

Chemical composition of the sediment from Lake 20 (Antarctica)

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ABSTRACT

Lake 20 (19,000 m²) is located on the coast of the Ross Sea, in the North-Central part of Victoria Land, and its surface is ice-free between the end of December and early February. Within the framework of the Italian National Research Programme in Antarctica, a study was made of the chemical composition of sediments from the lake, with the intention of using this information to contribute to a better understanding of the processes involved in the long range transport of pollutants and their role in global changes. A sediment core from Lake 20 (Antarctica), 18 cm long, was collected in 1994, sliced into 2 cm sections and analysed using X Ray fluorescence spectrometry for 17 elements (Si, Al, Ca, K, Fe, Mg, Ti, S, P, Pb, Zn, Cu, Ni, Mn, Cr, Na, Cl), by CHN Elemental Analyser for C and N, by Flameless Atomic Absorption Spectrometry for As, and by Cold Vapour Atomic Absorption Spectrometry for Hg. The chemical composition of the sediments is consistent with the known geochemical characteristics of the drainage basin. While the chemical analyses reveal that sedimentation in Lake 20 has changed through time, the variations along the core are most probably related to the climatic evolution of the area, to the consequent changes in weathering processes, and possibly to an increase in the primary productivity of the lake, rather than to anthropogenic influences on the biogeochemical cycles of the elements.

Key words: trace elements, sediments, Antarctica

1. INTRODUCTION

The continent of Antarctica may generally be regarded as a cold desert (Heywood 1984), with 98% of the land covered by ice; even in the warmest area, the temperature seldom exceeds 0 °C, and monthly mean temperatures range from - 12 to + 0.5 °C. Few areas of the continent therefore contain inland waters; those which are present were either left after the last glacial retreat, or formed by tectonic-volcanic activities (Heywood 1984).

Nevertheless, the existing lakes and pools are particularly interesting from a physical, chemical, and biological point of view, since they share some peculiar characteristics: well-defined boundaries, limited biodiversity, prolonged isolation from external influences due to the long duration of the ice-cover (Heywood 1984).

For this reason, within the framework of the Italian National Research Programme in Antarctica (started in 1985), the Istituto Italiano di Idrobiologia of the National Research Council has been carrying out a study of lakes in Antarctica (Guilizzoni *et al.* 1991, 1992; Libera 1993), to describe the limnological characteristics of about 60 different waterbodies from these remote areas.

Part of this study involved research on the chemical composition of the sediments from a few lakes, with the intention of using this information to contribute to a better understanding of the processes involved in the long range transport of pollutants and their role in global changes.

This paper reports the results of the inorganic chemical analysis of a sediment core collected in Lake 20,

on the coast of the Ross Sea, in the North-Central part of Victoria Land; it is the largest (19,000 m²) of the investigated lakes in the area of Tarn Flat. It is located in a cryptodepression (-70 m a.s.l.), at 74°58' S latitude and 162°30' E longitude, has a maximum depth of 3.5 m, and is fed by a small glacier (0.3 km²) in the watershed (2 km²; Libera 1993).

Previous studies (Guilizzoni *et al.* 1991, 1992) indicate that the lake surface is ice free between the end of December and early February, and different samples taken during melting time show a marked increase in the ionic content of the lake water (Tabs 1, 2). Furthermore, the water chemistry shows the influence of sea spray, since sodium and chloride are the main ions and the Na/Cl ratio (0.93) is close to the value for sea water (0.86).

2. MATERIAL AND METHODS

The bottom of Lake 20 is covered by a thick algae mat, over a limy sediment with some sand and a low content of vegetal material. No benthic fauna was observed (Guilizzoni *et al.* 1991).

In January 1994, a core 18 cm long was collected in the centre of the lake, at the maximum depth, using a gravity corer. The core was immediately frozen (-30 °C) and taken back to the laboratory in Italy, where it was sliced into 2 cm sections.

A subsample of each section was then dried at 60 °C, homogenised, and analysed by X Ray Fluorescence Spectrometry for 17 elements (Si, Al, Ca, K, Fe, Mg, Ti, S, P, Pb, Zn, Cu, Ni, Mn, Cr, Na, Cl), by CHN Elemental Analyser for C and N, by Flameless Atomic Ab-

sorption Spectrometry for As, and by Cold Vapour Atomic Absorption Spectrometry for Hg.

Tab. 1. Conductivity ($\mu\text{S cm}^{-1}$ 18 °C) and major ions ($\mu\text{eq l}^{-1}$) for Lake 20 at Tarn Flat (Guilizzoni *et al.* 1991, 1992). pH: field measurements; pH (A): pH measurement at ice-melt; pH (B): pH after equilibration with atmospheric CO_2 .

	20/12/88	24/01/89	29/01/89
pH			8.06
pH (A)	9.23	8.20	8.40
pH (B)	7.62	8.20	8.20
Alkalinity	417	1682	1507
Cl^-	902	437	2933
SO_4^{2-}	193	162	541
NO_3^-	2	14	8
NH_4^+	1	0	1
Ca^{++}	344	2445	1158
Mg^{++}	238	510	880
Na^+	978	391	2739
K^+	51	17	125
anions	1515	2295	4989
cations	1613	3364	4903
Conductivity	161	192	473

Tab. 2. Nitrogen, phosphorus and silica concentrations for Lake 20 at Tarn Flat (Guilizzoni *et al.* 1991).

	20/12/88	24/01/89	29/01/89
N-NO_3^- ($\mu\text{g l}^{-1}$)	30	190	107
N-NH_4^+ ($\mu\text{g l}^{-1}$)	9	5	15
Inorg. N (mg l^{-1})	0.04	0.20	0.12
Org. N (mg l^{-1})	0.12	0.00	0.10
Total N (mg l^{-1})	0.16	0.19	0.22
Total P ($\mu\text{g l}^{-1}$)	4	0	5
Si (mg l^{-1})	3.01	1.62	7.60

3. RESULTS AND DISCUSSION

The chemical analysis of the core (Tab. 3) indicates a mean composition very close to that of anorthosite for SiO_2 , CaO , MgO and MnO , and to that of granodiorite for K_2O , TiO_2 and P_2O_5 . These results are consistent with the available information on the lithology of the watershed, which consists mainly of granite, granodiorite, and metamorphic rocks (Carmignani *et al.* 1987; Libera 1993). However, Al_2O_3 is lower than in granodiorite and granite, Fe_2O_3 is higher than in monzonite, and Na_2O is much lower than in any igneous rocks.

In mineralogical terms (D'Argento *et al.* 1994), the sediments can be described as meta-alluminiferous ($\text{Na}_2\text{O} + \text{K}_2\text{O} < \text{Al}_2\text{O}_3 - \text{CaO}$) and alkali - potassic ($\text{K}_2\text{O}/\text{Na}_2\text{O} > 1$); according to the International Union of Geological Sciences classification, in the $\text{SiO}_2 - \text{Na}_2\text{O} + \text{K}_2\text{O}$ diagram they come into the andesite basaltic category.

For trace elements, such a comparison would be meaningless, since the reported composition of rock-forming minerals is highly variable (for instance, according to Salomons & Förstner (1984) in plagioclase the

range for Cu is 8-700 mg kg^{-1} ; for Zn, 1-50; for Pb, 1-70). However, in general the concentrations of trace elements in Lake 20 sediments are similar to or lower than in "lacustrine sediments" (Salomons & Förstner 1984) or soils (Bowen 1979), and could by no means pose a threat for living organisms.

To investigate the possibility of contamination due to human influences, the results were also compared with those reported for other Antarctic lakes.

Aceto *et al.* (1994) looked at the chemical composition of the sediments of Lake Carezza (close to the Italian base, at 74° 43' S latitude, and 164° 03' E longitude), along with that of a soil sample taken from the surrounding area (Tab. 4); they found "a very slight and insignificant difference", concluding that anthropogenic alterations are absent or have very limited effects.

The results from Lake 20 reveal much higher concentrations of Zn, Cu, and possibly Cr, and much lower ones of Pb and Ni. However, the differences indicated by these data alone might be the result of the different geochemical setting.

From the limnological point of view, the chemical elements detected in a sediment core may be classified in 5 different groups (Kemp *et al.* 1976): Conservative elements; Nutrients; Carbonate elements; Mobile elements; Enriched elements.

Conservative elements: major elements, like Si, Al, Ti, Na, K, Mg, Cl, whose content in the sediments is mainly controlled by the geochemical features of the drainage basin. Their concentrations are very high and seldom affected by direct human influence to any noticeable extent. In fact, in the Lake 20 core they are quite constant (Tab. 5), with a minimum in the 2-4 cm section (Al, K, Mg, Ti, Na). However, Si and Cl show a different pattern: the first decreases slightly from section 16-18 cm to section 8-10 cm, stabilises as far as section 2-4 cm, then drops sharply in the topmost layer. Cl shows a marked peak in the 6-8 cm section.

Nutrients: elements like organic C, P and N, necessary for the growth of aquatic plants. Organic carbon was not measured, but both total C and N show a peak at 10-12 cm, then decrease in the 2 to 8 cm part of the core, and increase again in the 0-2 cm section, reaching the same concentration as that measured at the bottom of the core. However, P behaves differently, more like the conservative elements, with a minimum at the 2-4 cm section.

Carbonate elements: carbonate C, Ca and the part of Mg not due to silicates, deriving from the weathering of carbonates in the watershed, or authigenically produced within the waterbody. Since in this study only total carbon was measured (see nutrients), and since Mg behaves like the other conservative elements, the trend for this group of elements can be described only by referring to Ca. This element shows an increase from the bottom to the top of the core, with a marked peak only in the topmost section.

Tab. 3. Chemical analysis (dry weight) of the core and reference values after Le Maitre (1976)⁽¹⁾, Bowen (1979)⁽²⁾, and Salomons & Förstner (1984)⁽³⁾.

	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	MnO	Cl	S	C	N
Core Mean %	51.06	12.18	12.94	2.94	6.52	2.27	0.51	0.16	1.13	0.06	0.13	<0.05	7.36	1.75
min	37.75	8.35	8.6	1.95	3.8	1.85	0.33	0.14	0.9	0.04	<0.05	<0.05	3.39	0.13
max	54.95	13.9	19.7	3.35	7.8	2.45	0.605	0.175	1.3	0.1	0.15	0.05	14.5	5.96
Gabbro ⁽¹⁾	51.05	15.76	9.75	0.95	11.68	7.73	1.14	0.24	2.43	0.12				
Anortosite ⁽¹⁾	51.12	26.29	12.69	0.66	3.31	2.16	0.65	0.09	3.20	0.05				
Monzonite ⁽¹⁾	63.65	15.9	4.24	4.13	5.42	2.05	0.79	0.25	3.79	0.10				
Granodiorite ⁽¹⁾	66.91	15.92	3.88	2.76	4.46	1.76	0.55	0.18	3.80	0.08				
Granite ⁽¹⁾	71.84	14.43	1.85	4.10	3.05	0.72	0.31	0.12	3.71	0.05	0.020	0.027	0.036	0.021
Basalt ⁽¹⁾	45.72	14.80	10.57	1.01	14.42	7.85	3.02	0.4	3.02	0.2	0.006	0.025	0.061	0.030

	Zn	Cu	Ni	Mn	Cr	Pb	As	Hg
Core Mean mg kg ⁻¹	101.5	59.6	12.5	442	40.4	<2	11.65	0.066
min	49.5	18.5	4.5	348	31	<2	11.02	0.031
max	190.5	167	19.5	806	45.5	2	12.68	0.141
Granite ⁽²⁾	52	13	0.5	400	4	24	1.5	0.08
Soil ⁽²⁾	75	50	80	950	100	14	6	0.06
Lacustrine Sediments ⁽³⁾	118	45	66	760	62	34		

Tab. 4. Comparison with Lake Carezza and Antarctica sediments. (1) Aceto *et al.* 1994; (2) Cosma *et al.* 1994

	Al (%)	Fe (%)	Ca (%)	Mg (%)	Na (%)	Mn (mg kg ⁻¹)	Fe/Mn
L. 20 (Mean)	6.45	4.56	9.250	1.371	0.841	442	110
L. Carezza ⁽¹⁾	3.13	2.33	0.066	0.077	0.988	323	72
Soil ⁽¹⁾ (around L.Carezza)	3.98	2.23	0.114	0.061	0.907	330	68
Antarctica ⁽²⁾ (sea sediments)		2.16				586	37

	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cr (mg kg ⁻¹)
L. 20 (Mean)	< 2	101.5	59.6	12.5	40.4
L. Carezza ⁽¹⁾	17.9	25.8	9.88	16.3	28.5
Soil ⁽¹⁾ (around L.Carezza)	21.3	27.5	13.4	17.0	28.6
Antarctica ⁽²⁾ (sea sediments)	12.7	108.0	25.3	24.2	27.7

Mobile elements: elements like S, Fe, and Mn in the sedimentary environment undergo chemical changes, mainly controlled by pH and redox conditions, which influence their mobility (increasing or decreasing their solubility). Mobile elements may decrease when the hypolimnion becomes depleted of oxygen and redox conditions favour the reduction to more soluble compounds. Fe/Mn ratio. In the core from Lake 20 Fe shows a minimum at the 2-4 cm section, whereas there is a marked increase in Mn in the 0-2 cm layer. For S, all data are below the detection limit.

Enriched elements: trace elements (Cu, Zn, Pb, Cr, Ni, Hg, As) widely used by man in industry, hence liable to be discharged at a rate which greatly exceeds the natural input. In this remote area, as expected, most of these elements behave like conservative elements; however, both Cu and Zn have marked peaks at the bottom of the core and at the 4-6 cm section. Hg shows

a different pattern, with minima at the 4-6 and 10-12 cm sections, and a sharp increase in the topmost layer.

Looking to the general chemistry of the sediments, the most prominent feature of the core profiles is the marked increase in Ca concentration. Since Mg does not follow the same trend, the Ca increase could be explained as an enhanced precipitation of CaCO₃ induced by an increase in alkalinity occurring during the periods when the lake is ice-covered. Ice cover reduces the exchange with the atmosphere, with a consequent rapid consumption of oxygen due to the decomposition of organic matter (Björck *et al.* 1993).

The precipitation of CaCO₃ may also be the result of a rise in pH due to photosynthetic activity; before the thaw. In fact, in Lake 20 pH reaches values higher than 10, then drops almost to 8, but for most of the time it remains in the range 8.5-9 pH units (Libera 1993). According to Lawrence and Hendy (1985, 1989), biogenic

Tab. 5. Chemical composition along the Lake 20 core.

cm	Si (%)	Al (%)	Ca (%)	K (%)	Fe (%)	Mg (%)	Ti (%)	Mn (mg kg ⁻¹)	Fe/Mn
0-2	17.65	5.27	14.08	2.24	4.27	1.30	0.25	806	53
2-4	24.08	4.42	10.90	1.62	2.66	1.12	0.20	386	69
4-6	24.47	6.03	10.15	2.24	3.92	1.33	0.27	455	86
6-8	23.66	6.75	10.11	2.53	4.41	1.45	0.30	404	109
8-10	24.03	7.04	9.47	2.66	5.18	1.48	0.32	380	136
10-12	24.47	6.96	8.61	2.62	4.65	1.42	0.32	349	133
12-14	25.53	6.93	7.00	2.62	5.07	1.42	0.34	383	132
14-16	25.27	7.36	6.79	2.78	5.42	1.45	0.35	403	135
16-18	25.69	7.25	6.15	2.70	5.46	1.39	0.36	412	132

cm	S (%)	Na (%)	Cl (%)	P (%)	N (%)	C (%)	C/N
0-2	<0.05	0.70	0.05	0.08	0.41	6.96	16.8
2-4	<0.05	0.67	0.02	0.06	0.18	3.84	21.7
4-6	<0.05	0.74	0.02	0.06	0.13	3.39	26.0
6-8	<0.05	0.93	0.30	0.07	0.43	3.92	9.1
8-10	<0.05	0.96	0.10	0.07	1.77	10.68	6.0
10-12	<0.05	0.89	0.02	0.07	5.96	14.54	2.4
12-14	<0.05	0.89	0.02	0.07	3.47	7.89	2.3
14-16	<0.05	0.93	0.05	0.07	1.54	7.07	4.6
16-18	<0.05	0.85	0.15	0.07	1.88	7.98	4.3

cm	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cr (mg kg ⁻¹)	As (mg kg ⁻¹)	Hg (mg kg ⁻¹)
0-2	<2.0	71.0	35.0	11.0	38.5	11.57	0.141
2-4	<2.0	49.5	18.5	4.5	31.0	11.42	0.060
4-6	<2.0	171.0	153.5	8.0	33.0	11.68	0.032
6-8	<2.0	72.5	30.0	11.0	42.5	12.68	0.057
8-10	<2.0	78.5	29.0	11.5	43.0	11.42	0.060
10-12	<2.0	82.5	30.0	18.0	41.5	12.11	0.030
12-14	<2.0	89.5	35.5	19.5	43.5	11.02	0.066
14-16	2.0	108.5	37.5	14.5	45.5	11.84	0.072
16-18	<2.0	190.5	167.0	14.5	45.5	11.08	0.079

CO₂ fixation (by phytoplankton or periphyton) induces the precipitation of carbonate minerals dominated by aragonite, with small amounts of high Mg-calcite.

The Ca contributed by gypsum should be almost negligible, because the S concentration is always lower than the detection limit of X Ray fluorescence spectrometry (0.05% S).

The main constituents of the sediment, Si, Al, K, Fe, Ti, and the trace elements Ni and Cr, all show a decreasing pattern from bottom to top the core, possibly due to an increase in the sedimentation of organic matter (acting as a "diluting" factor). In fact, the suggested recent climatic changes (Appleby *et al.* 1995) may have led to an increase in the primary productivity of the lake. This hypothesis seems to be supported by the increase in P concentration in the sediments. Moreover, the decrease in the Fe/Mn ratio, due to a decrease in Fe and an increase in Mn, points to a change in the redox

conditions at the water - sediment interface induced by an increased load of organic matter.

For Na, the suggested contribution from sea spray (Guilizzoni *et al.* 1992) does not appear noticeably to influence the sediment chemistry, and the element very likely derives from the weathering of the watershed. In fact, there is no correlation with Cl, which in turn shows some peaks possibly indicating past intrusions of salt water, followed by Na depletion and Cl bonding to the organic matter in the sediment (Bowen 1979).

Following another approach, useful suggestions regarding the time changes in the sedimentary environment emerge from an analysis of the metal/aluminium ratios (Bruland *et al.* 1974; Kemp *et al.* 1976). Assuming that human influences cannot alter the Al flux to the sediment, which is mainly due to the natural weathering of the rocks in the drainage basin, the metal/Al ra-

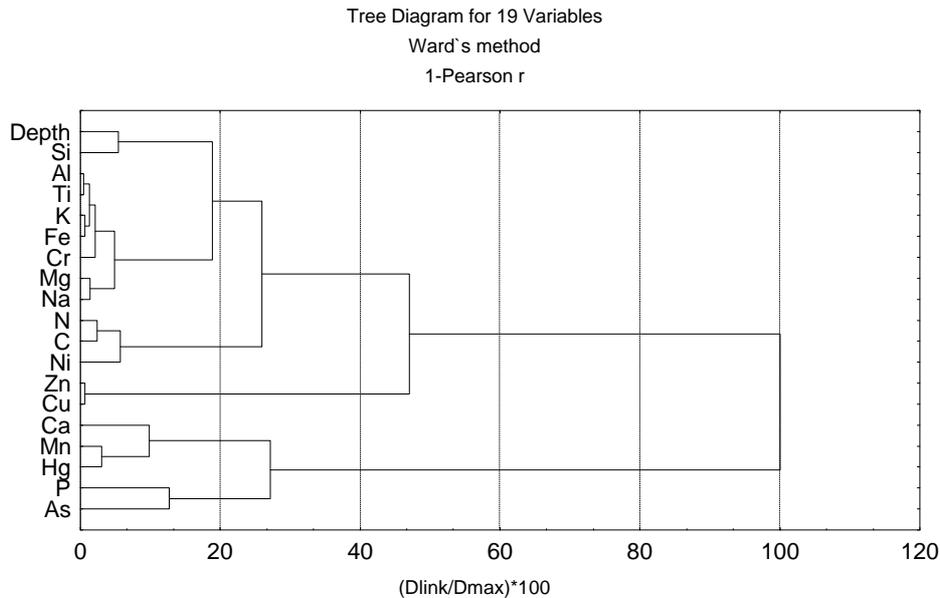


Fig. 1. Cluster analysis of the Lake 20 core.

tios will in fact change only if the metal and Al accumulate in the sediments at different rates.

This approach confirms that the Ca, Mn, and Hg accumulations show a marked divergence from that of Al, whereas for the other elements the sedimentation more closely follows that of the conservative element Al.

The cluster analysis (Fig. 1) also shows the common geochemical relationship of Al, Ti, K, Fe, and Cr (clay constituents), and between P and As; in addition, there is a cluster formed of Ca and Mn. Björck *et al.* (1993) attributed this relationship to the precipitation of mixed carbonates, calcite and rhodochrosite. Hg too seems to be associated with this cluster, probably for a co-precipitation of this element with autochthonous carbonates.

4. CONCLUSIONS

Radiocarbon dating (Orombelli, personal communication) indicates that the bottom of a 20 cm core from Lake 20 has an age of 1500 ± 50 years BP. As a rough estimate, the average sedimentation rate therefore corresponds to 0.013 cm y^{-1} , well in agreement with the reported rate of sedimentation, in the order of 0.1 cm y^{-1} or lower, for other lakes in Antarctica (Nedell *et al.* 1987; Squyres *et al.* 1991; Björck *et al.* 1993; Doran *et al.* 1994; Appleby *et al.* 1995).

According to Lyons *et al.* (1985), the increase in organic carbon and carbonates could be due to cold and/or dry periods, when the freeze-drying of the lake water and a reduced inflow decrease the ratio of allochthonous material to authigenically and biogenically produced material in the sediments.

Doran *et al.* (1994) report that a prolonged cold/dry period lasted between 1800 and 1500 y BP, and another

one has been identified prior to 1200 y BP. Possibly, the high measured total C values (organic + carbonate carbon) at the bottom of the core from Lake 20, and the peak at the 10-12 cm section, are related to these dry periods. The increase in total carbon is probably due to the high productivity of the lake, resulting in the sedimentation of organic matter of predominantly autochthonous origin, as reflected by the low C/N ratio (Björck *et al.* 1993).

On the other hand, the drop in Cl, from the maximum at the 6-8 cm section to the minimum at the 4-6 cm section, could be related to a wet period (resulting in a rise in the water level in lakes), that lasted between 750 and 400 y BP (Doran *et al.* 1994).

Considering that each sediment section probably covers at least 150 years, the highest concentrations for Zn and Cu, detected in the 4-6 cm section, definitely date back to the pre-industrial period. Hence, they reflect an increase in rock weathering/element sedimentation, rather than a contamination.

Björck *et al.* (1993) observed a higher erosional input in the period following the deposition of a tephra layer, dated at 720 y BP. For the Lake 20 core, the hypothesis of an increased sedimentation of allochthonous material around that time, at the 4-6 cm section, is further supported by the high C/N ratio of this section, explained by the input of allochthonous organic compounds (Björck *et al.* 1993).

Finally, the minimum at the 2-4 cm section, followed by the increase in the top layer of the sediments, may be due to climate warming over the past century, leading to greater erosion and increased precipitation of autochthonous material (Appleby *et al.* 1995).

In conclusion, the analysis of the sediment core from Lake 20 indicates that the chemical composition of the sediments is consistent with the known geochemical characteristics of the drainage basin, although it is true that the sedimentation rate in Lake 20 has changed in time. The variations along the core are most probably related to the climatic evolution of the area, to the consequent changes in weathering processes, and possibly to an increase in the primary productivity of the lake, rather than to anthropogenic influences on the biogeochemical cycles of the elements. It is only for Hg that the sharp increase in the topmost layer could suggest the long range transport of this contaminant.

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