TRACE ELEMENTS IN SOME NEW ZEALAND OILS AND CONDENSATES

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Abstract

Thirty-one trace elements were determined in 33 New Zealand oils and condensates from the Taranaki Basin. Concentrations of AL correlated strongly with "clay mineral" elements such as As,Ce,Cl,La, Mg,Mn, and Ti as well as with V. Although a Ni vs. V plot did not allow for discrimination of different oils and condensates, the abundances of both elements were extremely low and in the same range of values as Chinese terrestrial oils. A plot of Co vs. Ti provided some discrimination and showed that oils from Maui, Moki, and Pukearuhe wells were different from all other oils and condensates from the Taranaki Basin. A further parameter for classification of New Zealand crudes was afforded by a plot of the Co content of asphaltenes vs. maltenes.

Introduction

A knowledge of trace element abundances in oils and condensates is essential for several reasons: first, they can have an influence on the subsequent industrial processing of the oils and can themselves have an environmental impact; second, they can play a role in the elucidation of the origin of the oils and their possible migration patterns; finally, the trace element content can be used to classify the oils into families of similar genetic origin (Hodgson, 1954). Hitchon *et al.* (1975) and Hitchon and Filby (1984) were among the first to use the trace element content of oils to classify them into families. An earlier paper by Connor and Gerrild (1971) used a mixture of both trace element and hydrocarbon data in a more limited investigation. Ellrich *et al.* (1985) used the trace element content to group South German crudes, and Hirner (1987a) used both elemental concentrations and other parameters to group the oils into families.

The original work of Hitchon *et al.* (1975) involved the quantification of 22 elements by instrumental neutron activation analysis (INAA) in 88 Canadian oils from Alberta province. They subjected 11 of these elements (S,V,Cl,Na,Ni,Zn,Co,Mn,Se,Br,and As) to factor analysis, and concluded that the elements were controlled by maturation rather than migration processes.

The purpose of the present study was to apply trace element analysis to the classification of New Zealand oils and condensates that are of terrestrial origin (Cook,1987; Czochanska *et al.* 1988) and to attempt to place them into genetically related families linked to specific source rocks. Such work represents the first study of this type on non-marine oils and may increase our knowledge of genesis, maturation and migration of these local hydrocarbons.

The Study Area

The geology and sedimentary history of the Taranaki Basin (Figure 1) has been reported by Cook (1987) and King and Robinson (1988) and will not be discussed further in this paper except to mention that recent detailed chemical work (e.g. Cook, 1987; Czochanska *et al.* 1988) confirms a terrestrial organic source for Taranaki oils of which coals are the most probable source (Johnston *et al.* 1989).

Materials and Methods

A total of 33 oil samples were stored in sealed glass ampoules and the whole oils analysed either by instrumental neutron activation analysis (INAA) or graphite furnace atomic absorption spectrometry (GFAAS). The INAA analyses were carried out at the Nuclear Radiation Center of Washington State University at Pullman (WA), USA.

The GFAAS analyses were performed by a GBC 902 AAS instrument coupled to a GF 1000 graphite furnace and equipped with a PAL 1000 automatic sampling device. Oil samples were dissolved in toluene (1:4) and 3 µL aliquots (with multiple loadings of 1-10) were used.

Since trace elements are concentrated in asphaltenes (Hirner, 1987b), this fraction was removed from the whole oils by precipitation with n-heptane. After filtration the asphaltenes were redissolved in toluene and analysed as above. The maltenes (defined as total oils minus the asphaltene fraction - Hirner, 1987b) were analysed by taking the difference between elemental concentrations in whole oils and asphaltenes.

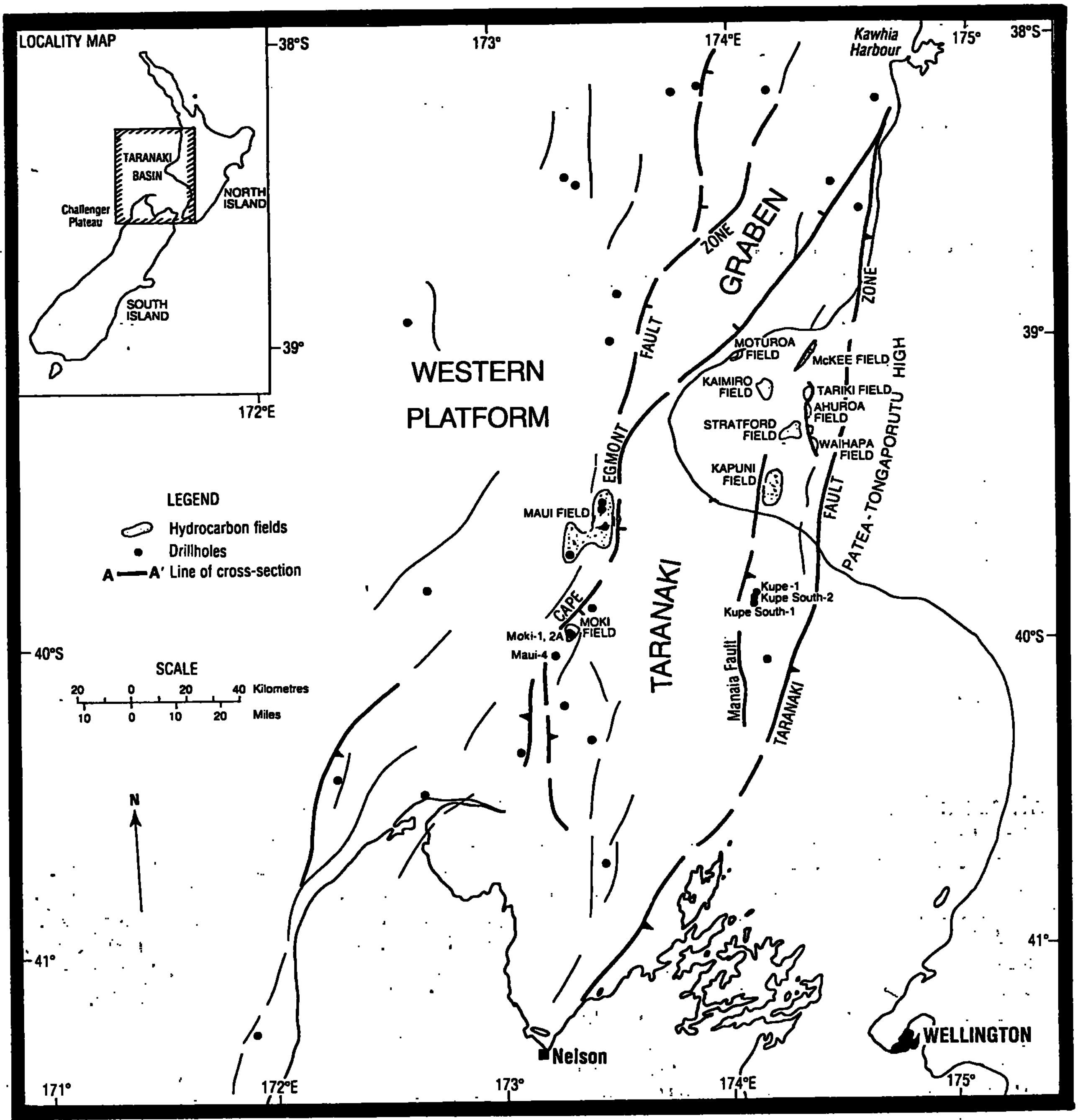

Figure 1: Map of the Taranaki Basin, New Zealand showing the position of the principal oil/gas fields and occurrences. After Pilaar and Wakefield (1984).

Results and Discussion

The analytical data

A list of the 33 New Zealand crudes that were analysed is given in Table 1. All were oils or condensates from the Taranaki Basin. The following 31 elements were quantified in the oils by INAA: Al, As, Ba, Ce, Cl, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, V, and W. Mean abundances ranged from 1.6 ng/g for Sm to 30,000 ng/g (30 µg/g) for Al. The mean Al and Ti concentrations (30 and 18 µg/g respectively) are somewhat higher than reported elsewhere (Barwise and Whitehead, 1983) for marine oils. For the sake of brevity the analyses are not tabulated but are represented in graphical form where appropriate.

Inter-elemental correlations

A correlation analysis of all 31 elements was performed. The highest mutual correlations ($P \leq 0.0001$) were between the elements Al, As, Ce, Cl, La, Mg, Mn, Ti, and V. Aluminium was correlated strongly with such "clay elements" as Ce, Cl, Fe, K, La, Mg, and Ti. It is possible therefore that these elements are derived from colloidal clay minerals distributed in the oils rather than being bound specifically to the oils themselves. There were few strong inter-elemental correlations between Co, Cs, Mo, Ni, Sb, Se, and Sr. If V is added to this list because of its known binding to porphyrins and other organic constituents of crudes, there is a pool of eight elements that might be of use in classifying oils.

Nickel and vanadium

The Ni and V content of marine-sourced oils is usually quite high. Tissot and Welte (1984) report values of up to 1200 µg/g V and 150 µg/g Ni in Boscan crude oil from Venezuela. Yu and Luo (1977) have reported much lower values for both elements (0.4 and 5.7 µg/g for V and Ni respectively) in Chinese crude oils from two terrestrial basins in Northwest China. This gave a V/Ni ratio of 0.07 compared with 3.8 for Kuwait crude (Yu and Luo, 1977). Our own mean values for V and Ni are 0.23 and 1.2 µg/g and are even lower than for the Chinese oils. A V vs. Ni concentration plot for New Zealand crudes and condensates (Figure 2) shows no discrimination between the different oils even though this pair of elements has often been used to group marine oils into families and to study maturation and migration patterns (Al Shahristani and Al-Atyia, 1972). The distribution fields for these two elements in local and overseas oils are shown in Figure 3. It is clear that our oils lie in a field well separated from marine oils and overlapping the terrestrial Chinese oils.

The low abundance of V, and to a lesser extent Ni, in New Zealand oils may be due to their low resin and asphaltene contents compared to marine oils.

Tissot and Welte (1984) have reported that some marine oils such as Baxterville crude, contain 100 % of the V in the porphyrins. However, some marine crudes such as La Luna (Venezuela) contain only 27 % of the V in the porphyrins (Erdman and Harju, 1963). Because the New Zealand oils were formed largely in a paralic environment there may be a small marine signature in some of these crudes. The variable vanadium content may possibly reflect a marine component. There is a very strong correlation between the Al and V content of the New Zealand oils (P=0.0001). This is also shown in a plot of Al vs. V concentrations (Figure 4). This close association would seem to indicate the presence of colloidal clays in the oil and it is more probable that the V content reflects clay minerals rather than a variable marine signature.

1. Tuhua-2 B.S.	2. Tuhua-2 A.S.
3. Tuhua-1	4. Urenui-1
5. Toe Toe-1	6. Tariki-1
7. Toe Toe-4	8. Toe Toe-2B
9. Toe Toe-3	10. Kaimiro-1
11. Stratford-1	12. Pukemai-2
13. Pouri-1	14. McKee-4
15. Tariki-1A	16. Maui-1
17. Maui-3	18. Moki-1
19. Republic-4	20. Taranaki-5
21. McKee-2	23. Galleon-1
24. Ahuroa-2	25. McKee-3A
26. Maui-4	27. Kupe South
28. Kapuni condensate	29. McKee condensate
33. Republic-1	34. Tuhua-2
35. Stratford-1	36. Pukearuhe-1
37. Moturoa-2	

Table 1: List of New Zealand crudes and condensates studied

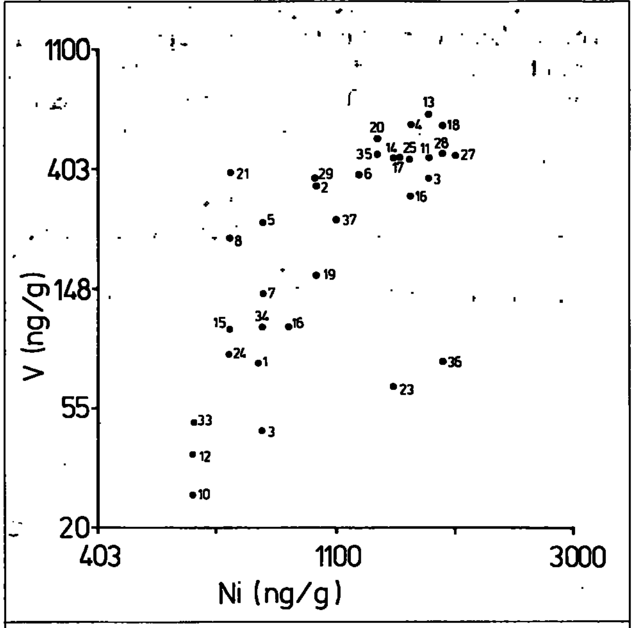

Figure 2: Plot of V vs. Ni concentrations in New Zealand oils and condensates. For key to numbers see Table 1.

Cobalt and nickel

Several computer-derived binary concentration plots of pairs of elements selected from the 31 that were quantified, were generated in order to attempt to select visually those that showed the most promise for classifying the oils. Among these, the most useful appeared to be Co vs. Ti (Figure 5). This plot appears to separate oils from Maui-1 and Maui-4, Moki-1 and Pukearuhe-1 from all others. The condensates

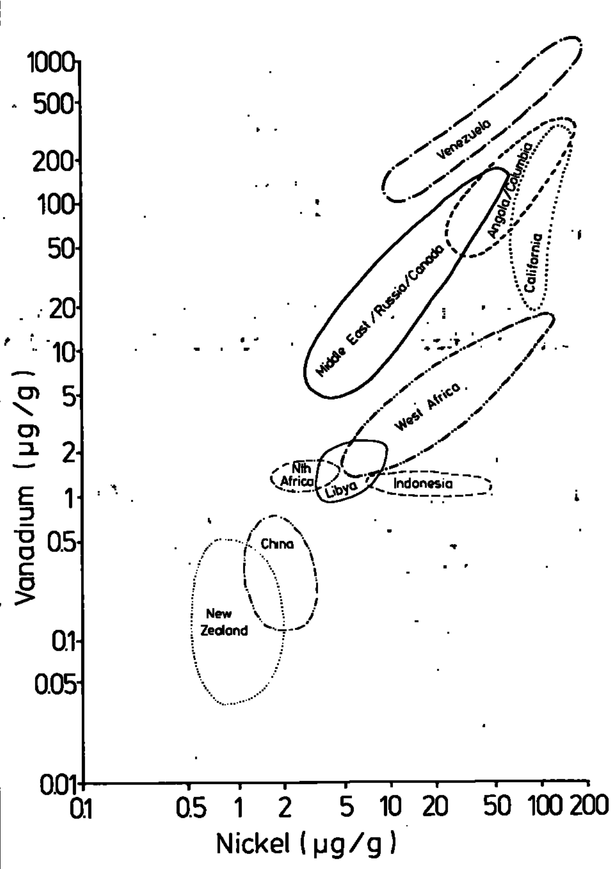

Figure 3: Plot of V vs. Ni concentrations in New Zealand and overseas oils and condensates. Modified from Tissot and Welte (1984).

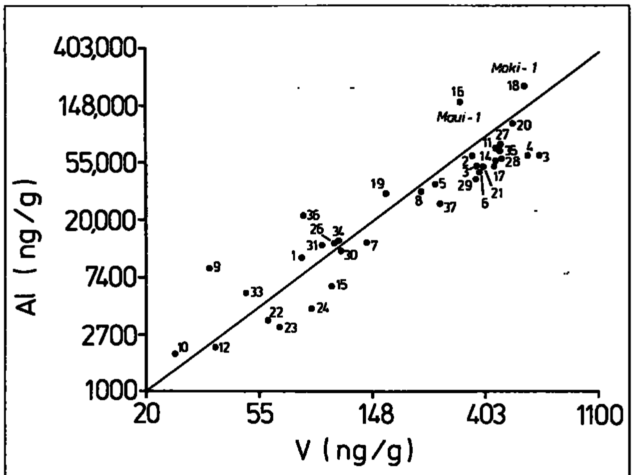

Figure 4: Plot of Al vs. V concentrations in New Zealand oils and condensates. For key to numbers see Table 1.

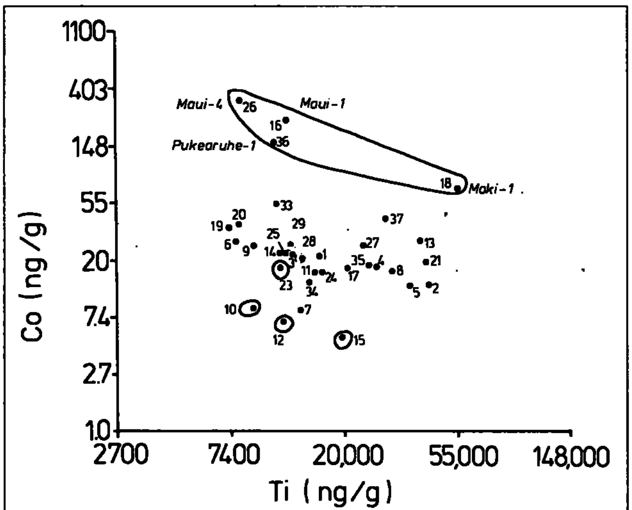

Figure 5: Plot of Co vs. Ti concentrations in New Zealand condensates (ringed) and oils. For key to numerals see Table 1.

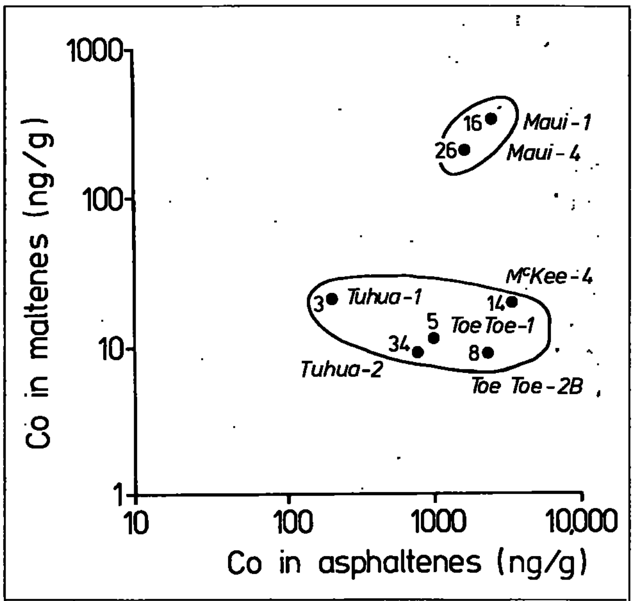

Figure 6: Cobalt concentrations in maltenes and asphaltenes separated from New Zealand oils. There is a clear separation between Maui oils and those elsewhere in the Taranaki Basin.

(circled in the figure) tend to be close to the origin as was to be expected because most of the trace element burden is concentrated in the high molecular weight asphaltene and resin fractions.

Cobalt in maltenes and asphaltenes

Hirner (1987b) has shown that the Ni, V, and Co content of maltenes and asphaltenes in South German oils could be used to classify them into two families. We have attempted the same by determination of Co in both of these fractions in New Zealand oils. We used Co only, because the V content of our oils is extremely low and the Ni content did not show great variation from sample to sample. Figure 6 shows a plot of Co in maltenes and asphaltenes of selected New Zealand oils. The graph clearly shows the good separation of oils from Maui-1 and Maui-4 from all other crudes and condensates.

Conclusions

On the basis of our accumulated data, we are of the opinion that with the exception of Maui-1, Maui-4, and Moki-1, all other oils and condensates from the Taranaki Basin are related to each other and are possibly derived from a common source. Maui-3 usually has a lower trace element content than Maui-1 and this may be due to its being a lighter oil with a lower asphaltene/resin component to bind trace elements. The similarity of most of the oils presupposes a common type of source rock and investigations are at present under way to assess the trace element content of these source rocks and to trace possible migration pathways of the oils formed from them.

Although the McKee (#29) and Kapuni (#28) samples are considered to be condensates, they have a higher trace element content than the other condensates and occur within the McKee distribution fields of the various figures (e.g. Figure 5).

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