

Observed trends in the chemical composition, $\delta^{18}\text{O}$ and crystal sizes vs. depth in the first ice core from the LoLc 1650 “Abisso sul Margine dell’Alto Bregai” ice cave (Lecco, Italy)

Michele Citterio^{1,*}, Stefano Turri¹, Alfredo Bini¹, & Valter Maggi²

¹Dipartimento di Scienze della Terra “Ardito Desio”, Università di Milano, via Mangiagalli 34, 20133 Milano, Italy

²Dipartimento di Scienze dell’Ambiente e del Territorio (DISAT), Università di Milano Bicocca, p.zza della Scienza 1, 20126 Milano, Italy

Abstract

A stratified clear ice deposit was drilled in an ice cave located at 2030 m a.s.l. in the Moncodeno area (Grigna Settentrionale, Lecco, Italy), and a 1.20 m-long ice core was recovered. Due to the topography of this cave the snowfalls cannot reach the ice deposit which is located at a depth of 80 metres below the cave entrance. Thin sections cut along the whole length of the core show significant textural evolution from equidimensional pluricentimetric at the top to columnar pluridecimeteric crystals near the bottom of the thickest stratum. The samples from the ice core follow a well-defined general trend with depth both in the $\delta^{18}\text{O}$ values and ionic concentration (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^-). We argue that the observed features are compatible with a “repeated freezing of shallow lakes” genetic model. The origin of the local deviations from the main trends observed at certain depths is discussed.

Keywords: ice crystallography, ice chemistry, stable isotopes, ice coring, Moncodeno, Italy.

Tendances observées dans la composition chimique, le $\delta^{18}\text{O}$ et les dimensions des cristaux par rapport à la profondeur dans une première carotte de glace de la grotte Lo Lc 1650 «Abisso sul margine dell’Alto Bregai» (Lecco, Italie)

Résumé

Une carotte de glace d’une longueur de 1,2 m a été prélevée d’un dépôt de glace transparente stratifiée d’une grotte localisée à 2030 m altitude dans la zone de Moncodeno (Grigna de nord, Lecco, Italie). Compte tenu de la topographie de cette grotte, la neige ne peut pas atteindre ce dépôt, car il est situé à une profondeur de 80 m. Des sections minces exécutées tout le long de la carotte relèvent une évolution texturale significative entre des cristaux equi-dimensionnels pluri-centimétriques se trouvant à la surface, et des cristaux columnaires pluri-décimétriques formés à la base de la couche la plus épaisse. Une tendance bien définie par rapport à la profondeur existe de même pour les valeurs du $\delta^{18}\text{O}$ et pour la concentration des ions (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^-). On considère que les caractéristiques observées sont compatibles avec le modèle génétique d’un «lac de regel répétitif». On discute l’origine des déviations locales à une certaine profondeur par rapport à la tendance générale.

Mots-clés: cristallographie de la glace, chimie de la glace, isotopes stables, carottage en glace, Moncodeno, Italie.

Introduction

The analyses carried out on the first ice core drilled in the ice block found at a depth of about 80 m below the entrance of the Lo Lc 1650 “Abisso sul Margine dell’Alto Bregai” ice

cave allowed us to determine the process responsible for the formation of the ice block (resulting from the repeated, complete freezing of shallow lakes one on top of the other to form a stratified ice deposit) and to set upper and lower limits to the age of the ice (see CITTERIO *et al.*, *this issue*, where more details about the cave and its ice deposit are given). This paper focuses on the trends observed from ionic content,

* corresponding author. E-mail address: michele.citterio@polimi.it

$\delta^{18}\text{O}$ values and crystal fabric of the ice, which offer interesting information regarding the freezing process during its development. In the following of this paper we will briefly describe the method used in measuring and plotting the data, and discuss the results; in the conclusive remarks we compare the three records and show the relevance of these findings for the study of the ice deposit.

Ice crystals size with depth

Several methods have been described in the literature for the measurement of ice crystals size, applied mainly to snow and glacier ice and usually involving the measurement of a certain number of crystals considered to be statistically representative. The crystal dimension can be expressed by specifying either the area of crystals or the length of the crystal diameter in thin section (*e.g.*, Gow, 1969 and JAKA, 1984), but

an underestimation problem exists for the general case of ice crystals not cut along their maximum section. Various approaches to this problem have been proposed, ranging from only counting the 50 apparently larger crystals (Gow 1969), to the use of correction factors chosen on the basis of the method adopted for the actual measurement of the apparent crystal size on the thin section plane (THORSTEINSSON, 1996, and references therein). Since we are mostly concerned with the variation of the crystal size, not with its exact value, we chose to measure and plot apparent crystal areas with a method easily applicable on our coarse grained ice: working on 1:1 scale photographs of the square, 10×10 cm wide thin sections, we superimposed a regular square grid and counted how many nodes each crystal was encompassing. Every node inside the perimeter of the thin section must be assigned to some crystal, so in case of nodes falling exactly on grain boundaries we credited "half a node" to each crystal. The results are plotted in Figure 1, which also features on the background a bar plot showing the percentage of the whole thin section surface occupied by a crystal of the indicated average size. This is particularly important, since sometimes the dimensions of the largest crystals in our samples greatly exceed those of the thin sections, thus leading to grossly underestimated average sizes. When only one or a few crystals are present, average apparent crystal areas can not be considered a reliable estimate both because these few big crystals extend outside of the thin section area up to an unknown extent and because of the small, statistically not representative number of the examined crystals. As a consequence of these considerations, the nearly exponential increase of crystal size with depth visible in Fig. 1 must actually be regarded as underestimated in the higher values. The very bottom of the plot, which shows an abrupt reduction in crystal size, has been recognized in the field and on the core to correspond to the upper part of the underlying ice stratum (CITTERIO *et al.* *this issue*).

Major ions profiles

From the plot of the major ions content vs. depth in the ice core (Fig. 2) it can be seen that during the earlier stages of water freezing the ionic content in the growing ice crystals is quite scarce and constant, with only the 1650-3 sample showing increased concentrations, which are of relevant amplitude mainly for alkali and Cl^- , whereas the plots of other ions only show a very modest undulation and ammonium even shows a very small depletion. Samples from 1650-10 to 1650-16 in most of the plots show abrupt changes which are not always present or coincident with those from other ions, with the interesting exception of the 1650-12 sample in which Cl^- and the alkali, together with Ca^{2+} , show a short high concentration peak. Starting from sample 1650-16, the values remain more stable until the largest peak observed in this ice core, which occurs at the 1650-20 and 1650-21 samples. This position coincides with the stratigraphic position of the bottom of the ice stratum.

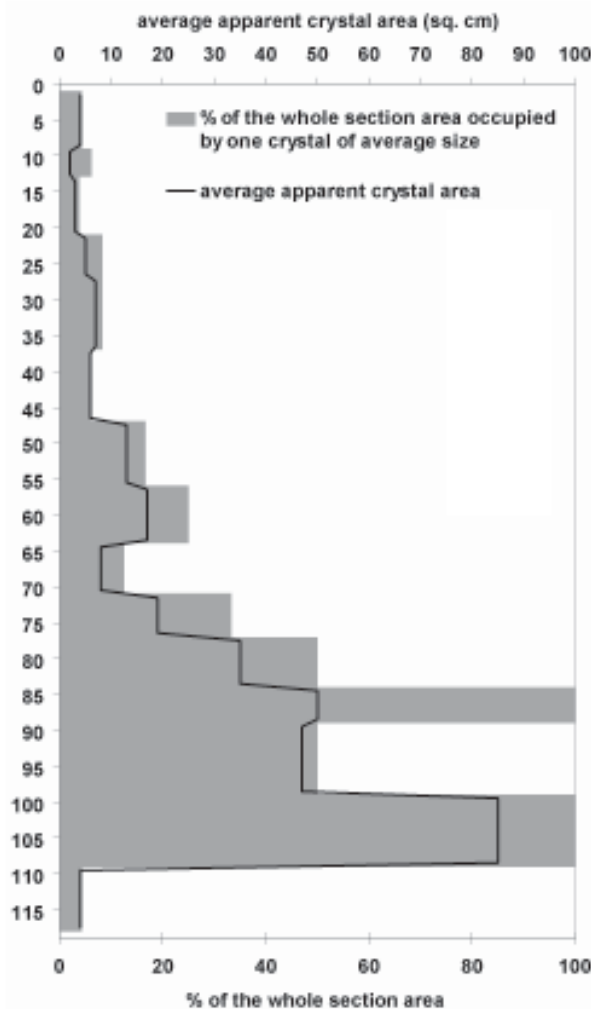


Fig. 1: Average size (area) of ice crystals vs. depth in the lake ice core from the P50 ice block in the Lo Lc 1650 ice cave.

Variation de la surface moyenne des cristaux de glace par rapport à la profondeur dans le lac de glace du bloc P50, grotte Lo Lc 1650.

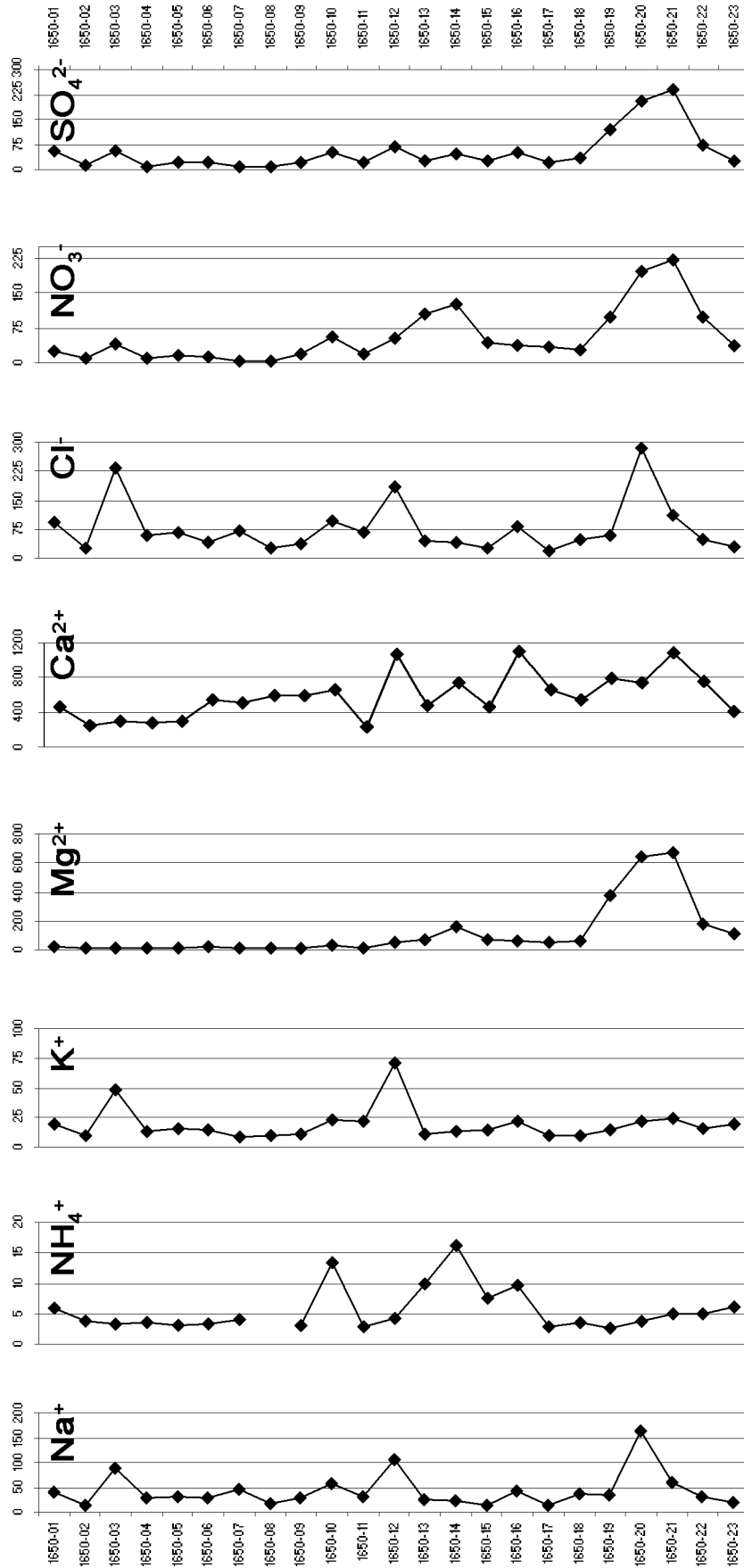


Fig. 2: Ionic contents vs. depth in the lake ice core from the P50 ice block in the Lo Lc 1650 ice cave. Variation du contenu ionique par rapport à la profondeur dans le lac de glace du bloc P50, grotte Lo Lc 1650.

This final enrichment can thus be interpreted as due to ice forming in the residual, solute-enriched water still present at the bottom when the lake was almost completely frozen. LORRAIN *et al.* (2002) showed a very similar ionic profile in an Antarctic glacier-dammed lake. As to the mode of occurrence of these ions in the ice, we have not carried out extensive investigations, but we observed that the bubbles present in the ice did not contain brines. It is possible that solutes expelled by the growing solid phase may have been trapped along crystal boundaries as hypothesized by LORRAIN *et al.* (2002), who also observed in the deepest part of a core some features similar to the brine-layer/ice plate substructures of sea ice, which were not observed in our thin sections. The presence of bubbles in some of the samples will be investigated to evaluate their role in causing the observed local deviation from the main trend.

Correlation coefficients computed for the 5 cm-thick samples are given in Table 1. Very high correlations (>0.90) exist between Na⁺ and Cl⁻, Mg²⁺ and SO₄²⁻, Mg²⁺ and NO₃⁻ and between SO₄²⁻ and NO₃⁻. In particular, Fig. 3 is a scatter plot of Na⁺ and Cl⁻.

δ¹⁸O profile

Figure 4 shows the evolution of the isotopic composition in the ice during freezing from top to bottom. A trend toward depletion in the heavy isotope is visible at the bottom, which is in agreement with findings in lake ice by LORRAINE *et al.* (2002) and is produced by isotopic fractionation between water and ice, with the preferential entry of water molecules containing ¹⁸O in the forming ice and the progressive depletion in heavy isotope of the liquid part of the system. Samples from 1650-9 to 1650-17 show a high variability in the δ¹⁸O values, an interval exactly centred on the samples having disturbances in the chemical content. The general trend is

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Na ⁺	1.00	-0.13	0.63	0.54	0.35	0.96	0.51	0.64
NH ₄ ⁺		1.00	-0.05	-0.04	0.28	-0.14	0.26	-0.03
K ⁺			1.00	0.05	0.34	0.69	0.13	0.26
Mg ²⁺				1.00	0.52	0.47	0.92	0.96
Ca ²⁺					1.00	0.24	0.54	0.58
Cl ⁻						1.00	0.46	0.60
NO ₃ ⁻							1.00	0.90
SO ₄ ²⁻								1.00

Table 1: Correlation coefficients matrix for the data plotted in Fig. 2.

Matrice des coefficients de corrélation pour les données de la Figure 2.

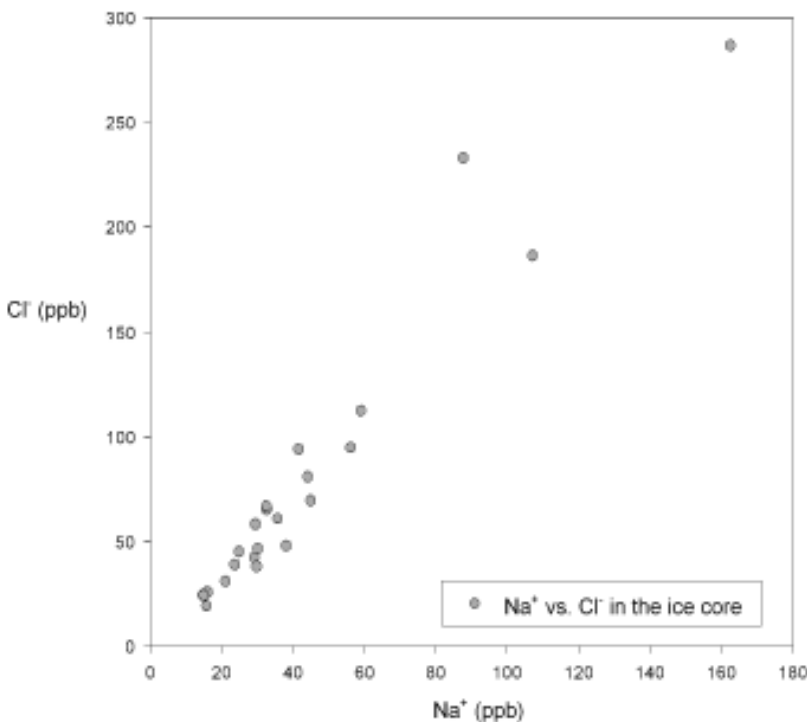


Fig. 3: Scatter plot of Na⁺ vs. Cl⁻ contents in the lake ice core from the P50 ice block in the Lo Lc 1650 ice cave.

Corrélation entre les contenus en Na⁺ et Cl⁻ dans la carotte extraite du lac de glace du bloc P50, grotte LoLc 1650.

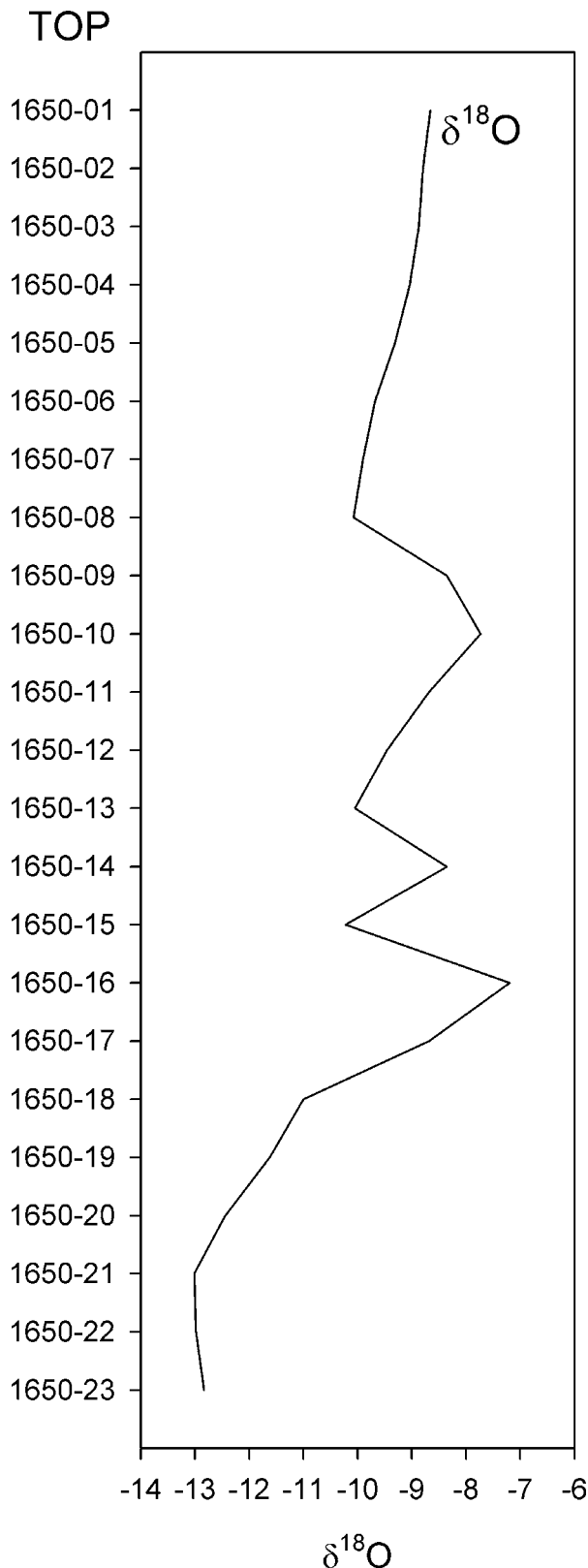


Fig. 4: $\delta^{18}\text{O}$ values vs. depth in the lake ice core from the P50 ice block in the Lo Lc 1650 ice cave.

Distribution des valeurs du $\delta^{18}\text{O}$ par rapport à la profondeur dans la carotte de glace extraite du bloc P50, grotte LoLc 1650.

depletion in the heavy isotope toward the bottom of the freezing lake, following the downward movement of the phase change boundary.

Discussion and conclusions

We have seen that trends have developed in the ice which all point to a genetic model of formed by the complete crystallization of lake water starting from the water-air interface and advancing downward in the water column. The expected signals are well expressed and include the following trends: (1) increasing size of the ice crystal with depth due to the growth of columnar ice; (2) solutes expulsion during crystal growth with late freezing of enriched residual water; and (3) isotopic fractionation from heavy ice at the top to light ice at the bottom. These trends heavily modified by an event that occurred in a "disturbed zone" between the depth of samples 1650-10 and 1650-16. This corresponds to a depth of about 50 to 80 cm below the top of the ice core; note that this is the depth below the present ablation surface of the P50 ice block, which does not coincide exactly with the stratigraphic top of the ice stratum (refer to CITTERIO *et al.*, this issue, for further details). The abrupt, fast nature of most of the observed changes taking place in the disturbed zone is being investigated on a second core by sampling at a three-fold increased vertical resolution. An explanation for such for such disturbances may be the opening of the system during freezing. For instance, some amount of new water could penetrate into the system under the already formed ice and mix with the residual "unfrozen" water. Hypotheses considering a slowing down or even a stop in the freezing process are unlikely to be able to produce such large effects: freezing was surely already taking place at low rates and one of the "heavy" peaks in the $\delta^{18}\text{O}$ profile is even richer in the heavy isotope than the samples from the top of the core. Further investigations should be carried out to define the distribution pattern of the ionic content in the ice; in particular, should salts be found along crystal boundaries or in any relation with bubbles, apparently anomalous values should be expected at samples containing a high amount of them.

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