

# **MODERN AND ANCIENT SABKHA ENVIRONMENTS - BORON ISOTOPES AS DISCRIMINATORS OF FACIES AND USES IN BASE METAL EXPLORATION**

**By**

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## **ABSTRACT**

Boron isotopic analyses were performed on samples of stromatolite representative of intertidal conditions within modern and Early Proterozoic sabkhas. The intertidal zone at Al-Khiran in southern Kuwait shows a range of  $\delta^{11}\text{B}$  values from 21.2-39.1 per mil. The stromatolites values are constrained between  $\delta^{11}\text{B}$  21.2-21.25 per mil and the brine medium in which they grow is characterized by values that range from  $\delta^{11}\text{B}$  25.6-39.1, or close to the seawater average. Both these data together with published  $^{18}\text{O}$  data, indicate a southwesterly trend towards lighter values for all isotopic systems, indicating an increasingly continental influence and precipitation of isotopically light carbon within the tidal creek. Their Early Proterozoic analogues from southern Africa have very different signatures, with a range of  $\delta^{11}\text{B}$  from 6.2-6.8 and indicating a more pronounced continental influence in pore water chemistry. These results have important implications for reconstructing palaeoenvironments where discrimination of facies is difficult in rapidly accumulating regressive/transgressive cycles. The observations have implications in exploration for stratabound Cu and stratiform Zn deposits in an evaporitic-sabkha setting where prediction on the continental/marine interface (and hence the ore itself) is critical to successful exploratory drilling.

## INTRODUCTION :

The Arabic word "sabkha" means *salt flats* and the word has become synonymous with all flat geomorphic surfaces sustained in deflational-depositional equilibrium by continuous fluxing of marine and continental waters. Proterozoic sabkhas were recognised as being part of the Arabian Gulf-type and with good reason. The environment is particularly important to understand the genesis of stratabound Cu deposits [1], whereby metals are precipitated in the shallow waters during fluxing under gravity of continental and marine waters. Older models for stratabound Cu deposits [2], stress the dominance of marine waters over continental waters in their origin. The bulk of the preserved mineralization in the Zambian Copperbelt exhibits features more compatible with syngenetic deposition of sulphides associated with decaying algal matter in marine lagoons [2]. The Great Arabian sabkha complex (extending almost continuously from Kuwait to the United Arab Emirates) can be classified based on its hydrological framework and in the distribution of the climatic/topographic variables. The southern African analogues are Early to Late Proterozoic in age and their recognition in the stratigraphic record is weaned from a few underground mining exposures and rare field outcrops but can be considered more akin to the *UAE-type* [2].

Recent sedimentation on the Abu Dhabi coastal flats provides the best Holocene analogues to ancient shallow-water carbonate and supratidal evaporite

sequences [3,4,5]. A typical Arabian Gulf sabkha is composed of subtidal, intertidal, and supratidal sediments accumulating on a broad shelf rimmed by organic reefs and algal sands. Traced from seaward to landward, the zonation begins with subtidal to intertidal sediments capped by supratidal evaporites. In the United Arab Emirates (UAE), sabkhas stretch for almost 150 kms along the coast and are forming in protected lagoons. The flats are characterized by four stromatolite belts each with its own morphological character: the oldest sabkhas are marked by the Upper Jurassic Hith Anhydrite, which is a widespread "marker" horizon in the Arabian Gulf found also in oilfields in Saudi Arabia and Qatar [3]. It is a product of evaporation in a shallow, hypersaline sea which extended as a giant playa system (72 million km<sup>2</sup>) along the southern margin of the Tethys Ocean [3].

In this paper an attempt is made geochemically to distinguish the continental sabkha environment from the dominantly marine environment. We focus on the algal mats of a modern intertidal sabkha environment where both marine and continental influences converge [6,7]. Proterozoic analogues are also investigated in an attempt to identify sites that exhibit dominantly marine influence, mixed seawater/continental brine, and dominantly continental influence and specifically the environment of ore deposition. Boron, because of its conservative nature during evaporation of seawater [8], is a potential indicator of brines residual from extensive

evaporation. Assuming the sabkha environment is 'diluted' by continental brines of lower salinity, significant isotopic contrast should be evident from fluids and authigenic minerals currently being precipitated in tidal creeks of Southern Kuwait. This fluxing of continental/marine waters in the sabkha environment should be discernible in the stratigraphic record where regressive/transgressive cycles rapidly change and isotopic system has not been disturbed.

### **Stratigraphy and sedimentology of sites in Kuwait**

The Al-Khiran area lies on the coast of the Arabian Gulf, 100 kms south of Kuwait city (Fig 1). The sabkha is dissected by three tidal creeks, displaying an average width of 0.75 km and extending 5.5 km inland. These creeks are the remnants of an old drainage system that was active during the Wurm glaciation. Seawater reaches the creeks between five Pleistocene to Holocene, oolitic, beach/dune ridges (Figure 2a). The oldest exposed sediments in the Al-Khiran area are continental, coarse-grained, siliciclastics derived from erosion of the Arabian peninsula which have transported seaward by fluvial processes. In contrast to the extensive continental sabkhas of the southern Arabian Gulf, the sabkhas of southern Kuwait are small and "pan-like" in character and have open hydrological systems (Figure 2b) [3 and 9] and in this respect they mirror the Proterozoic environments in southern Africa [2] the sabkhas formed in irregular pan-like

depressions originating in retreating lagoons containing evaporitic salts which may be covered temporarily with meteoric water and aeolian siliciclastics. Critical criteria for preservation are: (1) water table is above high water spring tide level and the flow of water is seaward (2) The annual recharge is large enough to maintain year to year stability of the sabkhas (3) Holocene sand ridges prevent total marine flooding and optimal fluxing is promoted enough to preserve the sabkha. The continental and marine sabkhas are telescoped into very narrow zones and the wide variation in facies observed is not recorded elsewhere in the Arabian Gulf [10]. It appears that the sabkha passes through phases of growth, stabilization and decay that are controlled by the hydrological characteristics of local and regional groundwater patterns [ 9 and 10 ].

### **Stratigraphy and sedimentology of sites in South Africa**

The earliest study on an incomplete facies of *UAE-type* occurring in the Early Proterozoic 2.3 Ga-old Transvaal Sequence, South Africa was made by [12]. Outcrops in the Griqualand West sub-basin of the Transvaal Basin contain sabkha-like accumulations of cryptalgal dolomites and are best exposed near Pering Zn-Pb mine and to the south near Boetsap (Fig. 1). An attempt at reconstruction of the environment during the deposition was made which is a compilation of drillcore logging and correlation of facies taken from old mine records and personal observations.

The Reivilo Formation is the best studied sequence in the Pering area since it hosts the Zn-Pb mineralization. The equivalent units of the Pering member in the southeast of the Griqualand West subbasin of the Transvaal Basin (Fig. 1) occur at the Boetsap section [12]. A logged section will suffice to summarize the main characteristics of the environments exposed at Pering and Boetsap and was used as a basis for the sampling programme. The main observation is that the younger parts of the succession (see Figure 4) have stromatolites that exhibit gigantism and extend from the photic zone down to subtidal environments. Subaerial exposure of the stromatolite zone is recognised from the presence of oolites, ripplemarks and desiccation phenonema.

Deposition of the lower RV1 member of the Reivilo Formation occurred mainly in intertidal to shallow subtidal environments on a tidal flat (see Fig.4). A marine transgression occurred towards the middle RV2 member of the Reivilo Formation onto which stromatolite megadomes developed. A second transgressive trend is noted towards the Upper Massive Dolomite (see Fig 4 ). Desiccation features are pronounced at the peak of the transgressive trend. Some shale intercalations are common and suggest a lagoonal phase since they are underlain and overlain by ripple dolomites, oolitic intercalations and edgewise conglomerates. A 'chicken-wire' textured rock is common in the section which is similar to evaporitic horizons in the Arabian Gulf sabkhas [13]. White

dolomite is the dominant lithology there is an association of laminated cavities, thrombotic stromatolites and ripple marks at Boetsap, suggesting that an intertidal deepening upward cycle is preserved there. Deposition during Reivilo time was restricted ultimately to a stable uniform tidal flat with shallow subtidal to intertidal deposition and a minor transgressive trend during which the megadome stromatolites were flourished deposited.

### **Sampling and Analytical techniques**

Samples of stromatolite from the intertidal zones of both Proterozoic and modern sabkhas were selected for boron isotopic analyses. Samples from the Reivilo Formation were collected during a field season in 1996 and access to the Pering open cast mine was provided by Shell South Africa. Stable isotope data is already available for drillcore samples in the same formation near to the open pit [13]. The aim of the sampling procedure was to identify and sample potential evaporitic horizons which could be compared with the Arabian Gulf environments. The most feasible structures in the field appeared to be vugs or druses which occur above and below thin shale horizons (see Fig. 4). These shale horizons are exposed in the mine sandwiched between stromatolite units and brecciated 'druzestone" horizons in the Pering member.

The sample preparation for the samples from Pering (South Africa) and the geochemical results obtained are described

in detail by [14] and are summarised in the following discussion. Thin sections of vugs were prepared prior to selection for isotope geochemistry. Individual carbonate phases within the vugs, in particular those associated with sphalerite mineralization, were difficult to identify using transmitted-light microscopy, and a combination of cathodoluminescence, and staining with Alizarin Red S was used to distinguish carbonate phases. All mineralogical identifications were made by XRD housed at the Department of Earth and Environmental Sciences, Kuwait University.

All boron analyses were performed at the Department of Hydrology labs at University of Arizona. The solid stromatolite samples from Al-Khiran and the South African localities were crushed and carbonates were handpicked prior to analysis. They are composed of calcite, aragonite and minor evaporitic minerals. Six water samples from the tidal creek were also analysed for trace elements and boron isotopic analyses. The samples from Pering (PR) and Boetsap (BOE) are recrystallized dolomite and ankerites with minor pyrites. BOE samples are clear dolomite extracted from a stromatolite.

20-40 micrograms of sample were dissolved in 1 N HCl, filtered and neutralized. B was extracted and B isotopic values determined by mass spectrometer on 20 ng of extract. The  $^{11}\text{B}/^{10}\text{B}$  ratios are reported as permil deviations ( $\delta^{11}\text{B}$ ) relative to the standard NBS SRM 951:

$$\delta^{11}\text{B} = [ \frac{^{11}\text{B}/^{10}\text{B}_{\text{sample}}}{^{11}\text{B}/^{10}\text{B}_{\text{NBS 951}}} - 1 ] \times 1000$$

The results for the standard are within error for the certified values of NBS SRM of 4.0436-4.0456 [15 and 16].

A precision of 0.5 per mil (1 sigma) was obtained on all isotopic analyses. The  $^{11}\text{B}/^{10}\text{B}$  for the NBS standard ranges from 4.04184-4.04653 over 10 runs and is in good agreement with the accepted value for the standard. In addition to the B isotopic analysis, brine samples were analysed for Na, Ca, Mg, K, Cl, S, bicarbonates and trace elements such as Cu, Pb and Zn.

## Results

The pH of the groundwater aquifer in the sampled zone at Al-Khiran varies from 7.0-8.3, dropping below 7 in the stromatolite zone. The boron concentration varies from 4670 ppb to more than 8000 ppb in the liquid brine samples (Table 1). The major and trace element concentrations of the six brine samples show the following ranges (Table 2); Na (13000 ppm- 46 000 ppm), Ca (547 ppm-2870 ppm), Mg (1540 ppm- 4830 ppm), and K ( 441-1950 ppm). Cu varies from 32.2-174 ppm, Zn values are <35.0 ppm and Pb is <110 ppm. Bicarbonates range from 59-165 ppm. Cl ranges from 21 000-91 000 ppm and  $\text{SO}_4$  from 2660-4880 ppm. The  $\delta^{11}\text{B}$  of the brine samples (30.5-39.3 per mil) are within the range of normal seawater (39 per mil.). The sediments from the tidal creek have concentrations below the detection limit of

the instrument and could not be determined. The  $\delta^{11}\text{B}$  on the other hand ranges from 20.8-21.5 per mil.

The concentration of B in the Proterozoic PR samples and duplicates is 266 ppm and BOE 237 ppb. The  $\delta^{11}\text{B}$  for these rocks ranges from 5.4-7.9 per mil in contrast to the Arabian Gulf samples.

### Discussion

Sabkhas and their associated hydrological regimes in the geologic record are of interest to both economic geologists (oil, gas, base-metals, sulphates: [2, 17, 18] and palaeoclimatologists [7]. Some authors [6] stressed that the sabkhas in southern Kuwait (Fig. 5 and 6) show dominant continental signature since waters form a distinct group isotopically different from local meteoric water and Pleistocene water. As in most sabkhas, the Cl-concentration in the brines increases steadily from both the seaward and landward sides towards a central plateau (Table 2; and [7]). This plateau in the area of samples C1-C2 suggests an apparent mixing of marine and continentally derived waters. There is hardly any gypsum precipitated at the watertable in the vicinity of this mixing zone and consequently the sulphate concentration is low. The flux of waters is also mirrored in the stable isotope and geochemical for the brines, published elsewhere [7, 10, 11] (Figure 5).

The facies changes within modern sabkhas are rapid and often interdigitated as encountered in Kuwait. Field

identification of the palaeoenvironments in older rocks is limited to scarce underground exposures and drillcores. For this reason, it becomes important to review the main characteristics of sabkhas.

In the Zambian Copperbelt, the sabkha environment is pivotal to understand the environment of precipitation of the stratabound Cu deposits. The deposition of the sulphides is a result of fluxing of marine and metal-rich continental groundwaters in the intertidal zone but there is no consensus on the precise role of stromatolites, evaporites, and local hydrology or on the timing of the precipitation of the metals [17, 18, 19]. However, switching from a transgressive to a regressive phase appears to be a common denominator among ore deposits. One of the reasons why so much controversy exists over the genesis of Proterozoic stratabound Cu deposits is that the fluid/rock interactions during diagenesis have been disturbed by epigenetic regional fluid-flow events [20]. Many of the models presented suffer in the first instance, from an inability to classify the local and lateral environment of ore deposition and its relationship with the aquifer. In one of the earliest but widely discussed models [17] proposed that the depositional environments of the Kupferschiefer, Roan and other evaporite-associated stratiform deposits may be likened to coastal sabkhas. He proposed that, during regression, oxidized terrestrial-formation waters at low pH mobilize metals from the underlying rocks and pass upward through  $\text{H}_2\text{S}$ -charged algal mat where precipitation takes place.

Stable isotopes of the sulphides and associated carbonates reflect the varying influence of marine and fresh water during transgressive and regressive phases of Ore Shale sedimentation [21,22], and in this instance anchoring sulphide precipitation to early marine diagenesis and not to epigenetic ascent of brines. Other ore deposit models [23] support the idea that ore-bearing horizons in the Alpine Triassic carbonate rocks of Spain are located at the transition between marine and continental evaporitic facies. Ore bearing horizons are located at two main lithologic transitions between predominant terrigenous continental sedimentation and marine sedimentation. This transition marks both a transgressive and a regressive cycle. The link between many carbonate-hosted ore deposits and pre-evaporitic tidal flat and lagoonal sediments in transition belts between continentally influenced and marine sediments is recognised elsewhere [22,23,24].

Boron isotopic analyses of carbonates and brines associated with sulphides should be an ideal discriminator between continentally - derived and marine-derived fluids in sabkhas and thus a discriminator of the dominant fluid involved in ore genesis. Several important studies have recognised boron isotope variation in sediments and brines in modern environments that may be prospective for metals [25, 26, 27]. Surface brines from the Dead Sea are characterized by high  $\delta^{11}\text{B}$  (55.7-57.4 per mil; cf., seawater of  $\delta^{11}\text{B} = 39$  per mil). Geological and other data suggest that the brines in the Dead

Sea are a residual product of evaporation of seawater. [25] proposed that depletion of elemental B and  $\delta^{11}\text{B}$  in some sediments relative to those values present in modern sediments may be the result of several causes. Firstly, recrystallization of calcite in the presence of groundwater depleted in boron and having a "terrestrial" low  $\delta^{11}\text{B}$  signature. Secondly, water-rock interactions in which a new isotopic equilibrium has been established:  $^{10}\text{B}$  would be partitioned into the tetrahedral species that incorporates preferentially into the carbonate, while  $^{11}\text{B}$  would be partitioned into the trigonal species, remaining in a liquid phase in low pH environments. Thirdly, secular variation in seawater  $\delta^{11}\text{B}$  values and boron contents in shallow marine environments.

42 water samples were analysed for boron isotopic signature from the Gulf of Mexico which showed a range in composition from +39 to +11 per mil [27]. The depleted samples relative to seawater were mostly Ca-rich. Boron in sediments was originally considered to be an indicator of paleosalinity, but research has shown that boron distribution in sediments is a function of mineralogy, provenance and particle size [27,28].

The unusually low values of boron for the BOE and PR samples in the Proterozoic of South Africa by comparison with worldwide data bases (Figure 6) suggests that one or more of the above processes were operative. Recrystallization of calcite could explain the low values since XRD

analysis identifies ankerite as the primary carbonate phase. If the ankerite was locally generated from transformation of magnesium calcite this precipitate should have a unique isotopic signature, as suggested by the fine development of the laminae on bedding planes (Figure 4). The Early Proterozoic sabkhas in this part of the Transvaal Basin appear to have experienced subaerial exposure and significant continental influences (Figure 7). The isotopic signatures indicate the non-marine dominated environment with supporting evidence from sedimentological data.

There are many examples of stromatolites associated with continental environments in the literature and a short discussion is warranted. Although rare occurrences are noted elsewhere in the geological record detailed facies analysis of non-marine stromatolites has been interpreted [19, 29]. The overriding feature in the preservation of these rare non-marine environments is principally caused by intermontane basinal/ rift settings which downthrow the sequence and promote rapid diagenesis. Syndepositional faulting of the basin can be recognised by rapid changes in facies. In the Transvaal examples from Pering at least 8 shale horizons occur within the Reivilo Formation and distinct tectonic features and syndepositional slumping occur indicating a steep palaeoslope. Although not proven, syndepositional faulting is proposed for the Pering Reivilo Formation suggesting further that stromatolite occurrences were evolving in a stressed changing environment. The

isotope signatures could represent changes in the flux of continental/marine waters in response to changing tectonic events. The presence of edgewise conglomerates, desiccation cracks etc. may mark the change from dominantly marine to dominantly continental influences. These abrupt facies changes can be seen clearly at Al-Khiran sabkha in Kuwait.

Bisotopes can be used with great confidence when discrimination of facies is difficult where transgressive and regressive cycles interdigitate in sabkhas.

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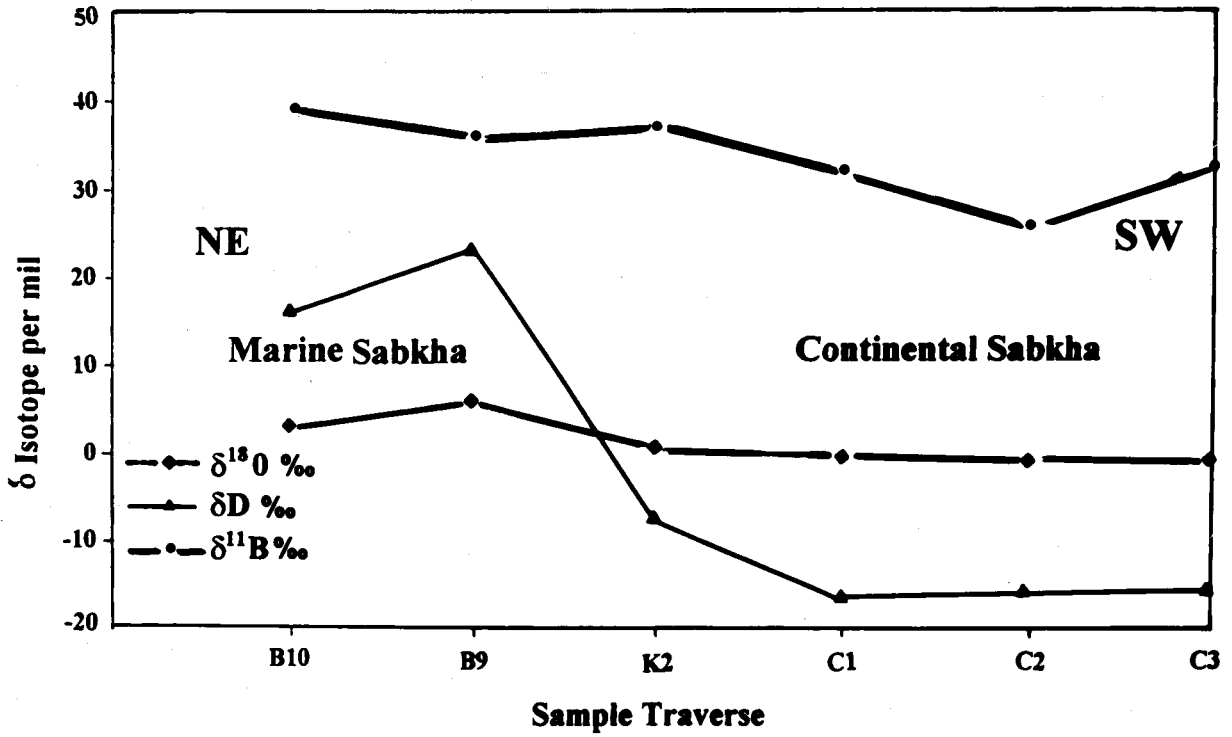
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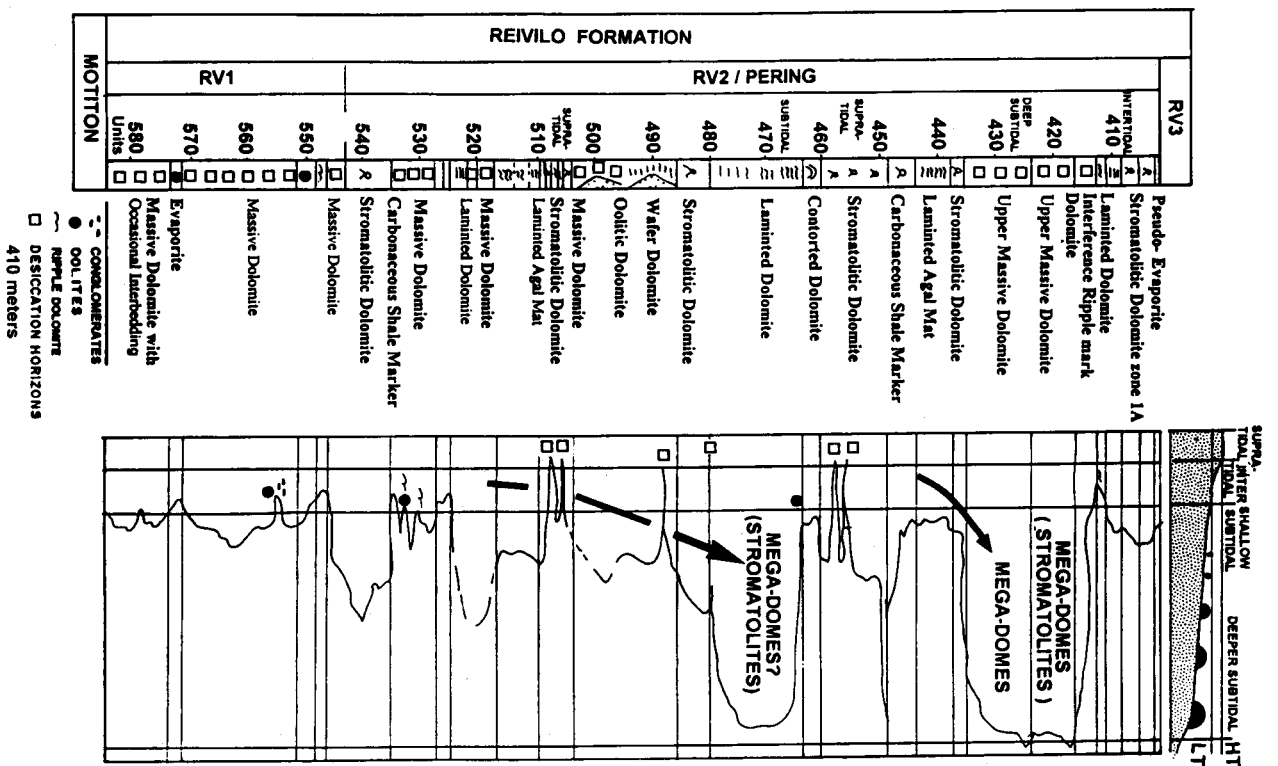
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




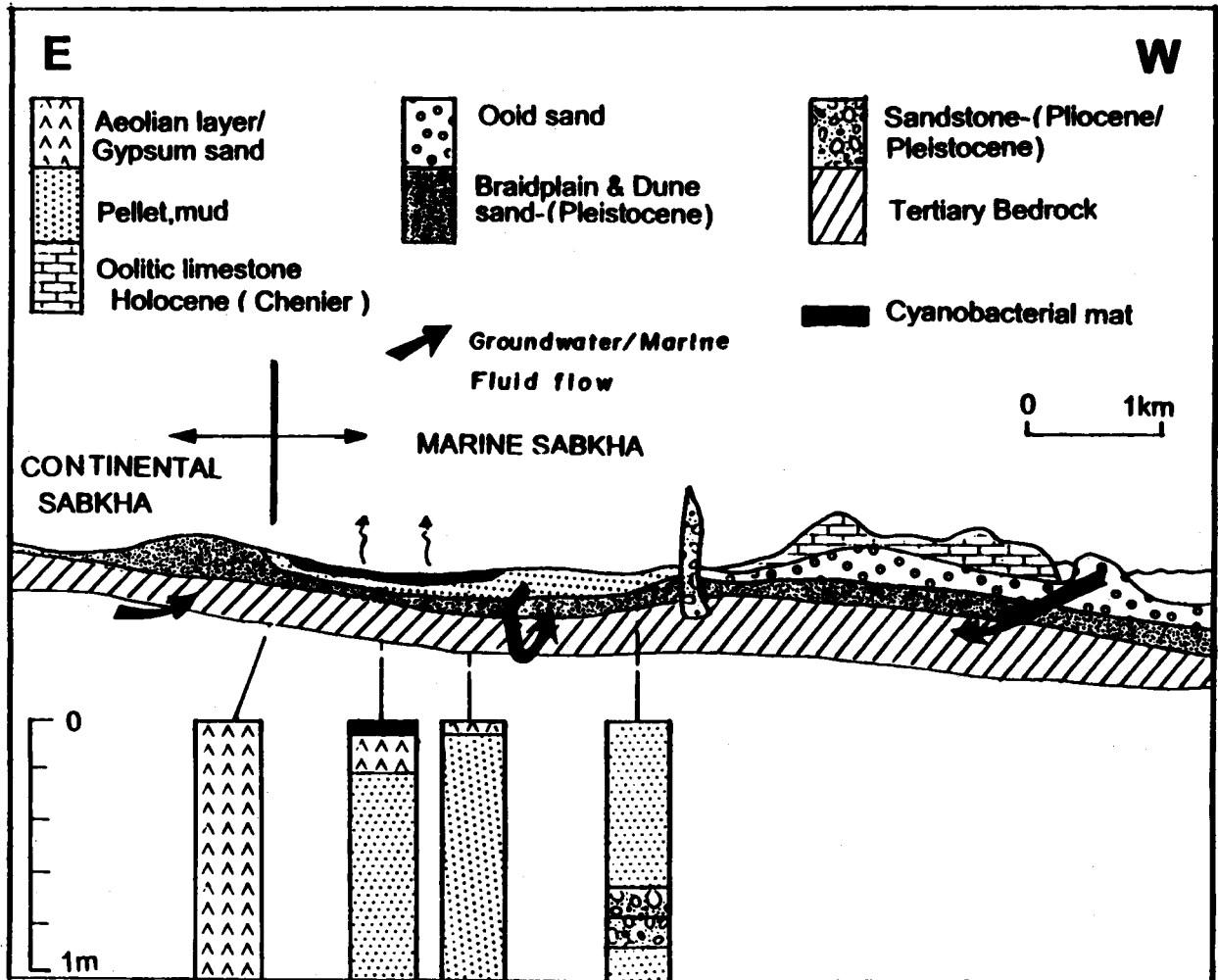
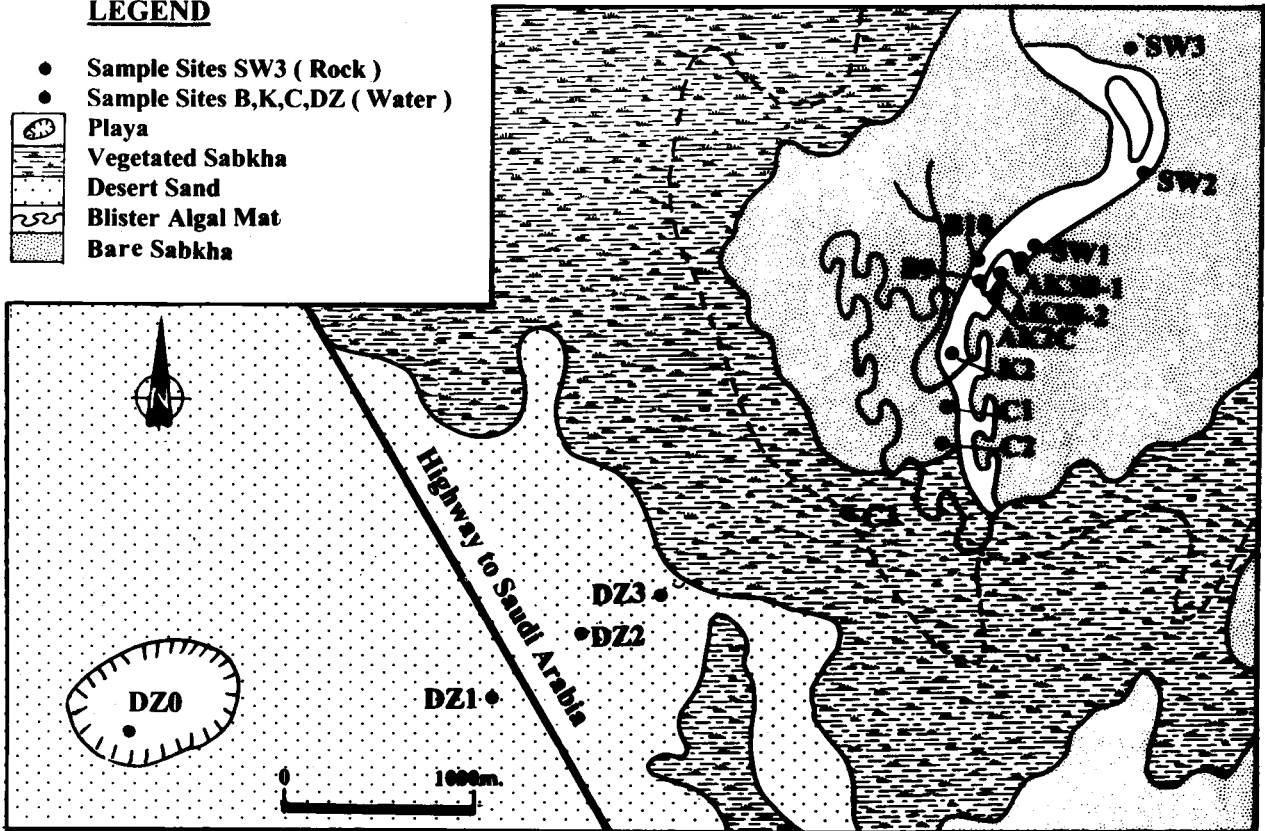
( Fig. 1 )



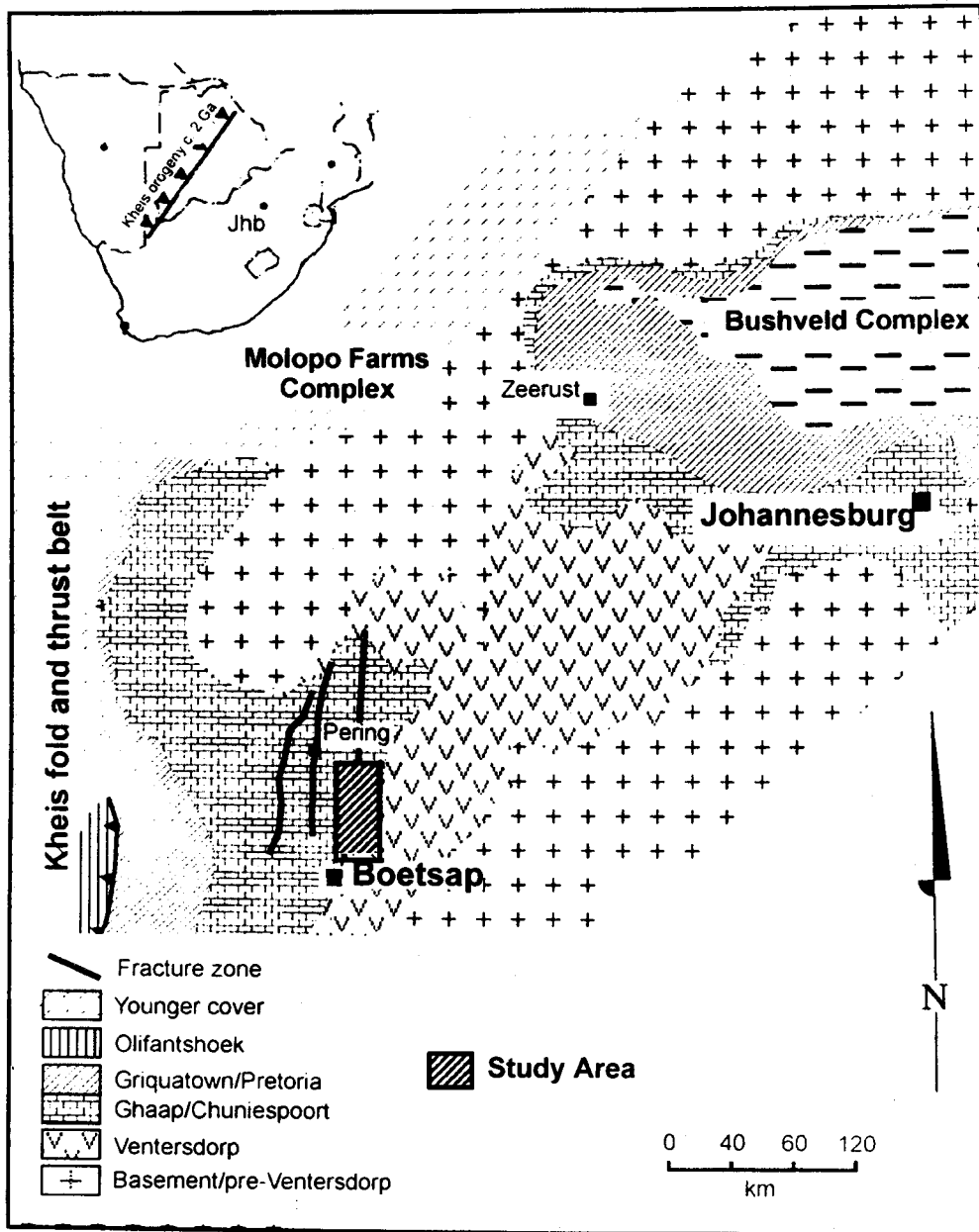
( Fig. 2 )

**LEGEND**

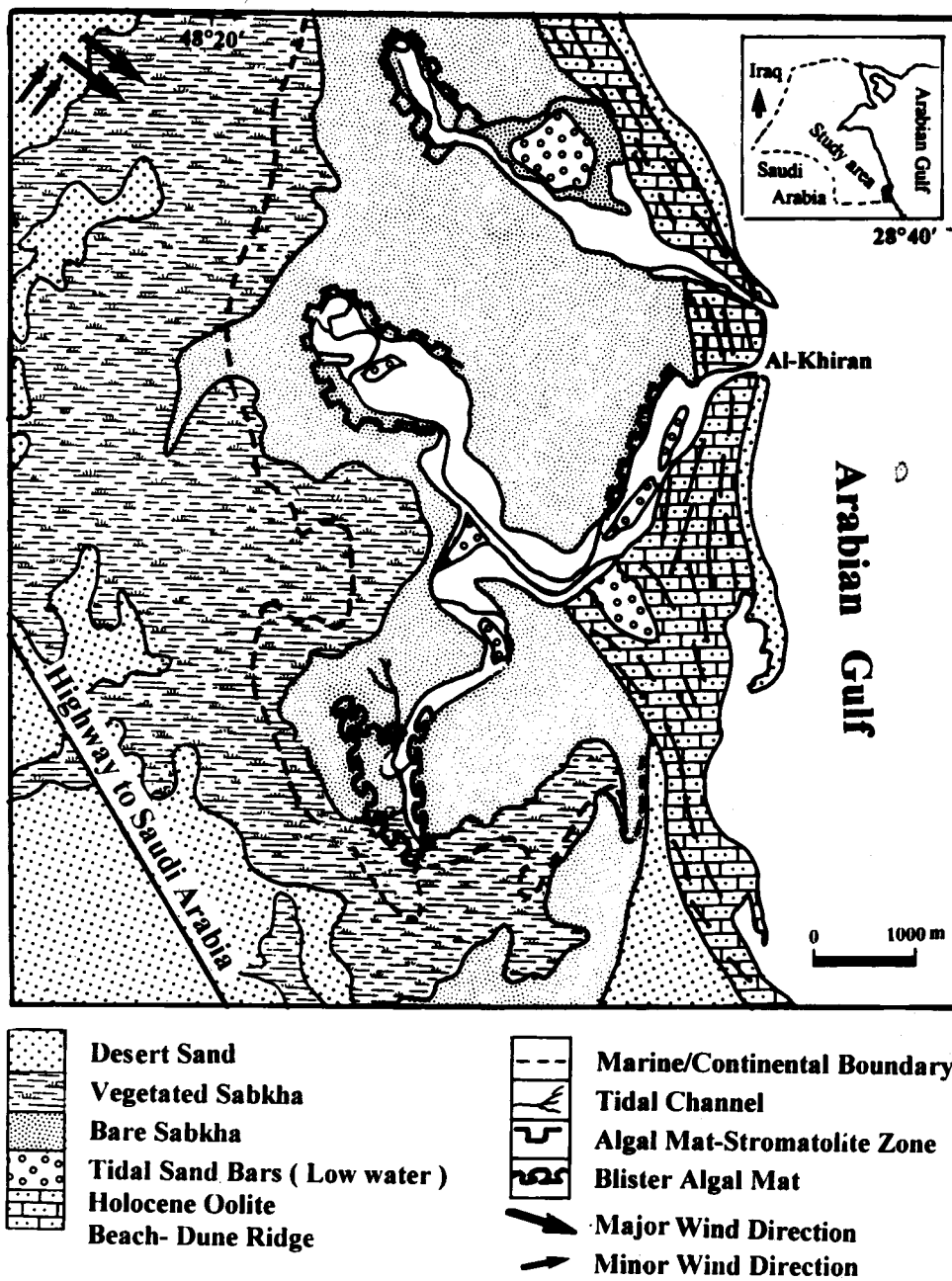
- Sample Sites SW3 ( Rock )
- Sample Sites B,K,C,DZ ( Water )
-  Playa
-  Vegetated Sabkha
-  Desert Sand
-  Blister Algal Mat
-  Bare Sabkha



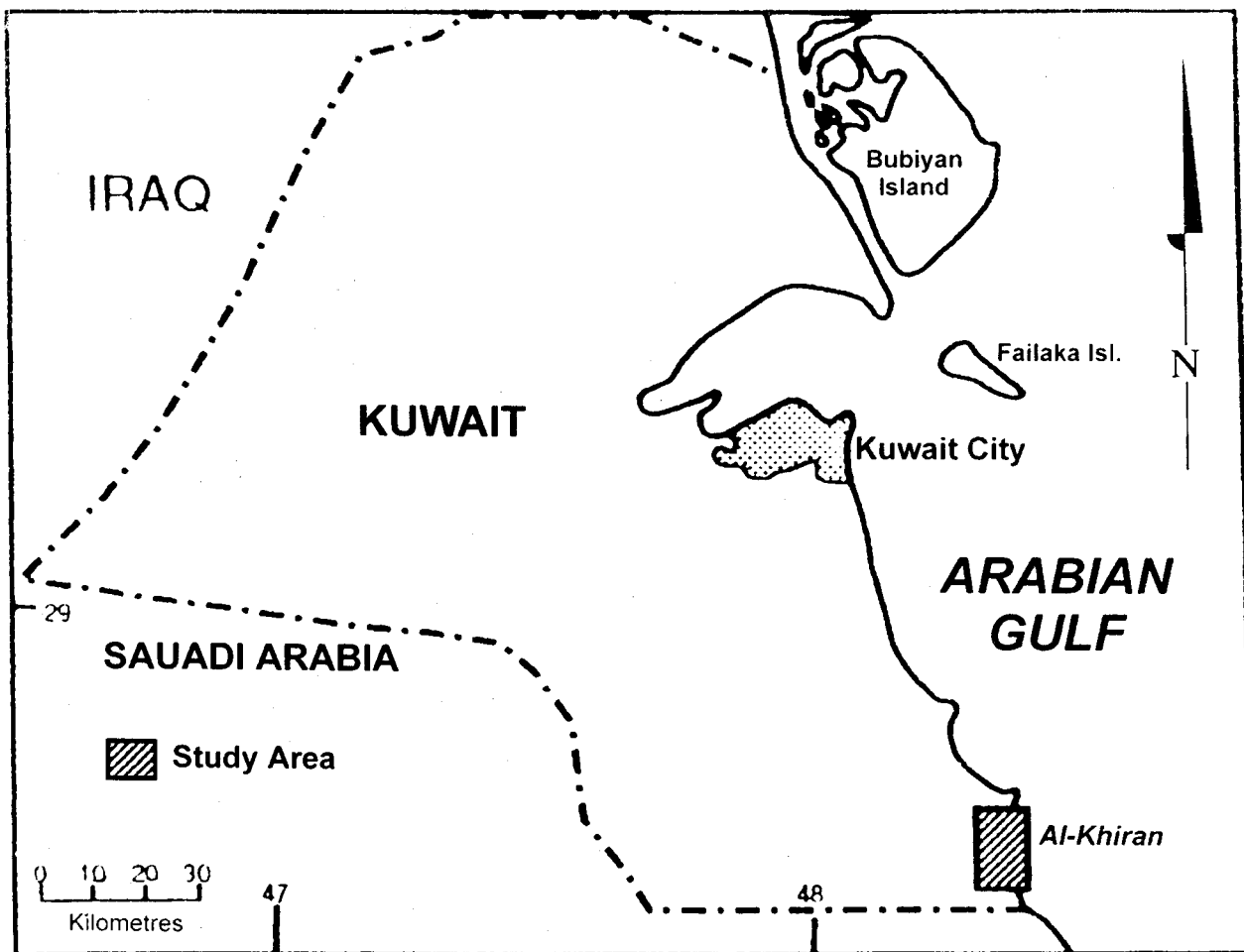
( Fig. 3 )



( Fig. 4 )



( Fig. 5 )



( Fig. 6 )

Table 1. Boron isotope data for samples investigated

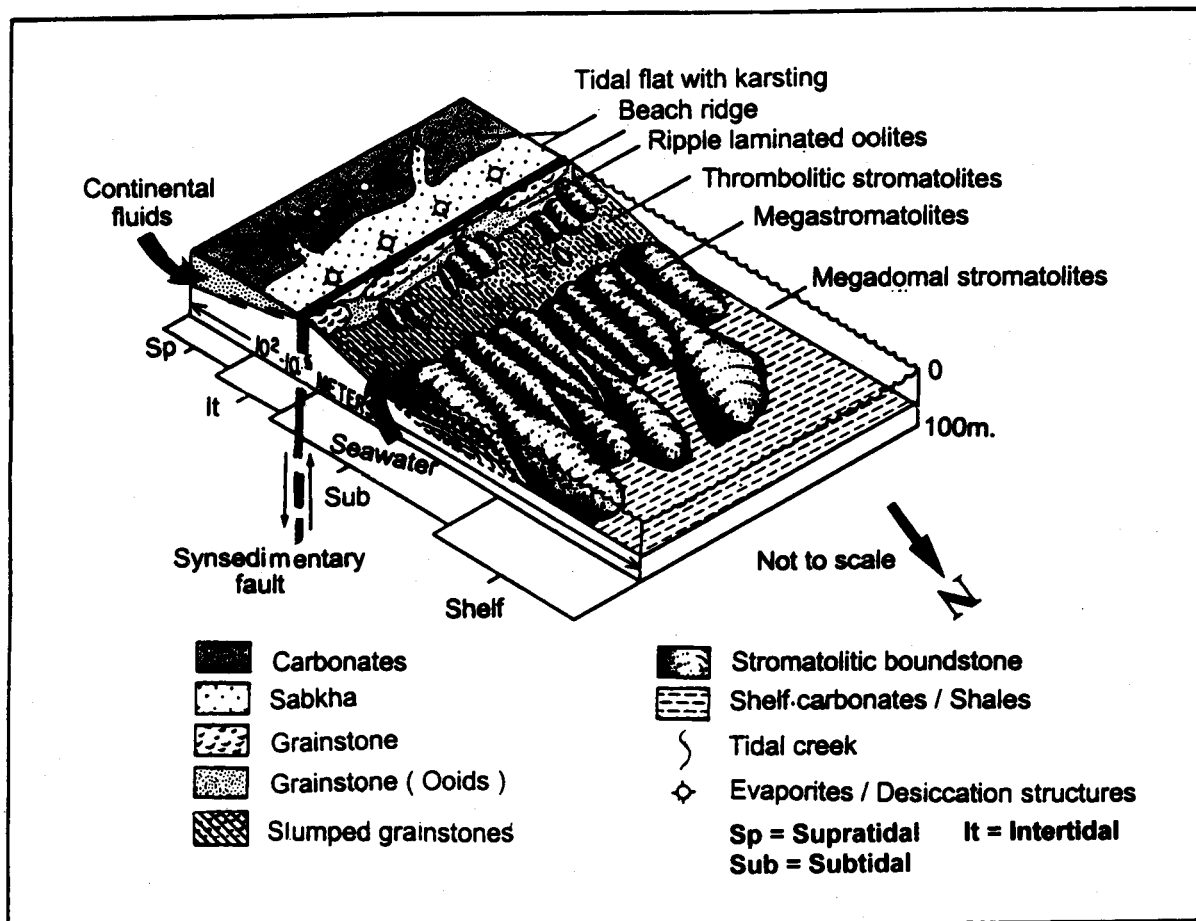
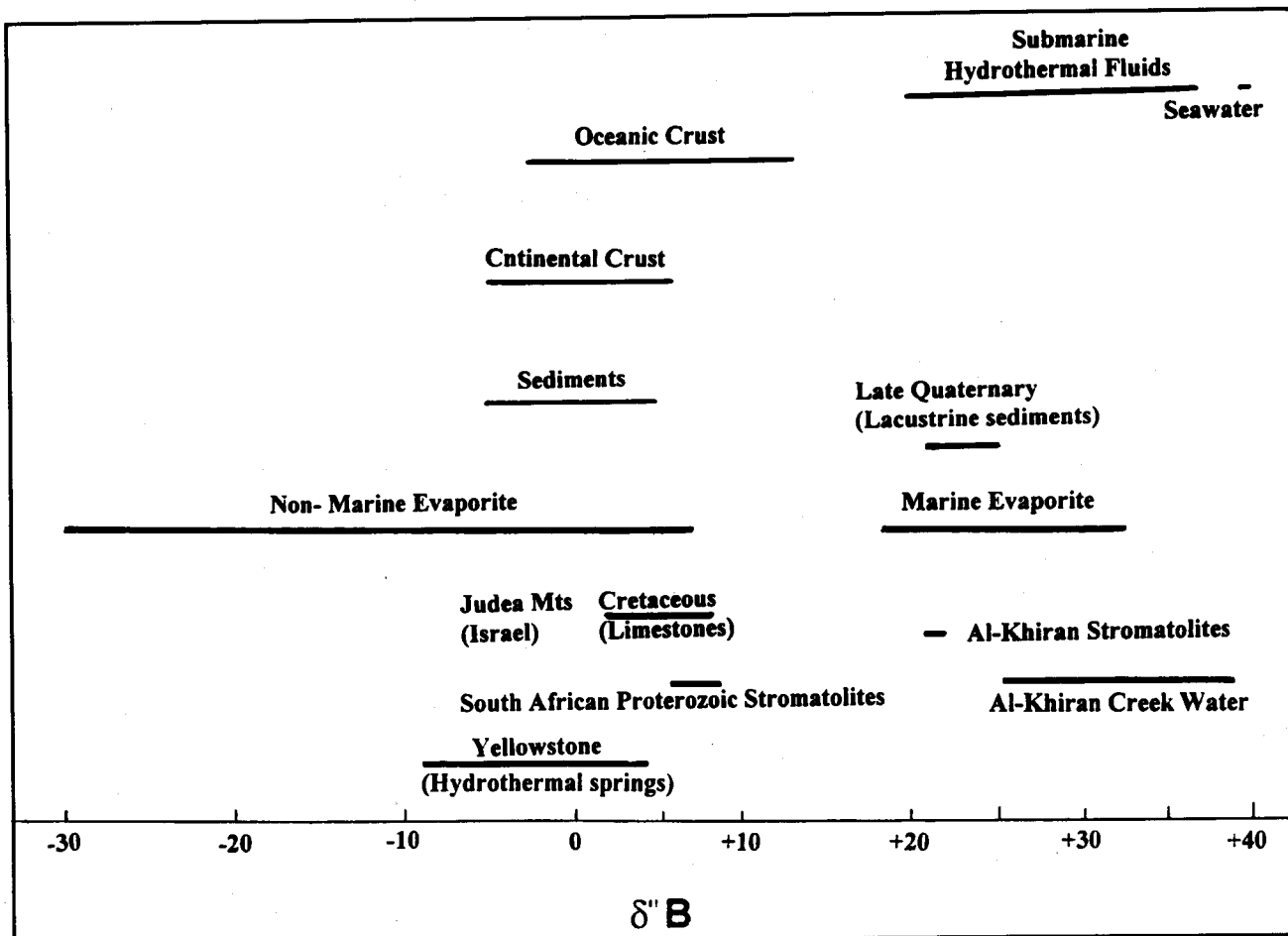
Region*	B ppb	$^{11}\text{B}/^{10}\text{B}$	$\delta^{11}\text{B}$
S.Africa			
PR-1	266	4.07099	6.8
BOE-1	237	4.06853	6.2
Kuwait			
B10	4670	4.20157	39.1
B9	6280	4.18954	36.1
BK2	8220	4.19194	36.7
BC-1	6430	4.16863	30.9
BC-2	5470	4.14694	25.6
BC-3	5680	4.14753	32.0
BDZO	9640	4.17319	25.3
BDZ1	7450	4.14231	24.1
BDZ2	5810	4.16354	29.7
BDZ3	7080	4.15302	26.4
AK-2C		4.12943	21.2
AK-3B1		4.12939	21.3
AK-3B2		4.12907	21.2
SW1	170	4.10296	14.5
SW2	160	4.10520	15.0
SW3	2150	4.12284	19.8

Samples B = brine, otherwise rock: BDZO = PLAYA

Sample Number	Na ppm	Ca ppm	Mg ppm	K ppm	Cu ppb	Zn ppb	Pb ppb	Alkalinity ppm	Cl ppm	SO <sub>4</sub> ppm	Salinity permil
B9	24400	1020	2590	807	174	<35.0	<110	128	32800	4730	90
B10	13000	547	1660	441	79	<35.0	<110	165	21800	2900	90
K-2	26000	1030	3220	1020	N.A.	<35.0	<110	130	59000	4880	-
C1	46100	2870	4830	1950	70.3	<35.0	<110	60	91900	2660	-
C2	27000	2720	2930	1190	32	<35.0	<110	59	46400	2920	-
C3	19200	2140	1540	637	66	<35.0	<110	154	31100	2740	50
DX3	14500	1830	1100	790	Nd	NA	NA	90	21500	2970	40
DX2	8330	1600	899	573	Nd	NA	NA	98	8600	2640	45
DX1	4730	1200	540	305	Nd	NA	NA	70	16800	2620	19
DX0	17400	1910	1720	1450	Nd	NA	NA	74	21600	3610	80

( Table 2 )





( Fig. 7 )