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Contrasting Forms of Iron and Phosphorus In the Bottom Sediments of middle and lower Bay of Quinte

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CONTRASTING FORMS OF IRON AND PHOSPHORUS IN THE BOTTOM SEDIMENTS OF MIDDLE AND LOWER BAY OF QUINTE

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ABSTRACT

A strong pyrite horizon in the bottom sediments of Middle Bay of Quinte is consistent with eutrophic summer-stratified waters. A strong nonapatite inorganic phosphorus (NAIP) horizon in Lower Bay sediments, 8 to 20 cm beneath the sediment-water interface, probably reflects an oxidizing horizon within the sediments. It represents a significant storage capacity for bioavailable phosphate ion.

NWRI Cont # 98-256

Management Perspective

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Current Status The in-place storage of sediment phosphorus in the Bay of Quinte was studied to find out whether there had been a change in iron phosphorus forms which would indicate changes in phosphorus recycling to the overlying waters. Core samples showed the onset of eutrophication was about around 1900. Most of the non-point source phosphorus is flushed through the upper Bay. This phosphorus is stored permanently in the lower Bay. This shows the importance of timing of the phosphorus loading in that the major non-point loads correspond with strong hydraulic loads. Furthermore, the work shows the mechanism by which the Upper Bay can clean up once the nutrient loads are reduced further.

Next Steps: The work will be communicated to the Bay of Quinte RAP process. The senior author has retired.

INTRODUCTION

The Bay of Quinte is a highly eutrophic elongated Z-shaped embayment on the northern shore of Lake Ontario (Fig.1). The impact of colonial settlement on water quality has been severe. For convenience of study, and supported by morphology and trophic levels, the bay may be sectioned into Upper, Middle and Lower Bays (e.g., Minns et al. 1986). Upper Bay, largely covering the stretch between Trenton and Napanee, is relatively shallow (maximum depth 5 m) and is well mixed in summer. Middle Bay, stretching from Hay Bay to a little east of Glenora, is deeper, and strongly stratified with marked oxygen depletion in summer. Lower Bay (Fig. 2) is deep (> 100 m), undergoes major water exchange with Lake Ontario, and is less eutrophic.

Here, we compare some chemical properties of the bottom sediments within each of the three sub-bays as a function of sediment depth beneath the sediment-water interface. The sediments of Upper Bay have been described earlier (Manning 1996). The significance of elemental horizons within the sediment column is explored. The aim of the work is to relate the main forms of iron and phosphorus in the sediments to depositional patterns and water quality in each bay.

EXPERIMENTAL

Bottom sediment cores were retrieved with a Benthos gravity corer on several different occasions between 1987 and 1993. All cores were sectioned on shore, immediately frozen, and later freeze-dried within two weeks of retrieval.

The experimental details on phosphorus fractionation, Mossbauer spectrometry, carbon and sulfur analyses have been described earlier (Manning *et al.* 1979, Williams *et al.* 1976).

^{210}Pb chronology was performed by Turner & Delorme (1989 a, b).

RESULTS

Middle Bay sediments

Middle Bay sediments are typified by a core collected from station 861A (Figs. 1,2) in September 1988. The Mossbauer spectra are best interpreted using four doublets (Manning et al. 1979), one broad central ferric iron, a sharp central pyrite (FeS_2), and two ferrous iron doublets (Fig. 3). The redox sulfate-reducing horizon begins at about 6 cm beneath the interface (Fig. 4), consistent with eutrophic waters, reducing sedoments and stratified waters. The conditions necessary for sedimentary pyrite formation did not exist prior to 26 cm burial, i.e., prior to 1900 . The pyrite depth profile is matched by that of total sulfur (Fig. 4). Approximately 50% of total sulfur is in pyrite.

The total phosphorus profile (Fig. 5) is quantitatively very similar to that of Warwick (1980) for a core retrieved from the same location in 1972. Since 5 to 8 cm of sediment would have been deposited in the 16 year interval (1972 to 1988), the phosphorus, as NAIP, is being continually recycled within the 0 to 6 cm surface layer (Fig. 5). The actual

rate of sedimentation is 0.025 % of 6.2×10^2 g m^{-2} yr^{-1} or 0.16 g m^{-2} yr^{-1}. The 0.025 wt% of NAIP in depoosited sediment compares with the 0.12 wt % NAIP in suspended sediment, and shows that most of the suspended NAIP is flushed through the Bay.

The iron and phosphorus profiles displayed in Figures 3 and 4 are reproduced, at least qualitatively, in cores collected from Hay Bay through Picton Bay to station 861A (Figs. 1, 2).

An intermediate zone

The core from station 861B, in terms of the forms of iron and phosphorus, shows different characteristics. The pyrite horizon is very weak, however, a prominent NAIP horizon occurs at 40 to 46 cm depth interval (Fig. 6). Reference to core 861A (Fig. 5) confirms a minor equivalent at 46 to 48 cm depth. This horizon dates to approximately 1830. Most of the NAIP is extracted in a dilute HCl wash, consistent with the presence of vivianite. The horizon may be a direct indicator of the massive land clearing during the major wave of colonial settlement.

Lower Bay sediments

Lower Bay sediments are typified by a core collected from station 898 in September 1989. The Mossbauer spectra show evidence of three doublets (Fig. 7), one marking ferric iron in hydrated oxide and clay minerals and two marking ferrous ions in clay minerals. There are no major iron horizons in the sediment column (Fig. 8). In contrast, a major NAIP horizon occurs between 8 and 20 cm depth of burial (Fig. 8). Quantitatively similar NAIP profiles occur in sediment from stations 899 to 891 (Fig. 2). These stations are in deeper water. Sediment cores from the shallower station 892 show no NAIP horizons except for the usual two-cm thick layer of enrichment at the sediment-water interface. Sediments at station 892 may be similar to those of the open lake.

DISCUSSION

No pyrite or NAIP horizons are present in the bottom sediments of Upper Bay (Manning 1996); the sediments are low in NAIP (0.035 wt %) with minor surface enrichment. The NAIP horizon in Lower Bay sediments may be of similar origin to the sharply defined peaks in the sediments of the central and eastern basins of lake Erie (Manning & Wang, in preparation). Like the Lake Erie peaks, the peak of the NAIP horizon in the station 898 core cannot be dated to the introduction of phosphorus controls in the mid-1970s (Fig. 8). The likelihood is that the Lower Bay NAIP horizon marks an environment of higher redox potential. There is, however, no coincident ferric iron maximum that would mark the zone of precipitation of hydrated oxides. Possibly the NAIP is bound up as the ferrous phosphate vivianite, $Fe_3(PO_4)_3.8H_2O$. To test for vivianite, which is soluble in dilute HCl, the 11 to 12 cm, 13 to 14 cm, and 14 to 15 cm sections of core 898 were washed with 0.2 M HCl and the sections then rinsed, freeze dried, and analyzed for phosphorus. Most of the NAIP was removed by the HCl wash, the residuals containing 0.066 wt %, 0.052 wt %, and 0.030 wt %, respectively. Hence, some of the NAIP could be present as vivianite.

The NAIP horizon is indicative of oxygen diffusion down to 15 cm sediment depth, and is consistent with a relatively low rate of decomposition of organic matter and a low rate of deposition of algal remains. The NAIP horizon should remain as permanent features of Lower Bay sediments.

The deeper edge of the pyrite horizon in Middle Bay cores (Fig.4) dates to approximately 1890. Pyrite is a product of strongly reducing conditions and sulfate reduction. The horizon may mark the onset of eutrophic conditions in the Bay.

ACKNOWLEDGEMENTS

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CAPTIONS FOR FIGURES

FIG. 1. Location of the Bay of Quinte and its three sub-bays.

FIG. 2. Station locations at the easter downstream end of Middle Bay and in Lower Bay. Dotted line marks the 36 m water depth contour.

FIG. 3. Mossbauer spectrum of 14 to 15 cm section of sediment from station 861A in Middle Bay.

FIG. 4. Pyrite, ferric iron, ferrous iron, and total sulfur profiles in sediment from station 861A.

FIG. 5. Phosphorus and organic carbon profiles in sediment from station 861A. Concentrations of NAIP are low in the sulfidic sections of core (8 to 26 cm sections).

FIG. 6. Phosphorus profiles in a core from station 861B, showing a significant NAIP horizon (at 40 to 46 cm), probably marking major land clearance in approximately 1830.

FIG. 7. Mossbauer spectrim of 4 to 5 cm section of core from station 898, showing one ferric doublet (main), and two ferrous iron doublets.

FIG. 8. Sediment depth profiles for forms of iron and phosphorus in a core from station 898 in Lower Bay. The NAIP peak is centred at 13 cm depth, corresponding to sediment laid down in approximately 1957, prior to phosphorus controls.

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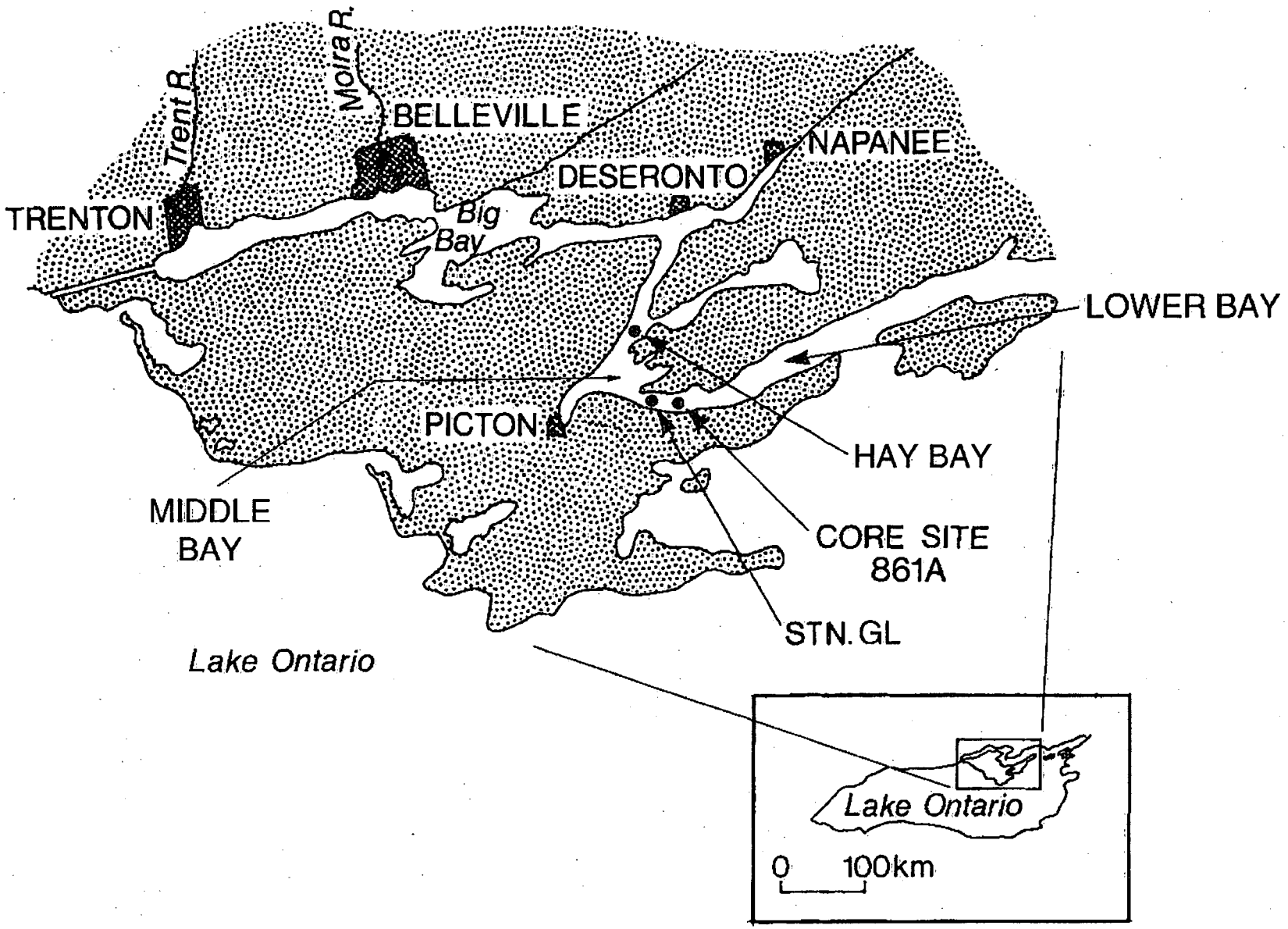
Trent R.
Moira R.
BELLEVILLE
NAPANEE
DESERONTO
TRENTON
Big Bay
LOWER BAY
PICTON
HAY BAY
MIDDLE BAY
CORE SITE 861A
STN. GL
Lake Ontario
Lake Ontario
0 100km

FIG 1

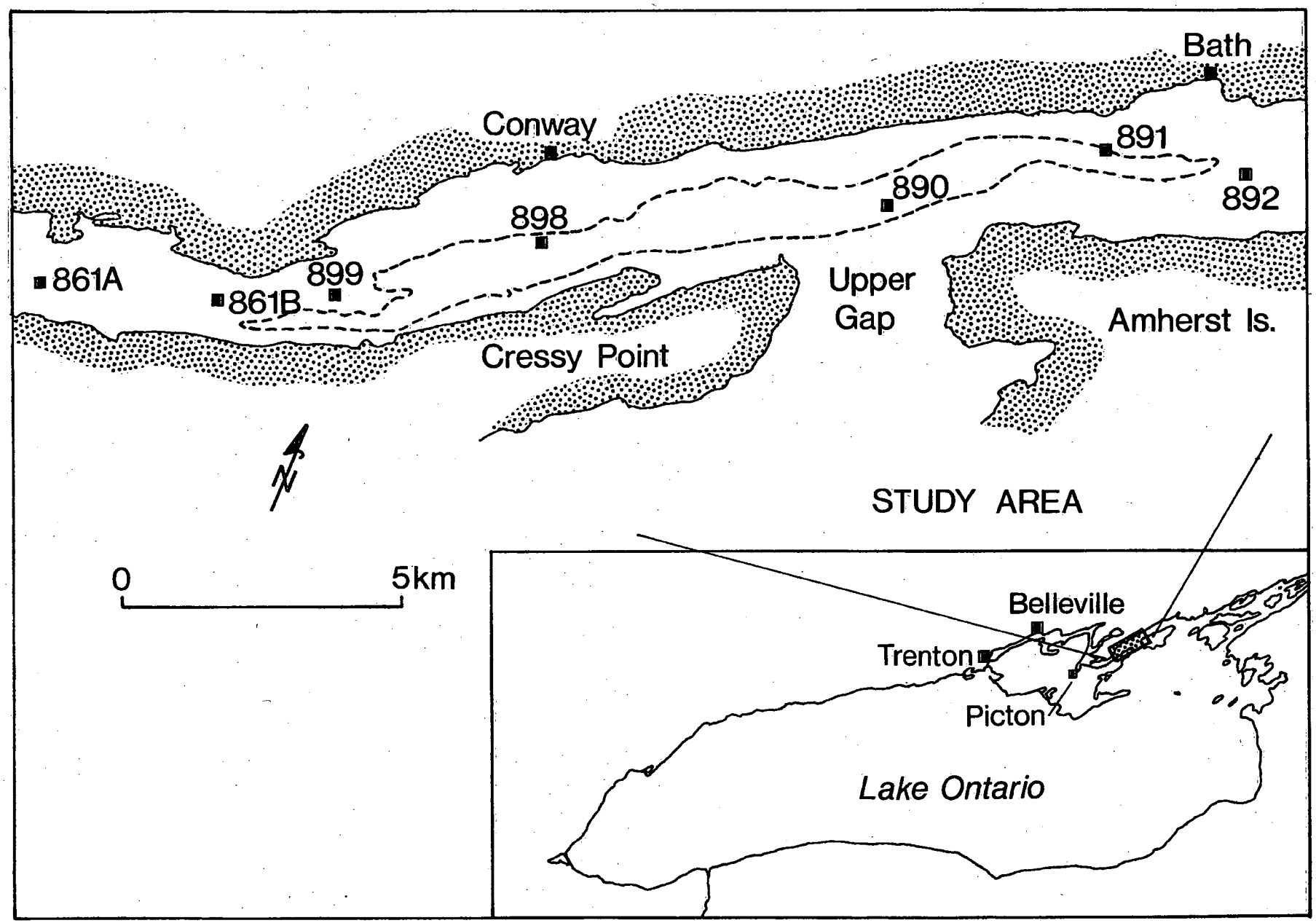
Bath
Conway
891
890
892
898
899
861A
861B
Upper
Gap
Amherst Is.
Cressy Point
STUDY AREA
0
5km
Belleville
Trenton
Picton
Lake Ontario

FIG. 2

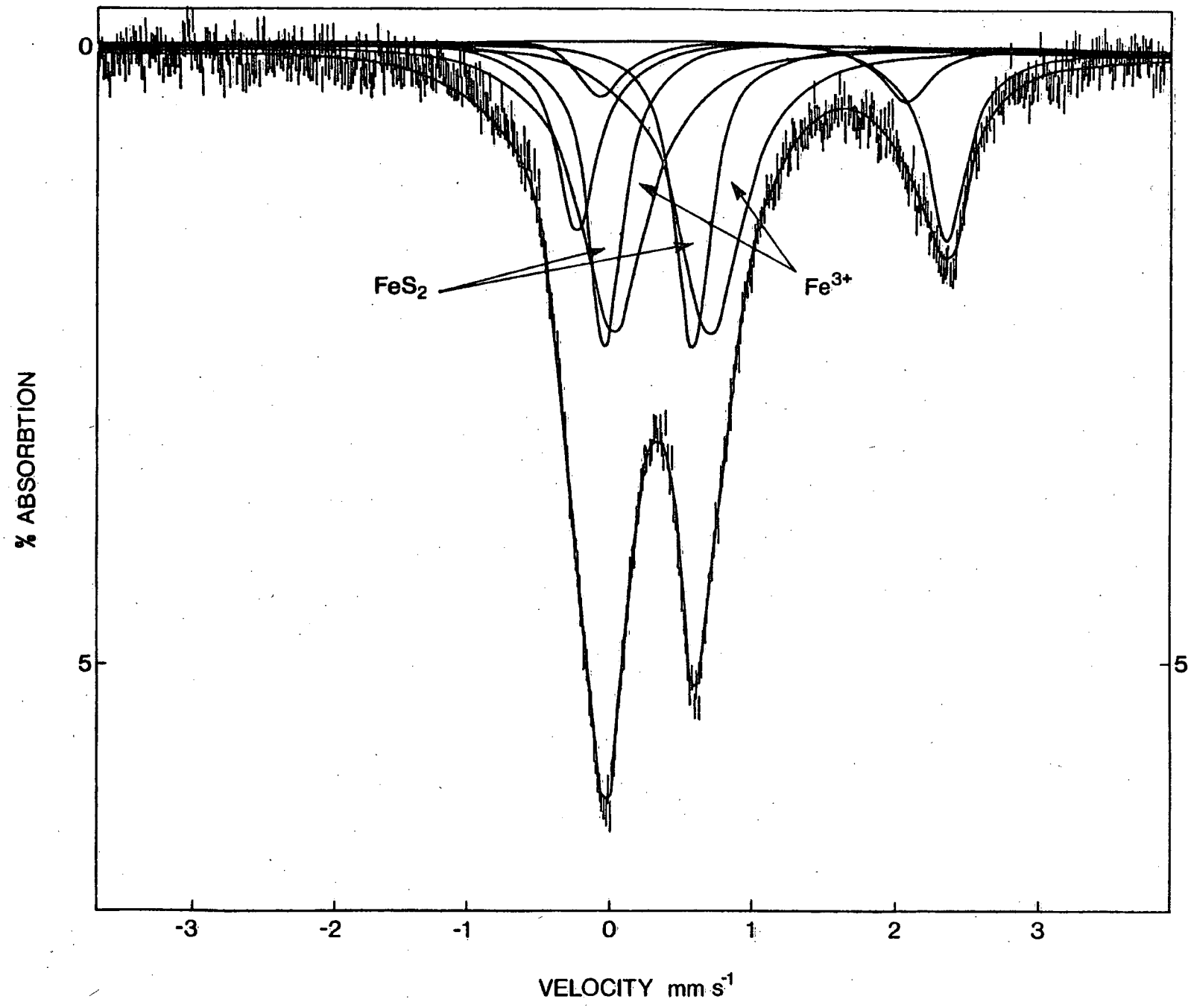

FIG. 3

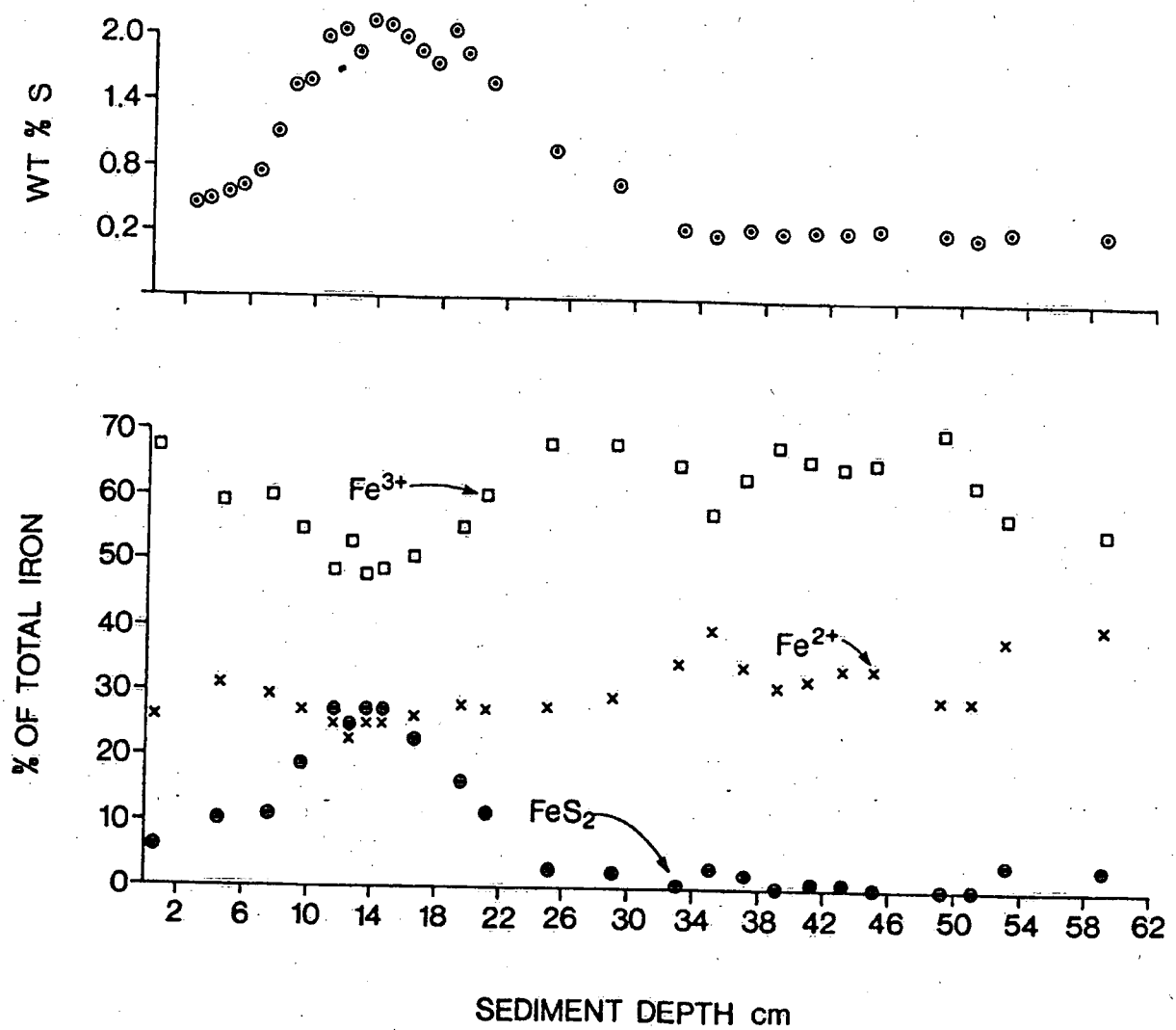
WT % S
2.0
1.4
0.8
0.2
% OF TOTAL IRON
70
60
50
40
30
20
10
0
Fe^{3+}
Fe^{2+}
FeS_2
2
6
10
14
18
22
26
30
34
38
42
46
50
54
58
62
SEDIMENT DEPTH cm

FIG. 8b.

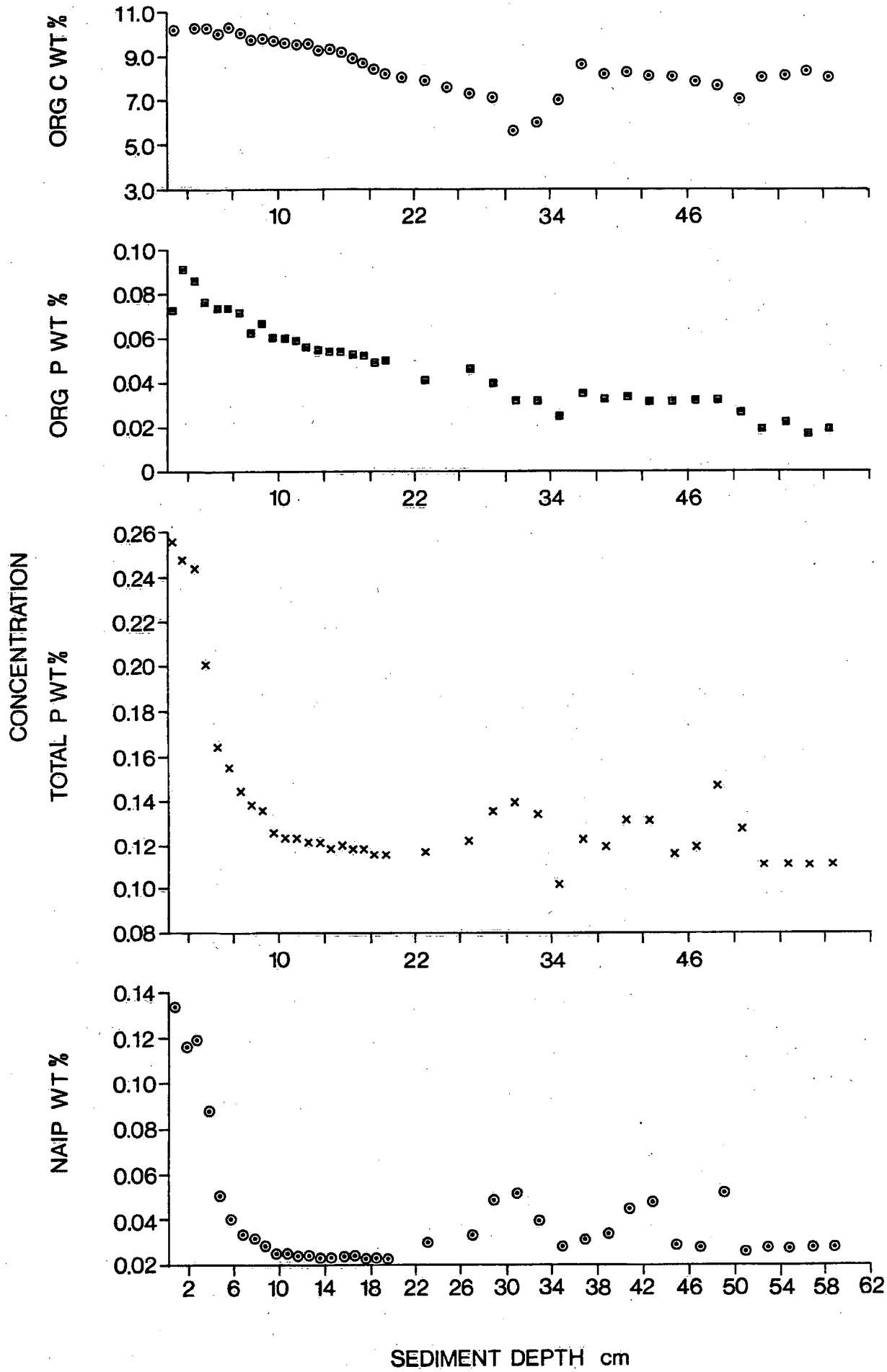
ORG C WT %
11.0
9.0
7.0
5.0
3.0
10
22
34
46
ORG P WT %
0.10
0.08
0.06
0.04
0.02
0
CONCENTRATION
TOTAL P WT%
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
NAIP WT %
0.14
0.12
0.10
0.08
0.06
0.04
0.02
2
6
10
14
18
22
26
30
34
38
42
46
50
54
58
62
SEDIMENT DEPTH cm

FIG. 5

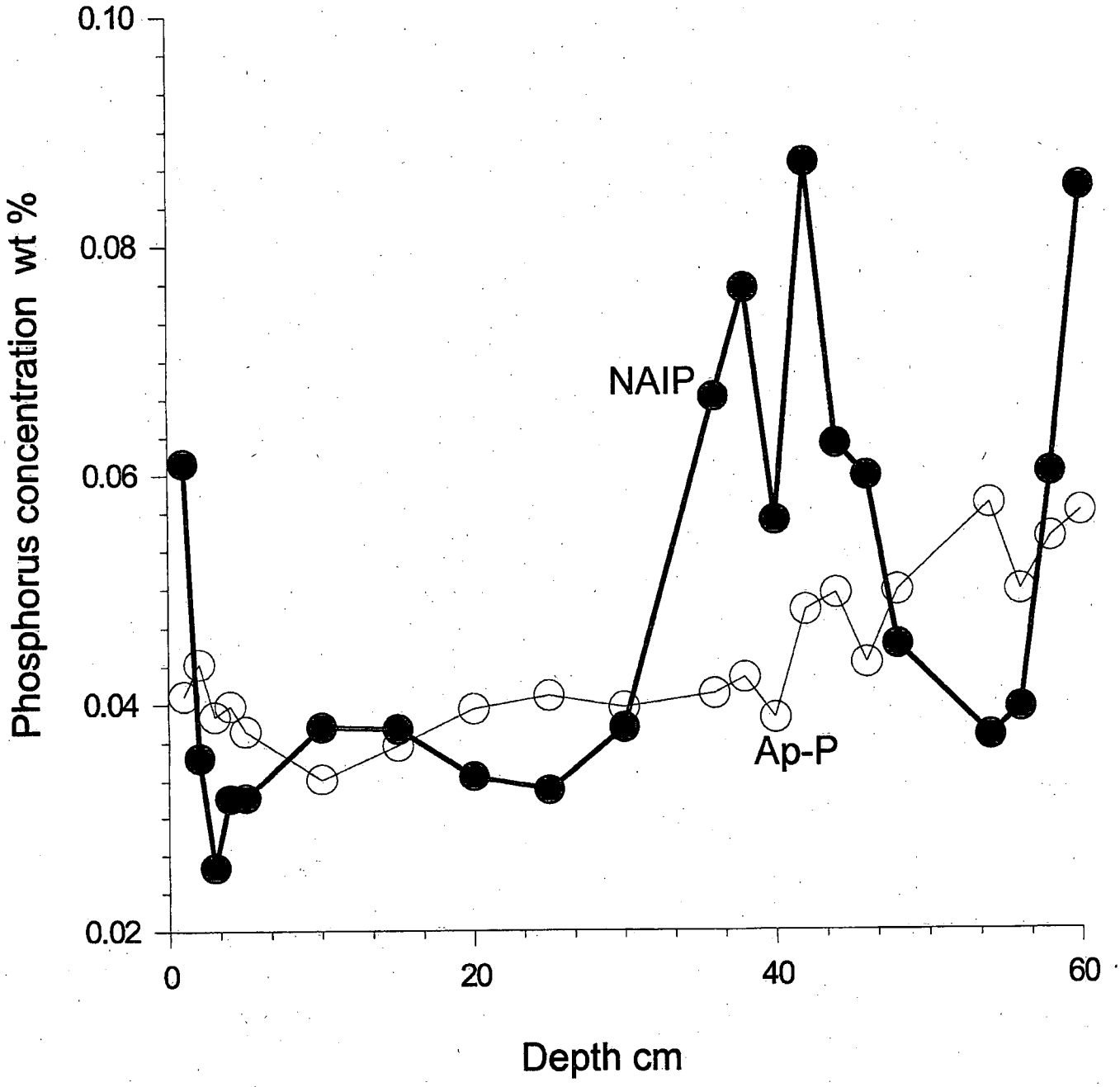
0.10
0.08
0.06
0.04
0.02
Phosphorus concentration wt %
NAIP
Ap-P
0
20
40
60
Depth cm

FIG. 6.

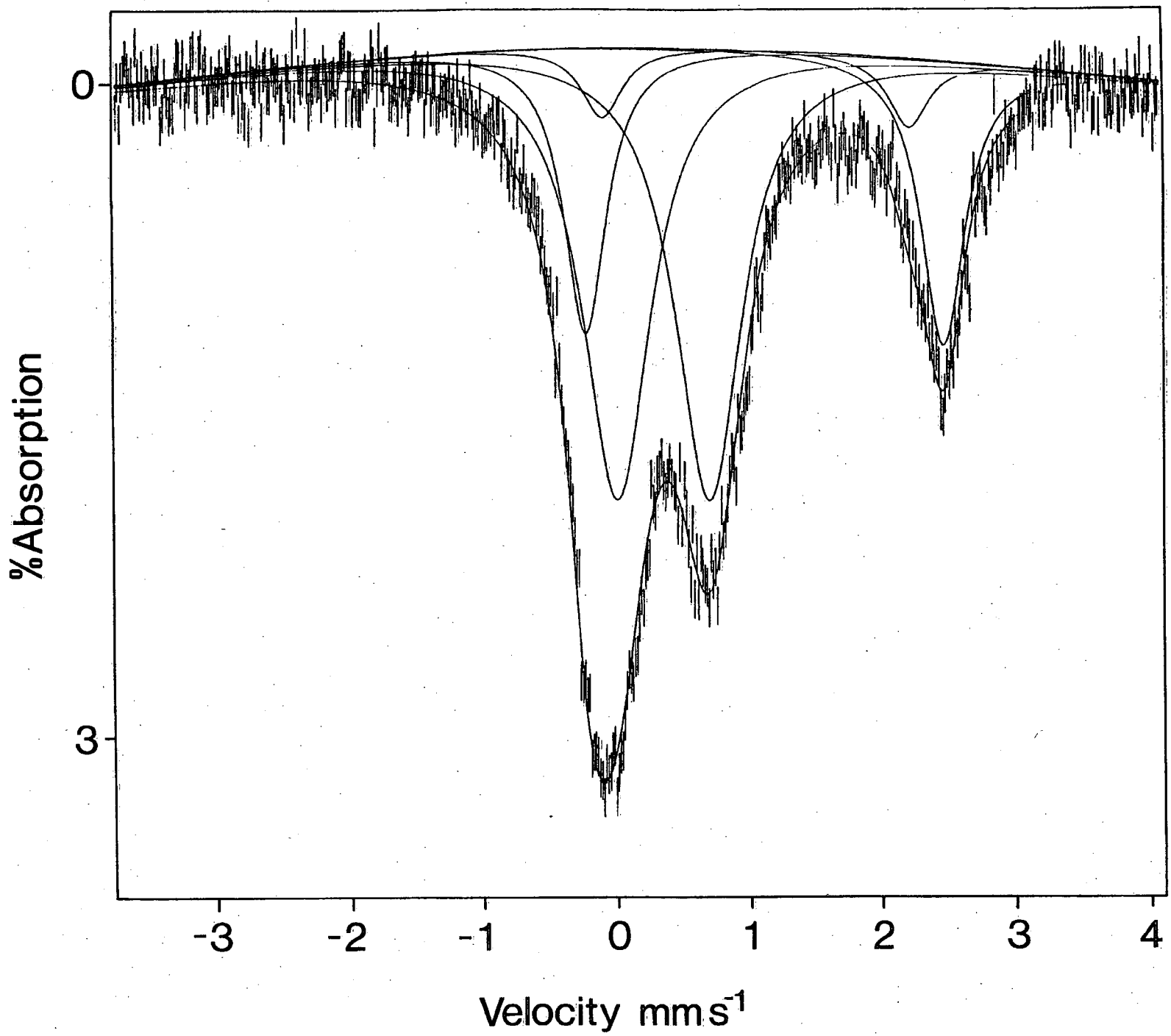

FIG. 7.

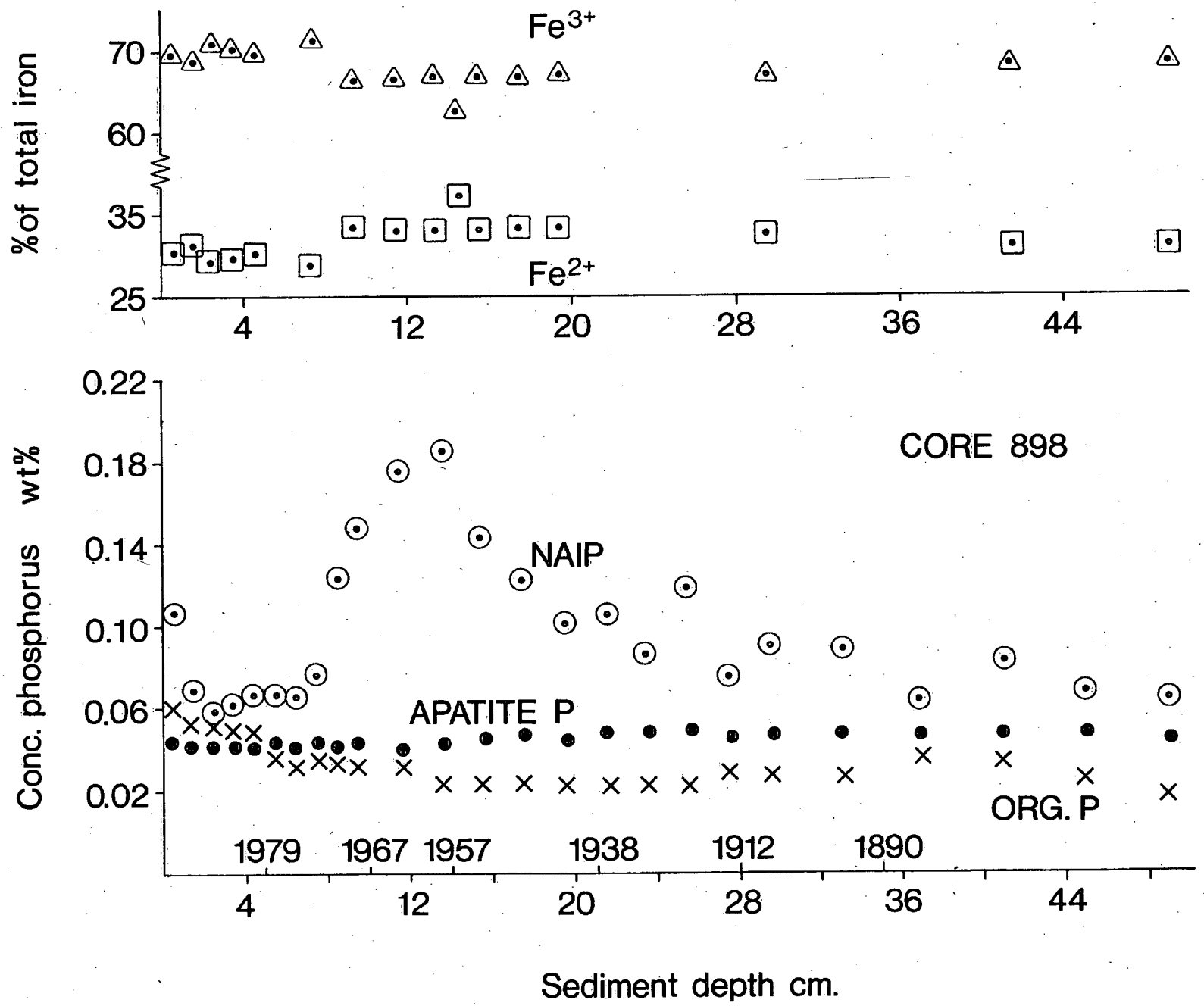
%of total iron
70
60
35
25
Fe3+
Fe2+
4
12
20
28
36
44
Conc. phosphorus wt%
0.22
0.18
0.14
0.10
0.06
0.02
CORE 898
NAIP
APATITE P
ORG. P
1979
1967
1957
1938
1912
1890
Sediment depth cm.

FIG 8

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