

Glaciological studies in Mexico, 60 years of academic work: A summary

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ABSTRACT

Glaciers have played a very important role in controlling the climate during most of the geologic history of our planet Earth. Of course, the glaciers have always been at higher latitudes (north and south), and some on high-altitude mountains. Current glaciers in Mexico are those inherited from the Last Glacial Maximum, (26000 - 19000 years before the present), increasing in size during the period of the Little Ice Age (1300 to 1850 common era), and they are unique in several ways; they are located at 19° north latitude, and they received snow precipitation from both the Pacific Ocean and the Gulf of Mexico (Atlantic Ocean). Research on glacial chronology, physical glaciology, and glacial geochemistry at Universidad Nacional Autónoma de México has provided valuable information on climate and environmental changes at different time scales, from millennial to decadal, and even annual. The first part of this work deals with the reconstruction of the glacial history in Mexico and establishing a glacial chronology from the Last Glacial Maximum to the Little Ice Age. The second part of this work focuses on monitoring recent changes (the last 60 years, 1960s to 2023) of the glacier extent on Iztaccíhuatl, Popocatepetl, and Citlaltépetl (the three highest mountains in Mexico), as well as having an updated inventory of all the glaciers at those mountains. Changes in glacier extent and thickness of ice are directly related to the increase in air temperature, variation in precipitation patterns, and glacier dynamics on some of the last glaciers of the northern tropics. The third part of this work focuses on a compilation of geochemical data from 17 years (from 2006 to 2013) of sampling ice (shallow ice cores) and snow at Iztaccíhuatl and Citlaltépetl glaciers. This database has the potential for providing interesting and useful information on natural and anthropogenic-induced changes related to the occurrence of heavy metals in tropical glaciers in the northern hemisphere of North

America. Black carbon concentrations analyzed in snow and glacier ice, and preliminary data on stable isotopes of Zn, also add information on natural vs. anthropogenic sources of heavy metals in central Mexico.

Keywords: Glacial chronology; physical glaciology; geochemical glaciology; Mexico; Iztaccíhuatl; Popocatepetl; Citlaltépetl.

RESUMEN

Los glaciares han desempeñado un papel muy importante en el control del clima durante la mayor parte de la historia geológica de nuestro planeta Tierra. Por supuesto, los mayores glaciares siempre han estado en las latitudes más altas (norte y sur), y algunos en las altas montañas. Los glaciares actuales en México son los heredados del Último Máximo Glaciar (26000 a 19000 años antes del presente), con avances considerables producto de la Pequeña Edad de Hielo (1300 a 1850 años de la era común), y son únicos en varios aspectos. Estos glaciares están ubicados a 19° de latitud norte y reciben precipitaciones de nieve tanto del Océano Pacífico como del Golfo de México (Océano Atlántico). La investigación que se ha desarrollado en la Universidad Nacional Autónoma de México en cronología glacial, glaciología física y geoquímica glacial, ha proporcionado información valiosa sobre los cambios climáticos y ambientales en diferentes escalas de tiempo, desde milenios, décadas e incluso anuales. La primera parte de este trabajo se enfoca en la reconstrucción de la historia glacial en México y en el establecimiento de una cronología glacial desde el Último Máximo Glaciar hasta la Pequeña Edad de Hielo. La segunda parte de este trabajo se enfoca en el monitoreo durante los últimos 60 años (desde 1960 y hasta 2023) de los cambios de extensión de los glaciares del Iztaccíhuatl, Popocatepetl y Citlaltépetl (las tres montañas más altas

de México), así como en tener un inventario actualizado de todos los glaciares de esas montañas. Los cambios del área glaciar y del espesor del hielo están directamente relacionados con el aumento de la temperatura del aire, la variación en los patrones de precipitación y la dinámica de los glaciares en algunos de los últimos glaciares del trópico norte (latitud 19° N). La tercera parte de este trabajo se enfoca en la recopilación de datos geoquímicos resultantes de 17 años (desde 2006 y hasta 2023) de muestreo de hielo (núcleos de hielo superficial) y nieve en el Iztaccíhuatl y el Citlaltépetl. Esta base de datos geoquímicos tiene el potencial de proporcionar información muy interesante y útil sobre los cambios ambientales, naturales e inducidos por el hombre, al analizar las concentraciones de metales pesados presentes en los glaciares de la zona tropical del hemisferio norte de América del Norte. Los análisis de las concentraciones de carbono negro (datos preliminares) encontrado en la nieve y el hielo de los glaciares, así como los análisis de isótopos estables de Zn, añaden información sobre las fuentes naturales vs. las antropogénicas de los metales pesados en el centro de México.

Palabras clave: cronología glaciar; glaciología física; geoquímica glaciar; México; Iztaccíhuatl; Popocatepetl; Citlaltépetl.

INTRODUCTION

Glaciers, the accumulation of snow transformed into ice that moves according to the bedrock and slope towards the ablation or melting zone, are formed when the snow-ice accumulation rate is greater than the snow-ice melting rate. This occurs when the average temperature of the snow-ice accumulation zone is below the freezing point (0 °C). These glacial processes occur, mainly, in polar and high latitude environments, currently in Antarctica (South Pole) and Greenland (Northern Hemisphere), which are called continental glaciers due to their large continental extension and their thickness of ice of several kilometers. But also, high mountains all over the world, depending on latitude and altitude, have glaciers, which can be hundreds of meters thick, in some cases, and tens of kilometers long. Snow precipitates in the accumulation zone together with micrometric solid particles (atmospheric aerosols) and gasses that accumulate in snow pores. Once precipitated, the snow undergoes many physical (crystalline) changes, from kilometers snow to firn and glacier ice. These crystallographic changes from snow to ice are a subject of study of physical glaciology (ice petrography) that we will not discuss further in this article.

Glaciation leaves evidence in the geologic record in the form of sedimentary features (moraines and erratic blocks), glacial lakes, and glacial erosion features (polished and striated bedrock), among others. Glacial processes are quite common in Earth history from the Precambrian to the Holocene. The glaciers of the past that have been the focus of research at Universidad Nacional Autónoma de México (UNAM), are those from the Late Pleistocene and Holocene, from the Last Glacial Maximum (LGM; 26000–19000 years before the present, BP) to the Little Ice Age (LLA; 1300 to 1850 years common era, CE), and to the present.

This article is divided into three major sections: 1) the glacial chronology of Mexican high mountains (glaciers of the past related to cold phases of the late Quaternary); 2) the current state of Mexican glaciers (physical glaciology); and 3) geochemical glaciology, preliminary data from chemical analysis of snow and ice from 17 years, and research work. These three fields of glaciology reflect the research that has been carried out at UNAM since the 1950s, and that is currently in progress with active projects and postdocs programs at the Institutos de Geografía, Geología, Geofísica, Física, and Centro de Geociencias.

GLACIAL CHRONOLOGY

Since the mid 19th Century, evidence of past glaciation has been one of the major sources of paleoclimatic information. The discovery that alpine glaciers were substantially larger in the relatively recent past highlighted the changing nature of climate and prompted the study of Quaternary environments and climates (Imbrie and Imbrie, 1979). The analysis of past glaciation is one of the proxy records capable of providing quantitative estimates of climate change for paleotemperatures.

Compared to the mid and high latitudes, the study of glaciation in the tropics progressed slowly during the 20th century. As everywhere, it relied on relative dating criteria and limited use of radiocarbon due to the scarcity of organic matter in high mountain environments, hampering the correlation with other records of environmental change. However, with the development of dating techniques, in particular cosmogenic nuclide dating, numerous chronologies of glaciation have been established for tropical mountains over the past 30 years (Heine, 2019).

In Mexico, after pioneering efforts to identify evidence of past glaciation (e.g., Böse and Ordóñez, 1901) and to establish a relative chronology for Iztaccíhuatl mountain (De Terra *et al.*, 1949), a formal glacial sequence was first proposed by White (1962). Subsequent work on Ajusco mountain (White *et al.*, 1990), on Popocatepetl mountain (White, 1981a), and the equilibrium line altitude of glaciers of the three mountains (White, 1981b) added radiocarbon dating and estimates of temperature change to the chronology, thus allowing for correlations with the glacial advances of North America (White, 1987; White *et al.*, 1990).

Heine (1975a, 1983, 1988, 1994) developed an independent glacial chronology for Malinche volcano based on tephrostratigraphy and radiocarbon dating, and subsequently, he expanded it to Iztaccíhuatl, Popocatepetl, Nevado de Toluca, and Citlaltépetl mountains. The original chronology of Malinche (Heine, 1975a) includes five glacial advances spanning the last 36000 ¹⁴C years and correlations with the glacial events defined by White (1987).

In the last two decades, a glacial chronology based on the *in-situ* accumulation of the cosmogenic nuclide ³⁶Cl (Phillips, 1995) has been developed for Iztaccíhuatl, Cofre de Perote, Tancitaro and Nevado de Toluca mountains (Figures 1 and 2; Vázquez-Selem, 2011; Vázquez-Selem and Heine, 2011; Vázquez-Selem and Lachniet, 2017). This has allowed correlating the glacial chronology of central Mexico with those from other mountains of the Americas (Lachniet and Vázquez-Selem, 2005; Palacios *et al.*, 2020) and with other proxy records from the region such as pollen, diatoms and speleothems (Lozano-García and Vázquez-Selem, 2005; Caballero *et al.*, 2010; Lachniet *et al.*, 2013).

Extent of Glaciation

In his pioneering study of modern glaciers in Mexico, Lorenzo (1964) listed eight volcanoes of the Trans-Mexican Volcanic Belt (TMVB) with traces of past glaciation: Nevado de Colima, Nevado de Toluca, Ajusco, Iztaccíhuatl, Popocatepetl, Malinche, Cofre de Perote, and Citlaltépetl. Heine (1975a) added Telapón and Tlaloc to this list and two sites of northern Mexico with probable glaciation: Peña Nevada in Nuevo León and unidentified mountains in southern Durango.

To date, Late Pleistocene glaciation has been documented and mapped with different degree of detail on the following volcanoes of the TMVB (Figure 1), from west to east: Nevado de Colima (Lorenzo, 1961), Tancitaro (Vázquez-Selem, 2011), Nevado de Toluca (Heine, 1975a, 1994), Ajusco (White *et al.*, 1990), Iztaccíhuatl (White, 1962, 1981b, 1987; Heine, 1975a, 1988; Vázquez-Selem and Heine, 2011), Popocatepetl (White, 1981a; Heine, 1975a, 1983; Espinasa-Pereña and Martín-del Pozzo, 2006), Malinche (Heine, 1975a, 1988), Citlaltépetl (Heine, 1975b, 1988) and Cofre de Perote (Vázquez-Selem, 2011; Carrasco-Núñez *et al.*, 2010). Other mountains with clear traces of

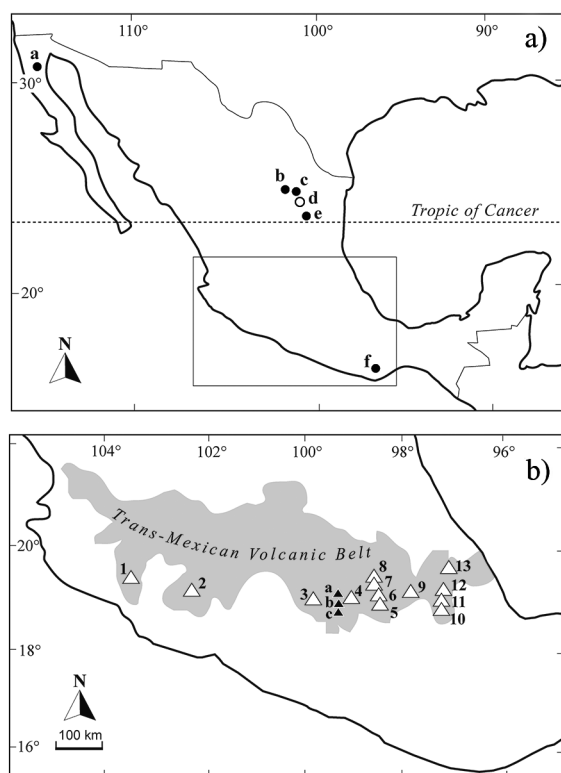


Figure 1. a) General location map showing mountains outside the Trans-Mexican Volcanic Belt with demonstrated glaciation (open circle) and probable glaciation (black circle): a. San Pedro Mártir (3000 m a.s.l.). b. La Viga (3700 m a.s.l.). c. La Marta (3690 m a.s.l.). d. Cerro Potosí (3720 m a.s.l.). e. Peña Nevada-Pico San Onofre (3500–3550 m a.s.l.). f. Quie Yelaag-Quixobee (3700 m a.s.l.). b) Location of mountains of the Trans-Mexican Volcanic Belt with evidence of late Pleistocene glaciation (open triangle) and probable mid Pleistocene glaciation (black triangle). The three highest mountains (underlined) supported glaciers in the early 21st century. 1. Nevado de Colima (4240 m a.s.l.). 2. Tancítaro (3840 m a.s.l.). 3. Nevado de Toluca (4650 m a.s.l.). 4. Ajusco (3940 m a.s.l.). 5. Popocatepetl (5450 m a.s.l.). 6. Iztaccíhuatl (5220 m a.s.l.). 7. Telapón (4060 m a.s.l.). 8. Tláloc (4120 m a.s.l.). 9. Malinche (4440 m a.s.l.). 10. Sierra Negra (4580 m a.s.l.). 11. Citlaltépetl (5650 m a.s.l.). 12. Las Cumbres (3950 m a.s.l.). 13. Cofre de Perote (4220 m a.s.l.). a. San Miguel (3800 m a.s.l.). b. Las Cruces (3700 m a.s.l.). c. Zempoala (3690 m a.s.l.).

late Pleistocene glaciation yet to be studied are Tláloc, Telapón, Las Cumbres, and Sierra Negra (Figure 2). High mountains (higher than 4200 m a.s.l.) were glaciated during the early Holocene and the three highest ones (Citlaltépetl, Popocatepetl, Iztaccíhuatl) experienced significant glacier expansion in the late Holocene (Little Ice Age).

Geomorphological evidence (U-shaped valleys, cirque-like headwalls, narrow ridges or *arêtes*) suggests past glaciation in other mountains of the TMVB, but their lower elevation and more subdued morphology are indicative of glaciation prior to the Late Pleistocene. That is the case of three volcanic complexes near the SW corner of the Basin of Mexico: San Miguel (*ca.* 3800 m a.s.l.), Las Cruces (3700–3780 m a.s.l.), and Zempoala (3690 m a.s.l.; Figure 1b).

The record of glaciation has been partially obliterated on high mountains with persistent volcanic activity through the Late Pleistocene and Holocene, such as Citlaltépetl and Popocatepetl. Volcán de Fuego de Colima (3860 m a.s.l.) and Jocotitlán (3950 m a.s.l.) have elevations within the range of the Late Pleistocene snow lines of the region (3400–3950 m a.s.l., Lachniet and Vázquez Selem, 2005), but their Pleistocene-Holocene activity likely precluded the formation/

preservation of glacial features. The same applies to Tacaná volcano (4060 m a.s.l.) in southeastern Mexico (Figure 1b).

In northern Mexico glaciation has been demonstrated only for Cerro Potosí (3720 m a.s.l.), the highest Mexican mountain to the north of the Tropic of Cancer (Vázquez-Selem and Heine, 2011). Observations on aerial photos and Google Earth imagery suggest that other peaks of Sierra Madre Oriental in the same area probably supported small glaciers in the late Pleistocene, but convincing field evidence is still missing. This is the case of Peña Nevada-Pico San Onofre (3500–3550 m a.s.l.) and especially the north-facing flanks of La Marta (3690 m a.s.l.) and La Viga (3700 m a.s.l.; Figure 1a).

No geomorphological evidence of past glaciers exists for the Sierra Madre Occidental. Even the highest peaks, located in southwestern and west Durango (3200–3300 m a.s.l.) likely did not surpass the Late Pleistocene regional snowline, which was probably close to the snowline of Tancítaro peak (*ca.* 3400 m a.s.l.). In northwest Mexico the best case for Pleistocene glaciation is Sierra de San Pedro Martir in Baja California, due to its high latitude (31° N) and elevation (2900–3000 m a.s.l.). Cirque glaciers probably formed around the highest peaks, but field evidence is still missing.

The highest peaks of Sierra Madre del Sur in Oaxaca (Quie Yelaag and Quixobee), with an elevation of *ca.* 3700 m a.s.l., probably supported glaciers in the Late Pleistocene. However, their morphology as observed from air photos or satellite images is inconclusive.

In summary, glaciation during the Late Pleistocene (Marine Isotope Stage 2) was limited to the mountains of the TMVB, above 3800 m a.s.l., and to some peaks of the Sierra Madre Oriental, in NE Mexico, higher than 3600–3700 m a.s.l. Mountains of the TMVB peaking around 3700–3800 m a.s.l. show evidence of glaciation during a previous glacial cycle, presumably Marine Oxygen Isotope 6.

Timing of Glaciation

Since 1990 glacial geomorphology and chronology underwent a revolution with the development of cosmogenic nuclide dating (Granger *et al.*, 2013). Prior to that time, the possibility of dating a glacial advance or recession depended mainly on maximum or minimum limiting dates associated with radiocarbon or tephrostratigraphy. Cosmogenic nuclide dating made it possible to directly date geomorphic surfaces produced by glaciers, such as moraine boulders or glacially abraded bedrock. In central Mexico, the volcanic origin of the rocks of the TMVB allows for the use of the cosmogenic dating method of Chlorine-36 (³⁶Cl), a cosmogenic nuclide that does not require a specific mineralogy and that can be measured from whole rock (Phillips, 1995).

Iztaccíhuatl is the mountain with the longest record of glaciation in Mexico (White, 1987) due to its high elevation and its volcanic inactivity since *ca.* 80000 years BP (Nixon, 1989). The use of cosmogenic ³⁶Cl (nearly 120 age determinations), in tandem with tephrostratigraphy and eight radiocarbon dates (¹⁴C), resulted in a glacial chronology of the last 200000 years BP (Vázquez-Selem, 2011). In addition, the application of ³⁶Cl on Nevado de Toluca (Arce *et al.*, 2003), Cofre de Perote (Carrasco-Núñez *et al.*, 2010), and Tancítaro has allowed correlations of glacial deposits among different mountains, leading to a regional chronology (Vázquez-Selem and Heine, 2011). Figure 2 summarizes the glacial chronologies of different mountains in central Mexico and their correlation.

Overall, the main phases of glacial advance and moraine construction are related to cold events lasting several hundred to a few thousand years. Just as important from the paleoclimatic point of view are the phases of glacial retreat, produced by warming and in some cases drying conditions. From the LGM of the Late Pleistocene (26000–18000 years BP) through the early Holocene, the phases of glacial advance and retreat in central Mexico are overall synchronous

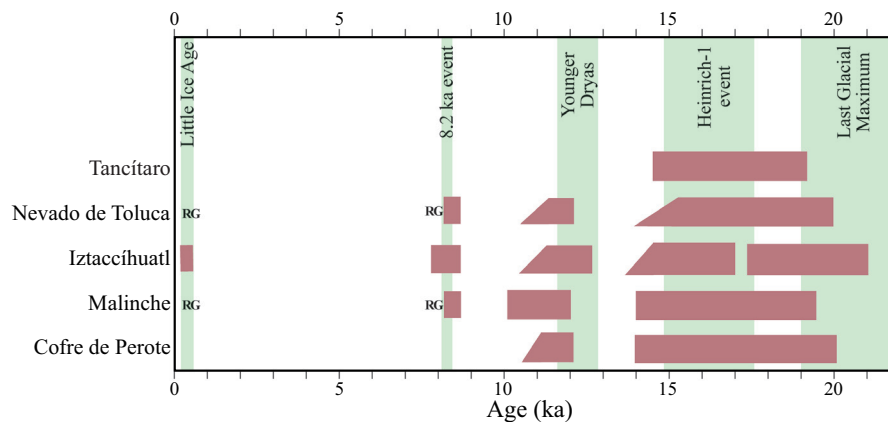


Figure 2. Correlation of glacial deposits of the mountains of central Mexico with global climatic events. Brown bars are glacial advances and moraine formation. RG: rock glacier formation. Green vertical bars are global climatic events. Ages for Iztaccíhuatl, Cofre de Perote, and Tancitaro mountains are based on cosmogenic ^{36}Cl dating (Vázquez-Selem and Heine, 2011; Vázquez-Selem and Lachniet, 2017); ages for La Malinche and Nevado de Toluca mountains are in calendar years BP, originally reported as ^{14}C years BP by Heine (1988).

to those of the northern tropics (Vázquez-Selem and Lachniet, 2017) and correlate well with the paleoenvironmental evolution of central Mexico (Caballero *et al.*, 2010). Also, glacial advances are in general coeval to major cold events of the mid-latitudes of the northern hemisphere, namely the LGM, Heinrich event 1 (17000–15000 years BP), Younger Dryas (12900–11700 years BP) and the 8200 years BP cold event (Palacios *et al.*, 2020).

However, major deglaciation in central Mexico did not start around 19000 years BP as in many other parts of the tropics and mid-latitudes, but rather after 15000 years, in coincidence with the Bolling-Allerod warm phase (14600–12900 years BP). The fact that glaciers on the highest mountains of central Mexico (> 5000 m a.s.l.) advanced during the Younger Dryas and the 9000–8000 years cold events, suggests that the northern tropics were substantially influenced by millennial-scale cooling phases of the mid and high latitudes of the Northern Hemisphere.

The most recent advance, recorded only on the three highest peaks of Mexico (> 5000 m a.s.l.), apparently is coeval to the Little Ice Age, a cold phase extending from ca. 1300 CE to ca. 1850 CE (Vázquez-Selem and Heine, 2011). However, ^{36}Cl dating of the moraines is still pending.

Based on the reconstruction of former glaciers, estimates can be made of their equilibrium line altitude (ELA). The ELA is generally located around the 0 °C isotherm, whereby its position can be used to estimate paleotemperatures. Estimates of ELA depression and related cooling have been made for different glacial advances of Iztaccíhuatl mountain (Vázquez-Selem, 2011). During the maximum glacier extent of the Late Pleistocene (21000–17000 years BP), ELAs in central Mexico were at 3400–3950 m a.s.l., depending on the mountain, which implies an ELA depression of ca. 1600–1000 m with respect to the regional modern ELA of ca. 5000 m a.s.l. A similar range of ELA depression has been found in the mountains of northern tropical America during the LGM (Lachniet and Vázquez-Selem, 2005). This observation suggests a cooling of 6–9 °C during the LGM in central Mexico, which is in agreement with global cooling estimated from other proxies (*e.g.*, Tierney *et al.*, 2020).

CURRENT STATE OF MEXICAN GLACIERS

As mentioned in the previous section, glaciers in Mexico have been present in the highest mountains of Mexico for thousands of years: Iztaccíhuatl, Popocatepetl, and Citlaltépetl. As early as 1923, Weitzberg (1923) mentioned that "periodic oscillations", like those of

the Popocatepetl glacier area, were observed in other glaciers of the world and that eruptive activity produced a slight decrease in glacier thickness. Robles-Ramos (1944) described the relationship of the Iztaccíhuatl glaciers with local meteorology. These ice bodies were studied for the first time between 1957 and 1958 during the International Geophysical Year. Lorenzo (1964) integrated the first Mexican glaciological inventory. White (1981a; 1981b) carried out studies on glacial fluctuations at Popocatepetl and Iztaccíhuatl volcanoes from the identification of existing and past equilibrium lines, estimating for the first time the magnitude of glacial retreat in Mexico. Later, Delgado-Granados (1997) presented an updated inventory of the glaciers of the Popocatepetl volcano based on field observations made between 1977 and 1992.

Glaciers of Iztaccíhuatl

Lorenzo (1964) measured the size of twelve glaciers using aerial photographs obtaining an extension of 1.4 km² (revised by Cortés-Ramos and Delgado-Granados, 2015). Delgado-Granados *et al.* (1986) found that three of these glaciers were extinct and the rest were described and classified. Delgado-Granados *et al.* (2005) reported for 1982 a total glacier area of 0.97 km², having lost an area of 20 % in 24 years. These authors studied one of the most representative glaciers of Iztaccíhuatl: the Ayoloco Glacier, reporting an area of 218340 m² for 1982 and of 140890 m² for 1998. Compared with the area reported by Lorenzo (1964), there is a 43 % glacier area loss in 40 years.

Schneider *et al.* (2008) updated the glacial inventory of Iztaccíhuatl volcano (Figure 3). The latter establishes a projection of the disappearance of these glaciers by 2020. Two years earlier, the Ayoloco glacier was declared extinct and only remnants of this glacier can be distinguished (https://www.dgcs.unam.mx/boletin/bdboletin/2021_349.html). At the time of this review, El Pecho is the only glacier remaining in this volcano which exceeds the projection proposed by Schneider *et al.* (2008). These authors clarified that although much of the glacial retreat is related to climate change, *in situ* observations suggest that geothermal heat fluxes and hydrothermal flows in the crater area should also be considered.

Thickness

Álvarez and Delgado-Granados (2002) studied the thickness of the La Panza glacier on Iztaccíhuatl using ground penetrating radar (GPR) to analyze the morphology of the ice substrate at depth and identified buried volcanic landforms as well. Subsequently, Delgado-

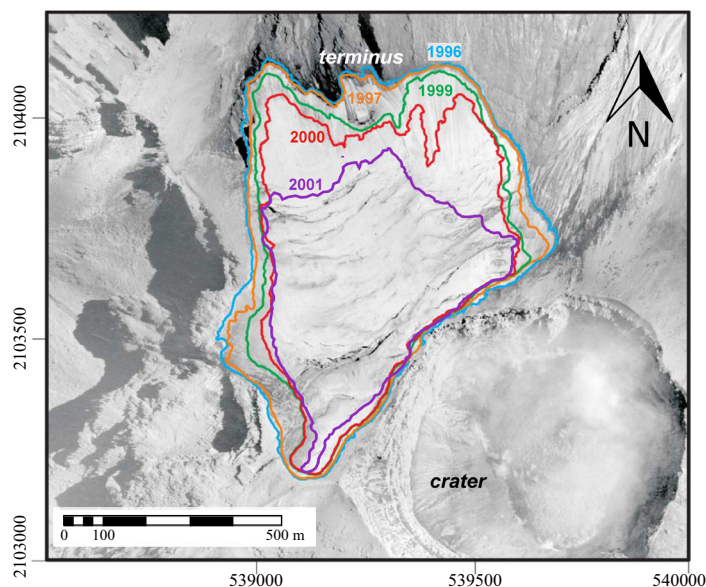


Figure 3. Recent changes in area size (1996-2001) in Popocatepetl Glaciers.

Granados *et al.* (2005), used a maximum thickness of ~70 m, and an average thickness of ~20 m of the Ayoloco Glacier to estimate a glacial volume of 4516400 m³ (Figure 3).

Glaciers of Popocatepetl

Lorenzo (1964) reported that the glacial area of Popocatepetl was 720000 m² and consisted of three glaciers: North Glacier (190000 m²), Ventorrillo Glacier (435000 m²), and Northwest Glacier (120000 m²). Delgado-Granados *et al.* (1986) and Delgado-Granados (1997) pointed out that the North Glacier was part of the Ventorrillo Glacier because they share accumulation and drainage areas. The Ventorrillo Glacier had four glacier tongues (Tezcalco I and II, Ventorrillo, and Herradura) with two crevasse systems. The northwest glacier had no crevasse system of its own; most of it was made up of ice with a high detritus content, and although it shared an accumulation area with the Ventorrillo Glacier, it drained to the west. According to White (1954), maximum accumulation occurred from November to January, with an additional period from June to September, with snow being the main form of nourishment, followed by hail (from June to August), and re-frozen meltwater to a lesser extent. This was confirmed based on field observations by Delgado-Granados *et al.* (1986) and Delgado-Granados (1997).

Changes in Popocatepetl Glaciers

From 1958 to 1982, a decrease of 22 % in glacier extension was noted on the Popocatepetl mountain, and from 1958 to 1996 the reduction in the area was 50 % (Delgado-Granados, 1996). Julio-Miranda *et al.* (2008) estimated that by February 2001, the remaining glacial area was only 29 % of that reported for 1958. The retreat of the altitude of the glacier front illustrates very well the disappearance of glaciers (Figure 4).

On December 21, 1994, an eruption began at Popocatepetl volcano characterized by volcanic explosions alternating with lava emissions. Julio-Miranda *et al.* (2008) established that phenomena associated with eruptive activity, such as the increase in heat flow under the glacial ice, the fall of tephra on its surface, and pyroclastic flows that moved over the glacier surface, caused its thinning, retreat and, in the final stage, its fragmentation between 1994-2001. The mass balance during the

eruptive stage of Popocatepetl was estimated with ice loss of 81491 m³ (1996-1997), 1884292 m³ (1997-1999), and 1280639 m³ (1999-2000).

Glaciers at Citlaltépetl

Lorenzo (1964) established the existence of nine glaciers covering an area of 9.5 km², the largest glacial area in the country. Cortés-Ramos and Delgado-Granados (2015) corrected cartographic flaws and reconstructed the 1958 glacial area, reporting an extension of 2.04 km². Cortés-Ramos and Delgado-Granados (2012; 2013) show that the Citlaltépetl glaciers were the largest contemporary ice bodies in the country. In 2007 they covered an area of 621230 m², the north glacier had a maximum length of 960 m and reached a minimum altitude of 5126 m a.s.l. Volcanic activity is not as important as in Popocatepetl and Iztaccíhuatl, although Delgado-Granados (2007) mentions that the glaciers have retreated considerably, mainly due to climatic variations, despite low-temperature fumaroles near the summit of Citlaltépetl. This volcano is not surrounded by large cities as is the case of Popocatepetl and Iztaccíhuatl volcanoes.

Cortés-Ramos and Delgado-Granados (2012) established some relationships between glacial retreat and net radiation on the glacial surface of Citlaltépetl, indicating that there are areas more vulnerable than others to glacial retreat as those on the west slope of the volcano. Continuing in this line, Ontiveros-González *et al.* (2015) highlight the

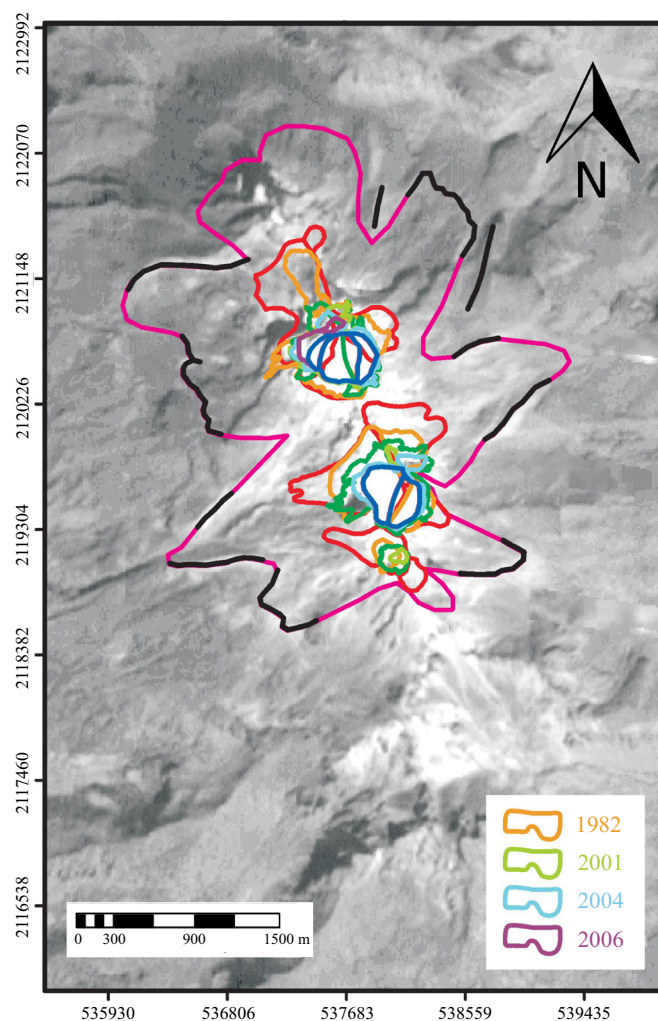


Figure 4. Recent changes in area size (1982-2006) in Iztaccíhuatl Glaciers.

close relationship and dependence of the calculated energy balance over the glacier surface with the measured net radiation. Using data from an automatic weather station located over the glacier surface (5100 m a.s.l.), these authors observed (during three years of records) that the calculated surface energy balance over that location correlated better with net radiation than with sensible and latent heat fluxes. From this result, the authors suggested that net radiation is the main component responsible for glacier shrinkage since this parameter controls the energy balance variability.

Glacier retreat at Citlaltépetl

From 1958 (2.04 km²) to 1989 (1.29 km²), the area of Glaciér Norte glacier disappeared by 36 %, following a loss rate slower than that occurred during the period of 1989-1998 (-0.04 to 1 km²). After 2005, this loss rate declined ten times (-0.004 to 1 km²) compared to that calculated during the 1990s and the mid-twenties (Cortés-Ramos et al., 2019). By 2017, this glacier had lost 71 % of its area coverage relative to 1958 (Figure 5).

Geodetic measurements show retractions of the glacier front from the end of the LIA to the present. Between 1958 and 1989, the elevation

of the glacier front changed at a rate of 3.7 to 1 m per year from 4640 to 4755 m a.s.l. A drastic retreat in one of the glacier tongues took place during the 1990's, separating this tongue from the main glacier body. The altitude of the glacier front changed from 4766 m a.s.l. in 1994 to 4965 m a.s.l. in 2017 when the accelerated retraction of the glacier had a maximum of +15 m per year during the period of 2005-2017. Cortés-Ramos and Delgado-Granados (2013) emphasized that the glacier front has moved steadily toward higher altitudes since 2001, similar to the global trend of glacier retreat (Zemp et al., 2007). Between 1990 and 2007, the glacier front rose ~100 m in altitude, corresponding with the disappearance of Jamapa and Chichimeco glacier tongues (Cortés-Ramos and Delgado-Granados, 2012; 2013).

Glacier depth

From a GPR profile conducted in 2006 (Ontiveros-González, 2018), a mean depth of ~19.5 m, a maximum of ~60 m, and a minimum approaching zero at the glacier edges were measured along the surface of the glacier. In 2016, a high-resolution GPR profile updated the maximum depth to ~80 m along a transverse transect at 5130 m a.s.l.

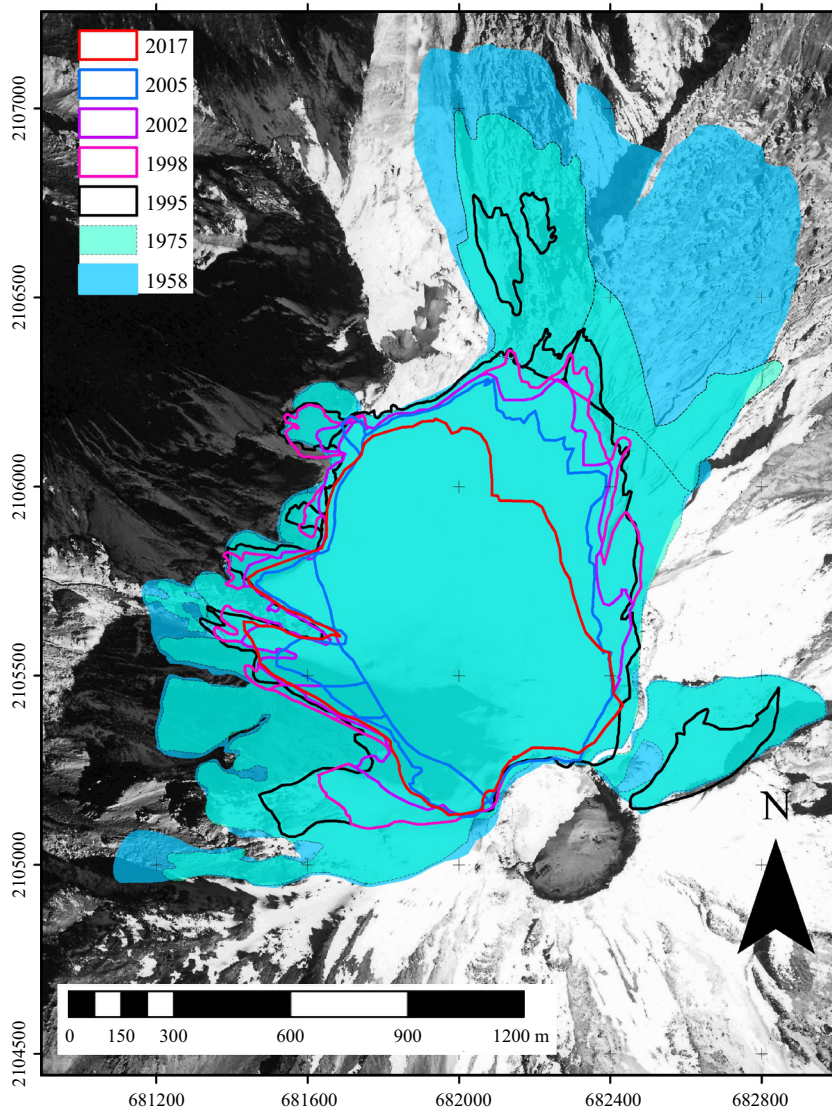


Figure 5. Recent changes in area size (1958-2017) in Citlaltépetl Glaciers.

Future prospects

Ontiveros-González (2018) proposed a projection for a possible scenario of the glacier volume evolution from 2016 based on an estimation of the glacier bed and the annual mass balance. In the proposed projection, between 2016 and 2020 the author expected a slight change over the depth found by the GPR profile and projected over the whole glacier, especially along the higher altitudes. Between 2021 and 2023, glacier thinning, and retraction is possible at the eastern and western edges, especially in the lower and middle elevations of the glacier surface. By 2023, the glacier bed will become visible around 5300 m a.s.l. By 2034 the glacier area will be reduced, representing 10% of the area that was present in 2016. In 2038 or 2039, the glacier volume would be 10% of the 2016 volume; then, the glacier surface will be fractionated into three parts. Finally, Ontiveros-González (2018) suggested that this fragmentation would mark the beginning of the glacier disappearance, leaving only small and scarce ice bodies above 5200 and 5300 m a.s.l.

According to Soto (2023), the accumulation zone of the Pico de Orizaba glacier system has not existed since 2019, which has caused the outcrop of the rock bed. Exposure of the bedrock increases solar energy transference as heat to the adjacent ice and snow, causing an increasing melting. At the same time, it prevents the flow of ice towards the ablation zone, causing an accelerated retreat of the glacier front. So, the current surface of the glacier is $\sim 0.46 \text{ km}^2$.

Periglacialism on Iztaccíhuatl

Andrés *et al.* (2010; 2011; 2012a; 2012b) emphasize the non-existence of continuous permafrost at Iztaccíhuatl due to the altitude of the volcano, recognizing the occurrence of isolated and discontinuous segments between 4600 and 5000 m a.s.l. Periglacial processes at Iztaccíhuatl volcano are based on soil thermal data and the presence of permafrost above 4900 m a.s.l. There are temperature records in Popocatepetl soils that allowed them to identify areas of discontinuous permafrost 200 m above the reported for Iztaccíhuatl. The air temperature at Iztaccíhuatl correlates with soil temperature data over a ten-year period, resulting in the periglacial zone of the volcano beginning at 4400 m a.s.l. with regions of discontinuous and isolated permafrost between 4600 and 5000 m a.s.l., depending on the orientation of the slopes.

Periglacialism on Popocatepetl

Delgado-Granados (1997) reported the existence of permanently frozen ground where landslides occurred due to hydric saturation or soliflujión. Delgado-Granados (1997) identified four areas of this type of soil in Popocatepetl: Norte (69000 m^2), Yancuecole (43000 m^2), Las Cruces (119000 m^2) and Coyotes (8000 m^2).

Periglacialism on Citlaltépetl

As early as 1975, the presence of fossil permafrost was reported between 4600 and 5000 m a.s.l. (Heine, 1975a), although it could begin above 4000 m a.s.l. when vegetation reaches its upper limit. He also mentioned that some terminal moraines above 4600 m a.s.l. could be rock glaciers. Based on air, soil, and glacier base temperature data, as well as on the correlation of insolation and albedo, together with documented critical elements, the lower limit of continuous permafrost has been documented at 4880 m a.s.l. and discontinuous permafrost above 4780 m a.s.l. on the northern slope of the volcano, as well as 4963 and 4863 m a.s.l. respectively on the southern slope. Due to the altitude of 4700 m a.s.l. of the glacial ice line until 1975 on the north face, the isolated portions of discontinuous permafrost must be the product of that glacial retreat (Soto-Molina *et al.*, 2019). The possible existence of basal permafrost inside the main Citlaltépetl glacier can

be suggested because the basement in the deepest part (115 meters) is preserved at $-2.48 \text{ }^\circ\text{C}$ throughout the year without registering the minimum temperature oscillation. Seasonal temperature ranges influence the shallower parts without crossing the melting point barrier (Soto-Molina *et al.*, 2019).

Recent studies (Soto-Molina and Delgado-Granados, 2020) indicate that periglacial activity at the Pico de Orizaba starts above 4584 m a.s.l., with the presence of cryoclasty that gives rise to the debris cones, sometimes flowing down. Additionally, at the northern slope, the lower limit of discontinuous permafrost is located at 4880 m a.s.l. and continues at 4963 m a.s.l.; while on the southern slope, both are located 100 m higher. More studies are needed on the Mexican cryospheric environment, particularly at the highest mountains of the country (*e.g.* the recent studies at Cofre de Perote volcano, which recreate the glacial cover and periglacial dynamics surface at the end of Late Pleistocene; Victor Soto, 2023, personal communication).

GLACIAL GEOCHEMISTRY

Snow precipitates together with micrometric solid particles (atmospheric aerosols) and gasses that accumulate in snow pores. Once precipitated in the glacier, the snow undergoes many physical (crystalline) changes forming ice of various types. Among the principal constituents of atmospheric aerosols precipitated in the snow, and accumulated (recorded) in glacial ice are: 1) Na, Cl, Mg, K, SO_4 and many others elements, basically from marine source; 2) SiO_2 , Ca, Fe, Al, Mg, and many more elements from atmospheric dust; 3) C and heavy metals due to natural forest fires; 4) SiO_2 , Ca, Mg, Fe and many more compounds and elements derived from volcanic ash from local, regional and even global events (large volcanic explosions spew micrometer volcanic ash at high altitudes (10 to 20 km high) and can travel around the planet in a few weeks); 5) Fe, Ni, Pt and platinum-group elements and other metals derived from meteorite impacts; 6) all elements and compounds derived from human activity (industry, hydrocarbon burning, agriculture, pesticides, fertilizers, etc.); 6) atmospheric gasses (natural and anthropogenic gasses: O_2 , CO_2 , CH_4 , SO_2 , NO_2 , chlorofluorocarbons (CFC), etc.) that are trapped in ice pores during the crystalline transformation from snow to ice; and 7) cosmogenic elements (atmospheric cosmogenic isotopes which are formed due to cosmic ray impact with atoms of atmospheric gasses, *e.g.* ^{14}C , ^{10}Be , ^{36}Cl , and others). In addition, precipitation temperature (summer precipitation-near $0 \text{ }^\circ\text{C}$, or winter precipitation - temperatures from -10 to $-60 \text{ }^\circ\text{C}$, depending on latitude and altitude) can also be determined on the basis of stable isotopes of water (Deuterium and ^{18}O). To this date (2023) there are also stable metal isotopic measuring techniques for several transition metals (*i.e.* Fe, Zn, Cu, Hg, Cd, Mo, Cr; Bullen, 2011). The ratio between a pair of stable metal isotopes allows us to relate isotopic fractionation with different geochemical processes and, ultimately, differentiate metal sources in the glacial record (natural or anthropogenic sources).

In this section, we will discuss four techniques of glacial geochemistry: black carbon, metal geochemistry, stable isotopes of metals and atmospheric stable isotopes (^{10}Be). These techniques are currently used to monitor climate-environmental records and anthropogenic impact, as well as the use of ^{10}Be to relate climate change with solar activity variations.

Black Carbon

Black Carbon (BC) is an aerosol characteristic of the troposphere formed basically by the incomplete combustion of fossil fuels. The BC is taking great importance as a parameter to consider in the

environmental climate impact of short time in glacial areas. Due to its light-absorbing properties, BC can darken the surface of snow or ice, affect the energy balance, and affect the melting rate of a glacier mass. Drilling, extraction, and analyses of glacial ice cores in different glaciers (continental and mountain) show a dramatic increase in BC since the 1850's and continuously during the 20th and 21st centuries, consistent with fossil fuel-based industrial development. From 1970 onwards, a decrease in BC was detected in glacial areas of Europe and Antarctica and is assumed to be due to actions taken since the Clean Air Act. However, data from Himalayan glaciers show a continuous increase of BC in snow and ice. Because of its color, snow reflects most of the incident solar radiation. BC, like other solid materials, darkens the snow when deposited, decreasing the fraction of solar radiation reflected and increasing the solar radiation absorbed. In turn, more absorbed energy generally implies more melting of the glacier mass. Sources of black carbon are the burning of wood, carbon, and fuel oil, as well as other industry-related activities such as mining. This material can travel thousands of kilometers suspended in the air, so there is no region on earth where some amount of black carbon is not deposited, and its presence on glaciers is permanent, although its concentration may vary throughout the year. The retreat of glaciers cannot be explained by the presence of black carbon alone, but it is significantly related to climate change. There are several well-accepted methods for measuring the amount of black carbon deposited on snow surfaces. These methods have in common the sampling that is then passed through a filter for subsequent analysis by different techniques. One is the light-absorption heating method (LAHM) which is used to accurately quantify the impact of light-absorbing particles on snow (Schmitt *et al.*, 2015). The premise behind this method is to estimate the amount of light energy that the particles will absorb that will cause increased melting or sublimation. Since snow is completely absorbing in the thermal infrared wavelength range, the most critical wavelengths to consider are in the visible range. The LAHM technique does not discriminate between BC and dust. Therefore, values derived from the LAHM technique should be treated as "effective black carbon" (eBC), which means that the visible light absorption capacity of the particles on the sample filter is equivalent to a given amount of BC.

Figure 6 shows the average concentrations of black carbon for snow, glacier ice and high mountain lakes and springs from Iztaccihuatl and Citlaltépetl, Mexico; Cordillera Blanca, Peru, and Cordillera Real, Bolivia, for 2019 and 2022 seasons. The BC measurements were carried out in the Laboratory of Environmental Geochemistry, Centro de Geociencias, UNAM. Bars indicate the averages of BC equivalent content (mg/kg) for all the sampling sites. The red square indicates the range of annual BC content as reported for samples from the Cordillera Blanca, Perú (Guillermo Ontiveros, 2023, personal communication; Schmitt *et al.*, 2015).

Heavy Metals

For about 6000 years, we have been using metals such as Cu, Fe, Zn, Au, Ag, and others, for our industrial and human society development. Since the Industrial Revolution (1700's) we have considerably increased the number of metals we use in modern technology and industrial processes. But in the last 40 years, the number of metals used in modern technology has risen to around 68 (a good example of their use in modern technology is in our mobile devices, computers, electric cars, batteries, and other devices). On the other hand, some metals such as Ca, Mg, Fe, Cu, Co, Cr, Zn, Mo, Li (among others) are basic in the metabolic processes of plants, animals, and even humans. As mentioned above, these metals floating in the troposphere, as millimetric particles, are deposited in glacier snow and ice, forming an environmental record.

A very extensive database of heavy metals in ice cores has been obtained from Greenland, Antarctic, and Alpine snow and ice cores. But Lonnie Thompson and his team from Ohio State University, started drilling ice cores in the Peruvian Andes (tropical or low-latitude glaciers). They have gathered a geochemical database for nearly 40 years, dated 22000 BP (Last Glacial Maximum), to the Little Ice Age (1300 to 1850 CE). The most important conclusion of these works indicate that the metal source is mainly from rock and soil dust, but other sources are needed to be explained (Ferrari *et al.*, 2001, Thompson, 2017). The current standard analysis of heavy metals in glacier ice and snow is carried out by using the sensitive ICP-MS technique, which can detect fractions of ppm. Ice cores in mountain glaciers have been drilled in the Andes, Alaska, Kilimankaro, Alps and Himalaya, but UNAM research is just starting to collect data of heavy metals in the small Mexican Glaciers. These glaciers are unique because they are the only ones at 19° north latitude in the world. Their geographical location, proximity to one of the largest metro areas in the world (Mexico City), industrial zones, and snow precipitation conducted by the convective patterns coming from the Gulf of Mexico and the Pacific Ocean, both in winter and summer storms, offers a good opportunity to analyse the anthropogenic impact on atmospheric precipitation recorded in glacier snow and ice. For the last decade, surface snow and glacier ice (borings and shallow cores at 1 m depth) have been sampled in Iztaccihuatl and Citlaltépetl for geochemical and isotopic (Deuterium and ^{18}O) analyses.

Considerable concentrations (micrograms/liter) of Zn, Cu, Fe, among other metals, and Nitrates have been detected. Table 1 shows a summary of the average concentrations of V, Cr, Ni, Cu, Zn, and Pb for Iztaccihuatl and Citlaltépetl snow and ice above 5000 m for 15 years of sampling and monitoring metals in the glaciers (Carrillo-Chavez *et al.*, 2023). Table 2 shows a comparison between the average metal content in a drill core of 120 m depth in Sajama Glacier, Bolivia (Ferrari *et al.*, 2001) with the average metal content from the Mexican mountains (Carrillo-Chavez *et al.*, 2023). V, Cr, and Pb are an order of magnitude greater in Mexican mountains with respect to data for Sajama, Bolivia. Zn and Cu concentrations are up to three orders of magnitude higher in Mexican glaciers. These higher concentrations in snow and ice from Mexican glaciers with respect to Sajama have several possible explanations: 1) The core samples from Sajama are of much greater depth and represent much older ages (22000 yr BP for

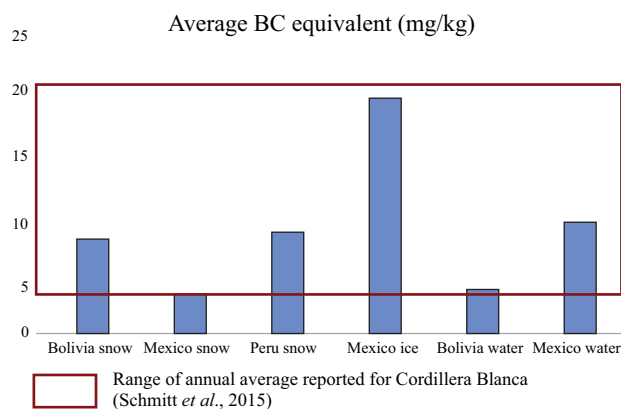


Figure 6. Average concentrations of black carbon (BC) for samples collected in the year 2022 and analyzed at the Laboratory of Environmental Geochemistry, Centro de Geociencias UNAM. Bars indicate the averages of BC equivalent content (mg/kg) for all the sampling sites. The red square indicates the range of annual BC content as reported for samples from the Cordillera Blanca, Perú (Schmitt *et al.*, 2015).

Table 1. Summary of selected geochemical analyses for V, Cr, Ni, Cu, Zn, and Pb for Iztaccíhuatl and Citlaltépetl mountains during seasons of 2006 to 2021. Concentrations are in micrograms per liter (ppb). Carrillo-Chavez *et al.*, 2023. Avg.: Average.

Year	Location	Sample/depth (cm)	Altitude (m a.s.l.)	V	Cr	Ni	Cu	Zn	Pb
2006	Iztaccíhuatl	Snow (20)	3500–4720	0.50	0.20	0.30	0.10	5.40	0.00
2007	Iztaccíhuatl	Core (10–150)	5100	0.50	1.00	7.50	2.89	39.12	0.35
2007	Citlaltépetl	Core (10–150)	5100	1.90	1.60	6.80	25.70	118.84	0.60
2008	Citlaltépetl	Core (10–80)	5100	0.60	0.50	5.58	4.64	38.24	0.31
2021	Citlaltépetl	Core (10–100)	5150	0.00	1.02	0.00	8.50	31.06	0.00
Avg.				0.70	0.86	4.04	8.37	46.53	0.25

the 120 m depth; 8000 yr BP for 100 m depth; 1650 CE for the 60 m depth and 1897 CE for the 40 m depth (Ferrari *et al.*, 2001). In fact, the samples for depths 120, 100 and 80 m, could be taken as base values due to natural sources (dust, ashes from fires, volcanic ashes, and other natural sources). The 40 m depth data (1987 CE) show a slight increase for the elements V, Cu, Zn, Pb and may be due to an increase in industrial activity in Bolivia or the area around. On the other hand, 1) the Iztaccíhuatl and Citlaltépetl samples are from the period between 2006 and 2021, and represent the great industrial activity in central Mexico; 2) the proximity of Mexican glaciers to important industrial areas (oil, automotive, metal-mechanical) and to one of the largest metropolitan areas in the world (Mexico City) may explain these higher concentrations; and 3) the Popocatepetl volcano is very close to Iztaccíhuatl (15 km) and not far from Citlaltépetl (142 km away). Popocatepetl has been intermittently active since 1994 with periodic eruptions of gasses, ash, and other volcanic material. Volcanic ash eruption (material with trace metals) and circulation in the upper troposphere easily allow the accumulation of ash metals in the snow and glacial ice of the high mountains of Mexico.

Stable Metals Isotopes

Traditional environmental stable isotopes have been used for several decades (Deuterium, ^{18}O , ^{13}C , ^{15}N and ^{34}S). However, with technological advances in mass spectrometry during the last 20 years, the isotopic system of transition metals has been investigated to understand important issues such as tracking sources and fates of metal contaminants and the development of geochemical and biogeochemical isotopic signatures. In general, stable isotopes of metals in the environmental samples (water, soil, organic matter, snow-glacial ice) contain valuable information about the sources of metals (natural or anthropogenic) and the geochemical processes that have affected the samples. We will focus only on four of the stable isotopes of transition metals that are currently used for signatures in the environment, and their application in glacial geochemistry: Zn, Cu, Fe, and Hg.

Zinc (Zn)

Zinc is an element widely used in modern industry, from alloys, fertilizer, paints, electronics, and other industrial and technological uses. Zn is also an important trace element essential in plant, animal, and human metabolic processes. Zn has five stable isotopes ^{64}Zn (48.63% natural abundance), ^{66}Zn (27.90%), ^{67}Zn (4.10%), ^{68}Zn (18.75%), and ^{70}Zn (0.62%). The most commonly used isotopic ratio is $^{66}\text{Zn}/^{64}\text{Zn}$ which in geological materials varies approximately 2‰. Variations in the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio (isotopic fractionation) are a good indicator of geochemical processes and sources of Zn to the environment. Figure 7 shows a comparison of isotopic composition (range of $\delta^{66/64}\text{Zn}$) for ZnS

(sphalerite ore), Zn in sediments of mine tailings, Zn in anthropogenic materials, Zn in hydrothermal vent fluids, Zn in seawater and the first preliminary published ($\delta^{66/64}\text{Zn}$) data for snow and glacier water from Iztaccíhuatl and Citlaltépetl, Mexico, and Cordillera Blanca, Peru (Sivry *et al.*, 2008; (Bermin *et al.*, 2006; John *et al.*, 2007, 2008; Sivry *et al.*, 2008; Black *et al.*, 2011). The first preliminary published ($\delta^{66/64}\text{Zn}$) data for snow and glacier water from Iztaccíhuatl and Citlaltépetl, Mexico, and Cordillera Blanca, Peru (Calvo-Ramos *et al.*, 2023) also are included in the comparison of Figure 7. The samples from Iztaccíhuatl (Izta Panza 220704), Citlaltépetl (CA-2 and Agua Piedra Grande), and Cordillera Blanca (5/Peru) seem to be related to natural sources (atmospheric dust). However, sample CA-1 (Citlaltépetl) seems to be related to an anthropogenic source (possible micro-particles from hydrocarbon combustion). More $\delta^{66/64}\text{Zn}$ data for snow and ice samples from high mountains in Mexico and Peru are being processed for publication, which will allow a better understanding of the natural vs. anthropogenic source (Alejandro Carrillo-Chavez, personal communication, 2023).

Copper (Cu)

Copper was one of the first metals to be used by humans (along with Au and Ag). Today Cu has many industrial applications: electrical wires, electronics, metal alloys, paint, pipes, and in coins. Cu is part of a relatively small group of metallic elements that are essential for human health. Copper and other metals are necessary for normal metabolic processes. Thus, the human diet must supply regular amounts for their absorption. Cu has two stable isotopes: ^{63}Cu (69.17% natural abundance) and ^{65}Cu (30.83%). In natural materials, the measured range of $^{65}\text{Cu}/^{63}\text{Cu}$ is about 9‰ for solid samples and 3‰ for water samples (Larson *et al.*, 2003; Borrok *et al.*, 2008). The microbe *Acidithiobacillus ferrooxidans* has been documented to be

Table 2. Comparison between the average metal content in a drill core of 120 m depth in Sajama Glacier, Bolivia (Ferrari *et al.*, 2001) with the average metal content from the Mexican mountains (Carrillo-Chavez *et al.*, 2023). Concentrations are in micrograms per liter (ppb). See the text for details and possible explanations of the differences.

Metal	Sajama 120 m	Sajama 100 m	Sajama 60 m	Sajama 40 m	Iztaccíhuatl Surface	Citlaltépetl Surface
V	0.06	0.15	0.071	0.10	0.50	0.83
Cr	0.03	0.05	0.01	0.02	0.60	1.04
Ni	n/r	n/r	n/r	n/r	3.90	4.13
Cu	0.09	0.24	0.06	0.15	0.15	12.95
Zn	0.27	0.23	0.21	0.38	22.26	62.71
Pb	0.03	0.09	0.06	0.36	0.18	0.30

partly responsible for copper fractionation (Mathur *et al.*, 2005). Novak *et al.*, 2016, used Cu and Zn stable isotopic fractionation ($\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$) to fingerprint sources and dispersion pathways of pollutants in the air using snow from Central Europe.

Mercury (Hg)

Mercury was widely used in thermometers and other scientific devices, amalgams for dental restorations, Hg vapor lamps, cosmetics, and liquid mirror telescopes. Historically, Hg has been widely used in gold mining operations. Today, because of its toxicity, the use of mercury is banned in most countries of the world, but its presence in the environment is still considerable. Mercury and its compounds (*e.g.*, monomethyl mercury (MeHg) and mercuric chloride) are extremely toxic and can be easily ingested by inhalation or absorption through the skin and mucous membranes. Mercury has seven stable isotopes: ^{196}Hg (0.15 % natural abundance), ^{198}Hg (9.97 %), ^{199}Hg (16.87 %), ^{200}Hg (23.10 %), ^{201}Hg (13.18 %), ^{202}Hg (29.86 %), and ^{204}Hg (6.87 %). The measured range of $^{202}\text{Hg}/^{198}\text{Hg}$ in natural materials resulting from mass-dependent fractionation (MDF) between coexisting Hg groups is approximately 7‰. In addition, the stable isotopes of Hg exhibit considerable mass-independent fractionation (MIF), in which the odd isotopes ^{199}Hg and ^{201}Hg behave differently from the even isotopes in certain chemical reactions such as photochemical reduction (Bergquist and Blum 2007; Blum, 2011), leading to significant enrichments and depletions of the odd isotopes relative to the even isotopes in environmental Hg reservoirs. Blum (2011) notes that most environmental applications of Hg isotopes are related to (1) interpretation of the isotopic composition of MeHg present in sediments and organisms, or (2) interpretation of the isotopic composition of Hg(II) associated with sediments or deposited on the

land surface or in a water body. Zheng *et al.* (2021) used Hg stable isotopes to reveal the sources of atmospheric Hg in the high arctic (snow precipitation during the polar spring from 2011 to 2015).

Cosmogenic Isotopes (^{10}Be)

^{10}Be is not a stable beryllium isotope, rather it is a cosmogenic Be isotope formed when cosmic rays (high-energy neutrons and protons from astronomical sources) collide atmospheric O_2 and N_2 molecules and trigger a series of nuclear reactions (spallation processes). The most useful Be isotopes for use in geosciences are the short-lived ^7Be (half-life 53.1 days) and the longer-lived ^{10}Be (half-life 1.4 Ma; Nishiizumi *et al.*, 2007). Because the cosmic rays that cause the initial cascade of neutrons and protons in the upper atmosphere responsible for the spallation reactions are attenuated by the mass of the atmosphere itself, cosmogenic Be production rates are three orders of magnitude higher in the stratosphere than at sea level (Masarik and Beer 1999, 2009). Therefore, most of the cosmogenic Be production takes place in the upper atmosphere (5–30 km). Once cosmogenic Be forms in the atmosphere, it precipitates in rain, snow, hail, and dry deposition. Cosmogenic Be production rates vary inversely with solar activity because increased solar output strengthens the Earth's magnetic field which acts as a shield and deflects cosmic rays. On timescales of decades, production rates vary by approximately 25 % with the 11-year solar cycle, but over the course of hundreds of years, production rates can vary by a factor of two or more due to longer timescale cycles in the sun activity (Koch and Mann, 1996; Vonmoos *et al.*, 2006). As cosmic rays are deflected poleward, cosmogenic Be production rates are a factor of three to five higher in polar air than in equatorial air (Harvey and Matthews, 1989; Masarik and Beer, 1999), depending on altitude. Thus, polar atmospheres have higher amounts of cosmogenic

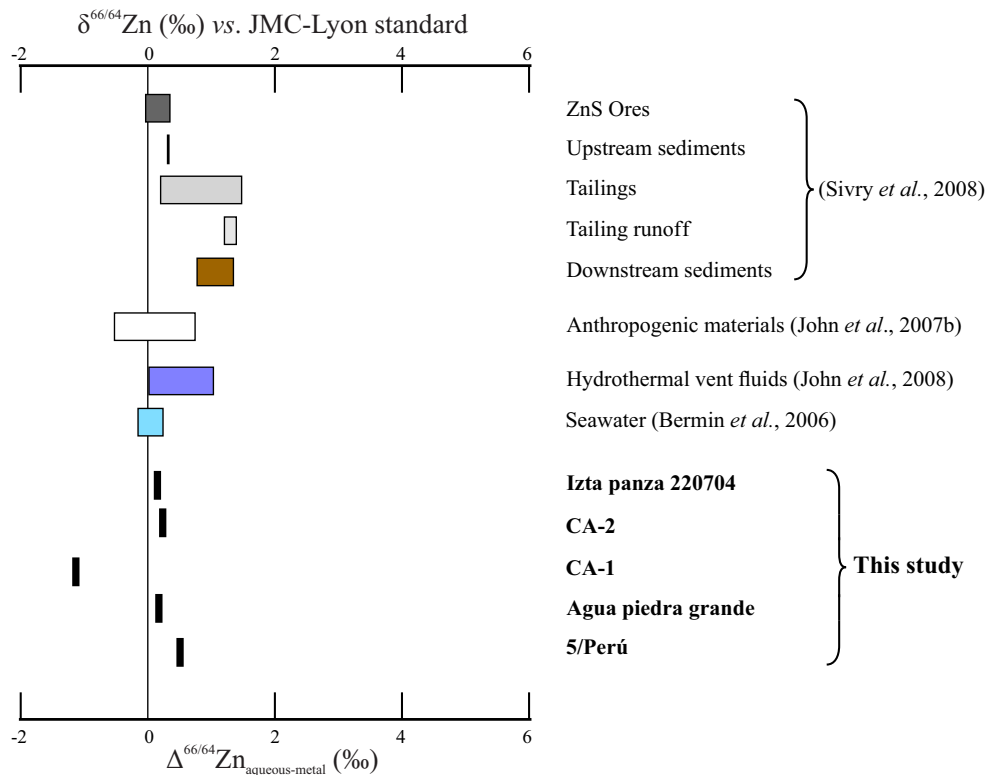


Figure 7. Comparison of isotopic composition (range of $\delta^{66/64}\text{Zn}$) for different natural sources of Zn (Sivry *et al.*, 2008; John *et al.*, 2007a; Bermin *et al.*, 2006), a compilation of anthropogenic materials (John *et al.*, 2007), and the first preliminary published ($\delta^{66/64}\text{Zn}$) data for snow and glacier water from Iztaccihuatl and Citlatepetl, Mexico, and Cordillera Blanca, Peru (Calvo-Ramos *et al.*, 2023). Modified from Black *et al.*, 2011. See texts for discussion.

Be, but precipitation rates are generally very low. The strong gradient of cosmogenic Be production with atmospheric elevation causes seasonal variability (at least in some latitude belts) in ^7Be and ^{10}Be deposition. This has been evident in midlatitudes, as injections of stratospheric air into the troposphere during the spring of each year result in higher concentrations of cosmogenic Be in meteoric waters (Husain *et al.*, 1977). Snow usually has higher cosmogenic Be isotope concentrations than rain, possibly due to the larger surface area of snowflakes compared to raindrops, and to the higher production of cosmogenic Be at higher altitudes in the atmosphere (McNeary and Baskaran, 2003). The nearly constant production rate of cosmogenic Be isotopes in the atmosphere (Leya *et al.*, 2001; Vonmoos *et al.*, 2006) and the reactive nature of Be atom particles (You *et al.*, 1989) make meteoric cosmogenic Be nuclides a valuable tracer of a wide range of chemical, physical, meteorological, and solar activity variation processes, which are recorded in continental and mountain glacier ice sheets over time periods ranging from tens of years to hundreds of thousands of years. These data, complemented with other climatic and environmental records at local, regional, and global levels, provide valuable information on the climatic variations of the Earth over the indicated time span.

CONCLUSIONS

Glaciers have shaped the highest mountains of central Mexico throughout the Late Quaternary (22000 BP to 2023 CE). In the last decades, UNAM-based research on past and modern glaciers has provided valuable information on glacier chronology for the last 20000 years, The glacier changes during the last 73 years are reported in detail, and their chemistry (environmental pollution) during the last 17 years also is reported.

The reconstruction of glacier change at millennial time scales requires the use of state-of-the-art dating techniques, namely cosmogenic nuclide dating. This has allowed for the development of robust chronologies and thereby correlations between the glacial records and other proxies of climate and environmental change (local, regional, and global) from the Last Glacial Maximum to the Little Ice Age.

Monitoring modern glaciers on the three highest mountains of Mexico since the middle of the 20th century has been one of the most important sources of information on the impact of climate change on tropical mountains. The analyses of glacier area, thickness, and elevational change have shown the close linkages between climate warming and glacier dynamics on some of the last glaciers of the northern tropics.

Using glacier ice as an archive, geochemical analyses on these lingering glaciers aim to provide valuable data on environmental change and anthropic disturbance for the last few decades.

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