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THE MARMOLADA GLACIER: AN INVESTIGATION OF NATURAL WEATHERING AND ANTHROPIC PRESSURE THROUGH CHEMICAL ANALYSES OF MELTING WATER AND ICE

ABSTRACT: VIGANÒ A., DOSSI C., MATTANA U., MARTIN S., MONTICELLI D. & POZZI A., *The Marmolada Glacier: an investigation of natural weathering and anthropic pressure through chemical analyses of melting water and ice.* (IT ISSN 0391-9838, 2003).

A sampling campaign on Marmolada Glacier (Dolomites, Italy) was undertaken on 7-8 september 2001, in order to collect samples of ice, snow and surface waters for chemical analyses. Such analyses, conducted on the field with portable electroanalytical instrumentation and in the analytical laboratory, suggested the occurrence of strong chemical interactions between melting waters and the limestone bedrock. Evidence for a strong anthropic pressure on the glacier, related to winter and summer sport activities, is also reported.

KEY WORDS: Glacier, Anthropic pressure, Marmolada, Alps.

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Nei giorni 7-8 settembre 2001 è stata effettuata una campagna di campionamento di ghiaccio, neve ed acque superficiali sul ghiacciaio della Marmolada (Dolomiti) che ha interessato sia la zona di accumulo delle precipitazioni nevose sia quella di ablazione del ghiacciaio alle fronti occidentale, centrale ed orientale. Le analisi chimiche effettuate sia direttamente sul ghiacciaio mediante strumentazione elettroanalitica portatile che in laboratorio, hanno messo in evidenza le interazioni chimiche che avvengono tra le acque di fusione del ghiaccio e le rocce carbonatiche del bacino, e gli effetti dell'elevato impatto antropico legato all'attività sportiva praticata sul ghiacciaio sia d'inverno che d'estate.

TERMINI CHIAVE: Ghiacciaio, Impatto antropico, Marmolada, Alpi.

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INTRODUCTION

Geographic and geomorphologic setting

The Marmolada Massif is located in the Dolomites (Venetian region, NE Italy) at the boundary of the Belluno and Trento provinces. This mountain ridge represents the divide between the hydrographic catchment basins of the River Piave and Adige. The Marmolada Massif includes several peaks higher than 3000 meters, the highest being Punta Penia (3343 m a.s.l.). The Marmolada mountain range is bounded northwards by the deep and large Fedaia basin (Fedaia Pass: 2056 m a.s.l.), whereas it is bounded southward by the Contrin and Ombretta valleys, the latter starting from the Ombretta Pass (2704 m a.s.l.). The streams situated on the western side of the massif are tributaries of the Avisio River (Adige system), while the eastern ones are tributaries of the Pettorina River (Piave system) (Mattana, 1995, fig. 1).

The Marmolada Glacier is the largest glacier of the Dolomites and it extends on the northern side of the massif; a 600-1000 meter high and five-kilometre long very steep rock wall represents instead the southern side. The watershed between Adige and Piave water systems is developed just in the middle of the glacier (see fig. 2).

The Marmolada Massif is composed of fossil-rich clear limestones known as Calcarea del Latemar and Calcarea della Marmolada Formations of Upper Anisian-Ladinian age, derived from a carbonatic shelf and detritic material accumulated at the shelf bottom toward the basin and minor volcanic effusions of Ladinian age (Leonardi & alii, 1968). The frontal glacial basin is developed above the Calcarea del Latemar Formation (Caputo & alii, 1999).

At present, the Marmolada Glacier has a trapezoidal shape and extends over 2.6 km² (it is 1.5 km long and 2.5

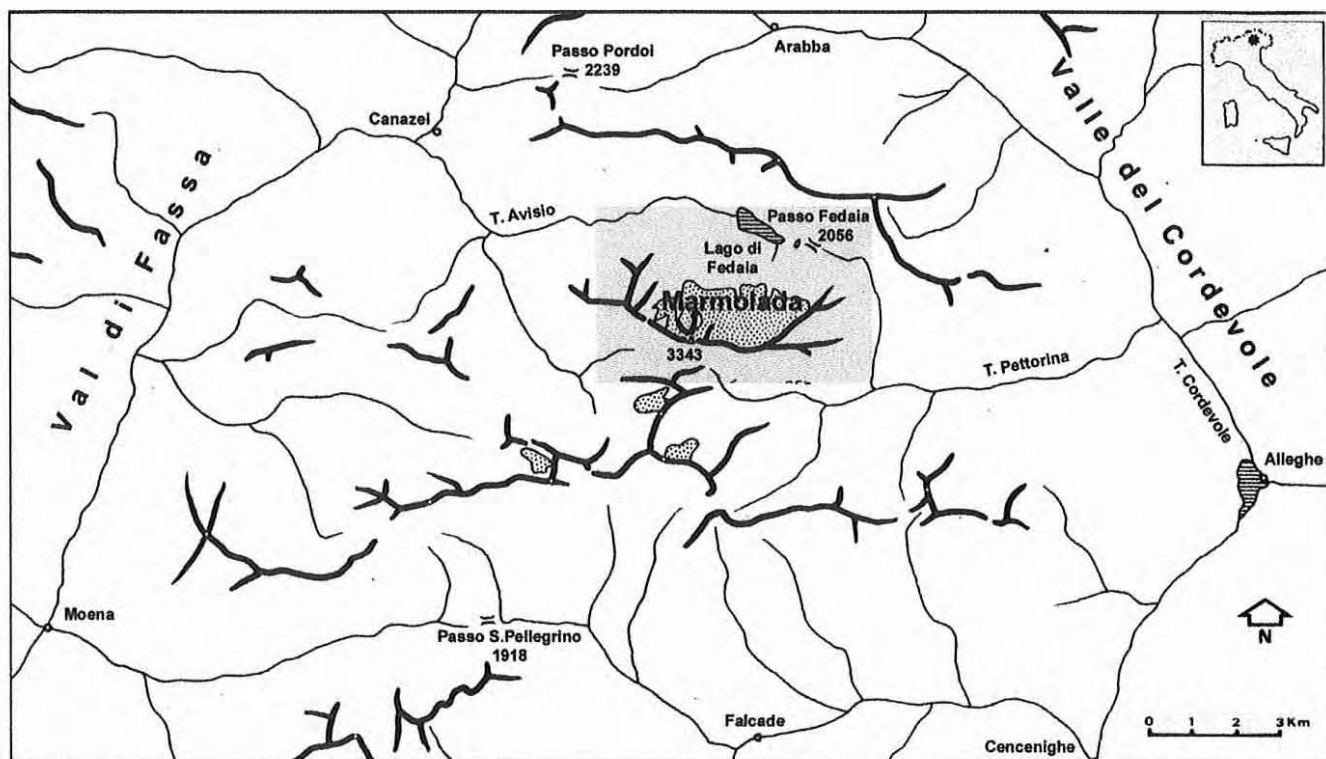


FIG. 1 - Geographic setting of the Marmolada Massif.

km large, at maximum) with an average dip of 53%. On the western front the glacier extends between 3340 and 2490 meters of altitude (Mattana, 1995). It is constituted by an upper elongated zone separating into three tongues, which descend northwards in the direction of the Fedaiia Lake. The central tongue is located between Sasso delle Undici to the east and Sasso delle Dodici peak to the west, within high and steep ridges. At present, due to the very scarce snowfall during the winter and the high summer temperature, the three tongues are disappearing and their fronts are retreating inducing a relevant change in the glacial morphology of the basin.

The goals of this work are both to study the geochemical features of the Marmolada system with particular focus on the chemical reactions between ice, melting water and carbonatic rock, and to evaluate the human impact on the glacier using simple chemical analytical parameters.

The chemical analyses of ice, snow and surface waters have been integrated with a morphological analysis of the glacier and the related proglacial area, carried out by researchers of the University of Padova during the annual survey of the Comitato Glaciologico Italiano.

EXPERIMENTAL SECTION

Sampling sites were chosen so as to cover the whole front of the Marmolada Glacier, from the western to the

eastern end. Seven significant sampling sites for ice, snow and melting water were selected and their locations are reported in fig. 2.

- Site M1) ice sample taken from a crevasse near Pian dei Fiacchi (2780 m a.s.l.), above the arrival of the chair lift coming from Fedaiia Pass;
- Site M2) superficial snow fallen in the previous days (15 cm layer), in the same position as site 1;
- Site M3) ice sample taken at the Western front at a 40 cm depth (2675 m a.s.l.);
- Site M4) melting water from the stream exiting the small glacial basin below Punta Penia, after the water has flown for about 200 m on rocks;
- Site M5) ice sample from a serac of deep blue ice in the Central front (2550 m a.s.l.) from a depth of 10 cm;
- Site M6) ice sample on the eastern front (2640 m a.s.l.) from a depth of 10 cm;
- Site M7) water collected from the small lake at the end of the eastern front (2630 m a.s.l.), 1 meter from the shore and at a depth of 20 cm.

Ice, snow and water samples were collected in low-density polyethylene bottles (capacity 250 mL). The bottles were cleaned by soaking in diluted ultrapure nitric acid (HNO₃ Suprapur, Merck) and then rinsed with sever-

al portions of ultrapure MilliQ water (Millipore MilliQ System, 18 M Ω -cm resistivity).

Ice was sampled by an ice axe, which was previously cleaned with deionised water: the uppermost layer of ice was discharged, as it is likely to be heavily contaminated. Snow was collected by dipping a large mouth bottle into it, while water was sampled directly by hand.

Hardness, alkalinity and the physicochemical parameters (temperature, pH and conductivity) were determined in the aqueous samples on the field. Temperature and pH were measured through a portable Hanna HI9025C pHmeter and conductivity through a portable Hanna HI9033 conductivity meter: both instruments were calibrated daily on the field. Hardness and alkalinity were determined through Aquamerck portable kits from Merck Eurolab.

The concentrations of major ions were determined in the laboratory by means of ion chromatography (IC761 from Metrohm, Herisau, Switzerland): this technique is, in fact, largely employed for ice and snow analysis (see Legrand & *alii*, 1993 and Huben & *alii*, 2001). A Phenomenex StarIon A300 column was used for anion separation with a flux of 1.5 mL/min of a carbonate/bicarbonate elu-

ent (1.8 mM Na₂CO₃ + 1.7 mM NaHCO₃). Cations were separated on a Metrohm Metrosep Cation 1-2 column with an eluent composition of 4 mM tartaric acid and 1 mM dipicolinic acid and a flux of 1.0 mL/min. The measured limits of detection (LOD) are 3 μ g/L for anions and 10-25 μ g/L for cations.

Bicarbonate determination was performed by titrating the sample with 0.01 M hydrochloric acid through a computer based automatic titrator developed in our laboratory (Dossi & *alii*, 2000).

RESULTS AND DISCUSSION

The results of the analyses of major ions highlighted the presence of pollutants like nitrate, nitrite and chloride that have to be certainly ascribed to the high anthropic pressure exerted on this glacier. In fact, the weathering of rock and sediments by itself is not able to account for the chemical composition of melting waters. The effects of human activities are evident on the glacier: plastic, vegetable and organic debris are clearly visible over the surface of the uppermost part of the glacier. The spreading of this

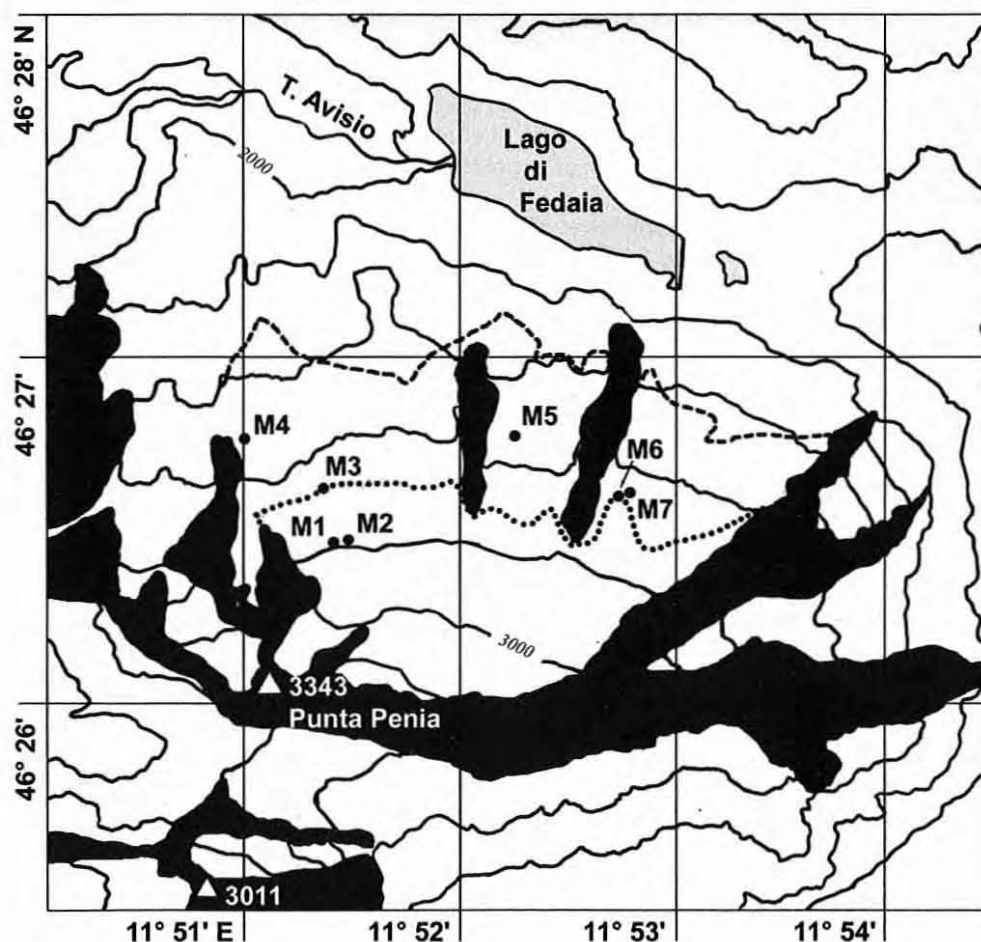


FIG. 2 - Simplified topographic map of the Marmolada Massif with sampling sites. The Last Glacial Maximum boundary (ca. 1850) is indicated by the dashed line; the 2001 position of the glacial front is indicated by the dotted line. Scale 1:25000, from sheet «La Marmolada» F.^o 11 II N.E., dai tipi dell'Istituto Geografico Militare (autorizzazione n. 5569, 12/04/2002).

TABLE 1 - *in situ* analytical data for surface waters

Analytical parameter	Stream water (site M4)	Small lake (site M7)
Temperature (°C)	4.4	5.5
pH	8.39	8.71
Conductivity (µS/cm)	81.9	71.2

TABLE 2 - Bicarbonate concentrations measured in ice, snow and water samples

Site	Sample nature	Bicarbonate concentration (mg/L)
M1	Deep ice	0
M2	Surface snow	-0.3
M3	Deep ice	17.3
M4	Melting water	27.9
M5	Deep ice	0
M6	Deep ice	3.3
M7	Melting water	34.1

pollution downhill to the whole glacier is anyhow to be expected because of the ablation action of the glacier increased by the steepness of the slope. Winter and summer skiing are practised since many years and several ski lifts, cablecars and cableways have been built increasing steadily the anthropic pressure on this glacier. Moreover, the residual snow pack still present on most of the Alps at the end of the summer of 2001 did not allow an effective assessment of the annual advancement or retirement of the glacier front.

The results of the *in situ* analyses of the water samples M4 and M7 are shown in tab. 1. pH values higher than 8 were observed, in accordance with previous measurements (Ek, 1966 and Fairchild & *alii*, 1994). These high values of pH are frequent in carbonatic bedrocks because of the solubility of calcium and magnesium carbonates in melting waters in which CO₂ is likely to be at the equilibrium with the atmosphere. The presence of carbonates leads to the buffering of the mineral acidity deriving from acid rain,

which would have otherwise decreased the values of pH between 5.5 and 6.5 as it is observed in crystalline bedrock.

To gain a deeper insight, the concentrations of bicarbonate ions were determined in all the samples and the results are reported in tab. 2. The highest concentrations of bicarbonates were measured in surface melting waters, as the interaction between water and rock is much stronger than between ice and rock. The strong weathering of carbonatic rocks is evidenced by the direct relation between pH values (8.39 and 8.71) and the concentration of hydrogen carbonates (27.9 and 34.1 mg/L) measured for samples M4 and M7. On the other hand, the ice and snow samples have very low or even negative carbonate concentrations. This latter result is not an analytical error, but it is related to the presence of mineral acidity in the ice and snow samples, leading to a negative intercept in Gran's plot. In fact, nitrogen oxides («NO_x») and sulphur dioxide (SO₂) are known to oxidise in the atmosphere and lead to the formation of nitric and sulphuric acid after reacting with water (Legrand & Mayewski, 1997, Preunkert & *alii*, 2000, and references therein). Modern techniques of ion chromatography were thus employed to determine the chemical composition of the samples in term of major ions and, hence, to gain a better understanding of the chemistry of this system. The results are reported in tab. 3 (Novo & Rossi, 1998 for a comparison to other Alpine sites). As a first consideration, very low ion concentrations were measured in ice and snow samples and, for some of them, they resulted even lower than the limit of detection (see Experimental).

Melting water samples exhibit instead much higher concentrations of the analysed ions because of the strong chemical weathering of carbonatic rocks. Calcium and magnesium carbonates are in fact quite easily solubilised by both the carbon dioxide dissolved in water, and nitric and sulphuric acids deriving from atmospheric depositions. Both mechanisms lead to the formation of soluble hydrogen carbonates of calcium and magnesium. It should also be noticed that these two mechanisms act synergistically, as the attack by mineral acidity strongly eases the subsequent dissolution by carbon dioxide.

Beside calcium and magnesium, the concentration of sulphate ions is also higher in melting waters with respect

TABLE 3 - Major anion and cation concentrations determined by ion chromatography

Site	Sample nature	Ion concentrations (mg/L)							
		Chloride Cl ⁻	Nitrite NO ₂ ⁻	Nitrate NO ₃ ⁻	Sulphate SO ₄ ²⁻	Sodium Na ⁺	Potassium K ⁺	Calcium Ca ²⁺	Magnesium Mg ²⁺
M1	Deep ice	0.141	< LOD	0.205	0.189	0.111	< LOD	0.057	< LOD
M2	Surface snow	0.026	< LOD	0.400	0.087	< LOD	< LOD	< LOD	< LOD
M3	Deep ice	0.395	0.043	0.251	0.068	0.231	0.066	5.52	0.069
M4	Melting water	0.157	< LOD	1.80	0.520	0.118	< LOD	7.84	1.31
M5	Deep ice	0.094	< LOD	0.074	0.045	0.125	< LOD	0.249	< LOD
M6	Deep ice	0.078	< LOD	0.156	0.030	0.106	< LOD	1.11	< LOD
M7	Melting water	0.200	0.040	1.40	0.406	0.213	0.067	9.58	1.37

to the ice and snow samples. The presence of this ion is to be ascribed to two sources. On the one hand, the presence of SO_4^{2-} in ice and snow is due to the oxidation of sulphur containing compounds during the combustion of fossil fuels. On the other hand, the dissolution of rocks containing sulphates, like gypsum (CaSO_4), leads to a strong enrichment of this ion in melting waters. In fact, calcium sulphate is much more soluble than the corresponding carbonate, in the absence of CO_2 and acidity too (Kegley & Andrews, 1998) and can thus be released more easily from rocks.

It should also be noted that the highest levels of chloride ion were determined in the sampling sites more stressed by human activities, i.e. sites M3 and M7. The first is located near a busy track close to the cable lift arrival and the latter in a cold area favourable for summer skiing, right below extensively used lifts: the presence of chloride, together with sodium, is in fact a good indicator of human and animal wastes.

Non-negligible concentrations of nitrite ions (NO_2^-) are another fingerprint of human pollution of sites M3 and M7. Nitrite is a metastable and very toxic species produced by bacteria during the oxidation of proteins according to the sequence: protein - ammonium - nitrite - nitrate. Nitrite is thus an important indication of pollution due to organic matter. Moreover, NO_2^- is suitable for this kind of studies, as it can be determined at very low levels by means of portable instrumentation with the precision and sensitivity required by environmental research.

CONCLUSIONS

The environmental observations and chemical data collected during the yearly survey of the Marmolada Glacier gave interesting clues about the dry and wet accumulation mechanisms of the atmospheric pollutants and about the weathering of rocks by ice and melting waters. The evaluation of simple chemical like major ion concentrations proved to be a powerful tool for the assessment of the pollution on the glacier surface: in the investigated area, a very high level of pollution was registered. Moreover, the canalisation of melting waters, used for supplying both the hydroelectrical power plant and the devices used for artificial snow production, completely hinders a more detailed study of the water-rock interactions along the ice stream, from the glacier margin to Fedaiia Lake.

A better assessment of the effect of human activities on the reduction of the glacier mass can be accomplished by studying trace elements like iron, copper and manganese and their reactivity with organic matter in water through speciation analysis (Achtenberg & alii, 1997).

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