Studies on element bonding forms in sediments from the Reykjanes Ridge (59°N-60°N)

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With 4 figures and 2 tables in the text

Abstract: The chemical composition of sediments from the Reykjanes
Ridge is controlled by allochthonous and autochthonous processes. The
surface sediments are characterized by relatively high contents of calcium-
oxide and strontium. Calcium and strontium dominate in the carbonate
phase due to the high content of biogenic carbonate. A high percentage
of iron and manganese are bound to oxides and hydroxides. An indication
of hydrothermal activity was not observed. A considerable portion of ad-
sorbed barium is transported in clay minerals. The higher amounts of
aluminium in glacial sequences indicate an enhanced input of terrigenous
material; the increase of stable bonding elements points toward the large
influence of detrital minerals. The distinct differences in the bonding
characteristics of elements in these marine sediments in comparison to
fluvial and coastal deposits could be due to the different environmental
conditions.

Zusammenfassung: Die Elementzusammensetzung in den Sedimenten vom
Reykjanes-Rücken wird durch allochthone und autochthone Prozesse be-
stimmt. Die Oberflächensedimente sind durch relativ hohe Gehalte an
Calciumoxid und Strontium gekennzeichnet. Die überwiegend karbonatische
Bindung von Calcium und Strontium ist auf den dominierenden Anteil bio-
genen Karbonats zurückzuführen. Eisen und Mangan liegen mehrheitlich
als Oxide bzw. Hydroxide vor. Hydrothermaler Einfluß konnte nicht nach-
gewiesen werden. Barium ist zu einem beträchtlichen Teil in adsorbierter
Form an Tonminerale gebunden. Die höheren Aluminiumwerte in den gla-
zialen Sedimenten dürften vorwiegend auf einen verstärkten terrigenen
Eintrag zurückzuführen sein; gleichzeitig erhöht sich dadurch auch der An-
teil an stabilen Elementbindungen im Sediment. Die deutlichen Unter-
schiede in den Elementbindungsformen dieser vollmarinen Sedimente im

Vergleich zu fluviatilen und küstennahen Ablagerungen ist die Folge der jeweils unterschiedlichen Sedimentationsmilieus.

1. Introduction

Apart from authigenic formation, element distribution is mainly controlled by two processes in the North Atlantic: on one hand by detrital input from continental weathering and on the other hand by biogenic input in the form of calcareous and siliceous organisms. Besides the biogenic, detrital and hydrogenic contents the volcanic components at the Mid-Oceanic Ridge (MOR) can be of great importance. The occurrence of the various minerals and particle associations in the MOR sediments causes different geochemical compositions that can record changes in the depositional and environmental conditions. Geochemical investigations on sediments from the Mid-Atlantic Ridge in the TAG area at 26° N (CRO-NAN 1972, RONA 1976, CRONAN et al. 1979, SHEARME et al. 1983), in the area between 27° N - 30° N (MURTON et al. 1994) and from the Steinaholl area at 63° N (GERMAN et al. 1994) have shown that the hydrothermal input is important here. LACKSCHEWITZ et al. (1994) divided the sediments north of Iceland into a biogenic, terrigenous and volcanic component using geochemical and mineralogical data, while the sediments south and east of Iceland were divided into a biogenic and two lithogenic components by GROUSSET et al. (1982).

We present the results of chemical studies on sediments from the Reykjanes Ridge between 59°N and 60° N (Fig. 1). The area between 55° N and 66° N has been shaped by complex hydrographical conditions that account for the areas complicated sea-bottom topography (TUCHOL-KE 1985, KUPTSOV & BARTENEVA 1988). An overview of the simplified circulation pattern of the surface and deep-sea water masses is given in Fig. 1.

In the working area the Mid-Oceanic Ridge is marked by an active spreading zone with a central depression (ENDLER & LACKSCHEWITZ 1993). The depression shoulders are 200-300 m. The north-westwards and south-eastwards sloping ridge flanks are structured into basins and highs parallel to the ridge. Occasionally, also seamounts occur.

The focus of the investigations presented lies on the registration of the geochemical variability of sediments in the mid-oceanic Reykjanes Ridge area. This allows to quantify the composition and spatial distribution of local enrichment and impoverishment of metals and to characterize the geochemical and facial conditions of sedimentation.

2. Methods

The sediments investigated were taken with a large box corer and a giant gravity corer in the area of the Reykjanes Ridge between 59° N and 60° N during the RV "SONNE" Cruise 82 (SO 82) and RV "Professor Logachev" Cruise 09 (LO 09). Sediment sampling and lithological description were done aboard (ENDLER & LACKSCHEWITZ 1993, WALLRABE-ADAMS & LACKSCHEWITZ 1993).

Time control of the core SO 82-5 is based on high resolution oxygen isotope stratigraphy (unpubl. data). The composition of major and trace
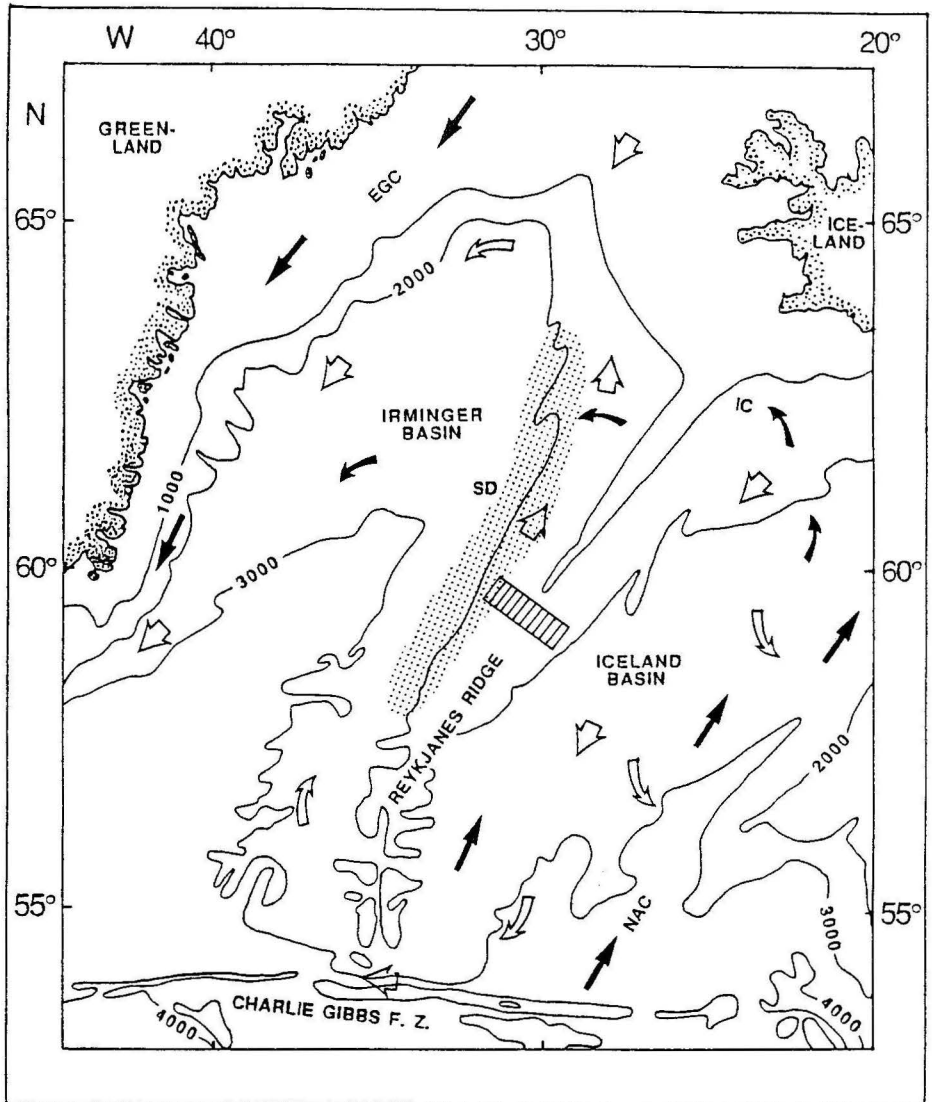
Fig. 1. Surface water and deep water circulations in the western North Atlantic (hatched area = study area) (from GEHRKE et al. 1994).

elements was analysed in all samples. Bulk sediment samples were oven-dried at 60 °C and then pulverized. The major element composition was measured with a Philips X-ray fluorescence spectrometer (XRF). For XRF analysis the pulverized sediments were dried at 1000 °C and melted using a mixture consisting of 4 g lithiumtetraborate ($Li_2B_4O_7$) and 1 g sediment. 12 international standards were used for calibration. The trace element composition was analysed with ICP/MS (VG Plasma-Quad PQ 1). For this purpose the sediment was dissolved with a $HF-HClO_4$-aqua regia attack (GARBE-SCHÖNBERG 1993). Accuracy of the results was controlled by measuring the international standard reference material "MESS 1". Further geochemical precision was achieved by determining bond types of various elements. The elemental phase distribution was analysed by means of selective chemical extraction. According to the methods by TESSIER (1979) and FÖRSTNER (1983) six characteristic types of element bonds were distinguished for extraction: adsorption and exchange of cations, carbonatic, easily (Mn oxides) and moderately (Fe oxides) reduceable phases, organic fraction or sulfides and residual fraction.

3. Results and discussion

Description and composition of the recent surface sediments

The composition of the recent surface sediments is primarily characterized by pelagic sedimentation (GEHRKE et al. 1994, WALLRABE-ADAMS & LACKSCHEWITZ 1993). In particular, these are brownish, sandy silty clays with a high percentage of calcareous biogenic components (planktic foraminifers, coccoliths). The sediments from the central ridge flank (SO 82-6) and from the lower slope of the southeastern seamounts (LO 09-15) are striking due to their high percentage of sand and low percentage of clay, while clearly increased percentages (<10 weight%) of quartz particles were encountered in the sediments from station SO 82-6 (GEHRKE et al. 1994). A low percentage of volcanic particles is only found in the sediments from the rift valley location LO 09-6. Location LO 09-14 has a very high percentage of clay (>90 %).

The sediments reveal generally relatively high percentages of calcium carbonate (50-60 %). The highest percentages of 60-70 % are measured in the surface sediments at the locations LO 09-9, -10 and -15. The percentages of organic carbon (C_{org}) lie between 0.4 and 0.7 %. Maximum values of C_{org} percentages of 0.9 to 1.2 % are reached in the surface sediments at the locations LO 09-14 and -18.

Distribution of major and trace element concentrations in the recent surface sediments

In Table 1 the geochemical composition of the recent surface sediments is given. Further possibilities of geochemical classification are provided by additional analysis of the mentioned element bond types. According to their spatial position the bond ratios of 9 elements for the surface samples are shown in Fig. 2.
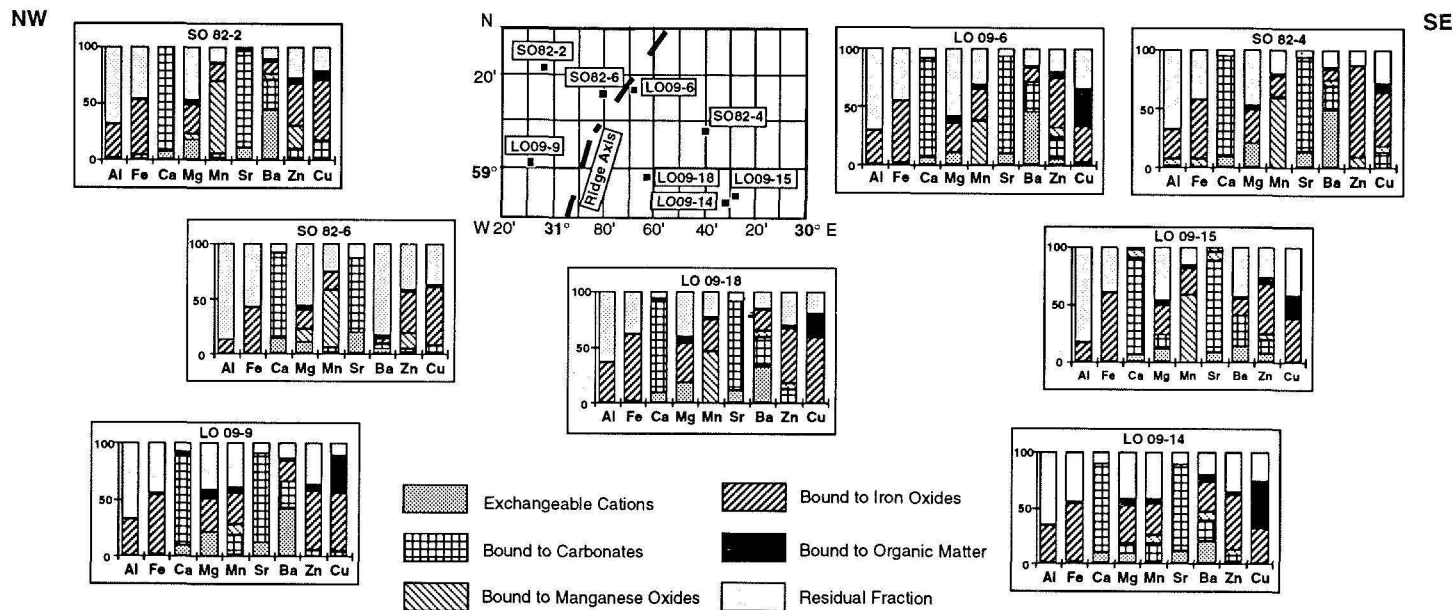
NW

SE

Fig. 2. Ratio of element bonding forms of surface sediments and location of sampling sites in the study area.

Table 1. Major and trace element concentrations in surface sediments from the Reykjanes Ridge. Major element concentration in %; trace element concentration in ppm.

Station	*Si	*Al	*Fe	*Ca	*Mg	*Mn	Sr	Ba	Zn	Cu
SO82-2	8.6	2.2	2.8	27.2	0.8	1400	1050	350	48	34
SO82-4	10.5	2.7	3.7	24.3	0.9	1300	940	244	61	37
SO82-6	19.0	4.9	4.5	14.2	1.6	1200	480	202	90	40
LO 09-6	9.5	2.3	2.9	24.6	1.0	715	1050	222	91	35
LO 09-9	14.9	2.7	3.9	17.0	1.1	580	971	586	78	44
LO 09-14	14.7	3.1	4.0	18.3	1.2	575	1030	574	83	34
LO 09-15	8.1	1.4	1.6	28.6	0.5	510	1000	164	51	10
LO 09-18	11.3	2.8	3.8	21.8	1.1	1000	1180	581	82	39

* Si = 0.467 SiO_2; Al = 0.265 Al_2O_3; Fe = 0.350 Fe_2O_3; Ca = 0.714 CaO; Mg = 0.603 MgO
Mn = 0.775 MnO

CaO, mainly linked with calcareous biogenic particles, and SiO_2, mainly represented by lithogenic components, have together mostly more than 50 % in the surface sediments. Apart from Ca, also Sr is primarily bound to the carbonatic phase due to the high content of biogenic carbonate. Aside from Al (1.4–4.9 %), Fe is the third most common element part with a percentage of 1.6–4.5 %. Fe mainly occurs in form of amorphic oxides. Especially, heavy metals such as Zn and Cu are bound to this moderately reduceable phase. The organically bound percentage of copper in the sediments at the locations LO 09-14 and –18 is linked with the C_{org} percentages increased there. Barium occurs mainly bound adsorptively or carbonatively, however, most percentages were measured in residual fractions at the locations SO 82-6 and LO 09-15. These samples are also characterized by an extremely low percentage of clay minerals (<10 %; GEHRKE et al. 1994). Thus, the possibility of a sorptive bond is reduced. Furthermore, compared to the average it is shown that especially Fe_2O_3, Cu and Ba are strikingly lowered in these samples. In sample SO 82-6 the relatively high percentages of lithogenic particles are bound to increased percentages of SiO_2, Al_2O_3, MgO and K_2O indicating an increased input of detrital aluminous silicates. In sediments of the North Atlantic an assessment of lithogenic components was carried out by METZ et al. (1988) using aluminium data.

Description and composition of Late Quaternary sediments

Core SO 82-5 collected on the northwestern flank of the Reykjanes Ridge is characterized by brown and olive coloured pelagic sediments intercalated by spicule-rich layers (ENDLER & LACKSCHEWITZ 1993).

Occasionally, thin sandy layers or lenses are interlayered in core SO 82-5. Stratigraphic control is mainly based on oxygen isotope data. Additional stratigraphic information is provided by a volcanic ash. This volcanic ash from Iceland is present as a cm-thick sandy layer at 4.93 m and marks an age of 57.5 ka (RUDDIMAN & McINTYRE 1984). While the upper 40 cm of the core SO 82-5 have relatively high percentages of calcium carbonate (30-40 %), the other sediments of up to 5 m are characterized by distinctly lower percentages (<20 %). The percentages of C_{org} range from 0.2-0.5 %.

Distribution of major and trace elements in Late Quaternary sediments

The sediments of the last Glacial in core SO 82-5 (100-500 cm) show distinct differences in the bonding characteristics of elements in comparison to the sediments of younger Holocene (upper 60 cm). The glacial sediments are characterized by a high percentage of all their elements that is bound to the residual fraction (Fig. 3). The clearly higher percentages of Al compared to the Holocene indicate a high percentage of aluminous silicates (Table 2). Apart from the carbonatic bond, Ca shows a relatively increased clay mineral-fixation due to low $CaCO_3$ percentages in the glacial sediments.

The percentages of Ba in the sediments of the Reykjanes Ridge (Table 2, 300 to 500 ppm) are in the same order to the values of Ba in sediments from the Norwegian-Greenland Sea (PAETSCH 1991). In the core SO 82-5 at 57.5 ka a high percentage of Ba is bound to the residual phase, which is connected with the high percentage of rhyolitic glass particles in this sample, because they are extremely enriched with incompatible elements such as Ba. On the other hand, in Holocene sediments Ba is mainly bound to clay minerals due to the exchange of cations. The high percent-

Table 2. Major and trace element concentrations in sediments of core SO 82-5 from the Reykjanes Ridge. Major element concentration in %; trace element concentration in ppm.

Depth (cm)	*Si	*Al	*Fe	*Ca	*Mg	*Mn	Sr	Ba	Zn	Cu
1	8.3	1.9	2.5	23.0	0.7	762	1000	422	84	35
51	14.8	4.5	4.4	10.0	1.5	664	483	462	135	67
101	21.8	7.3	6.4	7.4	1.8	679	282	331	141	46
181	23.0	7.3	6.7	6.1	1.8	713	228	289	179	45
411	24.3	7.0	6.8	5.6	1.9	759	250	361	132	42
493	23.8	6.5	5.6	7.4	1.4	864	338	339	138	45

* Si = 0.467 SiO_2; Al = 0.265 Al_2O_3; Fe = 0.350 Fe_2O_3; Ca = 0.714 CaO; Mg = 0.603 MgO

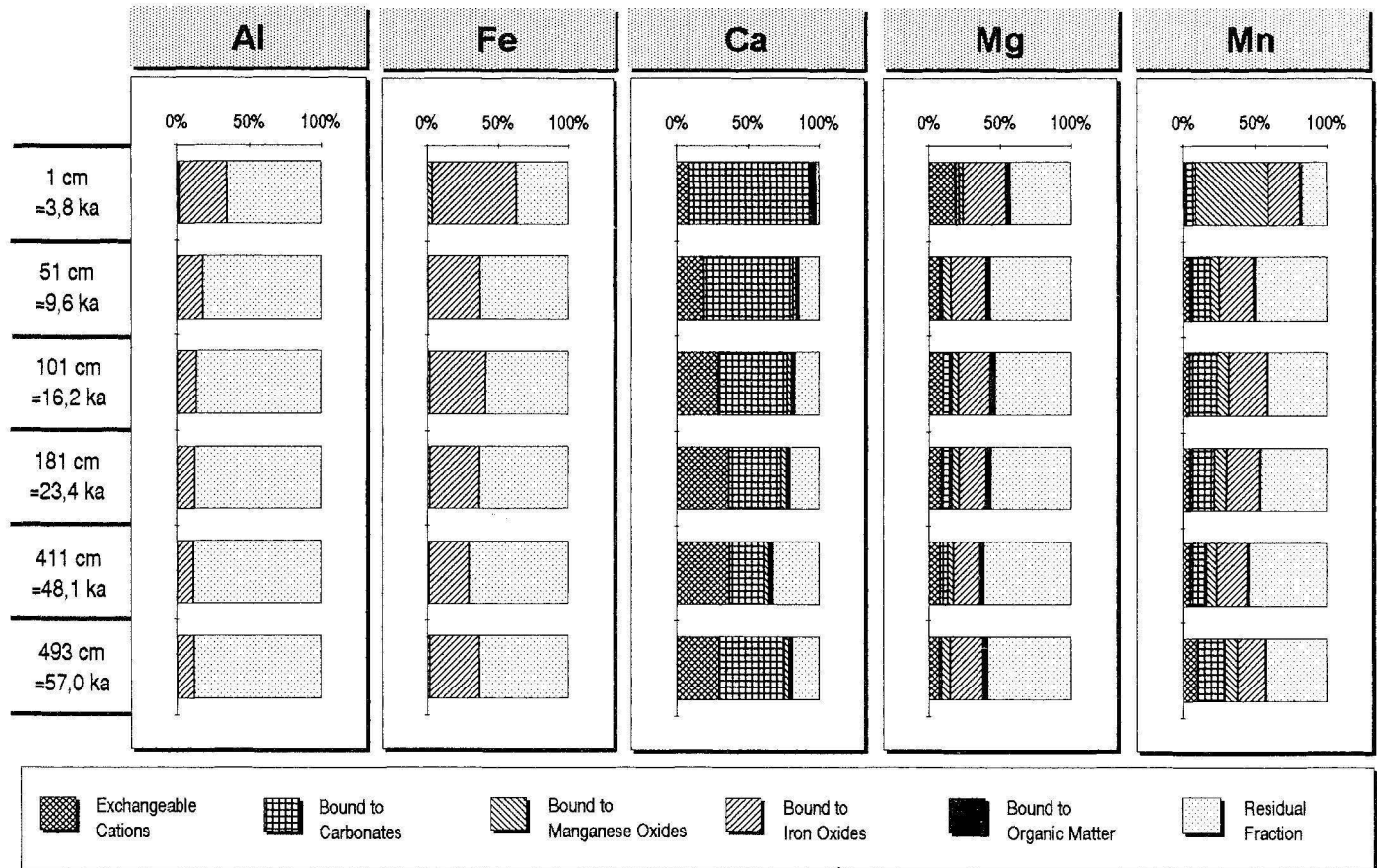Mn = 0.775 MnO

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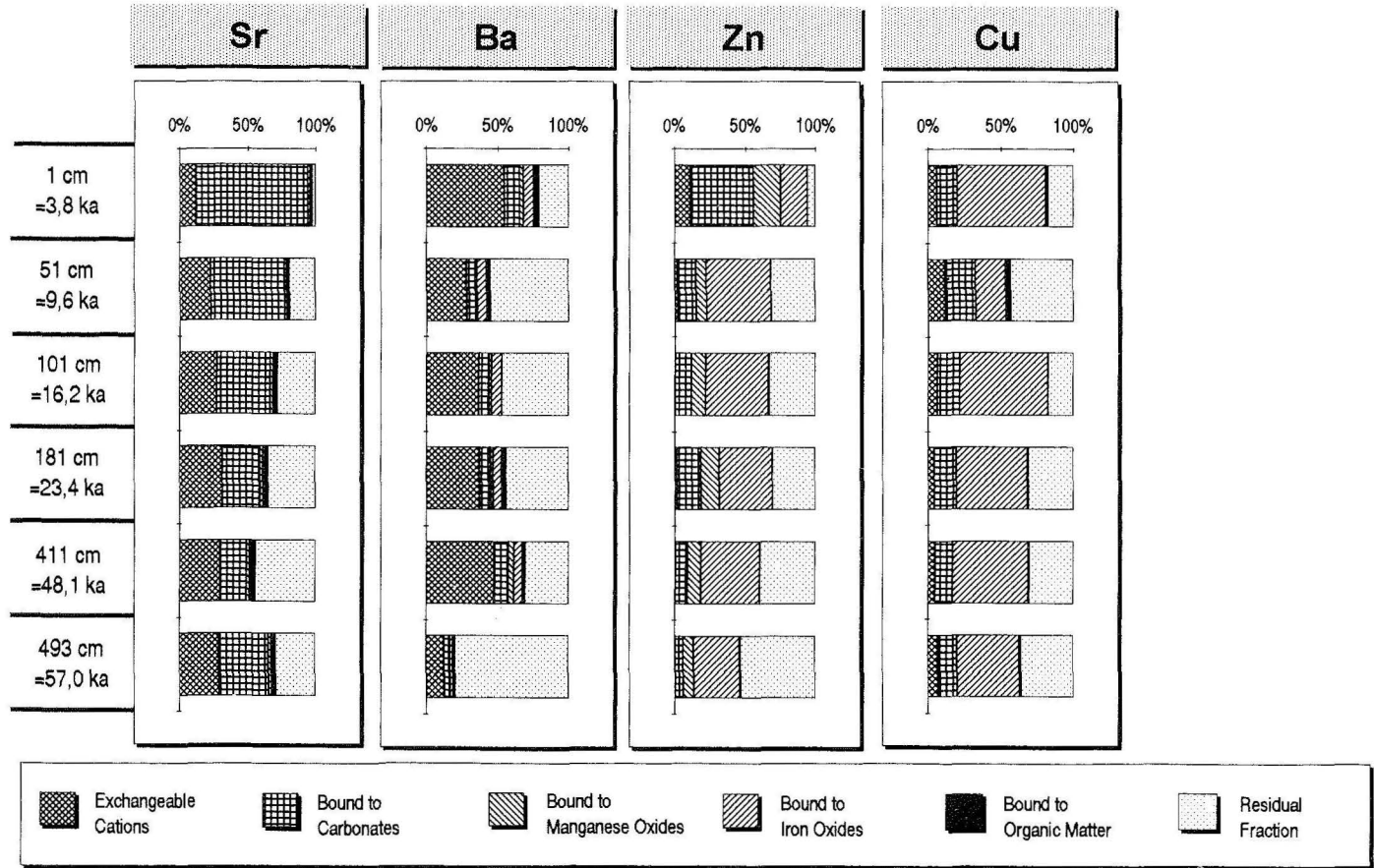Fig. 3. Ratio of element bonding forms of sediments from the core SO 82-5 and their changes with time.

Fig. 3 (continued).

age of carbonatic particles in the Holocene sediments causes mainly carbonatic Ca and Sr bonds. Also Zn shows a distinct increase in this kind of bond.

Comparison of geochemical facies with other areas of sedimentation

The average phase-specific distribution of elements in the surface sediments of the Reykjanes Ridge by comparison with the phase percentages of Fe, Mn, Cu and Zn in the sediments of the Arcachon Basin (France; EL GHOBARY & LATOUCHE 1986), the Lower Rhine (Germany; FÖRSTNER & PATCHINEELAM 1976) and the Pacific (FÖRSTNER & STOFFERS 1981) is shown in Fig. 4. Partly distinct differences in the heavy metal bond forms result from different sedimentary environments (marine, coastal, fluviatile). Most bonds of the elements in the surface sediments from the Reykjanes Ridge studied are mainly those to Fe oxides or hydroxides and those caused by formation of carbonates. Fe, Cu and Zn percentages are preferably bound to Fe oxides and hydroxides, respectively, while Al and Mg are mainly bound to siliceous particles. For the element of Ba mainly clay mineral-fixation is of importance (exchange of cations). In the sediments of the Reykjanes Ridge Mn is mainly bound to Mn oxides like in the sediments of the Pacific.

In contrast to the marine sediments from the Reykjanes Ridge, in the wadden sediments of the Arcachon Basin the heavy metals are bound to the organic, sulfic fraction (EL GHOBARY & LATOUCHE 1986), which can be explained by predominantly anaerobic conditions and the high percentage of C_{org} involved (3–4 %).

In the sediments from the Lower Rhine Fe and Cu have a high detrital-mineral bond (rock abrasion), while Zn has a preferably carbonatic bond due to the relatively high stability of $ZnCO_3$ in Eh-pH conditions of normal inland waters as well as the developed co-precipitation of this component with $CaCO_3$ (FÖRSTNER & PATCHINEELAM 1976).

4. Conclusions

The metals in the studied sediments from the Reykjanes Ridge are enriched by biogenic, detrital and hydrogenic processes. A hydrothermal influence was not detected.

From the distribution of relative concentrations of the quantified elements in the single extraction fractions it is obvious that some surface sediments have a greater similarity in its chemistry than the other samples. This points to spacially differentiated sedimentary ratios in the working area. Variations of the values of the grain sizes and of the C_{org} percentages explain some of the observed differences in the kinds of metal bonds, e. g. of Ba and Cu. In the surface sediments Ca and Sr dominate within the carbonatic phase; Zn and Cu are mainly bound to Fe hydroxides.

Analysing the distribution of elements in the single bond types, the higher bound percentage in the residual phase of all elements is striking in the glacial sediments. Especially for Al, clearly higher percentages are observed compared with the Holocene. Both is attributed to a higher input of lithogenic material where the elements are partly bound very tightly.
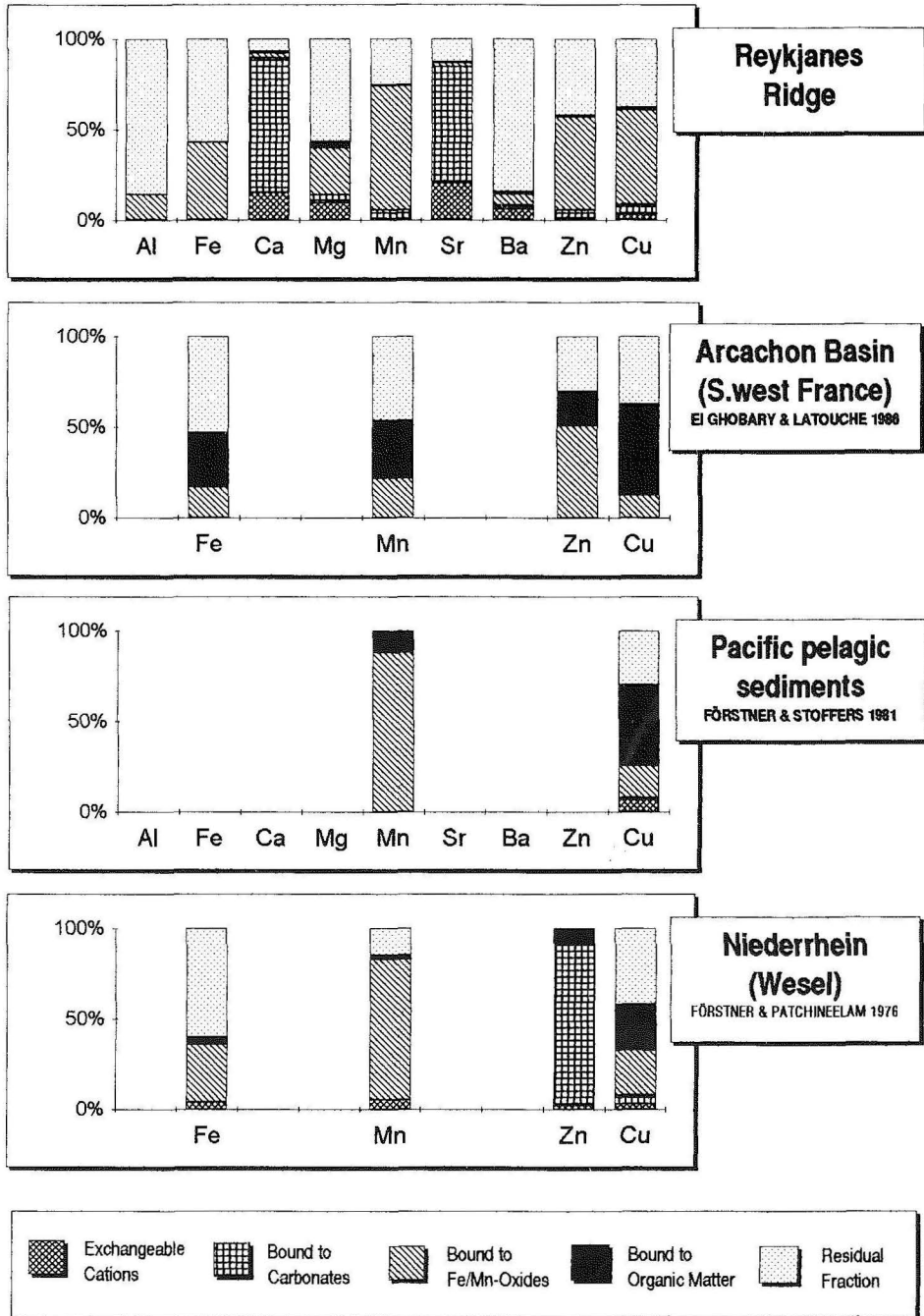
Fig. 4. Percentage of metal associations in surface sediments of three different chemical facies compared to the elemental phases of the Reykjanes Ridge deposits.

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