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# Mantle to surface degassing of alkalic magmas at Erebus volcano, Antarctica

Clive Oppenheimer [a,b,c,*], Roberto Moretti [d,e], Philip R. Kyle [f], Al Eschenbacher [f], Jacob B. Lowenstern [g], Richard L. Hervig [h], Nelia W. Dunbar [i]

[a] Le Studium, Institute for Advanced Studies, Orléans and Tours, France
[b] L'Institut des Sciences de la Terre d'Orléans, l'Université d'Orléans, 1a rue de la Férollerie, 45071 Orléans, Cedex 2, France
[c] Department of Geography, University of Cambridge, Downing Place, Cambridge CB2 3EN, UK
[d] Centro Interdipartimentale di Ricerca in Ingegneria Ambientale (CIRIAM) & Dipartimento di Ingegneria Civile, Seconda Università degli Studi di Napoli, Via Roma 29, 80131, Aversa (CE), Italy
[e] Istituto Nazionale di Geofisica e Vulcanologia, Sezione Osservatorio Vesuviano, Via Diocleziano 328, 80124 Napoli, Italy
[f] Department of Earth & Environmental Science, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA
[g] Volcano Hazards Team, U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA
[h] School of Earth and Space Exploration, Arizona State University, Box 871404, Tempe, AZ 85287-1404, USA
[i] Bureau of Geology and Mineral Resources, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

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## ABSTRACT

Continental intraplate volcanoes, such as Erebus volcano, Antarctica, are associated with extensional tectonics, mantle upwelling and high heat flow. Typically, erupted magmas are alkaline and rich in volatiles (especially $CO_2$), inherited from low degrees of partial melting of mantle sources. We examine the degassing of the magmatic system at Erebus volcano using melt inclusion data and high temporal resolution open-path Fourier transform infrared (FTIR) spectroscopic measurements of gas emissions from the active lava lake. Remarkably different gas signatures are associated with passive and explosive gas emissions, representative of volatile contents and redox conditions that reveal contrasting shallow and deep degassing sources. We show that this unexpected degassing signature provides a unique probe for magma differentiation and transfer of $CO_2$-rich oxidised fluids from the mantle to the surface, and evaluate how these processes operate in time and space. Extensive crystallisation driven by $CO_2$ fluxing is responsible for isobaric fractionation of parental basanite magmas close to their source depth. Magma deeper than 4 kbar equilibrates under vapour-buffered conditions. At shallower depths, $CO_2$-rich fluids accumulate and are then released either via convection-driven, open-system gas loss or as closed-system slugs that ascend and result in Strombolian eruptions in the lava lake. The open-system gases have a reduced state (below the QFM buffer) whereas the closed-system gases preserve their deep oxidised signatures (close to the NNO buffer).

## 1. Introduction

Erebus, the world's southernmost active volcano, offers an exceptional opportunity to examine the complexities that accompany degassing and evolution of magmas from deep to shallow levels. These include generic aspects of magmatic differentiation, redox evolution and eruptive transitions that are widely relevant to understanding other volcanic systems. Its long-lived anorthoclase phonolite lava lake has sustained emission of magmatic gases to the atmosphere for decades (Giggenbach et al., 1973) providing especially favourable circumstances for direct measurement of the magmatic system. Emissions rates of $SO_2$ have been measured by ultraviolet absorption spectroscopy since 1983 (Sweeney et al., 2008) and the relative abundances of many constituents of the plume (including gas and aerosol phases) have been measured using sampling equipment sited on the crater rim (Zreda-Gostynska et al., 1997) and open-path Fourier transform infrared (FTIR) spectroscopy (Oppenheimer and Kyle, 2008).

High emission rates of $CO_2$ from both the crater and a number of fumarolic ice towers scattered around the summit flanks have also been measured (Wardell et al., 2004; Werner and Brantley, 2003), revealing the presence of a $CO_2$-rich magma reservoir. The adjacent basaltic volcanic centres of Mt. Bird, Mt. Terror and Hut Point Peninsula on Ross Island are radially distributed at 120° around Erebus (Kyle et al., 1992), indicating generation of large volumes of parental basanite beneath Erebus, at the base of the thin (~20 km; Bannister et al., 2003) crust on which it is built. This supports the hypothesis that large quantities of mantle are required to account for the voluminous production of anorthoclase phonolite by differentiation (Kyle et al., 1992) and requires mantle upwelling, either as a ≥40-km wide plume (Kyle et al., 1992) or via decompression melting of (metasomatised) mantle during intraplate strike-slip tectonics (Rocchi et al., 2002, 2003, 2005).

One feature that makes Erebus particularly interesting from a degassing perspective is the evidence for extensive differentiation of magmas. Lavas on the upper parts of Erebus volcano are composed

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[*] Corresponding author at: Le Studium, Institute for Advanced Studies, Orléans and Tours, France. Tel.: +44 1223 333386; fax: +44 1223 333392.
*E-mail address:* co200@cam.ac.uk (C. Oppenheimer).

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predominantly of anorthoclase-phyric tephriphonolite and phonolite compositions (Kyle et al., 1992). Indeed, those erupted during the last 17 ka have a remarkably stable bulk phonolitic composition (Kelly et al., 2008). However, basanite, phonotephrite, and plagioclase-bearing tephriphonolite lavas crop out in eroded volcanic cones that form islands and sea cliffs on the southwest side of Erebus volcano and Hut Point Peninsula (Kyle et al., 1992; Moore and Kyle, 1987). Collectively, the lavas define a continuous fractionation series (referred to as the Erebus Lineage) from basanite to phonolite (Kyle et al., 1992).

Our principal aim here is to develop a coherent model for the magmatic plumbing system at Erebus. We analyse two principal datasets: surface observations of explosive versus passive degassing from the active lava lake, and the compositions and volatile contents of melt inclusions from a suite of Erebus Lineage and related rocks ranging from basanite to recently erupted anorthoclase phonolite bombs. The inclusion compositions mimic their associated whole rock chemistry, and document the evolution of the magmas. In light of the magmatic origin of $CO_2$ emitted from Erebus (Werner and Brantley, 2003), we use the pre-eruptive volatile content of this fractional-crystallisation sequence to build a framework for understanding the $CO_2$-dominated degassing of the magmatic system, and to interpret the composition of the emitted gas plume. Coupling of both deep and shallow signatures enables us to track volatile release right down to the lower lithospheric source of Erebus and its related volcanic centres. This provides valuable insights into the extent of degassing and its relationship with parental magmas at one of the world's most active intraplate alkaline volcanoes.

## 2. Methods

### 2.1. Samples

Samples for melt inclusion study were collected from Dry Valley Drilling Project (DVDP) cores extracted at Hut Point Peninsula (basanite), and from exposures on Inaccessible and Tent Islands (tephriphonolite), Turks Head (basanite, phonotephrite, tephriphonolite) and the summit of Erebus volcano (phonolite) (Moore and Kyle, 1987). A map of locations can be found in the Supplementary Material (Fig. 1). Samples DVDP 3–283, DVDP 3–295, AW82033, 7713, 97009, 97010, and 97011 are rapidly-quenched hyaloclastites with pristine melt inclusions. Sample 97006 is a highly vesicular lava-flow top. Sample 97018 is an anorthoclase phonolite bomb erupted in 1997, and EA1 is a crystal from a phonolite bomb. Only glassy inclusions lacking any signs of leaking or cracking were selected for study. Details of the samples and analyses of the whole rock samples are reported in Sections 1 and 2 of the Supplementary Material.

The concentrations of dissolved $H_2O$ and $CO_2$ in melt inclusions were measured by FTIR spectroscopy using a Nicolet Magna 750 at the U.S. Geological Survey in Menlo Park. Melt inclusions were prepared as doubly polished wafers ranging in thickness from 25 to 200 μm. Transmission infrared spectra were collected in the 1200–4000 $cm^{-1}$ range and measurements of total $H_2O$ (hydroxyl and molecular water) were made using the fundamental O–H stretch feature at 3550 $cm^{-1}$. Carbon dioxide was determined using the carbonate asymmetric stretch doublet near 1500 $cm^{-1}$ and 1400 $cm^{-1}$. Further details on analytical procedures are given in Section 3.1 of the Supplementary Material. The uncertainty of the total $H_2O$ and $CO_2$ analyses for most samples is ±11–12% and ±15–50%, respectively. Estimated uncertainties in $H_2O$ analyses are up to ±25% for some inclusions from the phonotephrite and tephriphonolite samples. The uncertainty of the carbonate determinations for the volatile-rich samples (DVDP 3–295, DVDP 3–283, 97009) is estimated to be ±15%. The quoted uncertainties are calculated from errors in the absorption peak height, inclusion thickness, density, and molar absorptivity. Replicate analyses of inclusions in DVDP 3-283a and DVDP 3-283b indicate reproducibility of better than ±2% for both water and carbonate. Individual raw FTIR analyses, calculated physical properties, and computed $H_2O$ and $CO_2$ abundances are reported in Tables 3, 4 and 6, respectively, of the Supplementary Material.

The concentrations of major elements and S, F and Cl in the melt inclusions were determined using a Cameca SX-100 electron microprobe at New Mexico Tech (Section 3.2 and Table 6 of Supplementary Material). Glass analyses were obtained with a defocused 15–25 μm beam and a 10 nA beam current and 15 kV accelerating potential. Errors for analyses of glasses are ±200 ppm based on replicate analyses of standard glasses, except for fluorine whose errors are ±1000 ppm.

### 2.2. Open-path FTIR spectroscopy of lava lake emissions

Open-path absorption spectra of the gas emissions were collected with a MIDAC Corporation M-4402-1 FTIR spectrometer sited on the crater rim, and using the lava lake as the infrared source, as described by Oppenheimer and Kyle (2008). Incoming radiation from the lake, ~300 m line-of-sight distant, was collimated with a 10-inch Newtonian telescope, and all spectra were recorded with a nominal 0.5 $cm^{-1}$ spectral resolution. Photographs of the lava lake and instrumental set-up are provided in the Supplementary Material (Section 4). The lava lake represents an unfaltering mid infrared radiation source while the very low humidity at the ~3700 m above sea level crater result in exceptionally 'clean' absorption spectra (i.e., there is very little interference from atmospheric water vapour).

The measurements presented here were made in December 2005, a period when intermittent Strombolian eruptions were occurring in the lava lake (around three per day that partially emptied the lava lake, hurling bombs, some more than a metre across, up to a few hundred metres beyond the crater rim). We focus on retrievals of $H_2O$, $CO_2$ and CO, which were made from transformed interferograms (collected with a time step of 1 s) using a code that simulates and fits atmospheric transmittance in discrete wavebands, specifically 2020–2100 $cm^{-1}$ for $H_2O$, $CO_2$ and CO (in addition to OCS). Uncertainties on these measurements are typically about 5% (e.g., Horrocks et al., 2001) but closer to 10% for measurements during explosions. Gas ratios are calculated from the raw column amounts after corrections are made for contributions of atmospheric water and $CO_2$ (Oppenheimer and Kyle, 2008). For our purposes, the ratio of $CO_2$/CO tracks redox conditions, while that of $CO_2$/$H_2O$ relates to the source depth of degassing. Of particular relevance here, we were able to measure the gas released by exploding gas slugs during the Strombolian activity, allowing comparison with the passive gas emission.

### 2.3. Modelling

The equilibrium saturation model used here was based on work of Moretti et al. (2003) for the C–O–H–S system, and incorporated: (i) a regular mixture approach to $H_2O$–$CO_2$–melt saturation (Papale et al., 2006); (ii) polymeric treatment of silicate melts for computation of sulphur solubility and speciation (Moretti and Ottonello, 2005; Moretti and Papale, 2004), and compatible oxidation state of iron in the melt (Moretti, 2005; Ottonello et al., 2001); (iii) multiple gas-phase species' equations of state (Belonoshko and Saxena, 1992); and (iv) mass balances for total (exsolved + dissolved) $H_2O$, $CO_2$ and S. All information is exchanged between the different modules, and composition and redox quantities are modified so as to zero model functions by means of a globally-convergent, non-linear method. This procedure ensures internal consistency and, critical to the Erebus case, permits application of the model to a wide spectrum of silicate melts. We also included a code for FeS precipitation based on the exchange reaction (Moretti and Baker, 2008):

$$FeO_{(melt)} + {}^1/_2S_2 \Leftrightarrow FeS_{(pyrrothite)} + {}^1/_2O_2. \quad (1)$$

This locates the FeS saturation surface in $P$–$S_{melt}$–$fO_2$ space, and at relatively oxidised conditions for which dissolved sulphur, $S_{melt}$, is not only constituted of sulphide.