15. GEOCHEMISTRY OF THE DIATOMACEOUS MUDS

The diatomaceous muds in the anaerobic basins of the continental shelf are the final stage of the geochemical cycle of uranium. A discussion on the geochemistry of the muds would be incomplete without mention of the behaviour of trace elements in the ocean water, because it is from this source that the elements were and still are being derived.

The abundances of metal ions in seawater are determined by the solubilities of their respective compounds. Concentra= tions of certain elements in seawater, relevant to this discussion, are given in Table 45.

TABLE 45: THE CONCENTRATIONS OF SOME ELEMENTS IN SEAWATER.
(KRAUSKOPF, 1956, p. 3, ALLEGRE AND MICHARD, 1974, p. 41)

Element	Concentration (ppm)
P	0,07
Mo	0,014
V	0,002
U	0,003

According to the calculated solubility products of elements in seawater, Krauskopf (1956, p. 9) reported that normal aerated seawater is undersaturated with respect to rare metals. In passing it is worthwhile to note that the oceans contain uranium resources equivalent to 4 000 times the total world reserves at 10 dollars per pound (Barnes and Ruzicka, 1972,

p. 162).

It is from the seawater that the diatomaceous muds
derived their high concentrations of certain elements. The
problem to be considered concerns the mechanisms involved
that were responsible for concentrating elements from a
source that is now known to be undersaturated. It is clear
that a mechanism based purely upon a solubility function
is entirely improbable.

The core samples analyzed in this investigation were
taken from the Walvis Bay Basin (Fig. 15) and the results
are given in Table 46.

15.1   Geochemistry of the Muds

The diatomaceous muds off South West Africa were the
subject of four major trace element investigations (Calvert
and Price, 1970; Baturin et al, 1971; Meyer, 1973; Veeh
et al, 1974) and the three most recent studies were primarily
concerned with the distribution of uranium.

Generally it has been shown that the distribution
of the diatomaceous muds is governed by upwelling currents,
creating a situation favourable for reducing conditions.
The presence of hydrogen sulphide is a manifestation of
such a system.

Using the mean concentrations of elements in Table 46
and comparing these with the concentrations of the elements
in seawater (Table 45), a concentration factor for the elements
in the muds was calculated (Table 47).

TABLE 46:   ELEMENT CONCENTRATIONS IN TWO CORES OF DIATOMACEOUS MUDS

SWA 30

DEPTH (m)	0-0,05	0,05-0,08	0,08-0,12	0,12-0,18	0,18-0,23	0,23-0,28	0,28-0,33	0,33-0,38	0,38-0,43	0,43-0,48	MEAN
P_2O_5 (%)	0,66	0,33	1,51	0,27	0,24	0,22	0,25	0,23	0,81	3,66	0,80
Mo (ppm)	26	32	23	31	26	29	39	39	33	22	30
V (ppm)	70	54	50	43	48	31	38	40	48	22	44
U (ppm)	17	16	22	28	37	18	21	27	40	37	26
LOI (%)*	22,4	20,0	18,1	17,1	16,7	16,1	15,6	17,5	22,0	17,6	18,3

SWA 50

DEPTH (m)	0-0,1	0,1-0,2	0,2-0,3	0,3-0,4	0,4-0,5	0,5-0,6	0,6-0,66	0,66-0,72	MEAN
P_2O_5 (%)	0,34	0,3	0,3	0,27	0,58	0,25	0,3	0,42	0,35
Mo (ppm)	24	26	25	19	28	24	23	16	23
V (ppm)	30	59	56	74	43	71	65	20	52
U (ppm)	14	21	16	24	43	43	25	18	26
LOI (%)*	16,6	17,3	15,4	13,4	13,8	15,8	14,0	8,4	14,3

* LOI = Loss on ignition at 500 $^{\circ}$C. This is regarded as being equivalent to the total
   organic matter concentration. Very Little $CaCO_3$ was present and was ignored.

It is clear that there is an enormous degree of concentration
of the elements in the diatomaceous muds with respect to the
seawater. Vanadium has the highest C_f value being more than
a factor 10 greater than molybdenum and more than a factor
2 greater than uranium. Molybdenum has the lowest concentra=
tion factor.

TABLE 47:   CONCENTRATION FACTORS, RELATIVE TO SEAWATER, FOR
            THE ELEMENTS IN THE DIATOMACEOUS MUDS

Sample	Element	Concentration Factor, C_f
SWA 30	Mo	$2,1 \times 10^3$
	V	$2,2 \times 10^4$
	U	$8,7 \times 10^3$
SWA 50	Mo	$1,6 \times 10^3$
	V	$2,6 \times 10^4$
	U	$8,7 \times 10^3$

     Krauskopf (1956) studied the removal of certain elements
from seawater and concluded that sulphide precipitation of
vanadium and molybdenum was unlikely, but that chemical
reaction with organic compounds appeared to be the most
likely mechanism. Kaplan (1974), reviewing the precipitating
mechanism for uranium, also pointed out that sulphide had
little or no effect in removing it from seawater. Furthermore
not all sediments rich in organic matter contain high uranium
concentrations, and he suggested a selective uptake by certain

organic compounds only.

Figs. 75 and 76 show the depth profiles of phosphorus pentoxide, molybdenum, vanadium, uranium and loss on ignition at 500 °C. The latter function is a measure of the total organic matter content. Comparison of the profiles for sample SWA 30 (Fig. 75) shows that there is a partial measure of coherence between some of the variables. Both vanadium and LOI (loss on ignition) follow the same pattern, with the exception of the value of 0,2 m, where the vanadium increases slightly. A similar increase in uranium occurs at the same depth, but in this case the increase is gradual and therefore uranium and LOI do not correlate above 0,25 m. Correspondingly, no significant change in molybdenum or phosphorus pentoxide is noted. Below 0,25 m a good coherence is seen between LOI, uranium, vanadium, and to a lesser degree, molybdenum. All variables with the exception of phosphorus pentoxide decrease below 0,4 m. The log of the core revealed that below 0,38 m a shelly zone was found and the high phosphate content is mostly due to the presence of skeletons. Baturin et al (1971) report similar findings.

The patterns of core sample SWA 50 (Fig. 76) show that both uranium and the organic matter (LOI) are very similar, which again emphasizes the role that organic matter plays in the precipitation of uranium. For the upper 0,25 m, molybdenum and vanadium have similar tendencies, but below, their trends diverge from that of LOI until 0,55 m, where a reconvergence of trend patterns reappears. At about 0,63 m the amount of organic matter decreases in accordance with an increase in phosphorus pentoxide and detrital matter.
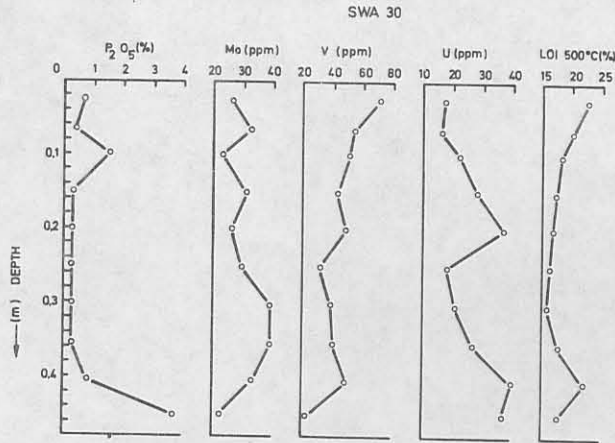
Fig. 75: Profiles through the diatomaceous mud for phosphorus pentoxide, molybdenum, vanadium, uranium and loss on ignition at 500 °C. (Borehole SWA 30)
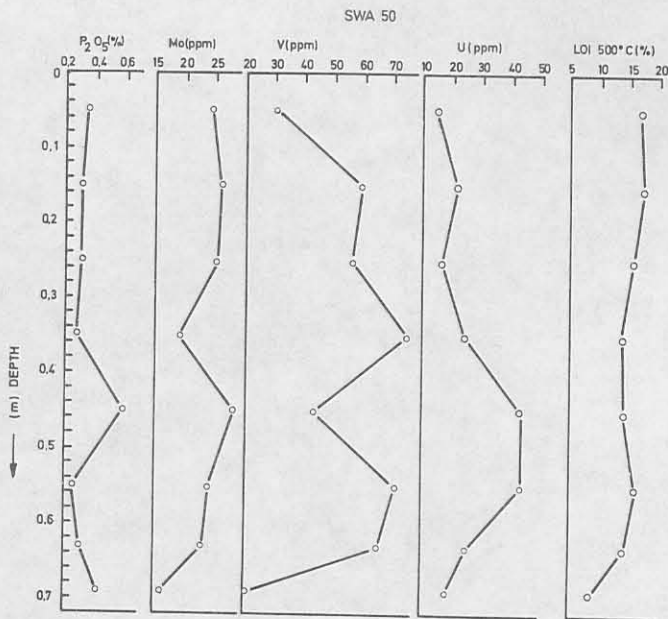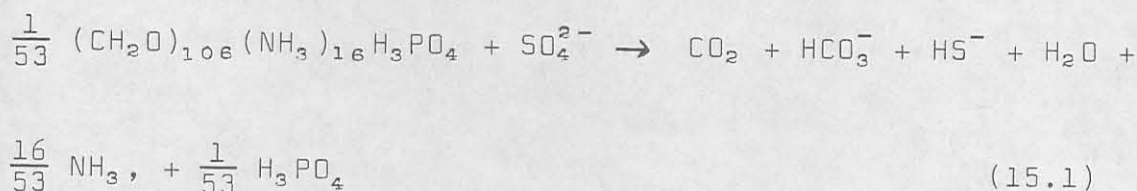

Fig. 76: Profiles through the diatomaceous mud for phosphorus pentoxide, molybdenum, vanadium, uranium and loss on ignition at 500 °C. (Borehole SWA 50).

It can be stated that it does appear that the organic
material is the chief precipitatory medium for these metallic
elements. Diverging patterns in places suggest that there
are more than one possible mechanism controlling the precipi=
tation of uranium, vanadium and molybdenum. Veeh et al (1974)
report that phosphate in the form of apatite co-precipitated
uranium.

A generalized equation for the decomposition of
average marine organic matter by bacterial sulphate
reduction is given in equation (15.1) (Ben-Yaakov, 1973, p. 88).

$$\frac{1}{53} (CH_2O)_{106} (NH_3)_{16} H_3PO_4 + SO_4^{2-} \rightarrow CO_2 + HCO_3^- + HS^- + H_2O +$$

$$\frac{16}{53} NH_3, + \frac{1}{53} H_3PO_4 \qquad\qquad\qquad (15.1)$$

Before organic complexing of the uranium can take place, it
must first be reduced from the hexavalent to the quadravalent
state. This is accomplished by the powerful reductant HS^-.
The mechanism for uranium reduction is given in equation
(15.2). It is likely that the UO_2 would be in an amorphous
form absorbed onto or reacted with an organic molecule.
Vanadium and molybdenum are not precipitated as sulphides
due to their relatively high solubility. The only mechanism
that remains is complex formation with an organic compound,
and the close coherence of both elements with LOI in sample
SWA 50 implies that an organic reaction took place.

$$2HS^- + [UO_2(CO_3)_2 \cdot 2H_2O]^{2-} \rightarrow H_2S + S^{2-} + UO_2 + 2CO_3^{2-} + 2H_2O$$

$$(15.2)$$
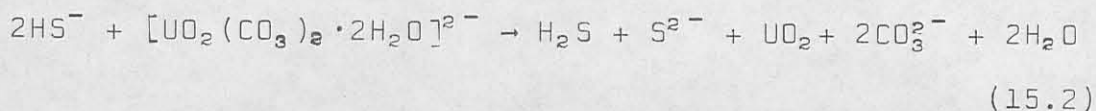
Normalizing the concentrations of molybdenum, vanadium and uranium with LOI reveals that there is a closer relation= ship between uranium and vanadium than between uranium and molybdenum (Figs. 77 and 78). The nature of the controlling precipitating mechanism for molybdenum and vanadium does not appear to be the same. Kaplan's remark (1974) that the concentration of uranium may be controlled by certain classes of organic compounds, may also apply to vanadium and molybde= num. Vanadium, however, seems to be more closely associated with those compounds that precipitate uranium.
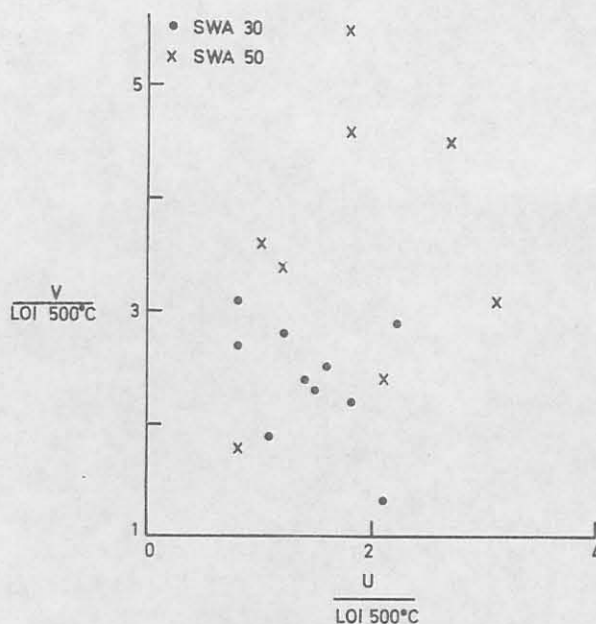

Fig. 77: Variation diagram of vanadium plotted against uranium for the diatomaceous muds. Normalized with loss on ignition at 500 °C.

Nissenbaum and Kaplan (1972, p. 570) suggested that marine organic matter is mostly the product of degraded plankton. The process of degradation takes place as a sequence of transformations in a sediment and is given as

follows, (1) Degraded cellular material → (2) water soluble
complexes containing amino acids and carbohydrates → (3)
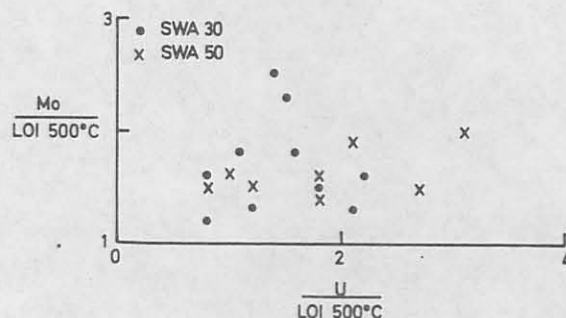fulvic acids → (4) humic acids → (5) kerogen.

Fig. 78: Variation diagram of molybdenum plotted
against uranium for the diatomaceous muds.
Normalized with loss on ignition at 500 °C.

The adsorption of vanadium and molybdenum may occur
at different stages within the degradation sequence. Through=
out the basin the nature of the degradation need not necessa=
rily follow exactly the same path due to some or other cause
and this would give rise to heterogeneties in the trace
element distribution patterns. Results (Rona, 1974) for
similar anaerobic sediments of the Black Sea show a closer
relationship between molybdenum and vanadium than do the
sediments in this study. Again this may be a case where
slight modifications in the organic degradation chain would
co-precipitate both molybdenum and vanadium in the Black Sea
in a sympathetic manner.

Meyer (1973) reports that there is a weak direct
relationship between uranium and phosphate. Figs. 75 and 76
give no indication that this is the case for the two cores
under study here.

The highest uranium concentrations in the submarine basins are situated opposite river mouths, past and present (Fig. 15). South of Walvis Bay the highest concentrations lie off old choked river mouths of the original Tsondab and Sossus Rivers respectively. It is certain that beneath the shifting sand dunes, water still flows, as the dunes are broken and disorientated in the region of ground-water flow (Fig. 1). These choked river valleys may be possible target areas for uranium exploration. From Walvis Bay northwards, the highest uranium concentrations lie opposite the Kuiseb, Swakop, Omaruru, Ugab, Unjab and Hoanib River mouths.

In the future, the diatomaceous muds may become an economic mining proposition, not only from the uranium aspect, but from the aspect of other metals as well (Table 48).

TABLE 48: MAXIMUM CONCENTRATIONS OF ELEMENTS IN DIATOMACEOUS MUDS (CALVERT AND PRICE, 1970, p. 594)

ELEMENT	CONCENTRATION (ppm)
Cu	129
Ni	455
Pb	32
Zn	337

Add to this list uranium, vanadium and molybdenum, and it certainly becomes more attractive, especially when considering the fact that all of these elements are directly associated

with the organic,and possibly the phosphate, fractions.
The selective dissolution of the organic matter and separation
of the metals from the inorganic fraction would provide a
significant concentrating factor.

15.2   Summary

Seawater is undersaturated with respect to rare
metals, whereas in the diatomaceous muds some elements are
significantly concentrated. The mechanisms for enriching
certain elements in the mud were considered. The distribution
of uranium, vanadium and molybdenum in the muds is hetero=
geneous and it was suggested that the presence of organic
matter was the main precipitating agent and that there was
selective uptake of these metals by particular organic
compounds.

Uranium is concentrated in the muds which are
situated opposite river mouths, past and present, e.g. the
Swakop River. The economic potential of the muds was discussed,
as other metals such as copper, nickel, lead and zinc are also
present in significant concentrations.