Geological Magazine: Higgs, Munday, Forbes, Crouch & Sagar: A geochemical and biostratigraphic approach to investigating regional changes in sandstone composition through the Paleocene-Eocene, Taranaki Basin, New Zealand Supplementary File S4

**Detrital Grains and Clay Minerals** 

A poorly defined negative association between the Al2O3 and SiO2 (A) is evidence for multi-mineral associations for Si and Al. SiO2 is largely concentrated in quartz and feldspar, while Al2O3 is largely concentrated in feldspar and clay minerals. The broad nature of the trend, together with the locally high Al2O3 for some sandstones, is interpreted to be due to the locally feldspathic or kaolinite-rich nature of these deposits. A minority of samples plot with low values of SiO2 and Al2O3, which is interpreted to be due to calcareous nature as illustrated by elevated concentrations of CaO (B).

A good positive correlation would be expected between Al2O3 and K2O if Al and K were primarily concentrated within clay minerals. However, taken together, the full dataset shows no clear relationship between Al2O3 and K2O (C). It is notable that Eocene sandstones plot with more scatter and a significantly higher K2O content than the Cretaceous, Paleocene and PM3b sandstones, which is interpreted to be due to higher K-feldspar in the younger samples. The older sandstone samples do show a reasonable Al2O3-K2O positive correlation, which could be evidence for with elevated illite/mica content in these deposits. Different Al2O3/K2O profiles are therefore interpreted to be primarily due to differences in mineralogical affinities, though it is unclear from this plot whether these differences are related to changes in source/provenance or weathering.

The ratio K2O/Rb is commonly used to give an indication of whether K is dominantly associated with K-feldspar or clay minerals; this is based on the assumption that Rb is relatively concentrated within illite/mica. A plot of K2O and Rb confirms that mudstone lithologies contain significantly higher Rb compared to the sandstones (D), and suggests that K2O and Rb have mixed mineralogical affinities; they are linked mainly with K-feldspar in sandstones, they are primariy linked with clay minerals and micas in mudstones. This is supported by the petrographic data showing that most sandstone samples have higher proportions of K-feldspar than illite and mica. Notably, higher K2O/Rb ratios are clearly evident in Eocene sandstones compared with both Paleocene and Cretaceous sandstones, which provides further evidence that K is primarily associated with K-feldspar in the younger strata, and associated with more significant clay minerals (illite/mica) in the older strata. A similar relationship is observed between Cs, which also is typically concentrated in clay minerals, and Rb. This plot (E) illustrates high Cs in mudstones due to high clay content, and different Cs/Rb ratios for sandstones of different ages.



## Clay and Carbonate Minerals

Mineralogical affinities for Ca, Mg, Fe, and Mn are harder to illustrate due to their common associations with a range of carbonate minerals, clays, feldspar and heavy minerals.

CaO versus MnO shows a poorly developed positive correlation in the sandstones (A). Particularly elevated values are likely to be concentrated in carbonates. However CaO and MnO within some of the Paleocene and Cretaceous sandstones is likely to be associated with Na-Ca plagioclase and heavy minerals. The absence of a stronger link between CaO and MnO may be taken as evidence that Mn has multiple mineralogical affinities.

The absence of significant relationships between MgO and CaO (B), and Fe2O3 and CaO (C) infers that both Mg and Fe are not primarily associated with calcite. A plot of MnO versys Fe2O3 (D) also shows a wide scatter of data; the high MnO samples are those with higher CaO and may be linked to carbonates, while the lower MnO samples show a broad positive relationship suggesting that in these samples the Mn and Fe have similar mineralogical affinities. A poor positive correlation between Fe2O3 and Al<sub>2</sub>O<sub>3</sub> (E) suggests that at least some Fe is linked to clay minerals, e.g., biotite and chlorite. This is further supported by a broad positive correlaton between MgO and Fe2O<sub>3</sub> (F) and illustrated by the available petrographic data. However, the absence of any strong correlations suggests that elements Ca, Mn, Mg and Fe all have multiple mineral affinities.



Strong positive relationships are observed between TiO2 and Nb and Nb and Ta, although there are at least two sets of samples with different Nb/TiO2 and Ta/Nb ratios (E & F). These elements are typically concentrated in heavy minerals such as anatase, rutile, sphene, and other Ti-bearing heavy minerals. The lower Nb/TiO2 rich heavy mineral indicator, binary plots indicate that these minerals are relatively enriched in the heavy mineral suite of Eocene sandstones over and Ta/Nb of Cretaceous to Eocene strata at Kupe South-4 and Kapuni-13 compared to the other study wells is most likely due to a change in provenance. Broad positive correlations are also observed between Ta and TiO2, Ta and Th, and Ta and U plots (G-I respectively), although these plots show more noticeable splits in the data, with higher TiO<sub>2</sub>/Ta, Th/Ta and U/Ta ratios in all Cretaceous-Paleogene strata from Kupe South-4. These graphs suggest that the elements have multiple mineral affinities. Notably, there is a split in the data from both sandstones and mudstones, suggesting that the different heavy mineral affinities affects both lithologies, albeit that total concentration is higher in the mudstones.



A strong positive relationship between Zr and Hf confirms that both elements are concentrated in zircon (A). There are weaker correlations between Zr and Th (B) and Zr and U (C), which suggests that some Th and U are associated with zircon but that these elements are also associated with other heavy minerals. A reasonably strong positive relationship between Th and U (D) may indicate that these two elements are associated with the same heavy minerals, e.g., zircon, apatite, monazite etc.

Further splits in cross-plotted data are recognised between Cr and other elements, e.g., Th, MnO, Be, and V (J-M). Positive correlations are observed for some of these elements, but with significantly different ratios displayed by some Eocene and Paleocene-Cretaceous sands. This is evidence for a stratigraphic change in composition that appears unrelated to well location and could possibly be a response to the effects of weathering/alteration.

The strong positive link between Y and HREE (N) infers that both elements exist in heavy minerals and is an indication of heavy mineral abundance; this is highest in the mudstones and older strata sandtones. Using HREE as an indication of heavy mineral abundance and TiO2 (Nb and Ta) as a Ti-Paleogene sandstones (e.g., O).

Ba is low in most samples although relatively high in samples from Kowhai-A1R and to a lesser extent Turangi-3 (P); these samples show a positive correlation with Eu suggesting that the positive Eu anomalie in these wells may be artefact. Other elements that appear related to Ba and Eu in these wells and that are likely include an artefact component are Cu and Mo.