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Review

Ice Core Methane Analytical Techniques, Chronology and Concentration History Changes: A Review

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Abstract: Ice cores are invaluable in paleoclimate research, offering unique insights into the evolution of the natural environment, human activities, and Earth's climate system. Methane (CH_4) is a crucial greenhouse gas, second only to CO_2 in its contribution to global warming, and is one of the primary anthropogenic greenhouse gases. Understanding historical CH_4 concentration changes is essential for predicting future trends and informing climate change mitigation strategies. By analyzing gas components trapped in ice core bubbles, we can directly examine the composition of ancient atmospheres. However, there are relatively few comprehensive reviews on ice core CH_4 testing techniques, chronology, and concentration history records. In response to this gap, our paper systematically reviews ice core CH_4 analytical techniques, chronology, and concentration history changes. Our review indicates that current research on CH_4 in non-polar ice cores is insufficient compared to polar ice cores, facing challenges such as high data dispersion, outlier frequency, and the presence of non-atmospheric signals. These limitations hinder our in-depth understanding of CH_4 signals in non-polar ice cores, and the reliability of atmospheric CH_4 concentration changes they reflect. To address these challenges, we propose exploring and applying advanced testing techniques, such as Continuous Flow Analysis technology, in non-polar ice cores. Additionally, we emphasize the research gap in utilizing CH_4 records for age determination in ice core chronology. Future research should focus on this area to advance our understanding of ice core chronology and the history of atmospheric CH_4 changes in non-polar regions, ultimately contributing to more effective climate change mitigation efforts.

Keywords: CFA; chronology; CH_4; global change; historical record

Citation: Song, J. Ice Core Methane Analytical Techniques, Chronology and Concentration History Changes: A Review. *Sustainability* **2023**, *15*, 9346. https://doi.org/10.3390/su15129346

Academic Editor: Marcelo Francisco Pompelli

Received: 13 April 2023
Revised: 27 May 2023
Accepted: 7 June 2023
Published: 9 June 2023

1. Introduction

Methane (CH_4) is a crucial greenhouse gas, the concentration of which is commonly expressed in the atmosphere as a mixing ratio in ppb (parts per billion). As one of the primary anthropogenic greenhouse gases contributing to global warming, its impact is second only to carbon dioxide (CO_2) [1]. Despite its shorter atmospheric lifetime and relatively lower emissions compared to other greenhouse gases, its global warming potential is 28 times greater than that of CO_2 [1–3]. Since the Industrial Revolution, the rapid increase in atmospheric CH_4 concentrations has raised significant concerns among scientists [4,5]. Consequently, international governments and the scientific community have proactively established a networked, long-term greenhouse gas observation system [6]. Modern measurements of atmospheric CH_4 concentrations began in the 1940s, while long-term observations can be traced back to the late 1970s [7]. Scientists have conducted a series of studies on the temporal and spatial distribution, as well as the long-term variation characteristics of atmospheric CH_4 concentrations, using long-term observation data [8,9]. Related studies have demonstrated that the global spatial distribution of atmospheric CH_4 concentrations is uneven and primarily influenced by the spatial distribution of emission sources [8,9]. As a result of significant advancements in the development of the global dynamic atmospheric monitoring system, the temporal and spatial distribution, as well as

the dynamic change characteristics of modern atmospheric CH_4, have been fundamentally understood.

However, during the geological history preceding the Industrial Revolution, the absence of modern atmospheric observation systems made direct measurements and records of atmospheric composition unattainable. Therefore, it is necessary to use proxy data for in-depth research in order to reconstruct the processes of ancient climate change. Currently, geologists utilize ice cores, ocean sediments, tree rings, corals, lake sediments, and stalagmites to reconstruct Earth's past climate changes [10–12]. Among these paleoclimate proxies, the air bubbles trapped in ice cores preserve abundant ancient atmospheric information, making them one of the key indicators for studying long-term changes in atmospheric CH_4 concentrations [13–15]. Compared to other paleoclimate proxy indicators, air bubbles in ice cores can stably preserve ancient atmospheric composition information over long periods, thus playing a unique and irreplaceable role in studying long-term changes in atmospheric CH_4 concentrations [13–15]. By examining CH_4 concentrations in ice cores, we can gain a better understanding of the atmospheric CH_4 concentration changes over thousands or even hundreds of thousands of years and further investigate the influence of natural and human factors on these concentrations. Moreover, it will help constrain biological processes in comprehensive climate forecast models.

Nowadays, there are relatively few reviews on ice core CH_4 testing techniques, chronology, and historical concentration records. Therefore, it is necessary to constantly summarize the latest research progress. In this review, we collected and screened the recent available literature from the database of ScienceDirect (accessed on 1 April 2023) and Google Scholar (accessed on 1 April 2023) by using the keywords "ice core" or "methane" or "CH_4", and the articles were grouped with different categories including "measurement", "chronology", "dating" or "concentration" to summarize the research on (1) ice core gas testing technology; (2) abnormal value of CH_4 in ice core and its causes; (3) ice core dating; and (4) historical records of CH_4 concentration in ice cores and its influence factors. In addition, current existing problems, knowledge gaps, and proposed suggestions for future research are included.

2. Ice Core Gas Testing Technology

Generally, ice core gas testing methods can be roughly divided into "discrete" and "continuous", as shown in Figure 1. Among them, the "discrete" ice core gas testing technology began in the 1950s [16]. The ice core samples used in this testing technique are discretely selected within the depth range of the entire ice core section. Currently, the melt-refreeze method is the most commonly used ice core CH_4 discrete testing system, and the normally testing process is as follows: First, the ice core sample, cut into 3–10 cm and 30–50 g pieces, needs to be placed in a specific container. The container is then sealed and vacuumized, followed by the gradual melting of the ice core sample. After it has completely melted, the temperature is adjusted to allow the sample to slowly solidify from bottom to top. Simultaneously, the gas released from the ice core will diffuse into the pre-pumped vacuum pipeline and quantitative tube, eventually being sent to gas chromatography equipment (GC) for detection. There were many studies have utilized this technique to test and analyze CH_4 in multiple ice cores in polar regions [17,18]. Globally, the research institutions that have mastered this technology mainly include the University of Bern (U-Bern), Switzerland [16,18–20], the Institute for Geosciences and Environmental Research (IGE, formerly LGGE) in Grenoble, France [15,21], Oregon State University (OSU) in the United States [22,23], Pennsylvania State University in the United States [24], etc. As technology advances, the accuracy of these testing systems has been continuously improving. For example, the testing accuracy of CH_4 at the University of Bern (U-Bern) has increased from about 20 ppb to about 10 ppb now, and the testing accuracy at the Oregon State University (OSU) laboratory has even reached about 3 ppb. Moreover, the testing efficiency of this technology is also constantly improving. For instance, the U-Bern laboratory has been able to perform testing and analysis tasks for over 16 samples at once,

while the OSU and IGE can accommodate single tests of 12 and 22 samples, respectively. It is worth noting that there are still differences in the test results of the melt-refreeze testing system between various research units. Studies have compared the melt-refreeze testing systems of different laboratories and found that even if ice core samples from the same ice core and the same depth are tested, the results still have a difference of 10–40 ppb. The reason may be related to differences in the tightness of testing systems [25,26]. This difference can cause a deviation from the true atmospheric CH_4 concentration, so further in-depth exploration is needed in the future. In addition, the sampling density of this testing method is usually only 1–2 m, which cannot meet the needs of continuous high-resolution ice core CH_4 testing [15,21]. At present, the typical resolution is 1 m, and the best resolution is 3–5 cm using continuous flow analysis (CFA). Therefore, CFA with high efficiency and continuous ultra-high resolution has become the main development direction of CH_4 testing in ice cores.

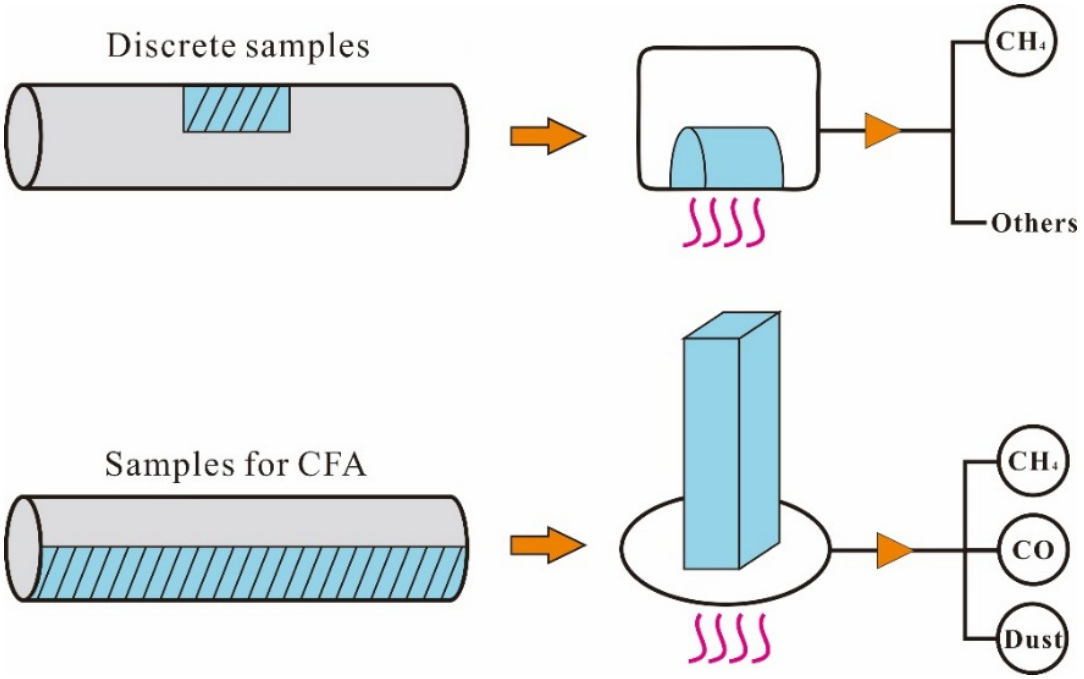

Figure 1. A comparison of discrete and continuous measurements of ice core gases.

CFA is an efficient ice-core gas testing technology. Its testing efficiency is more than 10 times higher than that of the melting-refreezing technology, and it can achieve continuous ultra-high resolution CH_4 concentration testing in ice cores [27,28]. With the help of this new testing technology, it is now possible to detect centimeter-level CH_4 concentration abnormalities in areas related to microbial activity [22,29]. In addition, the multi-parameter ice core gas testing technology has been able to simultaneously test gas components such as CH_4, N_2O, C_2H_6, and their isotopes. By comparing the values of different gas parameters, we can roughly judge whether the CH_4 concentration may be abnormal [30–32]. On this basis, researchers are still trying to correct the real CH_4 concentration in the ice core through the test results of other gases so as to more accurately restore the past atmospheric environment [30,32–35]. Currently, through the continuous improvement of testing technology, we can more accurately understand the changes in CH_4 concentration in the atmosphere in the past, which allows us to better understand the mechanisms of global CH_4 concentration changes. The University of Bern in Switzerland is the first research institution in the world to combine CFA technology with ice core CH_4 testing [27,28]. So far, the CFA test system at the U-Bern has undergone numerous improvements, not only meeting the requirements for ice core gas testing but also analyzing the physical and chemical indicators of ice cores, such as Na^+, Ca^{2+}, NH^{4+}, NO^{3-}, $SO_4{}^{2-}$, H_2O_2, and HCHO [27,28,36]. Additionally, the IGE is one of the earliest research institutions to use the CFA system for ice core gas testing, with

the primary test subjects including CH_4 and CO content [29,37]. Compared to traditional discrete testing technology, the CFA test system has three advantages. First, the testing efficiency of the CFA test system is higher than that of the discrete test system, with a simpler testing process and faster testing speed, which is more than 10 times the speed of traditional discrete testing. Second, the CFA test system can achieve ultra-high resolution testing at continuous ice core depths, which is crucial for identifying abnormal signals in ice core gas records. Finally, the modules of CFA testing equipment are usually connected in a non-fixed manner, allowing them to be easily removed or replaced. IGE fully exploited this feature and replaced the gas testing components of the CFA test system multiple times, transitioning from the earliest GC testing equipment to laser spectroscopy testing equipment, including the commonly used SARA testing based on OF-CEAS technology and commercial Picarro CFADS36 $CO_2/CH_4/H_2O$. These changes have improved the sensitivity of the tests while reducing the demand for samples [29,37]. It should be noted that, like all testing techniques (including melt-refreeze techniques) that use melting to extract gas from ice cores, a portion of the gas will dissolve in the meltwater during the CFA test, and 100% gas extraction cannot be achieved. Since CH_4 is a gas component with high water solubility, incomplete gas extraction will result in a lower CH_4 concentration than the actual concentration. Studies have shown that the actual gas extraction efficiency of the CFA test system is about 90%, which is lower than the traditional discrete melt-refreeze test technology. This means that the CH_4 concentration measured by CFA may be lower than the value measured by the traditional melt-refreeze technology. According to the current technical level, in CH_4 test research that does not require accuracy below 10 ppb, such as research aimed at establishing an accurate atmospheric CH_4 concentration gradient, those CFA test deviations caused by water solubility errors can usually be ignored [29]. In addition, the CH_4 concentration measured by the CFA test system is sufficient to meet the needs of most related studies, including the identification of non-atmospheric signals in ice cores, the analysis of the characteristics of atmospheric CH_4 concentration changes on different time scales, and the correlation of these changes with Antarctic ice cores. Table 1 presents the ice core CH_4 test and analysis methods currently adopted by major ice core research institutions worldwide.

Table 1. Important studies of ice core CH_4 and their measurement techniques.

Ice Core	Test Object	Institution	Test Method	Instrument	Sample Weight	SD	Resolution	References
Greenland Eurocore	CH_4	IGE	melt-refreeze	GC-FID	40 g	40 ppb	NA	[38]
Greenland GRIP	CH_4	IGE	melt-refreeze	GC-FID	40 g	37 ppb	NA	[39]
Greenland GISP2	CH_4	IGE	melt-refreeze	GC-FID	12–20 g	10 ppb	NA	[40]
Antarctica D47 and Byrd, Greenland GRIP	CH_4	IGE	melt-refreeze	GC-FID	40–50 g	20 ppb	NA	[41]
Antarctica Dome C	CH_4	U-Bern	melt-refreeze	GC-FID	~40 g	10 ppb	NA	[19]
Greenland NGRIP and GRIP	CH_4	U-Bern	melt-refreeze	GC-FID	~40 g	10 ppb	NA	[18]
Greenland NGRIP and GRIP	CH_4	U-Bern	melt-refreeze	GC-FID	~40 g	10 ppb	NA	[42]
Antarctica Dome C	CH_4	IGE&U-Bern	melt-refreeze	GC-FID	40–50 g	10 ppb	NA	[43]
Antarctica Dome C	CH_4	IGE&U-Bern	melt-refreeze	GC-FID	40–50 g	10 ppb	NA	[15]
Antarctica Talos Dome, Greenland NGRIP	CH_4	IGE&U-Bern	melt-refreeze	GC-FID	40–50 g	10 ppb	NA	[21]
Greenland GISP2	CH_4	OSU	melt-refreeze	GC-FID	35 g	15 ppb	NA	[44]
Greenland GISP2	CH_4	OSU	melt-refreeze	GC-FID	35 g	15 ppb	NA	[45]
Greenland GISP2	CH_4	OSU	melt-refreeze	GC-FID	62 g	~2 ppb	NA	[46]
Greenland GISP2	CH_4	OSU	melt-refreeze	GC-FID	62	~2 ppb	NA	[47]
Antarctica WAIS	CH_4	OSU	melt-refreeze	GC-FID	50–63g	2.8 ppb	NA	[23]
Antarctica WAIS Divide, Greenland GISP2	CH_4	OSU	melt-refreeze	GC-FID	60.5 g	2.4 ppb	NA	[22]
Greenland Eurocore	CH_4	U-Bern	crack	GC-FID	15 g	28 ppb	NA	[38]
Greenland GRIP	CH_4	U-Bern	crack	GC-FID	15 g	20 ppb	NA	[39]
Greenland GISP2	CH_4	U-Bern	crack	GC-FID	12–20 g	10 ppb	NA	[40]
Antarctica WAIS Divide	CH_4	U-Bern	crack	GC-FID	NA	5 ppb	NA	[10]
Greenland NEEM	CH_4	U-Bern	melt-activated carbon adsorption	GC-IRMS	~160 g	NA	NA	[30]
Antarctica Talos Dome	CH_4	U-Bern	CFA	GC-FID	NA	15 ppb	15 cm	[48]
Greenland NEEM-S1	CH_4	U-Bern	CFA	WS-CRDS	NA	8 ppb	5 cm	[49]

Table 1. *Cont.*

Ice Core	Test Object	Institution	Test Method	Instrument	Sample Weight	SD	Resolution	References
Greenland NEEM	CH_4	IGE&OSU	CFA& melt-refreeze	OF-CEAS, etc.	NA	3 ppb	5 cm	[50]
Greenland NEEM-S1	CH_4	IGE&OSU	CFA& melt-refreeze	OF-CEAS	NA	3 ppb	5.3 cm	[29]
Antarctica WAIS Divide	CH_4	IGE&OSU	CFA& melt-refreeze	OF-CEAS	NA	3 ppb	5.5 cm	[26]
Greenland GISP2	$\delta D\text{-}CH_4$	PSU	NA	XP-MS	1.1 kg	4.2‰	NA	[51]
Antarctica Taylor, Greenland GISP2	$\delta^{13}CH_4$	NIWA	NA	GC-IRMS	75–100 L	0.4‰	NA	[52]
Antarctica Dome C, Greenland NGRIP	$\delta^{13}CH_4$	U-Bern	NA	GC-IRMS	150–200 g	0.15‰	NA	[53]
Antarctica Dome C, Greenland NGRIP	$\delta D\text{-}CH_4$	U-Bern	NA	GC/P/IRMS	500 g	3.4‰	NA	[54]
Antarctica WAIS Divide, Greenland NGRIP	$\delta D\text{-}CH_4$	U-Bern	NA	GC/P/IRMS	500 g	2.3‰	NA	[55]
Antarctica Dome C, Talos Dome etc.	$\delta^{13}CH_4$	U-Bern	infrared radiation melting	GC-IRMS	~160 g	0.15‰	NA	[24]

Note: IGE represents Institut des Géosciences de l'Environnement, France; U-Bern represents the University of Bern, Switzerland; OSU represents Oregon State University, USA; PSU represents Pennsylvania State University, USA; and NIWA represents National Institute of Water and Atmospheric Research, New Zealand.

3. Ice Core Dating

Ice cores collected from high-altitude mountains, such as the Tibetan Plateau, the Andes, the Alps, and the Caucasus Mountains, are of great value in paleoclimate research [56–61]. The main reason for this is that these ice cores often contain information on the composition and climate conditions of the ancient atmosphere, which can reflect the history of historical climate changes. Their time span can even be traced back to the last ice age, which began about 70,000 years ago and ended about 11,500 years ago. This was a time of significant climatic change, with large ice sheets covering much of the Earth and a general trend towards global warming, punctuated by several rapid returns to glacial conditions. This period ended with the melting of these ice sheets and a rise in sea levels, leading into the current interglacial period known as the Holocene. Hence, the research findings from these ice cores are of great importance for understanding past climate changes, particularly those in middle and low latitudes. Moreover, these ice core records can be compared with other surrounding natural climate records (such as lake sediments, tree rings, etc.) to gain a better understanding of the local history of past climate changes [62]. Establishing an accurate ice core age framework is the fundamental prerequisite for the correct interpretation of ice core research results. Only by accurately dating ice cores can valuable paleoclimate information be obtained and compared with other climate records, leading to a better understanding of past climate change history [61]. Compared to polar ice cores, alpine ice cores in middle and low latitudes have a higher accumulation rate, and the time resolution of paleoclimate signals contained in them is relatively higher. In the records covering the upper part of the ice core for hundreds of years, the concentrations of stable isotopes, particulate matter, soluble ions, and black carbon, among other physical and chemical indicators, usually show obvious seasonal changes. These characteristics can be used to establish the age framework for the top several hundred years of the ice core [63–65]. In addition, ice cores contain records of radioactive isotopes such as ^{137}Cs and ^{3}H released by above-ground nuclear tests, and their distribution and activity peaks in ice core records can also be used to verify the accuracy of the upper part of the ice core [66–69]. However, the aforementioned dating methods are usually only applicable to the top area of the Tibetan Plateau ice core. As the depth increases, most of the Tibetan Plateau ice cores will experience rapid and non-linear thinning of the ice core sequence, which makes the identification of ice core annual layers very difficult [58,70,71]. To determine the chronology of the entire ice core, researchers usually combine glacier flow models with reference horizon methods [61,72]. The two-parameter glacier flow model (2p model) is one of the most commonly used glacier models and has been widely used to construct chronological frameworks for mid- and low-latitude ice cores [57,61,73,74]. To constrain a two-parameter glacier flow model, the ages of radionuclides (such as ^{210}Pb, ^{85}Kr, ^{39}Ar, ^{81}Kr, ^{14}C, and ^{36}Cl) and reference horizons (such as β activation peaks, ^{137}Cs peaks, tritium peaks, and volcanic ash layers) are usually used for information [65]. However, the 2p model assumes constant glacier accumulation rates and thinning coefficients, which may lead to large uncertainties in the age of deeper ice cores. Taking the Dunde ice core on the Tibetan Plateau as an example, the age of the bottom of the ice core is estimated to

be more than 100,000 years using the glacier flow model [73]. The age of the rock contact is 6240 ± 330 years [75]. Therefore, we still need to use other independent verification methods to verify the accuracy of the ice core age framework based on the 2p model.

At present, atmospheric signals in ice cores have become a new basis for determining the age of ice cores [76]. Because the global atmosphere is highly mixed, the atmospheric signals contained in ice cores in different regions should have strong similarities, which can be regarded as a reliable ice core age marker. Currently, the most commonly used ice core atmospheric signals mainly include oxygen isotope ratio (δ^{18}Oatm) and CH_4 concentration. Since oxygen has a long residence time in the atmosphere, about 1000 years, its signal does not change too drastically [76]; therefore, the δ^{18}Oatm in ice cores is usually used as an ice core age scale. In recent decades, the δ^{18}Oatm signal from ice cores has been successfully used to determine the age range of mountain ice cores, including the Sajama and Illimani ice cores in Bolivia, South America [77,78], the East Rongbuk ice core in the Himalayas [79], and the Chongce and Guliya ice cores in the West Kunlun Mountains [80,81]. It should be noted that there are still large uncertainties in the research of using δ^{18}Oatm technology to determine the age range of ice cores. The main reason is that different researchers use different data correction processes and data screening standards. For example, Hu et al. (2022) matched the ice core δ^{18}Oatm records with the high-resolution records of the Siple Dome ice core in Antarctica and determined that the oldest age of the Chongce ice core was 9799 years (1950 to present) [80]. In the same area, Thompson et al. (2022) matched the ice core δ^{18}Oatm records with the Antarctic WAIS ice core records, and the results showed that the age range of the Guliya ice core might exceed 16,000 years (1950 to present) [81]. The distance between the drilling sites of the Guliya ice core and the Chongce ice core is only about 30 km, and it is difficult to explain the large difference in the age range of the two ice cores. Compared with δ^{18}Oatm, the application of ice core CH_4 signal in ice core age determination is still less. Compared with δ^{18}Oatm, the residence time of atmospheric CH_4 is shorter, so it will show more obvious change characteristics on the multi-decadal scale to the century scale, which is more beneficial to the determination of the age frame of ice cores [76,82]. At present, the CH_4 signal in ice cores has played an important role in the study of bipolar ice core chronology synchronization, such as using it to synchronize a series of ice-interglacial features since the last glacial period in both hemispheres and fine-tuning the gas chronological framework of polar ice cores since the Late Holocene [22].

4. Historical Records of CH_4 Concentration in Ice Cores and Its Influence Factors

Nowadays, researchers have conducted studies on ice cores from various locations around the world, with important CH_4 research sites in ice cores illustrated in Figure 2. Based on geographical location, ice core research can be categorized into three groups: Antarctic ice cores, Greenland ice cores, and non-polar ice cores. In the following section, we will briefly summarize the relevant research findings related to CH_4 records in these three types of ice cores.

4.1. Antarctic Ice Core

In the realm of Antarctic ice core research, the study of air bubble inclusions holds significant importance. The Antarctic Dome C ice core research program commenced in 1979, while the Antarctic Vostok ice core research program was initiated in the early 1980s. The oldest CH_4 records in the Antarctic Dome C ice core date back to 800,000 years ago (Figure 3), while the earliest CH_4 records in the Antarctic Vostok ice core extend to 420,000 years ago [13–15,43]. These records offer crucial data support for understanding the patterns of global atmospheric CH_4 changes throughout geological history. Research has revealed that throughout past geological history, atmospheric CH_4 concentrations have exhibited a glacial-interglacial cycle with a period of 100,000 years [13–15,83]. During glacial periods, CH_4 concentrations exhibited a zigzag pattern of decline, while at the end of these periods, CH_4 concentrations demonstrated a rapid recovery trend. Atmospheric

CH_4 concentrations during glacial periods ranged between 320–350 ppb, while CH_4 concentrations during interglacial periods could reach 650–800 ppb. This glacial-interglacial cycle of Earth's climate may be associated with the Earth's orbital cycle. Owing to the influence of Earth's orbital eccentricity, global temperature, ice volume, oceanic and atmospheric circulation, and atmospheric records of CO_2, CH_4, and N_2O all exhibit changes on a timescale of 100,000 years [13–15].

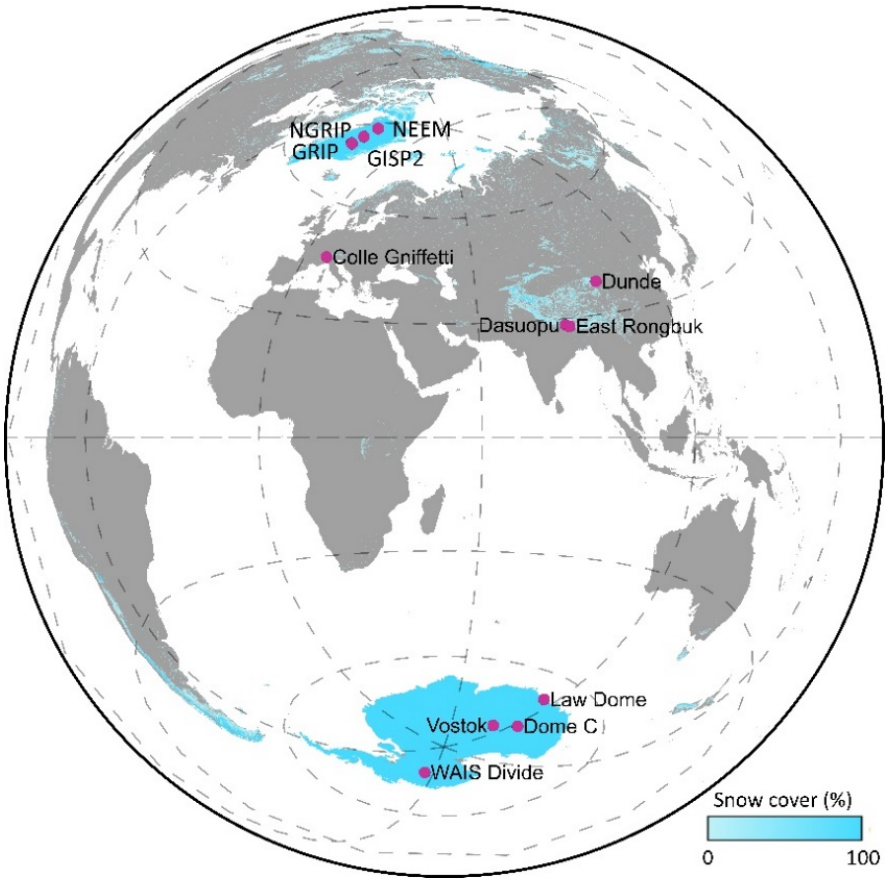

Figure 2. Location of major global ice core sites involved in CH_4 research. This figure presents the significant ice core sites involved in CH_4 research on a global scale, including Antarctica, Greenland, and some non-polar ice core locations. The surface snow cover data used is from the August 2020 TERRA/MODIS dataset with a resolution of 0.1 degrees. Related data can be obtained at the following website: https://neo.sci.gsfc.nasa.gov/view.php?datasetId=MOD10C1_M_SNOW, accessed on 20 May 2022.

Research has indicated that changes in global ice volume are the primary driver for glacial-interglacial variations in atmospheric CH_4 concentrations [84]. Examination of the atmospheric CH_4 balance between glacial and interglacial periods reveals that CH_4 absorption and sinks during interglacial periods are approximately 40% greater than those in glacial periods. Consequently, it is inferred that atmospheric CH_4 emissions during interglacial periods are 2–3 times higher than those during glacial periods. Throughout geological history, natural wetlands have served as the primary source of atmospheric CH_4, encompassing both boreal and tropical wetlands. As ice sheets in the northern hemisphere expand and contract periodically, the coverage area and CH_4 emissions of cold temperate wetlands will also undergo periodic changes. It has been estimated that prior to the Industrial Revolution, CH_4 emissions from cold temperate wetlands accounted for approximately 40% of total global emissions and played a dominant role in glacial-interglacial changes of atmospheric CH_4. Moreover, the northern hemisphere's tropical monsoon also played a significant role in the glacial-interglacial cycle of atmospheric

CH_4. According to China's loess records, the East Asian monsoon exhibits a significant 100,000-year cycle [84–86]. This cycle also results in the periodicity of tropical monsoon precipitation and CH_4 emissions from tropical wetlands.

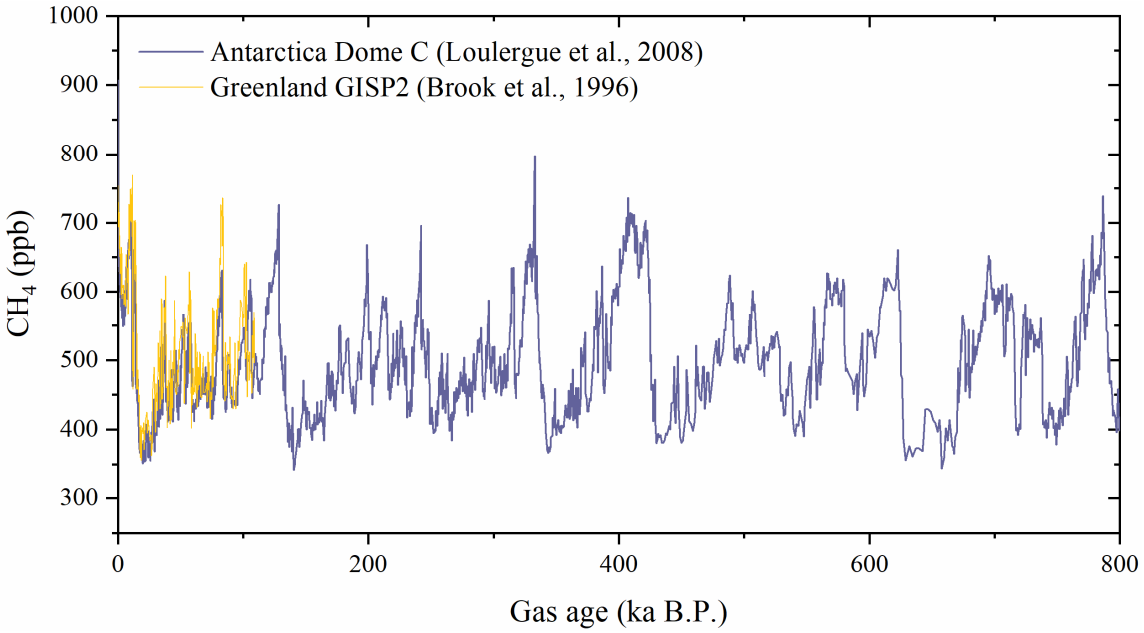

Figure 3. Historical variation characteristics of CH_4 concentration records in Antarctic Dome C and GISP2 ice cores [15,44].

In addition to cyclical changes between glacial and interglacial periods, CH_4 concentrations in Antarctic ice core records also exhibited a series of millennial-scale variations [15,87]. The magnitude of these millennial-scale changes in atmospheric CH_4 was approximately 100 ppb, which was significantly smaller than the magnitude of changes in CH_4 concentrations observed in glacial-interglacial fluctuations. Through spectral analysis of CH_4 records in the Dome C ice core, it was found that millennial-scale changes in atmospheric CH_4 occurred in periods of 20,000, 10,000, 8.2, 7.2, 6.6, 6, 5.5, and 4.2 millennia [84]. Researchers further investigated the causes of millennial-scale changes in atmospheric CH_4 concentrations and discovered that these periodic fluctuations are influenced not only by solar radiation during tropical summers but also by changes in global ice volume. Among these factors, tropical summer solar radiation can influence tropical monsoon rainfall, which in turn affects CH_4 emissions from tropical wetlands. The intensity of tropical summer solar radiation is influenced by the Earth's orbital precession factor, exhibiting a significant 20,000-year periodic variation. This can explain the 20,000-year period observed in the Dome C ice core CH_4 record. It is worth noting that the variation of summer solar radiation intensity in the tropical areas of the northern and southern hemispheres is in antiphase. When the summer solar radiation in the northern hemisphere weakens, the summer solar radiation in the tropical areas of the southern hemisphere increases. Therefore, the superposition of solar radiation factors during tropical summers in the northern and southern hemispheres will theoretically produce a semi-precession cycle of approximately 10,000 years. This can also explain the 10,000-year cycle observed in the CH_4 record of the Dome C ice core. In addition, changes in global ice sheets can also lead to variations in sea level and terrestrial hydroclimate, which in turn affect CH_4 emissions in cold temperate zones and tropical wetlands.

Under the influence of the Earth's orbit, the change in global ice volume exhibits a precession cycle of 20,000 years; however, this change typically lags behind solar radiation by 2 to 5 thousand years, adding a sense of complexity and wonder to our understanding of these natural processes. Generally, it takes several thousand years to build up an ice sheet starting from when orbital conditions are favorable because annual accumulation

is only a meter or so per year. When the influences of global ice volume and tropical summer solar radiation factors are combined, they theoretically produce atmospheric CH_4 change cycles of 30–26, 19, 16–12, 8–5.5, and 4.9–2.8 millennia. This finding aligns well with the change periods identified in the Dome C ice core CH_4 records, demonstrating consistency in the data [84]. Furthermore, as a significant greenhouse gas, CH_4 is not only influenced by climate change, but its fluctuations can also exacerbate climate change on both orbital and millennial scales. In conclusion, utilizing Antarctic ice core records to investigate changes in atmospheric CH_4 concentrations on orbital and millennial scales is of paramount importance.

4.2. Greenland Ice Core

Similar to the Antarctic ice core, the CH_4 research project involving the Greenland ice core was initiated earlier as well. At present, numerous Greenland ice cores have been investigated for CH_4, including the GISP2 ice core, NEEM ice core, GRIP ice core, and NGRIP ice core [44,50,87]. The timespan of these ice cores is shorter than that of Antarctic ice cores, and they primarily uncover the characteristics of atmospheric CH_4 concentration changes since the last ice age. Unlike Antarctica, these ice core records reflect changes in CH_4 concentration in the atmosphere at high latitudes in the northern hemisphere and are an important complement to those recorded in ice cores in the southern hemisphere [44,50,87]. Overall, the change trends of CH_4 records in Greenland ice cores are very similar to those in Antarctic ice cores. For example, the CH_4 data recorded by the GISP2 ice core over the past 110,000 years have shown multiple alternations of CH_4 concentrations ranging from 50 ppb to about 300 ppb. This is consistent with the glacial-interglacial CH_4 concentration changes of the last glacial period that have repeatedly appeared in Antarctic ice cores. The alternations, known as Dansgaard-Oeschger (D-O) events, are nearly synchronous in time between the Greenland ice cores and Antarctic ice cores, providing a more comprehensive understanding of the global CH_4 concentration changes during the last glacial period [44]. CH_4 records in ice cores are ideal for calibrating ice core ages because CH_4 is well mixed globally and exhibits rapid and significant global synchronous changes during some exceptional events [76,88].

Currently, some prominent features of the Dansgaard-Oeschger (D-O) events, Bølling-Allerød (B-A) and Younger Dryas (YD) events have been recorded based on ice core CH_4 concentrations. Researchers have successfully applied these features to age calibrations for several Greenland and Antarctic ice cores dating back to the last glacial age [89–91]. Building on the chronological synchronization of ice cores, it has become apparent that temperature changes associated with Dansgaard-Oeschger (D-O) events in Greenland ice cores exhibit a noticeable lag compared to corresponding events in the Antarctic by several millennia [89]. It is also important to note that, due to differing contributions from the northern and southern hemispheres to atmospheric CH_4 emissions, the CH_4 concentration in Greenland ice cores is typically higher than that in Antarctic ice cores from the same time period. At the same time, the difference in CH_4 concentration between the two hemispheres also changes due to the influence of variations in the proportion of CH_4 emissions in the tropics and high latitudes of the northern hemisphere. By studying the difference in CH_4 concentration between the two hemispheres, researchers can also assess the latitudinal differences in CH_4 emissions and further understand the contribution of natural factors to changes in CH_4 concentration. This is also an important direction for the current study of CH_4 in Greenland ice cores. Through in-depth analysis of the CH_4 concentration gradient difference recorded in the GISP2 ice core and the Taylor Dome ice core in Antarctica during the last glacial period, researchers found that changes in CH_4 emissions from the tropics and the cold temperate zone in the northern hemisphere contributed significantly to the change in the CH_4 concentration gradient during this period [45,92,93]. In addition, in the early and middle Holocene, the CH_4 concentration gradient between Greenland and Antarctica was larger than in other periods. This trend is basically consistent with the

trend of glacier retreat leading to the expansion of cold temperate wetlands in the northern hemisphere [41].

4.3. Non-Polar Ice Core

CH_4 records from non-polar ice cores also hold significant research value. By studying CH_4 records in polar ice cores, we have essentially gained an understanding of the distribution and variation characteristics of CH_4 concentrations in the northern and southern hemispheres throughout history. Meanwhile, CH_4 records in non-polar ice cores help us delve deeper into the distribution and variation of CH_4 concentrations at different latitudes, as well as their spatial distribution and variability [94]. Additionally, for non-polar ice cores situated near areas of human activity, we can gain a better understanding of the impact of human activities on changes in atmospheric CH_4 concentration throughout history by conducting relevant research. Finally, by examining the CH_4 record in non-polar ice cores, we can establish a more accurate chronological framework for these ice cores. In summary, the investigation of CH_4 records in non-polar ice cores contributes to our understanding of historical changes in atmospheric CH_4 concentrations on a global scale. It allows us to delve deeper into its relationship with early human activities and to enhance the accuracy of ice core chronology frameworks. At present, there are relatively few studies on CH_4 in non-polar ice cores, but some research has garnered attention, including the Colle Gnifetti ice core in the Alps and the Dunde ice core in the Qinghai-Tibet Plateau. In the following sections, we will discuss the research progress on CH_4 in these ice cores in detail.

4.4. Alpine Colle Gnifetti Ice Cores

The Colle Gnifetti ice core is located in the Swiss Alps at an altitude of 4450 m and serves as a valuable resource for studying historical climate change. According to research conducted by Stauffer et al. (2003), the CH_4 study of the Colle Gnifetti ice core used a melt-refreeze testing technique, melting the ice core under vacuum conditions and collecting air, and ultimately measuring CH_4 using a flame ionization detector. This study found that the trend of CH_4 concentration in the Colle Gnifetti ice core (the lower envelope of the test data) was very similar to the trend of CH_4 concentration in the GRIP ice core from Greenland between 500 and 2000 AD [20]. Therefore, researchers constrained the age of the CH_4 record from the Colle Gnifetti ice core based on the CH_4 record from the GRIP ice core. The results show that the age of the Colle Gnifetti ice core changed with depth, which was consistent with the basic characteristics of the rapid thinning of the annual layer of mountain ice cores as depth increases. In addition, the study also found that around AD 500 and between AD 1200 and AD 1400, the CH_4 concentration records of the ice core experienced multiple sudden rises and rapid declines, with a maximum variation of about 400 ppb. However, this signature does not appear in the GRIP ice core CH_4 record during the same period, and it is unlikely that atmospheric CH_4 concentrations have changed so drastically in such a short period of time. Therefore, researchers believe that this rapid change in CH_4 concentration is not a feature of the original atmosphere. Since CH_4 is a highly water-soluble gas component, the summer melting of ice cores may lead to relative enrichment of CH_4 in the melting layer. However, according to estimates, this melting phenomenon was not enough to cause such a drastic increase in CH_4 concentration. Therefore, researchers believe that the rapid change of CH_4 in the Colle Gnifetti ice core is likely to be caused by microbial activities in the ice core.

4.5. Dunde Ice Core on the Qinghai-Tibet Plateau

The Dunde Ice Cap is located in the Qilian Mountains in western China. In 1987, researchers drilled a 140 m long ice core sample here. The Dunde ice core is the first ice core in the Qinghai-Tibet Plateau glaciers to study ice core CH_4 [95]. Researchers selected 12 discrete ice core samples from the top 95 m and processed and analyzed CH_4 at the IGE. The testing technique used was the melt-refreeze method. The study reveals how the concentration of CH_4 in ice cores has changed over the past 800 years. The results showed

that the CH_4 records of the Dunde ice core in the past 200 years have the same significant upward trend as the CH_4 records of the polar ice cores, and the CH_4 concentrations of the two ice core samples in 1280 and 1800 were the same as the CH_4 concentration records of the Greenland ice core during the same period, all between 700–800 ppb. The similarity with polar ice core CH_4 records indicates that the Dunde ice core CH_4 records have the potential to reflect changes in atmospheric CH_4 concentrations in mid-latitudes. However, there are still some abnormally high concentration values in the CH_4 concentration records of the Dunde ice core, especially some values in the past 200 years are 500–600 ppb higher than the CH_4 concentration in the Greenland ice core during the same period. Modern atmospheric CH_4 research indicates that global atmospheric CH_4 concentration differences typically do not exceed 150 ppb. Therefore, the CH_4 concentrations in some Dunde ice core records may not represent true atmospheric information but are instead influenced by factors such as summer melting phenomena during ice core formation and microbial metabolic activity. The reliability of the CH_4 data recorded in the Dunde ice core still needs to be further verified, so it is difficult to provide accurate information on the historical changes of atmospheric CH_4 in the middle and low latitudes of the northern hemisphere. Nevertheless, the CH_4 study of the Dunde ice core proves that the Tibetan Plateau ice core has the potential to reflect changes in atmospheric CH_4 concentration, so researchers can try to carry out similar studies in other Tibetan Plateau regions to more accurately understand the historical characteristics of changes in atmospheric CH_4 concentration in the middle and low latitudes of the northern hemisphere.

4.6. Dasuopu Ice Core on the Qinghai-Tibet Plateau

Researchers drilled an ice core at an altitude of 7200 m in the Dasop Glacier in the Himalayas on the Qinghai-Tibet Plateau. Due to the region's high altitude, summer melt on the glacier's surface is limited, so the original atmospheric signal in the Dasop ice core may be effectively preserved. The CH_4 testing of the Dasuopu ice core was jointly conducted by the Cold and Arid Regions Environmental and Engineering Research Institute of the Chinese Academy of Sciences (now the Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences) and the IGE, both using the melt-refreeze testing method. Studies have shown that before the Industrial Revolution, the CH_4 concentration level in the Dasop ice core was relatively low. However, since the Industrial Revolution, its concentration has shown a rapid upward trend, which is not significantly different from the CH_4 record in the polar ice core. However, it should be noted that there was a brief pause in the upward trend of CH_4 concentration in the Dasop ice core from World War I to World War II, and this feature is not obvious in the polar ice core CH_4 record. This difference may be related to the reduction of CH_4 emissions in the middle and low latitudes of the northern hemisphere caused by human activities. In addition, the Dasopu ice core showed abnormally high CH_4 concentration values at certain depths, which were 500–600 ppb higher than the CH_4 concentration recorded in the Greenland ice core during the same period; this concentration anomaly may be related to summer melt that, although limited in scale at Dasopu, still left a noticeable signature of the melt layer. In this regard, the researchers tried to exclude these outliers from the test data, but even after correction, the data series still showed a larger data dispersion than the polar ice core. For example, the difference in CH_4 concentration at some adjacent depths can even reach 100 ppb, which is more than twice the range of concentration change in polar ice cores during the same period. Due to the lack of reference, the reliability of the CH_4 data from the Dasop ice core remains to be verified. Therefore, researchers suggest searching for new ice cores in the Himalayas of the Qinghai-Tibet Plateau or other areas for CH_4 research in order to obtain more reliable characteristics of atmospheric CH_4 concentration changes in mid-latitudes [96].

4.7. East Rongbuk Ice Core of the Qinghai-Tibet Plateau

The researchers also tested and analyzed the concentration of CH_4 in the East Rongbuk ice core located near Mount Everest. The East Rongbuk Glacier is located in the northeast

of Mount Everest. In 2001 and 2002, researchers drilled three ice cores from East Rongbuk, two of which were used to test and analyze the CH_4 concentration of the ice cores. Testing was performed using the traditional thaw-refreeze discrete testing technique and was done at the IGE [94,97]. After comparison, it was found that the CH_4 test results of the East Rongbuk ice core and the Dathorpe and Dunde ice cores all showed greater data dispersion than the polar ice cores. Due to the process of gas diffusion and gas sequestration in ice cores, the change characteristics of atmospheric CH_4 concentration recorded by ice cores should be gentle. Therefore, the CH_4 concentration records of the East Rongbuk ice core must contain some non-atmospheric signals. To identify and remove CH_4 outliers in ice cores, the researchers employed a series of criteria. First, they excluded 34 samples in the test sequence, as the standard deviation of repeated test results of these samples was greater than 20 ppb, which was likely to be affected by factors such as test error. In addition, they deleted the test results with pre-industrial concentrations greater than 1000 ppb because pre-industrial ice core CH_4 concentrations hardly exceeded 1000 ppb, except for those local contaminations caused by ice core microbial metabolic activities, etc. Finally, the study set the maximum increase rate of atmospheric CH_4 concentration as 17 ppb/year in 1981 and deleted all test data whose change rate exceeded this value. After the above data screening steps, there are only 15 data points left in the ice core CH_4 records of the past 1300 years. Nine of the data points were from before the Industrial Revolution, with an average concentration of 749 $\pm$ 25 ppb, which is 76 ppb lower than that of the Dassop ice core and more in line with the global CH_4 concentration gradient established based on the CH_4 concentration of polar ice cores. However, the amount of filtered data is small, and it is difficult to explore the characteristics of atmospheric CH_4 concentration changes on a century scale. In order to obtain more reliable data and better data screening results, we can refer to the CFA technology used in Greenland GISP2 and NEEM-S1 ice cores. This will allow us to obtain continuous ultra-high-resolution test results and provide a more reliable basis for studying atmospheric CH_4 changes in mid-latitudes [94].

5. Current Research Problems

CH_4 concentration records in ice cores are an important source of data for studying the characteristics of CH_4 concentration changes in the ancient atmosphere [15]. However, abnormal signals higher than normal atmospheric CH_4 concentrations may appear in the ice core test series, which will obviously affect people's understanding of the characteristics and changes of ancient atmospheric CH_4 concentrations [29]. Therefore, the non-atmospheric signals that may exist in ice cores have attracted widespread attention from relevant researchers [29,50]. In order to ensure the reliability of the data, researchers often check the abnormal signals in the ice core and analyze the causes of them. Earlier related research showed that the abnormally high CH_4 concentration may be related to the melting phenomenon of the glacier surface [98] because CH_4 is a gas component with high water solubility, and seasonal freezing and thawing will cause some ice core layers to melt, resulting in high CH_4 concentration [98]. However, with the increase of CH_4 measurements in ice cores and the improvement of analysis techniques, researchers found that there is no strict correspondence between the abnormal increase in CH_4 concentration and the occurrence of melting layers [10,20,99]. Some researchers have proposed other reasons for some abnormally high concentration values: First, this may be the modern atmospheric pollution caused by the laboratory atmospheric infiltration test system. Some abnormal values are significantly higher than the modern atmospheric CH_4 concentration. For example, in the CH_4 concentration test records of Greenland GISP2 and NEEM-S1 ice cores, some outliers with concentrations greater than 4000 ppb appeared, which were obviously not caused by modern atmospheric pollution [29,50,100]. Therefore, some scholars put forward another explanation, which is caused by the extra CH_4 produced by microorganisms in ice cores under anaerobic conditions [29,50,100], and studies on ice core methanogens and laboratory culture of ice core methanogens also confirmed this possibility [99,101,102].

Studies have found that the concentration of CH_4 in Greenland ice cores usually has local concentration anomalies, and the highest concentration can reach more than 2–3 times the atmospheric concentration of CH_4 in Antarctic ice cores during the same period [29,103]. Since such concentration differences are generally unlikely to occur globally over the same period, these anomalous signals are generally considered to be related to disturbances in the ice formation process and require special attention when researchers analyze the data [22,29,104]. At present, researchers usually use two methods to identify abnormal signals in Greenland ice cores: one is to identify outliers through continuous high-resolution test records, and the other is to realize simultaneous detection of multiple gas parameters in ice cores. They then compare whether the test concentration of CH_4 in the sample is abnormal [31].

With the deepening of the research, the researchers also found that abnormal CH_4 values are common in Greenland ice core samples with high dust concentrations [31,35]. For the reasons behind this phenomenon, the researchers proposed the following two possibilities: First, the dust particles in the Greenland ice core may come from the Taklimakan Desert [105], and CH_4 molecules produced by natural gas seepage may be adsorbed on the particle surfaces [31]. When the ice core samples were melted during the test, these attached CH_4 molecules may have been released from the surface of the dust particles, resulting in abnormally high CH_4 concentration values in the test results [31]. Secondly, organic matter may be attached to the surface of these dust particles, and this organic matter may be utilized by methanogens in the ice core or oxidized and decomposed under the melting test conditions, resulting in relatively high CH_4 concentrations in the test results [31,35]. It is worth noting that avoiding the method of melting can help avoid some abnormal situations, such as the oxidative decomposition of organic components attached to dust particles with the participation of meltwater [31]. However, the use of non-melting testing methods can also introduce pollution types, such as gas extraction using crushed ice core samples, which may lead to CH_4 hydrate decomposition and additional CH_4 release [41,49]. Therefore, most researchers still recommend using multiple testing methods for comparison in order to better test the data. In addition, controlling test speed is also an effective way to limit this type of contamination, so CFA testing techniques with faster testing speeds should outperform discrete testing techniques in controlling data quality [31].

It is evident from the above discussion that there are various types of anomalies in ice core CH_4 data, and the influencing factors are relatively complex. As a result, most research remains at a qualitative stage, and the optimal data processing method involves identifying these anomalies and analyzing them within the overall sequence [29,31,106]. Compared to polar ice cores, non-polar ice core data have greater potential for exploration [94]. However, at present, the characteristic analysis of CH_4 data in non-polar ice cores, especially the analysis of anomaly characteristics, is insufficient, which limits data quality to some extent. In order to better understand and apply ice core CH_4 data, it is necessary to conduct more in-depth investigations. This includes using new testing methods and approaches, exploring more accurate data anomaly characteristics, and developing more effective data processing methods. In all, it is clear that although researchers have conducted a certain amount of CH_4 research in non-polar ice cores compared with polar ice cores, the current research on CH_4 in non-polar ice cores is still insufficient. Specifically, the data dispersion and outlier frequency of CH_4 test results in non-polar ice cores are relatively high, and the preliminary judgment is related to the existence of non-atmospheric signals in ice cores. However, in conditions with low-resolution or discontinuous ice core CH_4 tests, accurately resolving interference from non-atmospheric signals is challenging. As a result, the reliability of atmospheric CH_4 concentration changes inferred from non-polar ice cores is not as high as that of polar ice cores. In addition, the current research on the specific cause and mechanism of this non-atmospheric signal is insufficient, which also limits our in-depth understanding of the CH_4 signal in non-polar ice cores.

6. Future Prospects

To improve the reliability of atmospheric information reflected by CH_4 records in non-polar ice cores, we need to further explore the application of advanced testing techniques such as CFA technology. With the establishment of ultra-high resolution and continuous ice core CH_4 test records, we can better distinguish non-atmospheric signals from atmospheric signals, thereby improving the ability of non-polar ice cores to reflect changes in atmospheric CH_4 concentration. Moreover, most of the current CH_4 records from ice cores have not been used to determine the age of ice cores. Based on the above, we make the following suggestions for future related research:

(1) Establish an ultra-high resolution ice core CH_4 concentration sequence and explore the types of CH_4 outliers in the test sequence and their identification methods. Currently, there are limited studies on atmospheric CH_4 concentration in non-polar ice cores, and the reliability of the existing research data is limited due to factors such as microbial activity in the core or other non-atmospheric influences. By further studying possible anomalies in ice cores and their sources and developing robust identification methods, we can improve the reliability of CH_4 records in ice cores. This advancement will provide more accurate data for studying changes in atmospheric CH_4 concentration in non-polar regions during historical periods, allowing a better understanding of the temporal and spatial dynamics of global CH_4 emissions and their potential drivers.

(2) Expand the application of ice core CH_4 concentration records in the field of mountain ice core chronology to enhance our understanding of climate history and the effects of various drivers on atmospheric conditions. Ice core chronology is crucial for determining the sequence of events and chronological frames in the ice core record. Currently, the establishment of continuous age frames for mountain ice cores primarily relies on the reference horizon method combined with the glacier flow model. However, this method has several limitations, including potential inaccuracies in age estimation and uncertainties in glacier dynamics.

Although studies on bipolar ice cores have demonstrated that CH_4 is an ideal ice core age marker due to its sensitivity to climatic changes and well-defined stratigraphic variations, CH_4 records from mountain ice cores have not yet been applied in this field. By incorporating CH_4 records as age markers in mountain ice core chronology, researchers can develop more accurate and robust age models, overcoming the limitations of existing methods. This advancement will not only enhance our understanding of climate variability and the underlying processes but also provide valuable insights into the regional and global impacts of past climate changes. Furthermore, improved mountain ice core chronology can contribute to the development of more effective climate adaptation and mitigation strategies, as well as inform future research on the links between climate change and human activities.

(3) Investigate the history of atmospheric CH_4 concentration changes in the mid-latitudes of the northern hemisphere, and examine its relationship with natural factors and early human activities to better understand the drivers of past and present climate changes. Studies have shown that CH_4 emissions in the atmosphere primarily originate from tropical wetland ecosystems in low and middle latitudes. However, the majority of research on CH_4 in ice cores has been concentrated on polar regions, including Antarctica and Greenland, leaving a knowledge gap in our understanding of CH_4 dynamics in non-polar regions. To address this gap, it is crucial to actively conduct research on CH_4 concentration changes in non-polar ice cores, enabling a more comprehensive understanding of the temporal and spatial variability of global CH_4 emission sources. This research will provide valuable insights into the roles of natural processes, such as wetland dynamics, permafrost thawing, and wildfires, in driving atmospheric CH_4 concentrations.

Furthermore, exploring the impact of early human activities on atmospheric CH_4 concentrations has become a critical area of study, as it sheds light on the long-term consequences of anthropogenic influences on the Earth's climate system. Investigating CH_4 records from non-polar ice cores will allow for a more nuanced understanding of

early agriculture, land-use changes, and other human activities and their contributions to atmospheric CH_4 levels. This knowledge can inform policy decisions and climate change mitigation efforts, as well as enhance our ability to predict future trends and develop adaptive strategies for a changing climate.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

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