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A theoretical framework for volcanic degassing chemistry in a comparative planetology perspective and implications for planetary atmospheres

Fabrice Gaillard ∗, Bruno Scaillet

Institut des Sciences de la Terre d'Orléans, CNRS/Université d'Orléans/BRGM, 1a rue de la Férollerie 45071, Orléans cedex 2, France

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Magmatic degassing is ubiquitous and enduring, yet its impact on both planetary surficial chemistry and how it may have varied among planetary systems remains imprecise. A large number of factors are likely to be involved in the control of magmatic gas compositions, leading roles being given to the redox state and volatile abundances in planetary interiors, and the fate of the latter during mantle melting. We however show that the pressure at which degassing occurs, that is the atmospheric pressure in most sensible cases, has a prime influence on the composition of subaerial volcanic gases on planets: high surface pressure produces N_2 - and CO_2 -rich and dry volcanic gases, while low pressure promotes sulfur-rich gases. In-between, atmospheric pressures close to 1 bar trigger volcanic gases dominated by H2O. This simple pattern broadly mirrors the atmospheres of Venus–Earth–Mars–Io planetary suite and constitutes benchmarks for the prediction and interpretation of atmospheric features of extra-solar planets. Volatile abundances within the planetary body interiors also matter but they play a secondary role. Furthermore, our analysis shows that any difference in redox conditions prevailing during partial melting tends to disappear with the degassing process itself, converging toward a unique – planetary oxygen fugacity – at the venting pressure.

A feedback relationship between volcanic gas compositions and atmospheric pressure implies a runaway drying during atmospheric growth; that is volcanic gases must become $CO₂$ richer as the atmospheric mass increases. This may explain some features of the Venusian atmosphere. On Earth, impact ejection of the atmosphere and CO₂-sink mechanisms, such as carbonate precipitation and plate tectonics, must have decreased atmospheric pressure allowing the reestablishment of water-rich volcanic gases.

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1. Introduction

Planetary atmospheres are most commonly considered as of either primary or secondary in origin [\(Zahnle](#page--1-0) et al., 2010). The first type corresponds to atmospheres with Sun(Star)-like composition, captured during the early stages of planet growth before dissipation of the Solar nebula, giving rise to a H_2 - and He-rich atmosphere equilibrated with a strongly reduced protomagma ocean at the surface [\(Fig. 1;](#page-1-0) e.g., Pepin, [2006; Matsui](#page--1-0) and Abe, [1986; Hashimoto](#page--1-0) et al., 2007). The second type corresponds to any primary atmosphere left over upon processes such as hydrodynamic escape, impact erosion [\(Lammer](#page--1-0) et al., [2008\)](#page--1-0), and to which have been added volatiles arising from either the planet interior, via degassing (Elkins-Tanton, [2008; Gaillard](#page--1-0) et

Corresponding author. *E-mail address:* gaillard@cnrs-orleans.fr (F. Gaillard). al., [2011\)](#page--1-0), or later meteorite/comet supply [\(Zahnle](#page--1-0) et al., 2010; [Hashimoto](#page--1-0) et al., 2007; [Schaefer](#page--1-0) and Fegley, 2010). In [Fig. 1,](#page-1-0) several types of processes fueling secondary atmospheres are illustrated, including the Magma Ocean stage [\(Elkins-Tanton,](#page--1-0) 2008; Gaillard and Scaillet, [2009; Hirschmann,](#page--1-0) 2012), which progressively shifted to volcanic eruptions emitting gas equilibrated under moderately oxidized conditions [\(Gaillard](#page--1-0) and Scaillet, 2009; Hirschmann, [2012; Gaillard](#page--1-0) et al., 2013; Yang et al., 2014). Equilibration with a quasi-inert planetary surface such as on present day Mars, or with an intensive biological activity such as on Earth constitutes a final atmospheric stage which is beyond the scope of our paper. Although the relative sequence of events is broadly known [\(Zahnle](#page--1-0) et al., 2010), estimating the individual contribution of each process to present-day atmospheres is a hard task and still widely debated field: in particular, whether planets of the inner solar system were born dry [\(Albarède,](#page--1-0) 2009) or wet [\(Zahnle](#page--1-0) et al., 2010; Drake and [Righter,](#page--1-0) 2002) is still open to discussion. For Earth, accretion simulations [\(Raymond](#page--1-0) et al., 2004) and geochemical

Fig. 1. The evolution of the planetary atmospheres. A helicoid projection illustrates the parallel growth of the planets and their atmosphere. For the planets, we present the magma ocean stage before and after core segregation, and the formation of the crust. For the atmosphere, we distinguished 4 successive types mostly inspired from (1): 1 – the nebular atmosphere (planetesimal stage); 2 – the magma ocean atmosphere (Hadean-stage of embryos and planets); 3 – the volcanic atmosphere (inflated by volcanic gases); 4 – mineral or biological atmosphere (once volcanic activity slowed down and other processes take over such as biological pumps or mineral–gas equilibria).

features (Albarède, [2009; Drake](#page--1-0) and Righter, 2002) hint at a late veneer of volatile-rich material having C, H and N isotopic ratios similar to that of primitive meteorites [\(Marty,](#page--1-0) 2012), which were subsequently folded into the deep Earth's mantle [\(Albarède,](#page--1-0) 2009). If true, such a scenario implies that the magma ocean atmosphere illustrated in Fig. 1 and discussed in Gaillard and [Scaillet \(2009\)](#page--1-0) or more recently in [Hirschmann \(2012\),](#page--1-0) must have been erased once the late veneer had supplied most of the C–O–H–S–N terrestrial inventory [\(Marty,](#page--1-0) 2012). Furthermore, we can reasonably assume that the atmosphere produced during a magma ocean stage must have had a small mass as most volatiles (C–O–H–S) would be contained in the huge molten reservoirs (silicate and metal; [Dasgupta](#page--1-0) et al., [2013;](#page--1-0) [Roskoz](#page--1-0) et al., 2013). It is therefore critical to address the mechanisms giving rise to the secondary volcanic atmosphere (Fig. 1) that resulted from igneous degassing once the late veneer has been incorporated in the mantle.

As illustrated on Fig. 1, a fundamental source of secondary atmospheres to all planets of significant size is magmatic degassing [\(Elkins-Tanton,](#page--1-0) 2008; [Albarède,](#page--1-0) 2009; [Gaillard](#page--1-0) and Scaillet, 2009; Hirschmann, [2012; Gaillard](#page--1-0) et al., 2013; Stanley et al., 2011). Within this context, it is during the late accretion steps, after the dissipation of the solar nebula and core segregation, hence from an already oxidized mantle (Trail et al., [2011\)](#page--1-0), that magma degassing began to significantly impact the atmosphere [\(Gaillard](#page--1-0) et al., [2013;](#page--1-0) Fig. 1). We consider that this degassing results from basalts formed by partial melting of a mantle that has already ingested the late veneer. This is the starting point of our analysis. To the best of our knowledge, the major volatiles released by planetary basalts belong to the C–O–H–S system as these atoms can be stored at significant concentration levels in the source regions of basalts and constitute *>*90% of magmatic gas produced on Earth [\(Symonds](#page--1-0) and Reeds, 1993), whereas other volatile species exist at much lower concentrations [\(Marty,](#page--1-0) 2012). In spite of a relatively poor knowledge of its behavior in magmatic system, we added nitrogen species in a few selected calculations in order to broadly illustrate the behavior of this important component of terrestrial atmosphere [\(Libourel](#page--1-0) et al., 2003; [Russel](#page--1-0) and [Arndt,](#page--1-0) 2005; [Marty,](#page--1-0) 2012). Minor species not included in our approach are [\(1\)](#page--1-0) the halogens (F, Cl, Br*...*), the reason being that their solubility behavior (i.e. the fugacity–composition relationships) in basalts remains unknown but we recognize their likely high importance in the magmatic degassing of Martian volcanoes (Filiberto and [Treiman,](#page--1-0) 2009), [\(2\)](#page--1-0) noble gases, since both their abundances in the Earth mantle [\(Marty,](#page--1-0) 2012) and their solubilities in basalts (Libourel et al., [2003; Miyazaki](#page--1-0) et al., 2004;

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