

MINERALOGICAL, GEOCHEMICAL, AND ISOTOPIC TOOLS FOR THE RECONSTRUCTION OF SUBGLACIAL AND MARINE ERUPTIVE PALEOENVIRONMENTS IN ANTARCTICA

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ABSTRACT

The Antarctic continent plays a key role in all the paleoclimatic reconstructions, and affects also the climatic evolution of lower latitudes. Therefore, knowledge of the past evolution of Antarctic ice cover is crucial for all the (paleo)climatic reconstruction.

The study of Cenozoic eruptive sequences in northern Victoria Land is a significant source of information about the presence, extent, thickness and type of this ice cover. In combination with $^{40}\text{Ar}/^{39}\text{Ar}$ dating, the eruptive environment can be used to draw a picture of ice sheet dynamics in the past. This is particularly true for cold regions where there is little or no surviving evidence for ice cover.

In the field, determination of the eruptive paleoenvironment of a volcanic sequence (*e.g.* submarine *vs.* subglacial eruptions) could be a difficult task owing to occurrence of ambiguous sequences of volcanic lithofacies. We propose a new, helpful approach in the determination of eruptive environment, represented by the use of chemical and isotopic composition/evolution of glasses and authigenic minerals in water-cooled lavas to determine the original eruptive paleoenvironment (freshwater *vs.* seawater).

The studied products are from Melbourne and Hallett volcanic provinces in northern Victoria Land and vary from hyaloclastite breccias to lapilli tuffs, characterized by variable degree of alteration. These products have been first characterized by petrographic investigations, mineralogical determinations (XRD) along with chemical analyses (SEM-EDS) on sideromelane, palagonitized glasses and secondary mineral phases such as zeolite, smectite. Then, analyses of specific indicator of eruptive environments have carried out, such as stable isotope systematics (D/H, $\delta^{18}\text{O}$) on handpicked glasses and plagioclase crystals separated from the juvenile lapilli along with altered hyaloclastite matrix and B contents on zeolite-rich matrix. (Na+K)/Ca of zeolites and glasses, B content and D/H isotopic ratios on altered matrix and $\delta^{18}\text{O}$ on glasses and plagioclase, coupled with $^{40}\text{Ar}/^{39}\text{Ar}$ data, furnish fundamental information about the evolution of the ice cover during the last 10-12 Ma in northern Victoria Land.

INTRODUCTION

The study of eruptive paleoenvironment of a volcanic sequence can represent a fundamental tool for paleoclimatic reconstructions. At present-day the climate change has a worldwide relevance, and the only way to try to understand the probable climatic evolution is to investigate the past. Current researches on this topic are concentrated on paleoclimatic study of ice cores in Antarctica and Greenland, and marine sediments, integrating stable-isotopes paleotemperature reconstructions from cryosphere-atmosphere records. In the last decades, these investigations are leading to a significant advancement in paleoenvironmental reconstruction even if facing many difficulties such as: complex and expensive logistic (drilling ice or marine sediments in complicated environments), less than 1 million year limit for ice cores, no climate indicators on terrestrial environment.

The Antarctic continent plays an important role in the Earth's climate variations, affecting the climate evolution of lower latitudes and constituting a natural laboratory where temperature variations and evolution are recorded. The volcanic rocks outcropping in Antarctica represent a significant repository of information about the occurrence of ice in the past; in fact, they can register chemical and isotopic variations due to magma-ice or magma-seawater interaction during eruption.

In this work, a multidisciplinary approach has been used to discriminate different eruptive paleoenvironment of volcanic sequences sampled in the Hallett and Melbourne Volcanic Province in northern Victoria Land (Antarctica). This research project takes inspiration from a recent paper written by Johnson & Smellie (2007) on the use of chemistry of zeolites as proxy for eruptive paleoenvironment. This study is not only an application of this pioneering proxy-methodology but it is also the first substantive test of that methodology using a large dataset of new analyses from a different volcanic terrain in other part of Antarctica, and including the first B, δD and $\delta^{18}O$ for volcanic rocks in an eruptive environmental study.

These way, gather different knowledge, some completely new, about magma-ice-water interaction and chemical variations during the eruptions. The field observations coupled with chemical, isotopic and geochronological data provide fundamental information about the evolution of the ice cover during the last 10-12 Ma.

PALEOCLIMATE

The climate change, today, is a topic of worldwide relevance. In the last decade many studies have been carried out, and a lot of hypotheses have been formulated on the temperature evolution of the Earth. These global variations are felt and recorded, particularly, in the polar areas, where the ice masses continuously draw a picture of this fluctuation. In the climate system, the cryosphere (which consists of snow, river and lake ice, sea ice, glaciers and ice caps, ice shelves, ice sheets, and frozen ground) is intricately linked to the surface energy budget, the water cycle, sea level change and the surface gas exchange. The cryosphere integrates climate variations over a wide range of time scales, making it a natural sensor of climate variability and providing a visible expression of climate change. Its relevance for climate variability and change is based on physical properties, such as its high surface reflectivity (albedo) and the latent heat associated with phase changes, which have a strong impact on the surface energy balance. The presence (absence) of snow or ice in polar regions is associated with an increased (decreased) meridional temperature difference, which affects winds and ocean currents. Because of the positive temperature-ice albedo feedback, some cryospheric components act to amplify both changes and variability. However, some, like glaciers and permafrost, act to average out short-term variability and so are sensitive indicators of climate change. Elements of the cryosphere are found at all latitudes, enabling a near-global assessment of cryosphere-related climate changes.

The Arctic area shows the clearest evidence of this variation with the intense reductions in Arctic sea ice extent (Fig. 1). Similar alerts come from the changes of the Antarctic ice cover that affects the climate evolution of lower latitude. Given this, it is not surprising that the poles are also where much of the research concerning global climate change is taking place.

Paleoclimate in Antarctica

Antarctica is a superb natural laboratory for the investigation of climate changes, coupling general climatic elements (*i.e.* orbital variations, greenhouse gas concentration, precipitation change) and

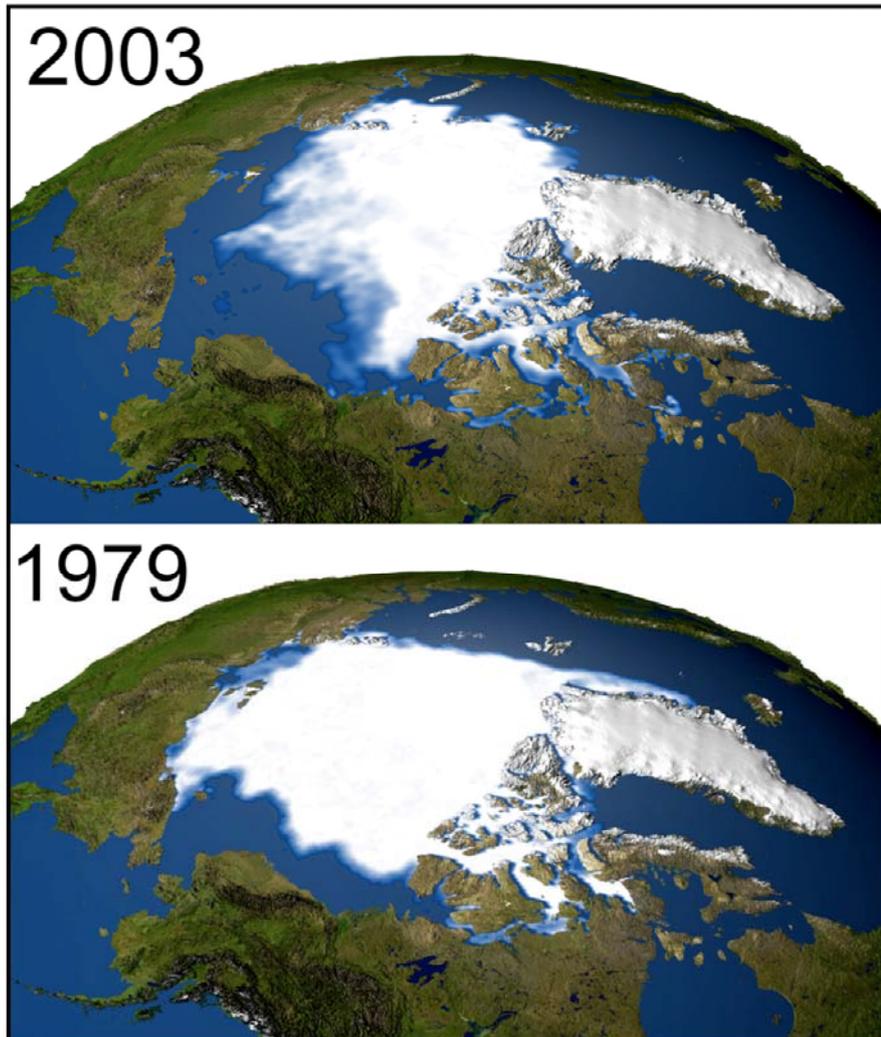


Fig. 1 - Arctic sea ice variations 1979-2003 (www.earthobservatory.nasa.gov).

geodynamic factors, both regional such as the opening of oceanic gateways, and local such as the creation and uplift of mountain ranges (DeConto & Pollard, 2003). The role of polar position of continental Antarctic plate is fundamental, but not fully sufficient to explain the development of the ice sheets, being the position reached in late Cretaceous whereas the ice sheets did not develop until Oligocene time. The set-up of the Antarctic circumpolar current following the opening of the Drake Passage is considered a possible trigger to the main Antarctic glaciation. On the other hand, geodynamic factors like the tectonomagmatic evolution of the West Antarctic Rift System (WARS) (Behrendt *et al.*, 1991; Finn *et al.*, 2005; LeMasurier, 1990; Rocchi *et al.*, 2002), could give rise to the evolution of the Antarctic ice caps. Current research on these topics, in Antarctica, is focused on the forcing role of climate on environment, and aimed to understand how the Antarctic environment – particularly the ice sheets – react to climate variations. These investigations are leading to a significant advance in paleoenvironmental

reconstructions; integrating stable-isotope paleotemperature reconstructions from cryosphere-atmosphere records in the ice cores and hydrosphere record in marine sediments. However, all these methods encounter some difficulties such as: (i) the need for complex and expensive logistics for drilling ice or sediments in extreme environments like Antarctic plateau, ice-shelf (ANDRILL), open-ocean deep water (ODP), (ii) the less than 1 million year age limit for ice cores, (iii) the lack of measurements of climate indicators on terrestrial environment, (iv) the lack of accounting for the possible influence of regional geodynamic factors, such as horizontal and vertical tectonics.

MATERIAL AND METHODS

The studied samples have been collected in northern Victoria Land during the 2005-2006 Antarctic expedition (field season) as a joint operation between Programma Nazionale di Ricerche in Antartide (PNRA) and British Antarctic Survey (BAS). The sampling area (Fig. 2) is distributed along about 400 km, on the Ross Sea margin of East Antarctica, including areas of the Hallett and Melbourne Volcanic Provinces (HVP, MVP). The studied volcanic sequences are in a coastal key position capable to record

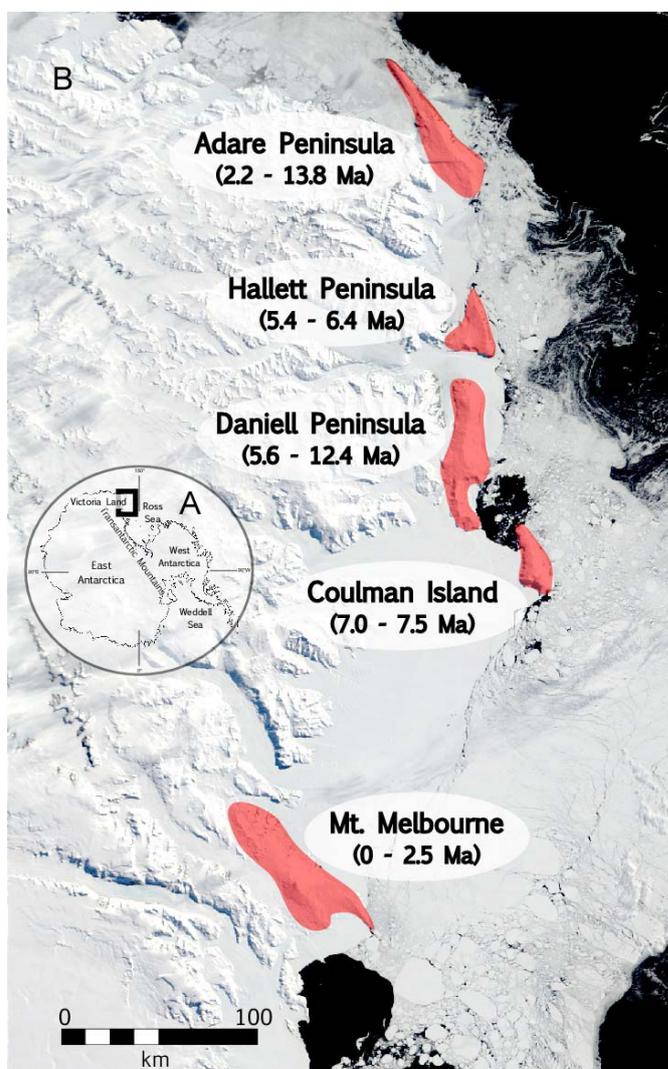


Fig. 2 - A) Antarctica schematic map and location of northern Victoria Land; B) aerial photo of northern Victoria Land. The red sectors represent the principal sampling areas. Age ranges after Armienti & Baroni (1999).

the icesheet or sea level fluctuation in the past; particularly the outcropping volcanic rocks can furnish paleoenvironmental information about the past 10-12 million years.

The sampling strategy was to collect rock samples from volcanic sequences representing magma-water-ice interaction, in order to obtain a potential significant database on the possible fluctuation of ice coverage in northern Victoria Land in the past. Estimates of former ice sheet thickness is one of the principal and most important outputs of lithofacies-based glaciovolcanic studies. However, environmental interpretations based on compositional criteria can also be important (Johnson & Smellie, 2007).

The samples are basanite/basalt - trachyte lavas, fine- or coarse-grained lapilli tuff, hyaloclastites, and pillow. After petrographic characterization, several samples have been selected for mineralogical, geochemical, geochronological and isotopic analyses. The idea was to recognize magma-water interaction considering the chemical and isotopic variation of zeolite-rich matrix, glass and plagioclase of hyaloclastites. From hyaloclastites, zeolite-rich matrix was separated by means of a micro-driller taking care to not include lava clasts/fragments in the powder. The powder obtained was used for XRD analyses, B contents and δD isotopic data. The clasts were crushed and glass and plagioclase were separated for $\delta^{18}O$ isotopic analyses. Glass fragments were concentrated by handpicking under a binocular microscope (excluding any fragment with evidence of micro-crystals and that were not optically clear). They were ultrasonically cleaned in deionized water and dried.

Concerning geochronology (^{40}Ar - ^{39}Ar systematics), alkaline lavas were crushed and a representative fraction was sieved to extract groundmass. Lava groundmasses were concentrated from the 150-250 μm and 250-350 μm fractions by handpicking under a binocular microscope, taking care to collect only fresh groundmass chips. In this way 150-200 mg of groundmass was gathered for 21 samples. After petrographic investigation two sanidine-rich lavas were selected to take out sanidine crystals for ^{40}Ar - ^{39}Ar analyses. The sanidine crystals were concentrated by means of a Franz Isodynamic separator, were sieved and separated from the 150-250 μm , 250-350 μm and 350-500 μm fractions by handpicking under a binocular microscope. Sample preparation and ^{40}Ar - ^{39}Ar data collection were carried out at IGG-CNR, Pisa.

RESULTS AND DISCUSSION

Collection of geochemical data started with SEM analyses on selected thin sections. The selection of the samples was made on the basis of the abundance of secondary minerals and extent of palagonitization. The chemistry of zeolites and glass, points out a lot of interesting linkages between the palagonitization process, taking place during or soon after the eruption, and the zeolitization. Examining the palagonitization development, it is frequently easy to distinguish the two different stages of palagonitization (gel-palagonite and fibrous palagonite). Gel-palagonite, as well as the different stage materials deriving from, it has a spectrum of chemical compositions showing relevant differences from those of the parent fresh glass. Gel-palagonite analyses show a general trend toward lower SiO_2 , Al_2O_3 , Na_2O , K_2O , CaO but higher TiO_2 and FeO concentrations of the parent glasses.

The zeolites occur as fibrous, elongated and blocky crystals (Fig. 3) and are almost all phillipsites with minor chabazites and analcite. The zeolites have been classified on the basis of alkali ratio using the triangular diagram Ca-Na-K (Ijima & Harada, 1969) (Fig. 4). The studied samples have been grouped into Hallett Volcanic Province (HVP), Melbourne Volcanic Province (MVP) and James Ross Island (JRI) samples.

The alkali ratios of zeolites, is a helpful key feature if used like a tool to discriminate the two

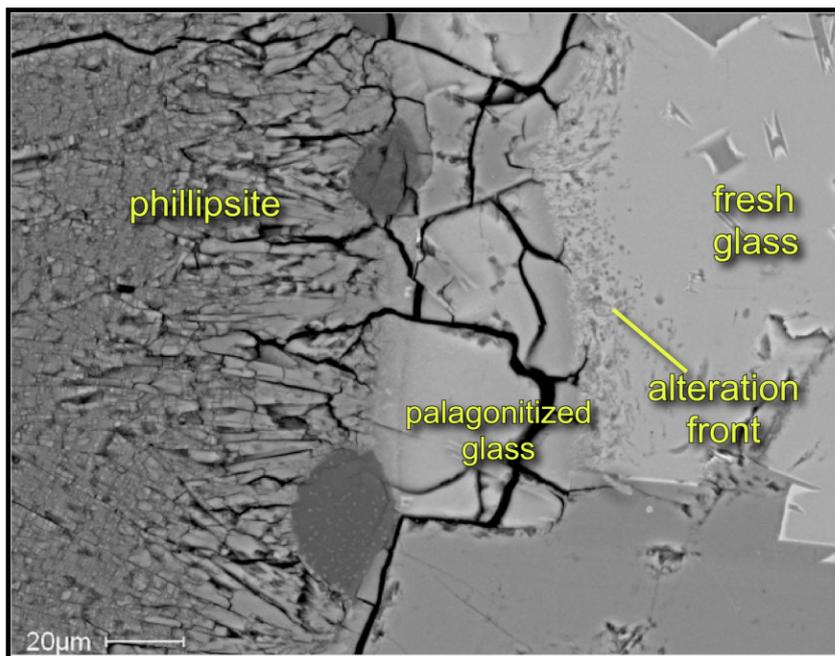
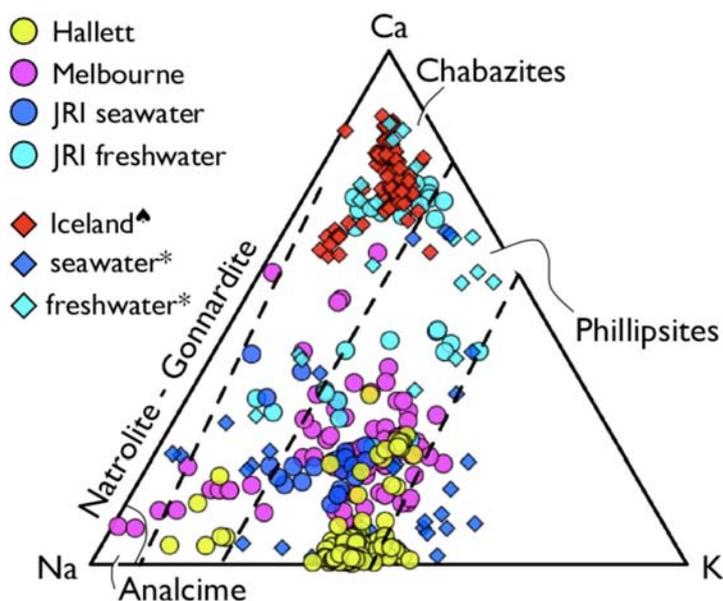


Fig. 3 - SEM picture showing the transition from fresh glass to palagonitized glass and zeolites.

Fig. 4 - Ca-Na-K zeolite triangular classification diagram after Ijima & Harada (1969), Smellie (2008), Johnson & Smellie (2007). Circles represent zeolite analyses made in this work. Diamonds represent literature data.



different eruptive settings (freshwater vs. seawater). The zeolite chemical data for the HVP and MVP have been plotted in diagrams considering alkali ratios, Si/Al and freshwater vs. seawater (Fig. 5). For comparison, in the diagrams are also plotted the JRI samples and literature data (Abollino *et al.*, 2001; Borghini & Bargagli, 2004; Johnson & Smellie, 2007; Smellie, 2008). The data distributions, plotted using the diagram $(Na+K)/Ca$ vs. Si/Al (Fig. 5), indicate that HVP zeolites have a more marine signature in comparison with those of MVP.

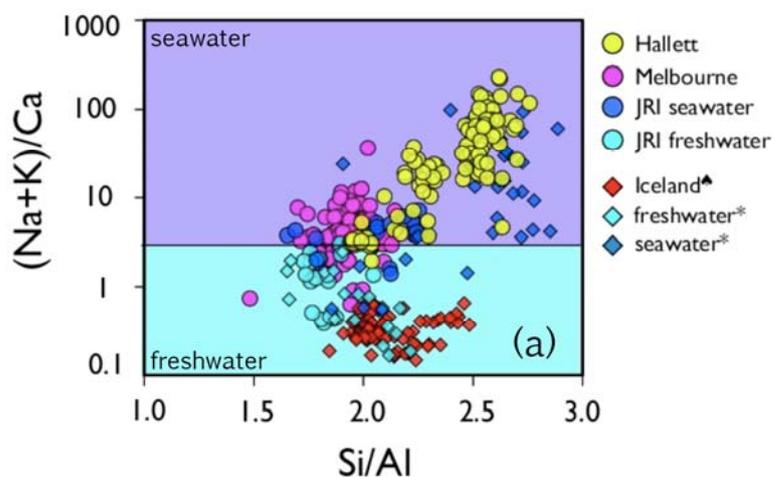


Fig. 5 - (Na+K)/Ca vs. Si/Al diagram for a) phillipsites, and b) chabazites. The (Na+K)/Ca ratio 3 is an empirical discrimination value to classify freshwater and seawater zeolites (Smellie, 2008; Johnson & Smellie, 2007). Circles represent zeolite analyses made in this work. Diamonds represent literature data.

The B analyses have been carried out on zeolite-rich groundmass of hyaloclastites from HVP, MVP and JRI. Boron is an element that can be used as a marker for the water-magma interaction in order to determine the paleoeruptive environment, because the boron is abundant in seawater (4.5 ppm; Stumm & Morgan, 1981) in comparison with freshwater boron content. The average of the boron contents for the HVP (-70.8 ppm) and MVP (-93.7) reveal clear differences between the two volcanic provinces. Apart from some samples more close to coastline, we can acknowledge that MVP samples have lower B content with respect to the HVP samples.

The isotopic analyses on zeolite-rich matrix, glass and plagioclase of lapilli, were performed to obtain information about different processes regarding magma-water interaction. A total of 40 zeolite-rich groundmass were analyzed to obtain the δD isotopic ratio, and 13 glass fragments and 13 plagioclase to obtain the $\delta^{18}O$ isotopic ratio. The analyzed samples come from HVP, MVP and JRI. The δD ratio varies from -43 to -119‰ but the variation range for HVP and MVP is different. The HVP samples show values from -56 to -92‰ with a median value of -69‰, whereas the MVP have more negative values, ranging from -71 to -120‰ with a median value of -93‰. The JRI samples have less negative values than MVP with δD ratio varies from -42 to -78‰ with a median value of -57‰.

The $\delta^{18}O$ isotopic ratios were measured for glass particles and plagioclase of hyaloclastite glassy clasts. The $\delta^{18}O$ ratio of glasses varies from 4.95 to 6.73‰ taking into account all samples. The $\delta^{18}O$ ratio of plagioclase, coming from the MVP, ranges from 6.5 to 8.5‰, whereas the sample coming from the HVP and JRI show higher values 6.4-12.3‰ and 16.5-21.3‰ respectively.

A total of 23 samples were dated. Ten lava groundmass and 1 sanidine for HVP samples and 11 lava groundmass and 1 sanidine for MVP. Step-heating technique was used to analyze lava groundmass splits and single-grain total fusion technique to analyze sanidine crystals. The MVP samples show ages ranging from 0.063 to 2.9 Ma and HVP ages ranging from 7.05 Ma to 9.95 Ma.

CONCLUSION

The ^{40}Ar - ^{39}Ar dating of HVP and MVP samples carried out from this work, give a great contribution to reconstruction of volcanic history in northern Victoria Land. The age distribution combined with reconstruction of eruptive paleoenvironment, contributes something important for

paleoclimatic evolution. The magma-ice-water interaction recorded by the HVP and MVP volcanic rocks gives information about ice sheet dynamics during the late Miocene and middle Pliocene- Pleistocene.

The interpretation of volcanic sequences in the HVP indicates an interaction with thin ice cover during eruption. The chemistry of zeolites records the interaction that occurred and suggest, as shown by high alkali ratios, B contents and isotopic values, an interaction with seawater or alkali-rich water. In this scenario, melting of snowbanks could generate alkali-rich water. In the Melbourne area, the analyses of volcanic sequences indicates that, during middle Pliocene, eruptions have occurred under a thick-ice cover. The chemical and isotopic data of zeolites for MVP samples show marine signature as indicated by zeolite chemistry and a subglacial or subaerial eruptive environment confirmed by the low B contents and high negative δD ratio. The marine signature of zeolites indicates a marine aerosol influence also on the MVP samples. The lower alkali concentration in zeolites in respect of HVP samples could be ascribed to the younger exposure age or sea level variations due to tectonic dynamics.

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