DIR-8-92

Cruise Report

ALPHA-HELIX Cruise

(20/08/91 - 26/08/91)

Forschungsstelle Meerestechnik
Institute for Applied Physics

Christian-Albrechts-Universität zu Kiel,Germany

Contents

1. Participants from Kiel: Urban Keussen, Rüdiger Thomas

2. Time schedule (for the Kiel participants)

15.08.91 (Thu)	departure Kiel, arrival Honolulu
19.08.91 (Mon)	first meeting with Vince Peterson, Peter Gorham, Bob Mitiguy; discussion of intended activities; installation of the Kiel equipment on board of ALPHA-HELIX
20.08.91 (Tue)	embarkation; first electrode test in the harbor;
11.30	departure
17.15	start of field measurements
23.30	failure of power supply
21.08.91 (Wed)	
03.00	return to Honolulu
08.30	arrival Honolulu; repair of power supply
12.15	departure
17.00	arrival at test station; start of measurements
21.08.91 -	
26.08.91 (Mon)	measurements according to the appended list (table 1)
08.00	end of measurements; return to Honolulu
14.00	arrival Honolulu; end of cruise
27.08.91 (Tue)	disembarkation
31.08.91 (Sat)	departure from Honolulu to Kiel
02.09.91 (Mon)	arrival Kiel

3. Experimental arrangement

The field experiments on board of RV ALPHA-HELIX were performed to test the behaviour of different electrodes and electrode combinations for the so called "seawater return" in the DUMAND experiment. Therefore the electrodes tested were made from Graphite (23 cm x 24 cm), from platinized Titanium (Platinum 20 cm x 20 cm), and from Iron (St 37 20 cm x 20 cm). The basic concept for the experimental arrangement consisted of one electrode suspended from the ship near the surface at a fixed depth of about 10 m (usually the anode), whereas the other was attached to a 3 conductor cable of about 5000 m length on a winch and was lowered to variable depths. The actual depth was controlled by an acoustic pinger which was attached to the cable just above the electrode.

The schematic wiring diagram for the experiment is shown in Fig. 1. The 2 electrodes at the left side of the figure are supplied with power from the DC-power supply at the right part of Fig. 1 (manually adjustable to about 4 A at 360 V). The applied voltage is measured at the outlet connectors of the power supply by an hand held digital multi-meter ("voltage"). The current in the circuit is measured by a high precision digital Hp-Multimeter 3478A ("current"; range with shunt resistor to 50 A). In order to avoid undefined cable resistances the voltage applied to the electrodes is measured directly at the electrodes, for the near surface one by an additional cable ("sense"), for the lowered electrode by using 2 of the 3 conductors of the cable in parallel for supplying power (2 x 180 ohm in parallel: cable resistance therefore 90 ohm) and the 3. for measuring the voltage ("power", "sense"). For the voltage measurement again an Hp-Multimeter 3478A is used. Both Hp-Multimeter are connected via IEEE-bus with a laptop computer ("Computer"). Therefore all measured data can be recorded automatically at well defined time intervalls and stored on floppy disks.

For the examination of I/U-relations of different electrode combinations the current was varied from 0.5 A to 4.0 A in steps of 0.5 A ("Characteristic" in table 1). The readings were taken 20 - 30 seconds after the new current setting had been applied when the electrodes had adjusted to the new current value and the instrument readings had become stable. For continuous measurements the data were taken at time intervalls of 5 minutes.

4. Results

A total of 32 different sets of data has been produced during the cruise (see table 1). Of these 13 were collected with Graphite-Graphite electrodes, 8 with Platinum-Platinum, 8 with Iron-Iron and 3 with Iron-Graphite combinations. 26 experiments were aimed at the current/voltage relation of the electrodes at varying depths (100 m, 1000 m, 2000 m, 3000 m, 4300 m), 4 experiments were performed to test the time dependent behaviour of the electrodes at constant current conditions (3.5 A) for time periods of 12 to 36 hours. 2 experiments finally were done with Graphite-Graphite electrodes and reversed polarity (cathode as top electrode, cathode as bottom electrode).

A selection of representative data is shown in Fig. 2 - 11. As can be seen from Fig. 2 - 4 the current/voltage-relations are very similar qualitatively for the three different electrode materials Graphite, Platinum and Iron. If inspected quantitatively certain differences in the measured data become obvious. The different electrode materials require different voltages for the same current, between 5.3 and 6.2 V for Graphite, 4.5 and 5.3 V for Platinum and 2.7 and 3.3 V for Iron, depending on the depth of the lowered electrode. Further there are significant differences in the voltage values for all three materials between the required voltage at 100 m depth and the voltages at the other depths.

Whereas the first difference is due to electrochemistry (different voltages of electrolytic disintegration of seawater with different electrode materials) the second can be interpreted by the considerable higher temperatures in the surface layer of the ocean and therefore by the higher specific electric conductivity of warm ocean water in comparison with cold one in greater depth.

The material based differences in the electrode behaviour are compared in Fig. 5, where the I/U-relation for 4 different electrode combinations (Graphite-Graphite, Platinum-Platinum, Iron-Iron, Iron-Graphite) are presented at the depth of 4300 m. Especially at maximum current (4.0 A) Iron electrodes required by far the lowest voltage (3.30 V), the voltage for Platinum electrodes is considerable higher (5.10 V), the highest voltage is needed for Graphite electrodes (6.00 V). The combination Iron(cathode)-Graphite(anode) requires about 300 mV less (5.70 V) than the Graphite-Graphite combination, due to a somewhat more favourable reaction of Iron in seawater with regard to electrolytic Hydrogen development.

In Fig. 6 the resistance of the seawater return between two Platinum electrodes is plotted versus the depth of the lowered cathode with the current as parameter. Though there is no significant dependence with depth or with the distance between the electrodes two facts in this plot should shortly be touched upon.

Firstly, the resistance of the seawater return is not constant but depends on the current (or the applied voltage) in the system. This somewhat peculiar observation is due to the non ohmic nature of a second class or electrolytic conductor like seawater between two Platinum electrodes (Tafel plot). Only at voltages higher than necessary for the electrolytic decomposition of seawater noticeable charge transfer at the electrodes happens and an ohmic current/voltage relation can be observed. Therefore the apparent resistance is high at low currents just above the voltage of disintegration, but becomes smaller with stronger currents at voltages significantly above the disintegration potential.

Secondly, the relatively strongest change in resistance with depth, if at all, seems to happen between 100 m and 1000 m. This observation is shown more clearly in Fig. 7, where the change in resistance for the electrode combination Platinum-Platinum at a current of 3.5 A has been plotted with more sensitive scale and suppressed zero point on the ordinate. As can be seen from the figure the resistance is increased from 1.23 ohm at 100 m to 1.38 ohm at 1000 m. At 4300 m the resistance is 1.425 ohm. As has been discussed already above the increase in resistance from 100 m depth to 1000 m is due to the correspondent decrease in water temperature from about 25 °C to 6-8 °C, which is of diminishing influence on the specific conductivity of seawter. The slight increase between 1000 m and 4300 m might be caused by the influence of increasing hydrostatic pressure on the electrolytic development of Hydrogen at the cathode.

In Fig. 8 - 11 finally the results of the 4 experiments for the time dependent behaviour of the 4 different electrode combinations are shown, lasting for about 15 hours (Graphite-Graphite; Fig. 8), 14 hours (Platinum-Platinum; Fig. 9), 19 hours (Iron-Iron; Fig. 10) and 34 hours (Iron-Graphite; Fig. 11). All experiments were performed at 4300 m depth with a current of 3.5 A. As can be seen from the graphs the time dependent changes in resistance of the 4 systems are limited to a few hundreds of one ohm and do not show any systematic variation with time.

5. Discussion and conclusions

From the presented results of the ALPHA-HELIX cruise in August 1991 it can be deduced that a variety of different electrode materials can be used for a seawater return in the DUMAND experiment. The 4 electrode combinations tested during the cruise, Graphite-Graphite, Platinum-Platinum (as platinized Titanium), Iron-Iron and Iron-Graphite (Iron as cathode), do not differ in their behaviour more than can be expected because of well known characteristic properties of the elements.

In contrary to metallic conductors, where with constant cross section the resistance varies proportional to the length of the conductor, the resistance of the seawater return does not depend on the distance between the electrodes. Small variations in resistance which have been observed during the lowering of one electrode (usually the cathode) from the vessel are based on corresponding variation in the state of seawater.

Of value for the design of electrodes for a seawater return is the current density which can be realized with an operational system. The active surfaces of the tested Platinum and Iron electrodes with dimensions of 20 cm x 20 cm were 800 cm^2 whereas the Graphite electrodes with dimensions 23 cm x 24 cm were exposed to the water only with one active surface of 550 cm^2. At maximum current of 4.0 A the current density for the tested electrode combinations therefore ranged from 5 - 7 mA/cm^2.

The absolute value of resistance of the seawater return depends on the current/voltage relation at the working point of the system and on the geometrical size of the electrodes. As has been shown in the evaluation of the measured data a total resistance for the seawater return of about 1 ohm can be realized with Platinum electrodes of 20 cm x 20 cm.

If a current of 25 A is to be transfered through the seawater return in the DUMAND design with a current density of about 5 mA/cm^2, Platinum electrodes of 20 cm x 100 cm will do with a slightly increased operating voltage at the electrodes of about 6.8 V and a current rating of 5.0 A (extrapolated data from Fig. 3). The resistance of the seawater return with these working data amounts to 1.36 ohm, resistance and voltage drop are therefore nearly neglegible in comparison with the corresponding cable data. If for mechanical reasons the electrodes, especially the cathode at 4500 m depth, should be smaller in size, 20 cm x 50 cm for instance, the current density has to be increased to 12.5

In concluding a few facts should be presented to the topic seawater electrolysis and electrode reactions. At the cathode Hydrogen-ions H^+ from the water are reduced to gaseous Hydrogen which because of the hydrostatic pressure at 4500 m depth stays in solution. At the anode the corresponding reactions are the development of gaseous Oxygen from OH^--ions and gaseous Chlorine from Cl^--ions. Chlorine gas because of its chemistry in water and the buffer action of seawater is not stable in seawater but is disproportioned into Chloride and Hypochlorite according to

$$Cl_2 + H_2O \; = \; HCl + HOCl$$

Hypochlorite again is disintegrated, especially with the additional action of light, into Chloride and Oxygen according to

$$2\,HOCL \; = 2\,HCl + \; O_2$$

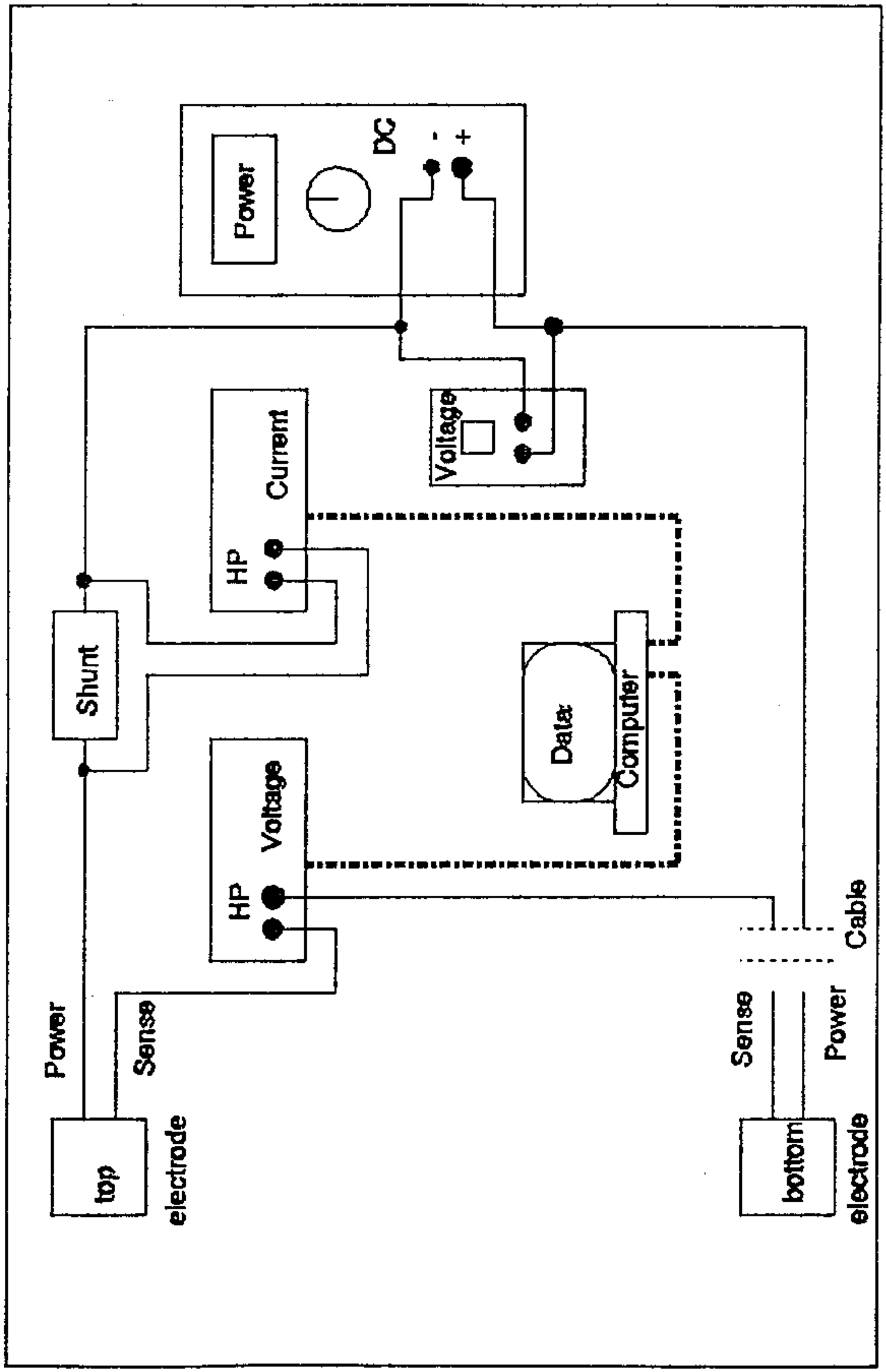
Therefor the overall balance of the anode reaction is the electrolytic development od Oxygen. The transfer of charge by the installation of a seawater return is performed via the disintegration of water into Hydrogen and Oxygen as electron exchange processes at the electrodes.

<u>Alpha Helix Cruise</u>

<u>Measurements:</u> (Cathode at the bottom)

	cathode - anode			
20.8.	Graphite-Graphite	100 m	4 A - 0.5 A	Characteristic
20.8.	Graphite-Graphite	4300m	4 A - 0.5 A	Characteristic
20.8.	measurement using 4 A at 4300m, power failure after 1 hour			
21.8.	Graphite-Graphite	100m	4 A - 0.5 A	Characteristic
21.8.	Graphite-Graphite	4300m	4 A - 0.5 A	Characteristic
21.8.-22.8.	Graphite-Graphite	4300m	3.5 A	12 hrs
22.8.	Graphite-Graphite	4300m	3.5 A	Cathode top (1.5 hrs)
22.8.	Graphite-Graphite	4300m	3.5 A	Cathode bottom (1 hrs)
22.8.	Graphite-Graphite	4300m	4 A - 0.5 A	Characteristic
22.8.	Graphite-Graphite	3000m	4 A - 0.5 A	Characteristic
22.8.	Graphite-Graphite	2000m	4 A - 0.5 A	Characteristic
22.8.	Graphite-Graphite	1000m	4 A - 0.5 A	Characteristic
22.8.	Graphite-Graphite	100m	4 A - 0.5 A	Characteristic
22.8.	Platinum-Platinum	100m	4 A - 0.5 A	Characteristic
22.8.	Platinum-Platinum	4300m	4 A - 0.5 A	Characteristic
22.8.-23.8.	Platinum-Platinum	4300m	3.5 A	15 hrs
23.8.	Platinum-Platinum	4300m	4 A - 0.5 A	Characteristic
23.8.	Platinum-Platinum	3000m	4 A - 0.5 A	Characteristic
23.8.	Platinum-Platinum	2000m	4 A - 0.5 A	Characteristic
23.8.	Platinum-Platinum	1000m	4 A - 0.5 A	Characteristic
23.8.	Platinum-Platinum	100m	4 A - 0.5 A	Characteristic
23.8.	Iron-Iron	100m	4 A - 0.5 A	Characteristic
23.8.	Iron-Iron	4300m	4 A - 0.5 A	Characteristic
23.8.-24.8.	Iron-Iron	4300m	3.5 A	17 hrs
24.8.	Iron-Iron	4300m	4 A - 0.5 A	Characteristic
24.8.	Iron-Iron	3000m	4 A - 0.5 A	Characteristic
24.8.	Iron-Iron	2000m	4 A - 0.5 A	Characteristic
24.8.	Iron-Iron	1000m	4 A - 0.5 A	Characteristic
24.8.	Iron-Iron	100m	4 A - 0.5 A	Characteristic
24.8.	Iron-Graphite	100m	4 A - 0.5 A	Characteristic
24.8.	Iron-Graphite	4300m	4 A - 0.5 A	Characteristic
24.8.-26.8.	Iron-Graphite	4300m	3.5 A	36 hrs

<u>Table 1</u>



Power
DC
-
+
Voltage
Current
HP
Shunt
Data
Computer
Voltage
HP
Cable
Power
Sense
Sense
Power
top
electrode
bottom
electrode

Figure 1

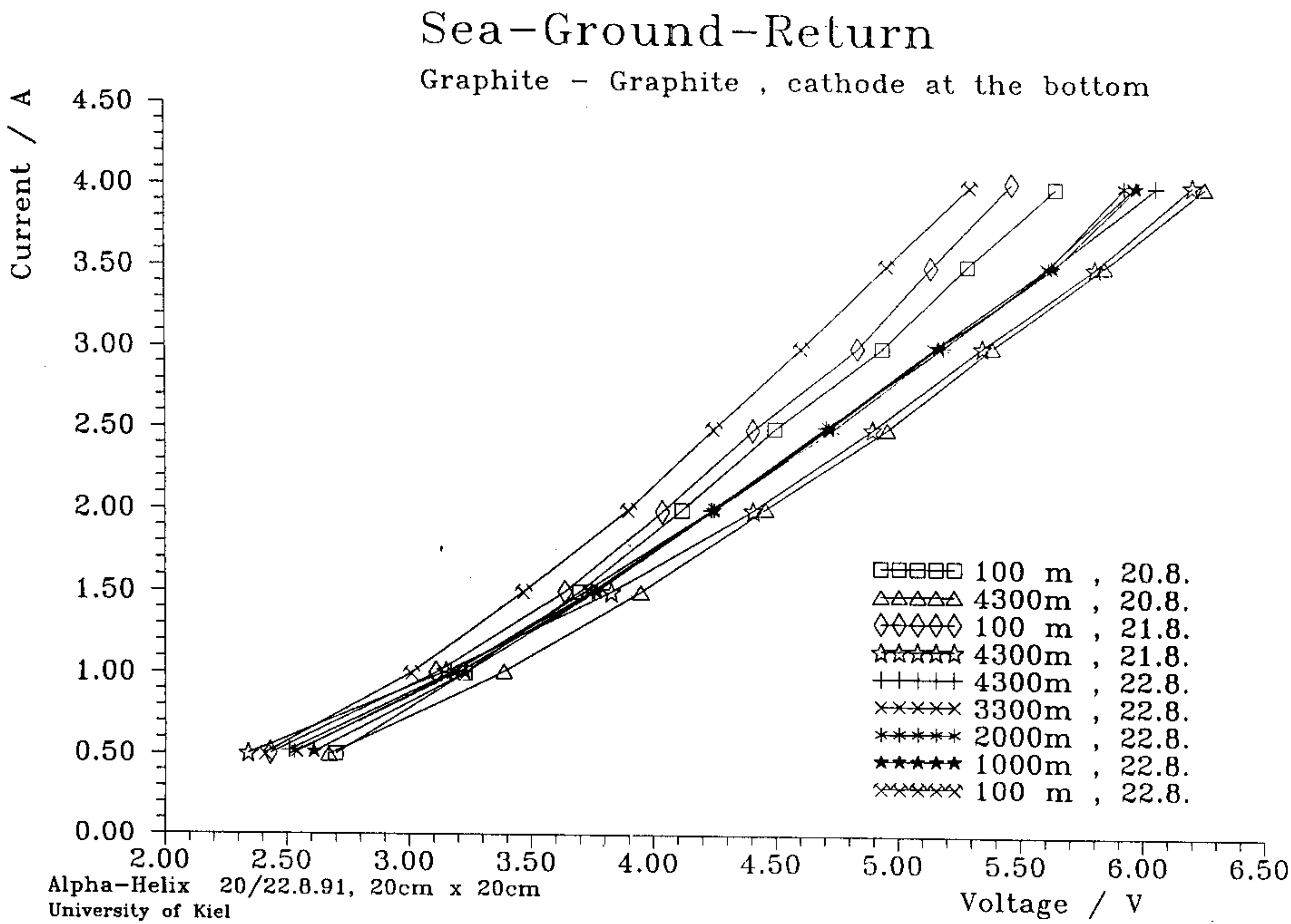

Sea-Ground-Return
Graphite - Graphite , cathode at the bottom
Current / A
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
Voltage / V
100 m , 20.8.
4300m , 20.8.
100 m , 21.8.
4300m , 21.8.
4300m , 22.8.
3300m , 22.8.
2000m , 22.8.
1000m , 22.8.
100 m , 22.8.
Alpha-Helix 20/22.8.91, 20cm x 20cm
University of Kiel

Figure 2

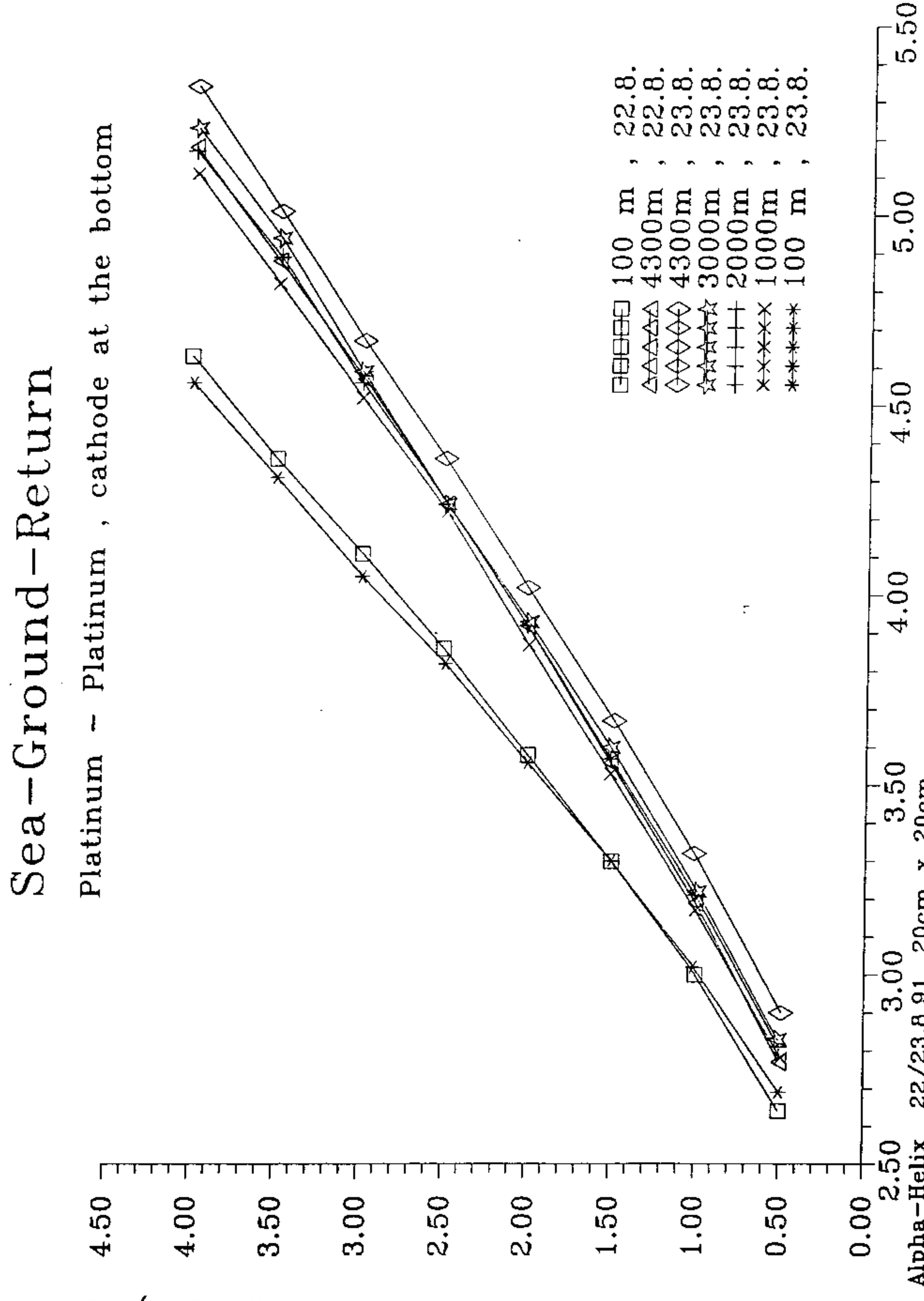

Sea-Ground-Return
Platinum - Platinum , cathode at the bottom
100 m , 22.8.
4300m , 22.8.
4300m , 23.8.
3000m , 23.8.
2000m , 23.8.
1000m , 23.8.
100 m , 23.8.
Current / A
Voltage / V
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
Alpha-Helix 22/23.8.91, 20cm x 20cm
University of Kiel

Figure 3

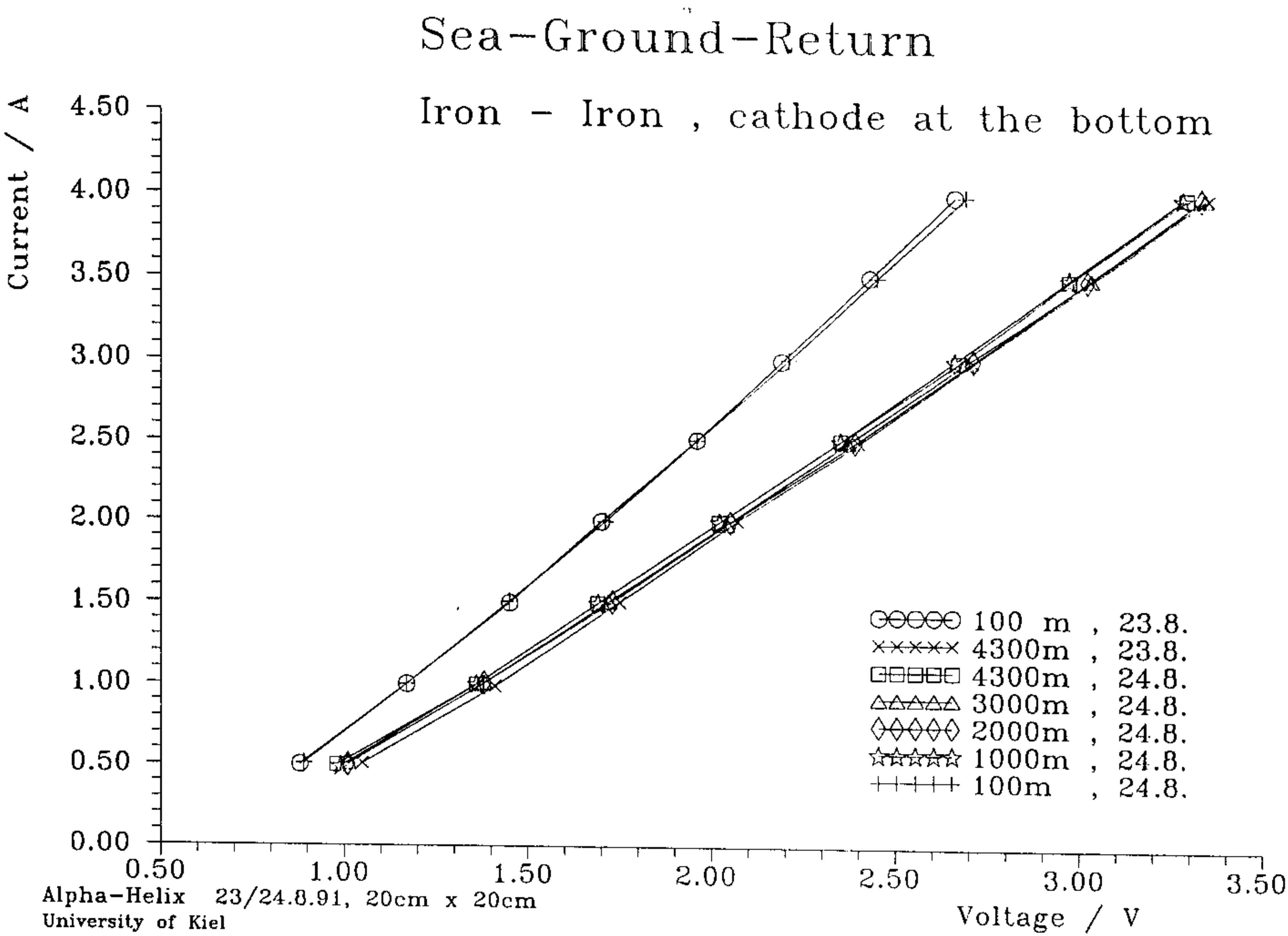
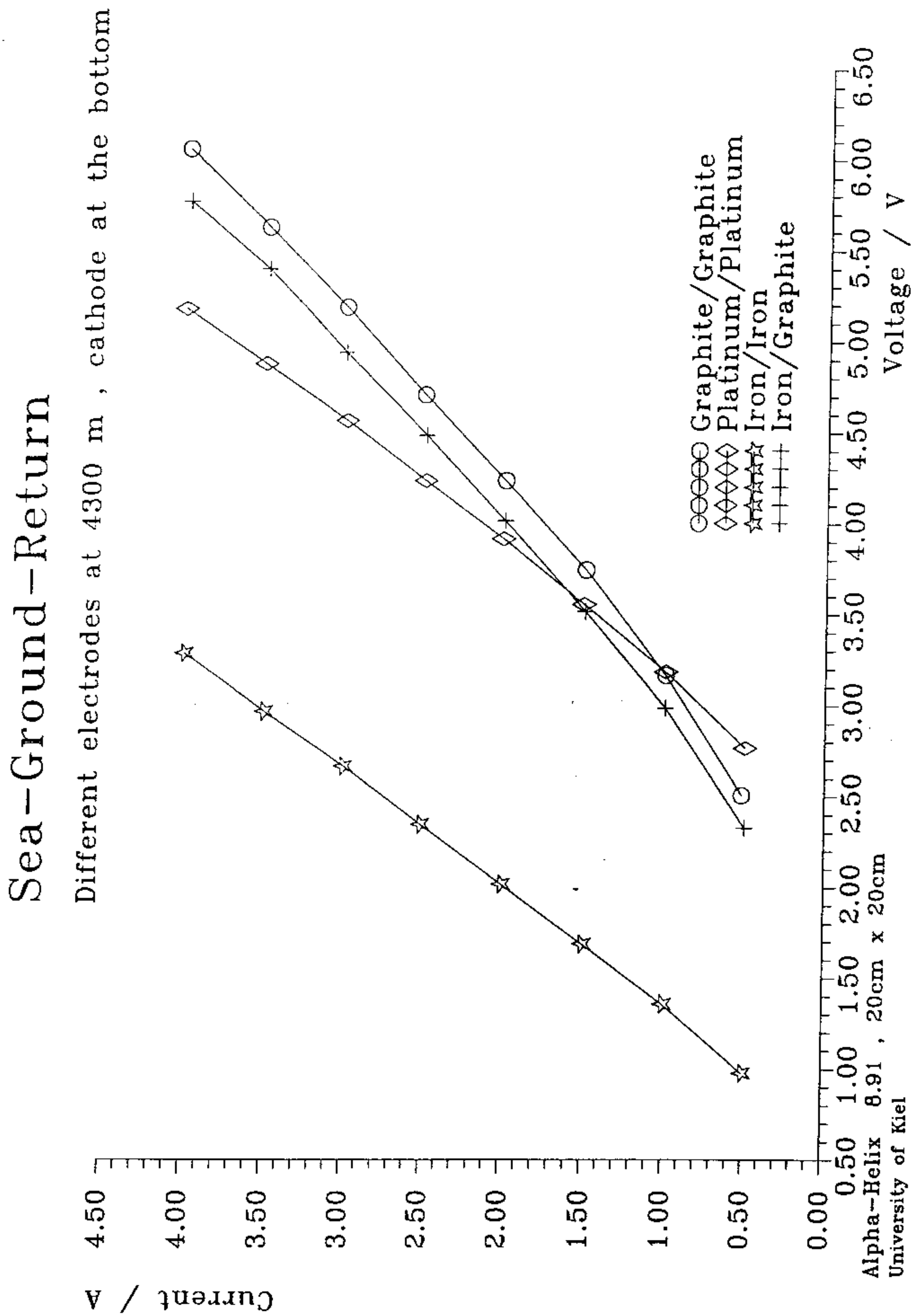

Sea-Ground-Return
Iron - Iron , cathode at the bottom
Current / A
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
Voltage / V
100 m , 23.8.
4300m , 23.8.
4300m , 24.8.
3000m , 24.8.
2000m , 24.8.
1000m , 24.8.
100m , 24.8.
Alpha-Helix 23/24.8.91, 20cm x 20cm
University of Kiel

Figure 4



Sea-Ground-Return
Different electrodes at 4300 m , cathode at the bottom
Current / A
Voltage / V
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
Graphite/Graphite
Platinum/Platinum
Iron/Iron
Iron/Graphite
Alpha-Helix 8.91 , 20cm x 20cm
University of Kiel

Figure 5

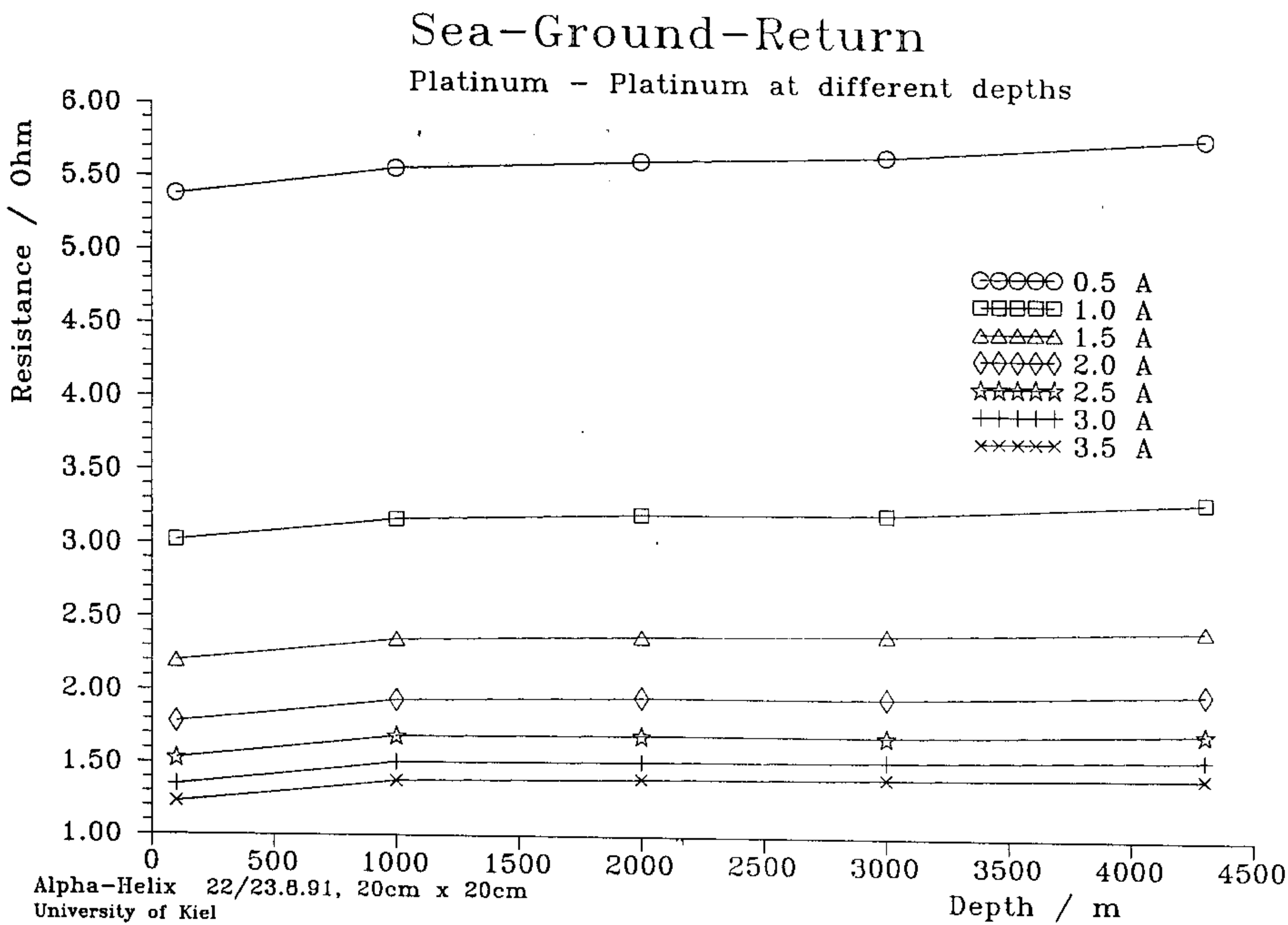

Sea-Ground-Return
Platinum - Platinum at different depths
Resistance / Ohm
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Depth / m
0.5 A
1.0 A
1.5 A
2.0 A
2.5 A
3.0 A
3.5 A
Alpha-Helix 22/23.8.91, 20cm x 20cm
University of Kiel

Figure 6

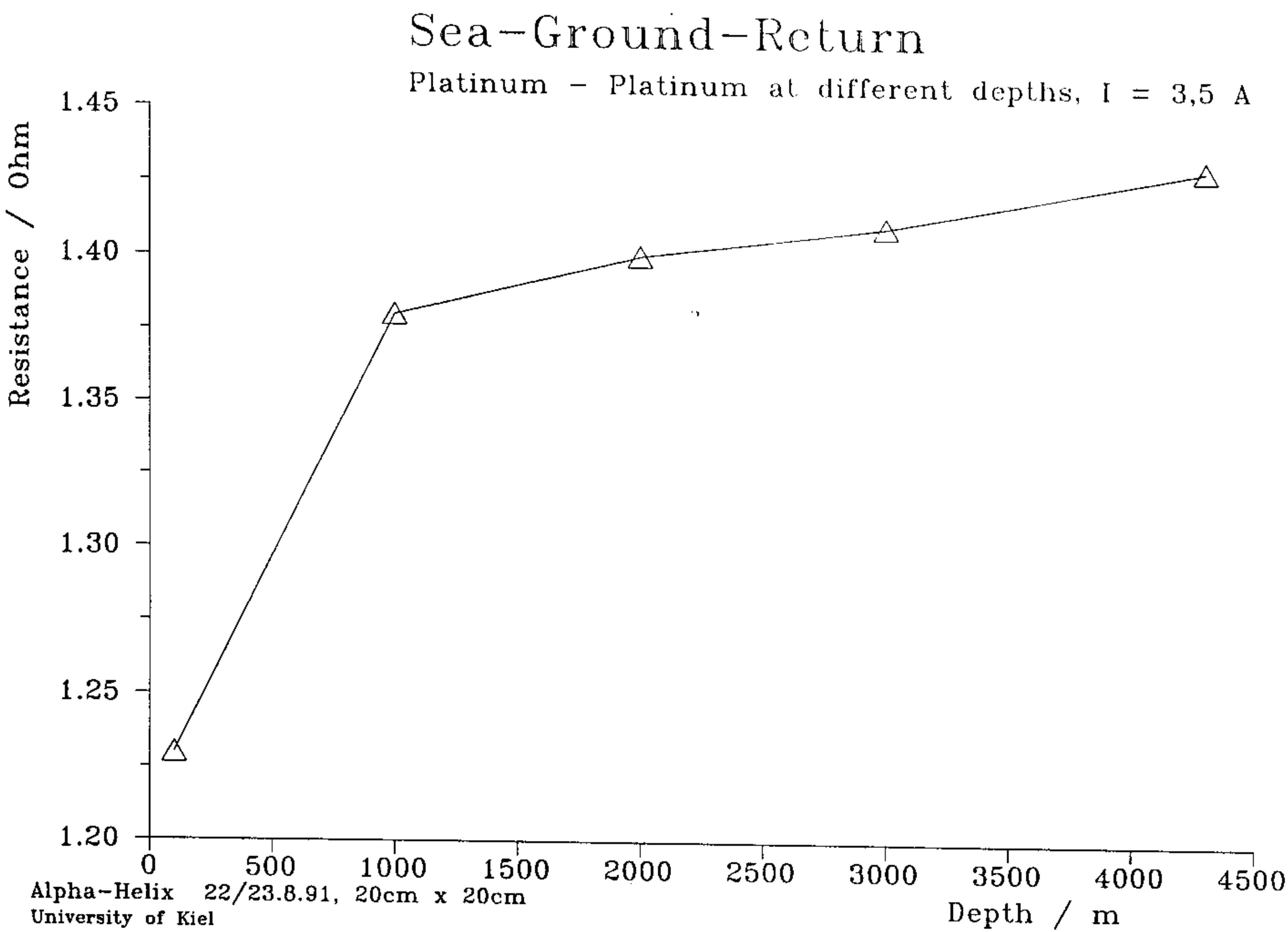

Sea-Ground-Return
Platinum - Platinum at different depths, I = 3,5 A
Resistance / Ohm
1.45
1.40
1.35
1.30
1.25
1.20
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Depth / m
Alpha-Helix 22/23.8.91, 20cm x 20cm
University of Kiel

Figure 7

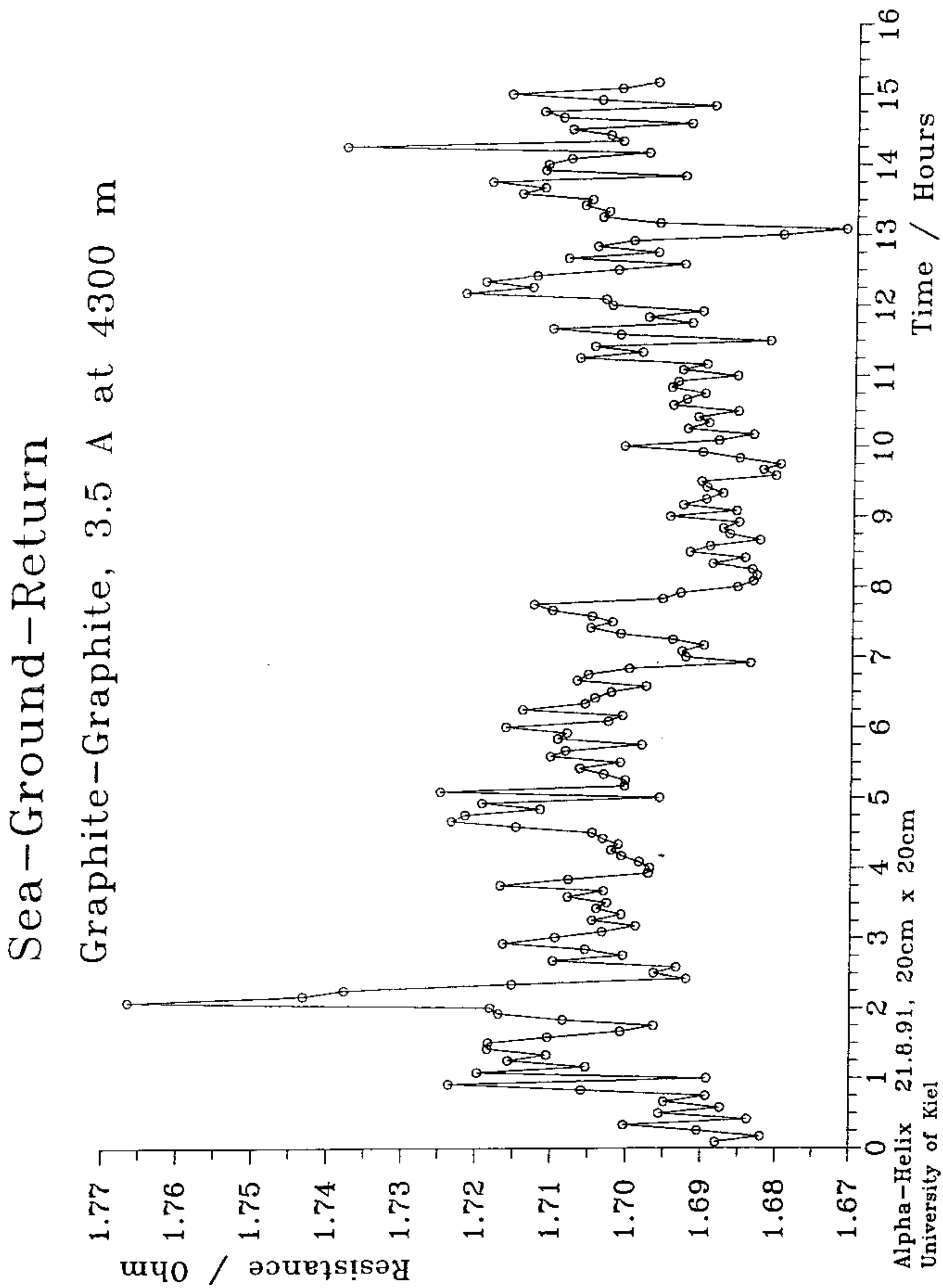
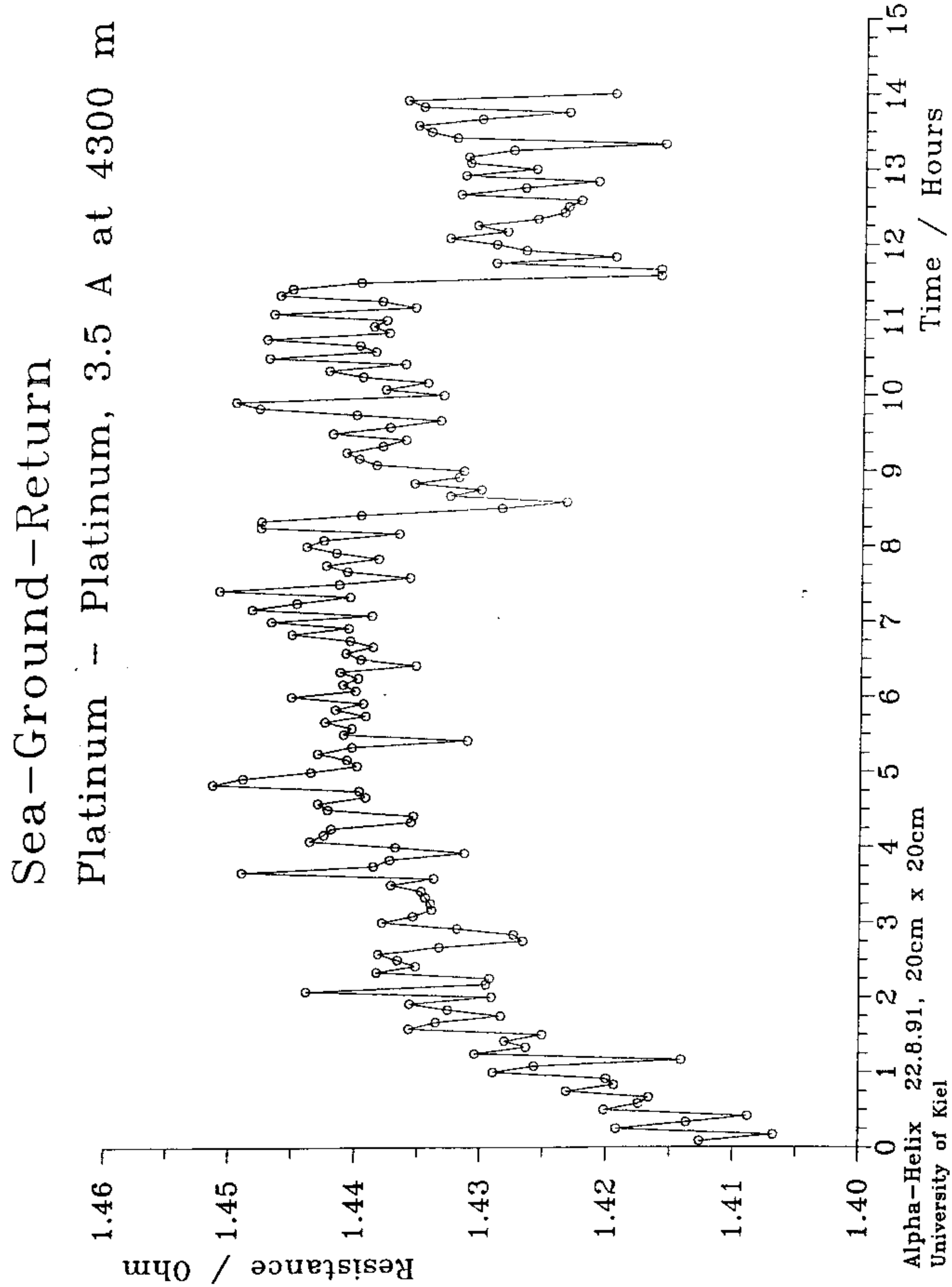

Sea-Ground-Return
Graphite-Graphite, 3.5 A at 4300 m
Resistance / Ohm
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.67
Time / Hours
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Alpha-Helix 21.8.91, 20cm x 20cm
University of Kiel

Figure 8



Sea-Ground-Return
Platinum - Platinum, 3.5 A at 4300 m
Resistance / Ohm
1.40
1.41
1.42
1.43
1.44
1.45
1.46
Time / Hours
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Alpha-Helix 22.8.91, 20cm x 20cm
University of Kiel

Figure 9

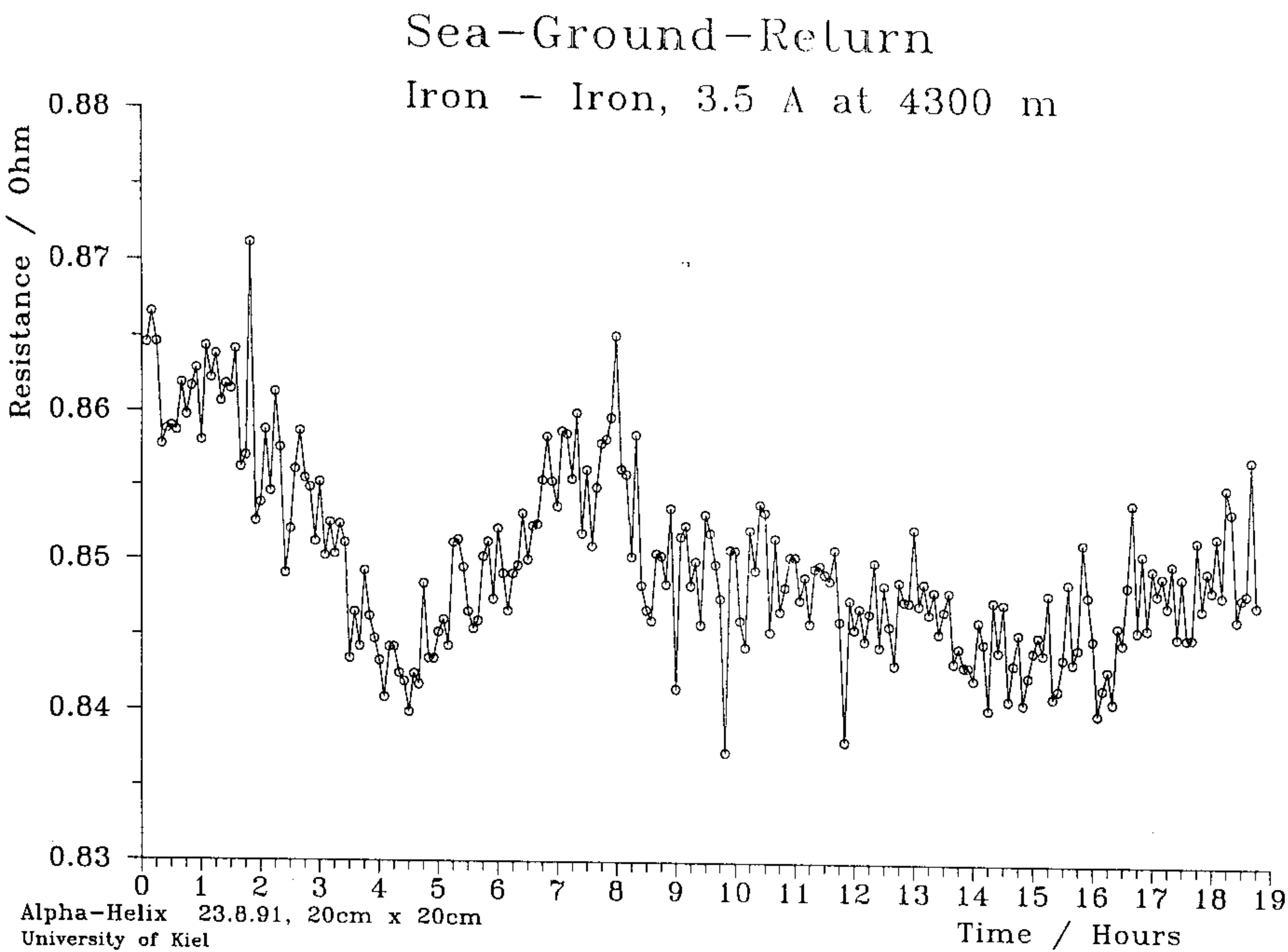
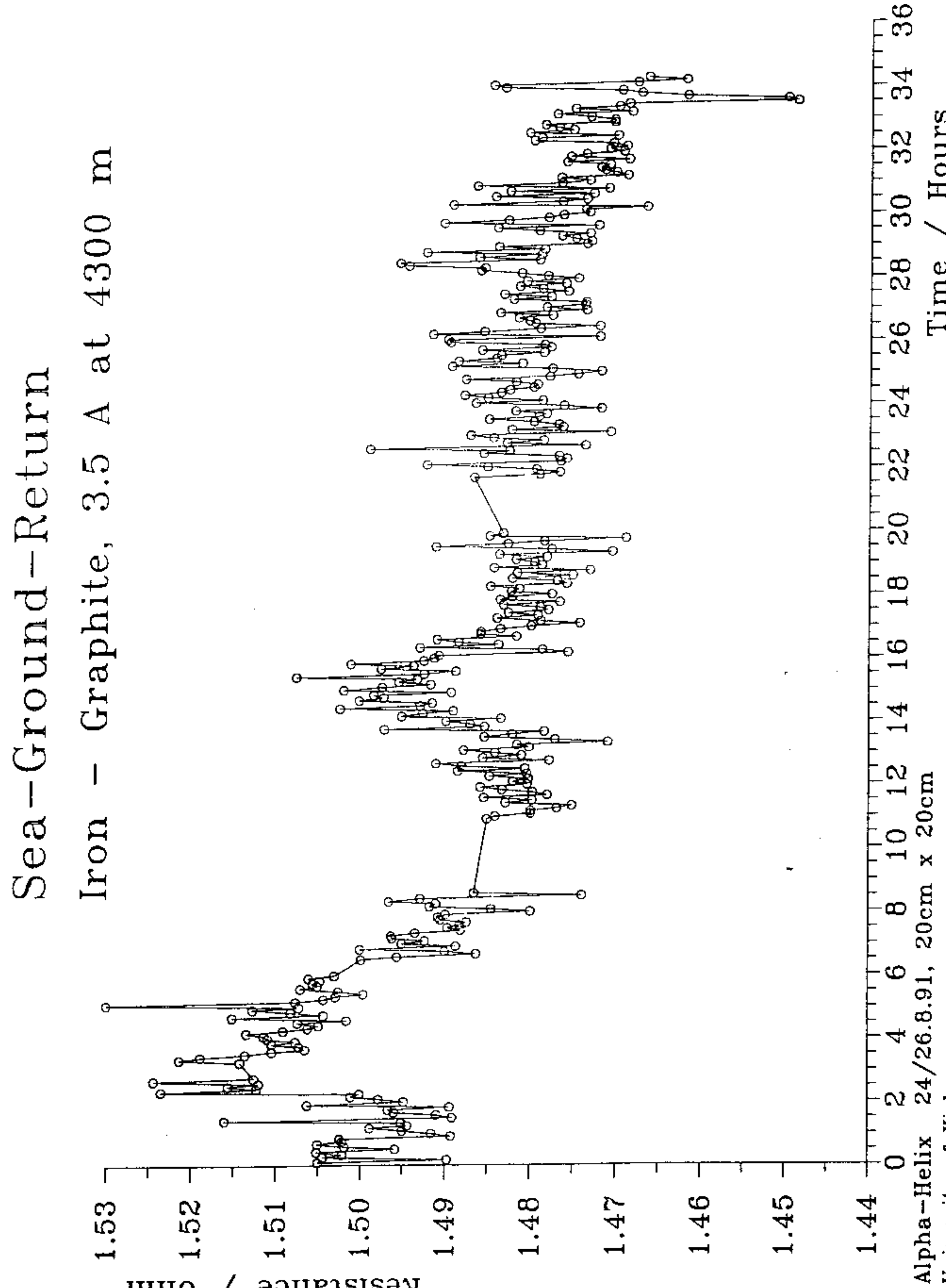

Sea-Ground-Return
Iron - Iron, 3.5 A at 4300 m
Resistance / Ohm
0.88
0.87
0.86
0.85
0.84
0.83
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
Time / Hours
Alpha-Helix 23.8.91, 20cm x 20cm
University of Kiel

Figure 10



Sea-Ground-Return
Iron - Graphite, 3.5 A at 4300 m
Resistance / Ohm
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.44
Time / Hours
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36
Alpha-Helix 24/26.8.91, 20cm x 20cm
University of Kiel

Figure 11