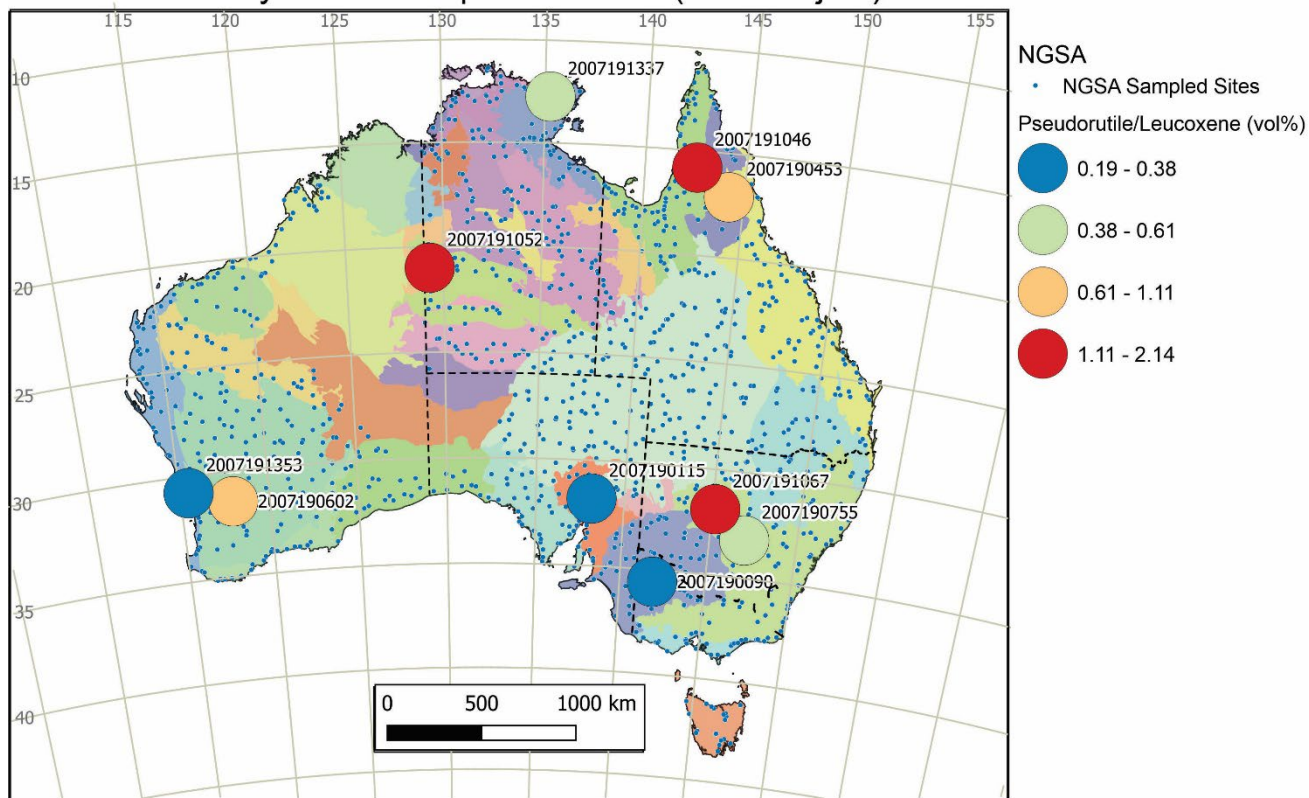
Heavy Mineral Map of Australia (Pilot Project)



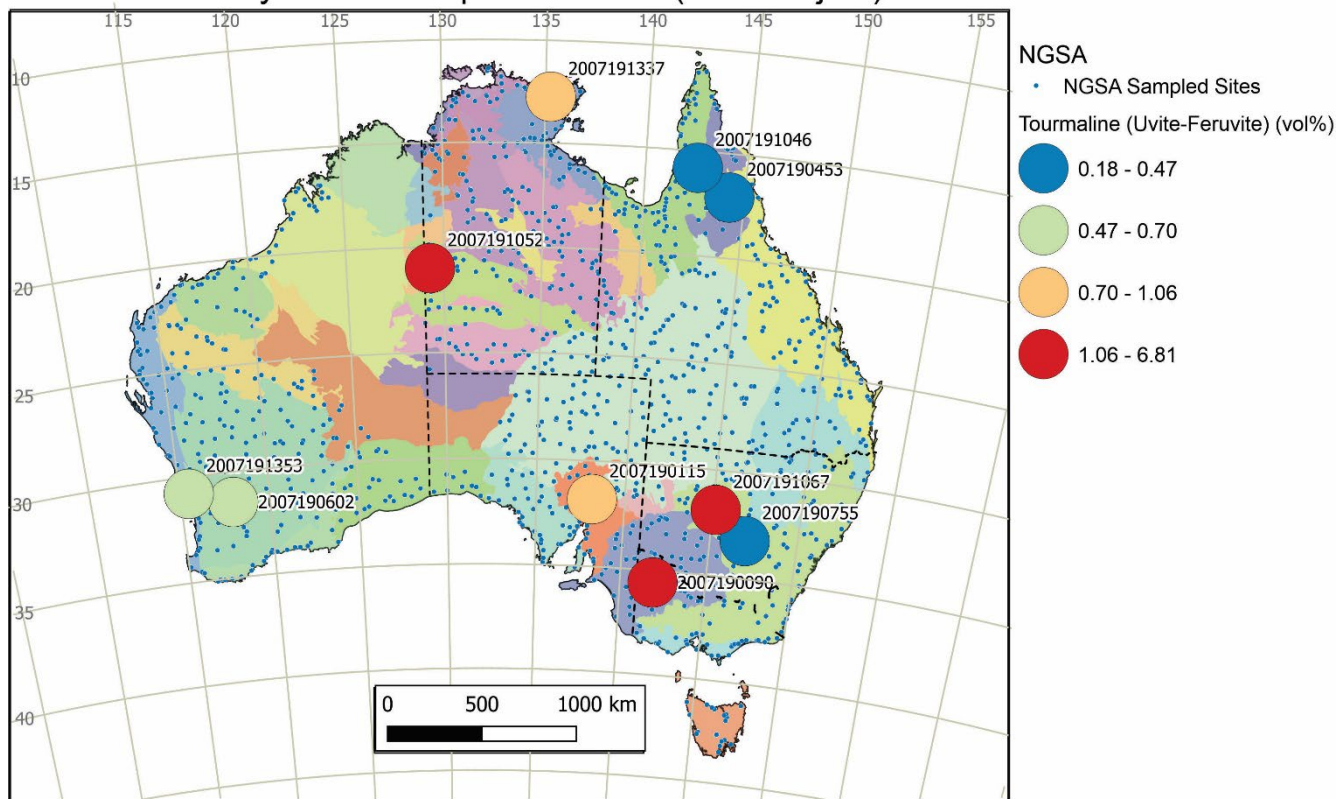
Heavy Mineral Map of Australia (Pilot Project)



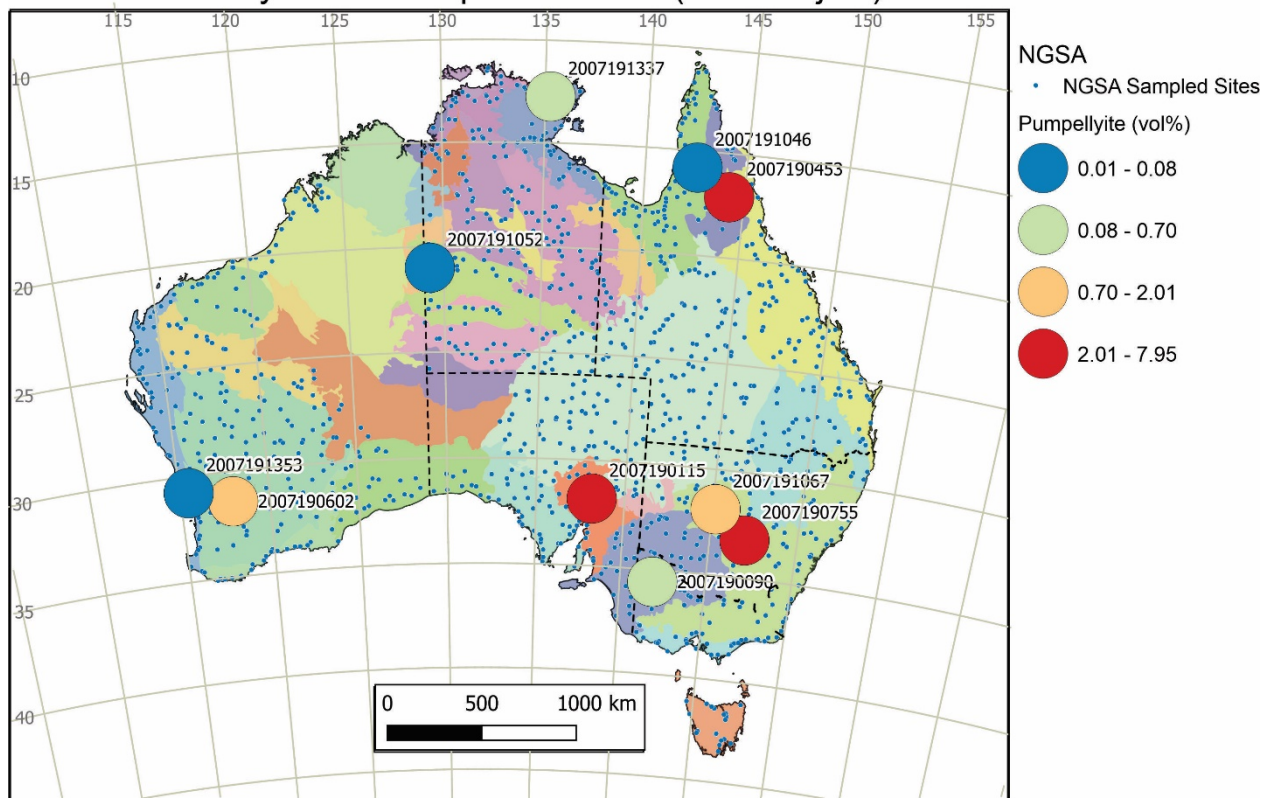
Heavy Mineral Map of Australia (Pilot Project)



Heavy Mineral Map of Australia (Pilot Project)



Heavy Mineral Map of Australia (Pilot Project)



Heavy Mineral Map of Australia (Pilot Project)

