GEOCHEMICAL EXPLORATION FOR VERTEBRATE FOSSILS USING fpXRF

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Introduction

Cenozoic freshwater limestone units within the Riversleigh World Heritage Area, Queensland, host a large array of Oligocene to Pleistocene mammals, birds, reptiles, amphibians, fish, invertebrates and plants. This includes unusual creatures such as the giant-toothed platypus *Obdurodon tharalkooschild,* the sun-bear-like *Nimbadon lavarackorum*, some of the world's largest birds and other megafaunal species (Archer et al. 1989, 2006) as well as many species of bats (Hand et al. 2005). The most productive fossil locations within the 100km^2 of limestone outcrop are the cave deposits developed within Cenozoic and Cambrian limestones and palaeo-lake or tufa dam deposits (Arena et al., 2004; Woodhead et al. 2014) for which there are some modern analogues (Figure 1). The fossils, ranging from articulated skeletons to exceptionally well-preserved single cells, are encased within secondary calcite deposits containing variable amounts (0–15%) of secondary Fe-oxides and phosphates (Arena et al., 2013; Matzke-Karasz et al., 2013). Weathered surfaces across the different limestones tend to be of similar appearance.

Figure 1. Lawn Hill Gorge with tufa barrage dams.

Since the early 1970s, exploration techniques for fossil deposits has largely been limited to observation of bone or tooth fragments on weathered surfaces, or the presence of materials such as flowstones and stalactites / stalagmites. Excavation of palaeo-cave or lake deposits then proceeds until the walls or basement of the deposits are reached. In 2013-2014 helicopter-based exploration for new deposits commenced on the western side of the Riversleigh area with limited success. This has prompted the question as to whether traces of finely divided bone material or phosphates derived from weathered bones (Nelson et al., 1986), guano, or other geochemical indicators of cave or lacustrine deposits can be geochemically detected on outcrops, where visible fossil material is otherwise absent. This question is addressed using fpXRF and is one of (if not the) first application of such technology in palaeontological exploration.

Methodology

The first step in this orientation study incorporated measurements on existing fossiliferous blocks obtained from various sites at Riversleigh, focussing on the main elemental discriminators – Ca, P, Sr, U, Zn, Pb, Ti and Zr – between fossiliferous and non-fossiliferous materials and the different depositional environments for the carbonate deposits. Analysis was undertaken using an *Olympus InnovX Delta Premium*. The second stage involved field measurements on exposed and weathered limestone surfaces along traverses that were conducted across known fossiliferous zones at *Creaser's Rampart* (mainly cave-fill deposits) and *JDM* (mainly lacustrine with some cave deposits) (Figure 2). At *Creaser's Rampart* the analyses were done on both raw weathered surfaces and the same surfaces after etching with conc. HCl in an attempt to increase the exposure of bone material, given that the penetration of fpXRF is typically <5 mm for minerals (Figure 3).

Figure 2. *Creaser's Ramparts* on Hal's Hill, within the D-Site Plateau. The traverse across the top of the cave deposit and adjacent walls is indicated.

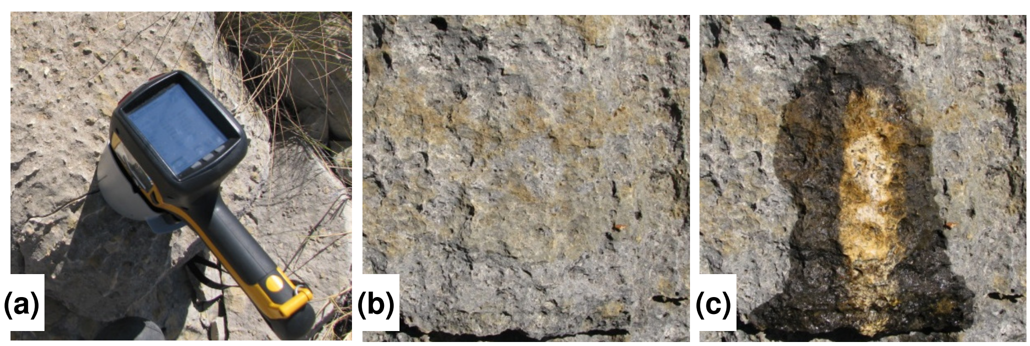

Figure 3. (a) Typical weathered surfaces of limestones in the Riversleigh area showing rillenkarren, with fpXRF measurement being taken; (b and c) Surface before and after etching with conc. HCl.

Results and Discussion

The best discriminators of P derived from bone or tooth material in the Riversleigh fossils are U and Sr. There are distinct trends for secondary phosphates associated with lower U and Sr concentrations (Figure 4). The patterns are not as well defined for Pb and Zn (both of which are typically elevated in bones and teeth). The small cluster of samples with high trace element values are from samples containing teeth.

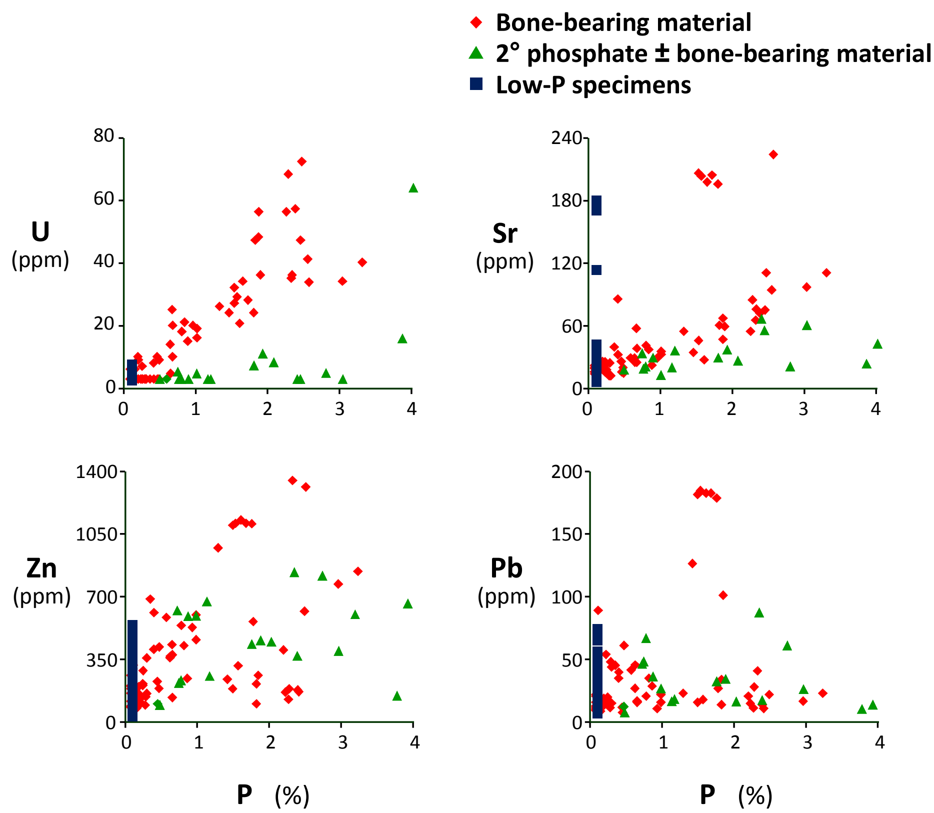

Figure 4. Relationship between P and other trace elements in fossiliferous archival block samples from Riversleigh.

The cave deposit at *Creaser's Rampart*, from which fossils have been recovered, displays strong differentiation from the adjacent wall rocks for a range for elements and ratios (Figure 5). The Pb and Ti/Zr patterns are related to the presence of fine-grained fossil fragments, different depositional environments and different source materials for the cave deposits compared with the wall rocks. Acid washing significantly increased the relative U concentration but decreased the other elements which may indicate exposure of bone and/or U-bearing heavy minerals.

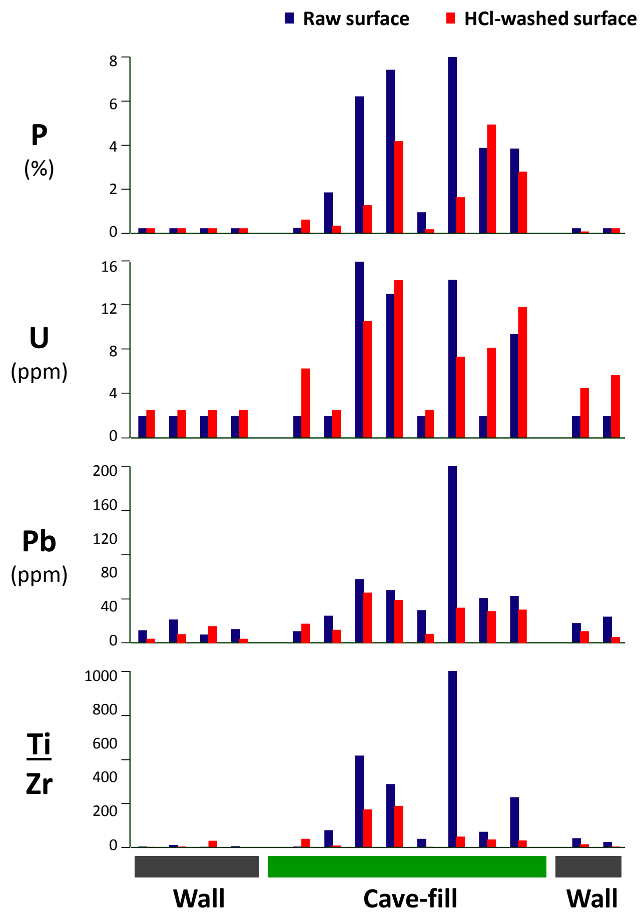

Figure 5. fpXRF measurements of P, U and Pb and Ti/Zr ratio for raw and acid-washed limestone surfaces in a traverse across *Creaser's Rampart*.

Data from the traverse across *JDM* displayed strong geochemical differentiation between the fossil-bearing and wall rock carbonates (Figures 6 and 7). However, in this case, P and U were below detection limits at nearly every point analysed. It should be noted that exposures with visible bone material were avoided. As for *Creaser's Rampart*, these patterns are interpreted to indicate different depositional environments and/or source materials entering the caves during in-fill processes, especially for immobile or heavy-mineral hosted elements (Ti, Zr, Y). There are also significantly higher amounts of secondary Fe minerals and hence elevated concentrations of Cu, Pb, Zn and other elements that strongly adsorb to Fe-oxyhydroxides.

Conclusions

Within the Riversleigh area, various fpXRF derived elemental abundances and ratios may assist in differentiating zones within the Cenozoic limestones containing vertebrate fossil fragments and/or secondary P-bearing minerals associated with the fossils or original depositional environment, from wall rock or non-fossiliferous deposits.

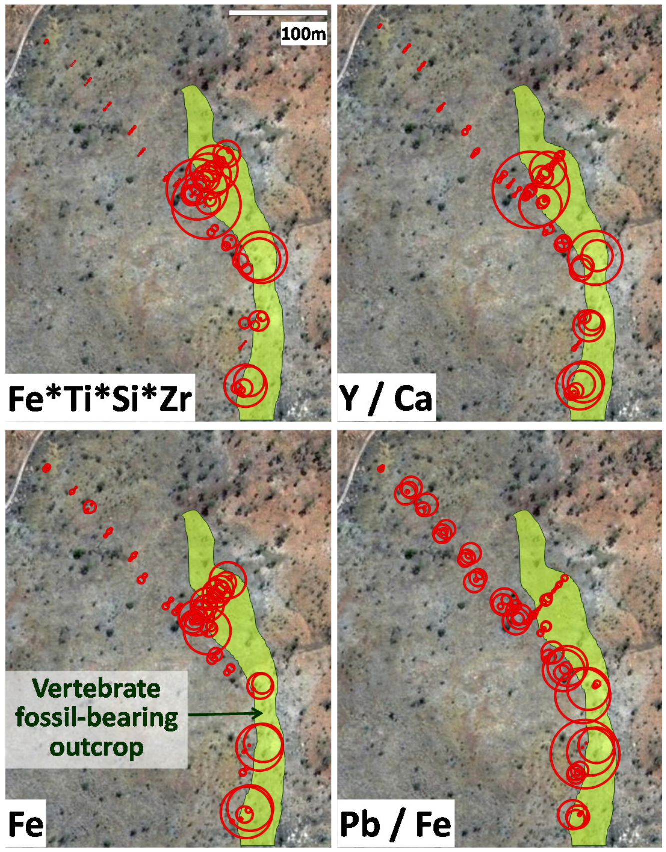

Figure 6. fpXRF data from traverse across the *JDM* Site, located on the central Gag Plateau, with fossiliferous cave deposit indicated in green.

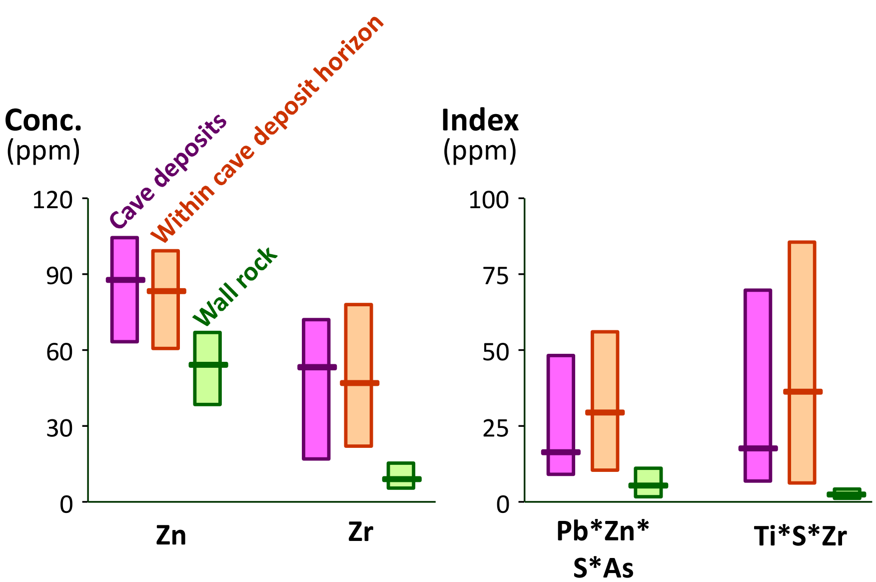

Figure 7. Comparative boxplots (Q1, Q2 and Q3) for fpXRF data from across the *JDM* cave deposit, adjacent to the cave within the lacustrine deposit horizon and extending out into the wall rock.

References

ARCHER, M., ARENA, D.A, BASSAROVA, M., BECK, R., BLACK, K. & 12 others, 2006. Current status of species-level representation in faunas from selected fossil localities in the Riversleigh World Heritage Area, NW Queensland. *Alcheringa: An Australasian Journal of Palaeontology*, **30**, 1–17.

ARCHER, M., GODTHELP, H., HAND, S.J. & MEGIRIAN, D., 1989. Fossil mammals of Riversleigh, Northwestern Queensland: Preliminary overview of biostratigraphy, correlation and environmental change. *Australian Zoologist*, **25**, 29–66.

ARENA, D.A., 2004. The geological history and development of the Riversleigh terrain during the middle Tertiary. PhD Thesis, UNSW, Australia.

ARENA, D.A., 2013. Exceptional preservation of plants and invertebrates by phosphatization, Riversleigh, Australia. Palaios, **23**, 495–502.

HAND, S.J. & ARCHER, M., 2005. A new hipposiderid genus (*Microchiroptera*) from an early Miocene bat community in Australia. *Palaeontology*, **48**, 371–383.

MATZKE-KARASZ, R., NEIL, J.V., SMITH, R.J., GODTHELP, H. ARCHER, M. & HAND, S.J., 2013. Ostracods (Crustacea) with soft part preservation from Miocene cave deposits of the Riversleigh World Heritage Area, NW Queensland, Australia. J*ournal of Systematic Palaeontology*, **11**, 789–819.

NELSON, B.K., DENIRO, M.J., SCHOENINGER, M.J. & DE PAOLO, D.J., 1986. Effects of diagenesis on strontium, carbon, nitrogen and oxygen concentration and isotopic composition of bone. *Geochimica et Cosmochimica Acta*, **50**, 1941-1949.

WOODHEAD, J., HAND, S.J., ARCHER, M., GRAHAM, I., SNIDERMAN, K., ARENA, D.A., BLACK, K.H., GODTHELP, H., CREASER, P., PRICE, E., 2014. Developing a radiometrically-dated chronologic sequence for Neogene biotic change in Australia, from the Riversleigh World Heritage Area of Queensland. Gondwana Research, online: http://dx.doi.org/10.1016/j.gr.2014.10.004.