ISOTOPIC COMPOSITION OF ICE AND SUBGLACIALLY PRECIPITATED CALCITE IN AN ALPINE AREA

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With 5 figures

ABSTRACT

Subglacially precipitated calcites, formed since 1860, are exposed by the retreating of the Tsanfleuron glacier in the Swiss Alps. They have been sampled together with different types of ice and water, for their isotopic composition. The isotopic study suggests that the initial water, from which calcium carbonate is precipitated by partial freezing, is produced by melting of the basal ice layer, not of glacier ice. Because of the wide range of isotopic composition of basal ice, some doubts are expressed on the possibility given by such subglacially precipitated calcites to determine the isotopic composition of Pleistocene ice sheets and to correct the paleotemperature scale.

ISOTOPENZUSAMMENSETZUNG VON EIS UND SUBGLAZIAL AUSGESCHIEDENEM KALZIT IN EINEM ALPINEN GLETSCHER

ZUSAMMENFASSUNG

Durch den Rückzug des Tsanfleurongletschers in den Schweizer Alpen werden subglazial seit 1860 ausgefällte Kalzite freigelegt, die so wie verschiedene Arten von Eis und Wasser auf ihre Isotopenzusammensetzung untersucht wurden. Die Ergebnisse deuten darauf hin, daß das Wasser, aus dem das Kalziumkarbonat ausgefällt wurde, aus basalem Regelationseis stammt und nicht aus dem eigentlichen Gletschereis. Wegen des weiten Bereichs der Isotopenzusammensetzung von basalem Eis muß die Möglichkeit angezweifelt werden, daß von subglazial ausgeschiedenem Kalzit die Isotopenzusammensetzung von pleistozänen Eismassen bestimmt oder die Paläotemperaturskala korrigiert werden könne.

LA COMPOSITION ISOTOPIQUE DE LA GLACE ET DES ENCROÛTEMENTS CALCAIRES SOUS-GLACIAIRES

RESUME

Nous avons étudié des encroûtements calcaires d'origine sous-glaciaire formés, après 1860, sur des roches polies dégagées depuis par le retrait du glacier de Tsanfleuron dans les Alpes suisses. Des analyses isotopiques des ces précipités et de différents types d'eaux et de glaces ont été réalisées. Elles indiquent que l'eau initiale, à partir de laquelle le précipité s'est effectué par suite d'un regel partiel, est produite par la fusion de glace basale et non de glace de glacier. La grande variabilité de la composition isotopique de la glace basale rend problématique l'utilisation de tels encroûtements calcaires pour déterminer la composition isotopique des calottes glaciaires du Pléistocène et corriger l'échelle des paléotempératures.

INTRODUCTION

    Subglacially precipitated calcites have attracted attention in recent years (Hallet 1976, Hanshaw and Hallet 1978, Hillaire-Marcel et al. 1979) for two reasons. Firstly, they are considered to be the direct consequence of the regelation sliding mechanism operating at the glacier base. Secondly, their oxygen isotopic composition may shed some light on the problem of the isotopic composition of Pleistocene ice sheets and on the correction of the paleotemperature scale. However, very few studies have been made on present-day sites of formation. In the case studied here, a survey of the isotopic composition of ice, meltwater and present-day precipitates has been undertaken.

THE TSANFLEURON SUBGLACIAL CALCITE

    The study was carried out at the Tsanfleuron glacier located northwest of the town of Sion in the Swiss Alps. This little plateau glacier covers an area of about 4 km² between 2420 and 2850 m a. s. l. and is principally underlain by Cretaceous limestones. It flows towards the east and, except for a small tongue 700 m long, it ends on the limestone plateau. It is fringed at its northern border by a marly limestone ridge reaching 3122 m at Oldenhorn. It was in recent time more extensive: a conspicuous end morainic ridge dated from 1860 runs parallel to the glacier margin about 1.6 km from the front (fig. 1).
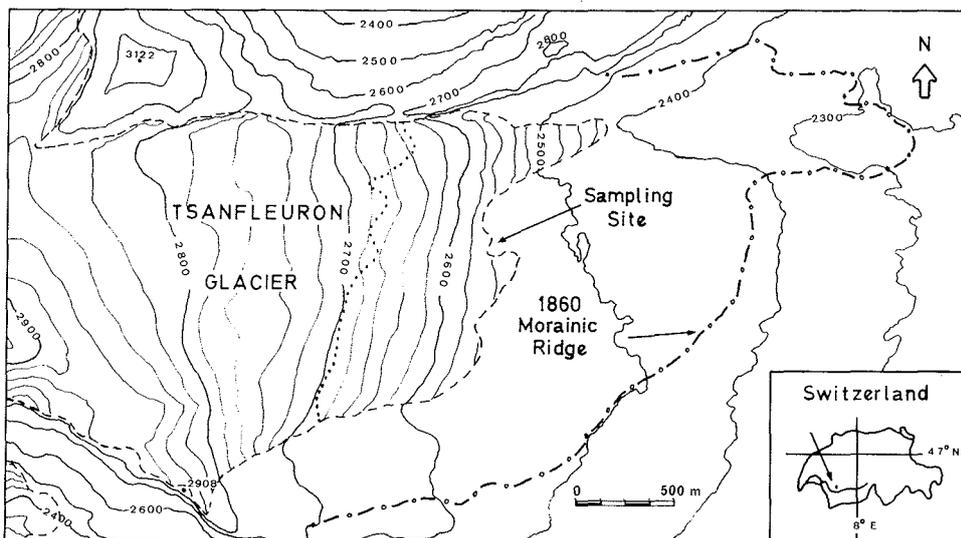

Fig. 1: Surface and bedrock topography of the Tsanfleuron glacier. Ice margin is shown stippled, snow line is dotted. At the sampling site indicated, ice and water were taken for isotopic studies

    In front of the glacier, a smoothed bedrock surface is carved into massive limestones that are, in some places, covered with thin debris. Downglacier from bedrock protuberances, the polished surface is overlain by a laminated carbonate deposit (fig. 2). This deposit is progressively less abundant as we go from the glacier margin to the

Fig. 2: Laminated subglacial carbonate deposit crusting the smoothed bedrock surface. Traces of the former ice-flow direction are visible on the deposit and on the bedrock surface, crossing calcite veins of the Cretaceous limestone. The diametre of the lens-hood is 6 cm

Fig. 3: Subglacial calcite precipitate with flutes and furrows parallel to the former ice-flow direction. The finger points to a stria scouring the bedrock and the deposit itself

1860 end moraine and disappears completely further downglacier. It is locally present on bedrock in natural subglacial cavities which temporarily exist at the glacier margin about 800 m from the snout. It is fluted and furrowed parallel to the former ice-flow direction. At some places the laminations, 10 to 100 μm thick, are visible in cross-section. Glacial striae scour sometimes the smoothed bedrock and the deposit itself (fig. 3). To account for these characteristics, it is apparent that, during its formation, this deposit must have been surrounded by ice with only a microscopic sheath of water separating it from the ice (Hallet 1976).

Optical examination in thin section indicates that it principally consists of calcite. Some clasts, particularly quartz, are incorporated into the deposit. These quartz particles with a maximum diameter of 100 μm might be present in the thin subglacial water film before their incorporation into the laminated calcite.

This type of carbonate deposit is explained by Hallet (1976) as being due to calcium carbonate precipitation at the eutectic point in freezing subglacial water at the lee side of a bedrock protuberance.

Samples of the precipitate and of the underlying Cretaceous limestone were analyzed for their isotopic composition in the Earth Science Laboratory of Quebec University at Montreal[1]. Results for $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ are given in table 1. The $\delta^{18}O$ values of the two types of material differ, the bedrock values being about 3 ‰ higher. This difference is related to the fact that calcite is not simply ground-up bedrock calcite but has gone through a solution phase. Furthermore, this difference implies that the carbonate has undergone an equilibration of its oxygen isotopes with a reservoir having an isotopic composition not in equilibrium with that of the bedrock carbonate (Hanshaw and Hallet 1978). On the other hand, the similar $\delta^{13}C$ values of the two types of material imply that no organic carbon was involved. The absence of vegetation along the glacier margin gives little likelihood for organically derived CO_2 to be incorporated into the meltwater under the glacier or at its front.

Table 1: Values of $\delta^{18}O_{PDB}$, $\delta^{18}O_{SMOW}$ and $\delta^{13}C_{PDB}$ for subglacial calcite and bedrock from the Tsanfleuron glacier area

Type of Samples		$\delta^{18}O_{PDB}$	$\delta^{18}O_{SMOW}$	$\delta^{13}C_{PDB}$
Bedrock	S 1	−4.41	25.82	−2.08
	S 2	−3.29	26.98	−2.75
	S 3	−4.36	25.87	−2.12
	mean	−4.02	26.22	−2.31
Subglacial Calcite	S 1	−7.72	22.42	−1.91
	S 2	−5.58	24.62	−1.90
	S 3	−7.37	22.77	−2.16
	S 4	−6.39	23.78	−1.33
	mean	−6.77	23.40	−1.83

Chemical analyses by X-ray fluorescence and by atomic absorption spectrophotometry after treatment with hot 1 N HCl indicate that the precipitate contains between 813 and 919 mg/g CaCO₃. A comparison of the ratios Ca/Mg and Ca/Sr in the deposit and in various types of water and ice from the Tsanfleuron glacier area

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[1] Thanks are due for this to Drs. J. Schroeder and C. Hillaire-Marcel.

(table 2) is suggestive of the selectivity of the precipitation process. The higher Ca/Mg ratios in the precipitate cannot indeed be due to the differential incorporation of cations in the growing ice giving rise to a residual water enriched in Ca since this cation is preferentially included into the ice (Malo and Baker, 1968).

Table 2: Ca/Mg and Ca/Sr ratios of ice, meltwater and subglacial calcite from the Tsanfleuron glacier area

Types of Samples	Number of Samples	Ca/Mg			Number* of Samples	Ca/Sr		
		Mean	Min.	Max.		Mean	Min.	Max.
Glacier Ice	14	9.73	1.26	25.00	4	149.25	125.00	200.00
Basal Ice	22	22.00	3.03	49.14	13	111.11	52.63	333.33
Meltwater	16	15.43	3.10	30.84	4	208.33	200.00	250.00
Subglacial Calcite	5	45.35	31.49	55.90	5	2702.70	1538.46	6250.00

* Sr analyses were performed only on some of the samples analysed for Ca and Mg.

CHARACTERISTICS OF ICE AND WATER SAMPLES

Ice and water samples were collected for isotopic analyses in two subglacial cavities accessible in 1980 at about 2550 m. a. s. l. (fig. 1).

Two main types of ice were sampled:

1. Ice layers 1 to 10 cm thick coating the floor of the cavities. Ice in these layers is bubble-free and particle-free with crystals about 1 cm long. These layers are sometimes deformed by the pressure of the glacier during periods when the cavities undergo size changes. Some of these layers are incorporated at the base of the glacier and, in this case, appear interbedded with fine particle layers. Together they constitute the basal ice layer (B. I. L.), (fig. 4).

2. Bubble-rich glacier ice appearing either at the ceiling of the cavities or at the glacier surface. For one of the two cavities visited in 1980, a crevasse connected the cavity with the glacier surface.

Sampling began with the removal of the uppermost centimetres exposed to the air. Stainless metal coring cylinders were then hammered into the ice. The samples were transferred into polyethylene bottles and allowed to melt. After melting was completed, the water was filtered through 0.45 μm Millipore filter and stocked into dark glass bottles to avoid possible slight diffusion through polyethylene in the course of time. Care was taken to entirely fill the bottles in order to minimize exchanges between water and entrapped air. Finally, the bottles were sealed with paraffin to prevent evaporation.

Meltwater running on the floor of the cavities and meltwater from supraglacial channels flowing either above the cavities or into the above-mentioned crevasse were also sampled with disposable polyethylene syringes and processed in the same way.

All samples were analysed at the "Centre d'Etudes Nucléaires de Saclay" in France for $\delta^{18}O$ and δD. Results are given in per mil versus S.M.O.W. Precision of the measurements is ± 0.1 ‰ in $\delta^{18}O$ and ± 0.5 ‰ in δD. Results are presented on a graph where $\delta^{18}O$ is the abscissa and δD the ordinate (fig. 5). On this figure, the ice
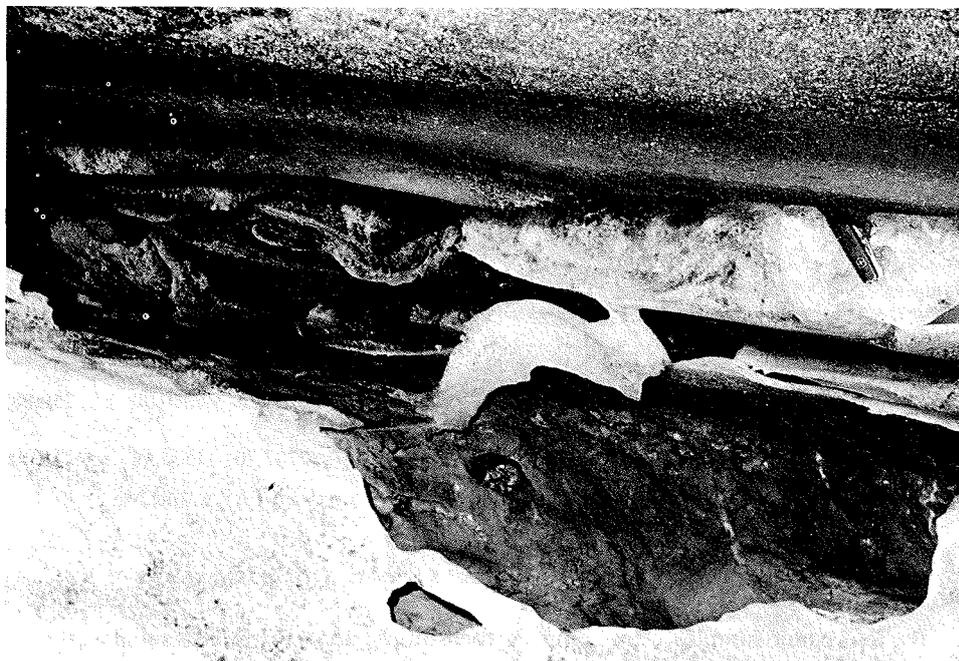
Fig. 4: A partial view of a subglacial cavity in which ice and water were sampled. Ice layers coating the bedrock floor are visible down left. At the level of the pocket-knife, deformed ice layers are being picked-up at the glacier base

layers coating the floor of the cavities constituting the B. I. L. are aligned on a straight line with a slope of 6.49 determined by linear regression. This slope is different from the well-known precipitation slope (S $\cong$ 8) and is characteristic of a freezing process as demonstrated by Jouzel and Souchez (1982).

COMPARISON BETWEEN THE ISOTOPIC COMPOSITIONS

The $\delta^{18}O_{PDB}$ of the subglacial calcites can be transformed into $\delta^{18}O_{SMOW}$ using the equation $\delta_{SMOW} = 1.03037 \delta_{PDB} + 30.37$ (Faure, 1977). The $\delta^{18}O_{SMOW}$ so obtained have a mean value of $+23.40$ ‰ and extreme values of 22.42 ‰ and 24.62 ‰ (table 1). Calcite precipitation in this subglacial environment is not the consequence of a rapid loss of dissolved CO_2 but is due to an increase of the ionic calcium concentration in residual water by freezing, the ions being rejected by the growing ice. Therefore, precipitation takes place in isotopic equilibrium with water. It is accompanied by a preferential incorporation of ^{18}O in the calcite that corresponds to a fractionation factor of 1.0347 for calcite and water at 0° C (Clayton et al., 1968). Using this factor and the average $\delta^{18}O_{SMOW}$ of 23.40 ‰ for the subglacial calcite, we obtain $\delta^{18}O = -10.92$ ‰ on the average for subglacial water in equilibrium with it. Extreme values obtained by the same method are -9.74 ‰ and -11.87 ‰.

Jouzel and Souchez (1982) demonstrated that, in the course of freezing, successively-formed frozen fractions are represented, on a $\delta\Delta - \delta^{18}O$ diagram, by points
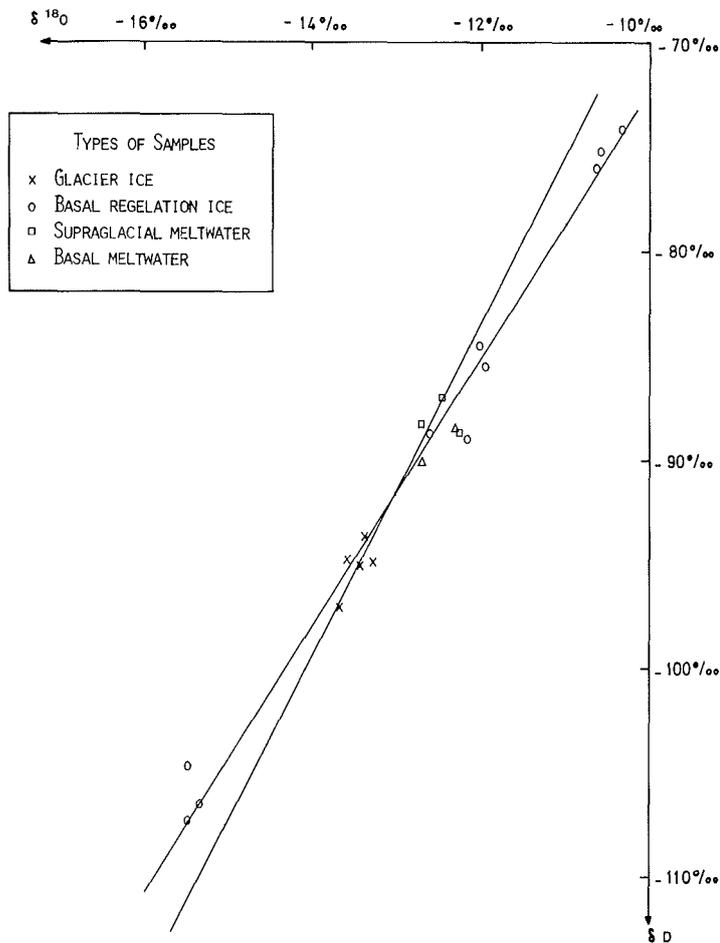
Fig. 5: δD—$\delta^{18}O$ diagram for ice and meltwater samples from the Tsanfleuron glacier

lying on a straight line with a specific slope, the first fraction being the most enriched in heavy isotopes. On the other hand, water in equilibrium with the growing ice is progressively impoverished in heavy isotopes. If initial water is partially frozen, the residual water will be enriched in $CaCO_3$ until saturation and eventually precipitation occurs. Moreover, this residual water is also progressively impoverished in heavy isotopes, if compared with initial water. Now, water in equilibrium with calcite is precisely this residual water so that it must be poorer in heavy isotopes than initial water. Impoverishment of residual water in heavy isotopes during freezing can explain that Gow et al. (1973) found water with a $\delta^{18}O$ value of 2 or 3 ‰ lower than ice at the base of the Antarctic ice sheet. This impoverishment of water during freezing can also be demonstrated experimentally. During a freezing experiment of a water sample from the Tsanfleuron glacier area, Jouzel and Souchez obtained a shift of 2 ‰ in $\delta^{18}O$ of the residual water along the predicted slope with progressive impoverishment in heavy iso-

topes of this water (personal communication). No agitation of the liquid was accomplished during the freezing experiment so that the conditions would more or less reflect those existing at the base of the glacier.

Now, subglacial water in isotopic equilibrium with the subglacial calcite has a calculated mean $\delta^{18}O$ value of $-10.92\ ‰$. Fig. 5 shows that, among ice layers due to refreezing, only those corresponding to a weak percentage of freezing may be richer in heavy isotopes. Since no fractionation occurs during the melting of ice (Friedman et al., 1964; Moser and Stichler, 1980), layers due to refreezing at the glacier base and water resulting from its melting have the same isotopic composition. Glacier ice samples were too negative to be, by melting, at the origin of the initial water.

Epstein and Sharp (1959) and Hambrey (1974) have shown that the isotopic composition of glacier ice varies along a transverse section across the glacier. We have not established such a transverse variation for the Tsanfleuron glacier. However, it is unlikely that glacier ice closer to the northern ridge, with a supposed higher $\delta^{18}O$, would be responsible for the isotopic compositon of subglacial water at the origin of the precipitates. The comparison between reconstructed flow lines and location of the subglacial calcites are not in favour of such an hypothesis. On the other hand, work done by the same authors, by Sharp et al. (1960), by Macpherson and Krouse (1967) and by Lawson and Kulla (1978) indicates that ice with the highest content in heavy isotopes — i. e. with the highest $\delta^{18}O$ — is located close to the equilibrium line at the glacier surface. Our sampling sites for glacier ice are about 500 m below the equilibrium line and mostly near the glacier base. Supraglacial water in channels flowing from upglacier and probably originating from near the equilibrium line was sampled above the cavities and where it disappears in a crevasse. This water has an isotopic composition similar to that collected on the floor at the margin. The $\delta^{18}O$ values are between $-12.25\ ‰$ and $-12.70\ ‰$. These values are too negative to be considered as those of the initial water giving rise to the precipitate by freezing.

CONCLUSION

Hanshaw and Hallet (1978) have shown that the $\delta^{18}O$ of subglacially precipitated calcite from near Blackfoot Glacier in Montana (USA) records the $\delta^{18}O$ of the ice from that glacier. Considering this point, they assume that it may be possible to determine the $\delta^{18}O$ of Pleistocene ice sheets on the basis of isotopic analysis of calcite formed under that ancient ice. This, in turn, would allow estimation of the $\delta^{18}O$ of the Pleistocene ocean and correction of the paleotemperature scale. Hillaire-Marcel et al. (1979) have studied, in that context, Pleistocene subglacial carbonate deposits in the Hull area (Quebec). Our study of a present-day case at the Tsanfleuron glacier margin in the Swiss Alps shows that things may be more complicated and that a large error is likely to be present for such an isotopic reconstruction. Indeed, the initial water from which calcium carbonate is precipitated by partial freezing is produced by melting of the basal ice layer which presents a large range of isotopic composition ($\delta^{18}O$ from -15.45 to $-10.35\ ‰$).

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