A golden era for volcanic gas geochemistry?

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Abstract

The exsolution, rise, expansion, and separation of volatiles from magma provides the driving force behind both effusive and explosive volcanic eruptions. The field of volcanic gas geochemistry therefore plays a key role in understanding volcanism. In this article, we summarize the most important findings of the past few decades and how these shape today's understanding of volcanic degassing. We argue that the recent advent of automated, continuous geochemical monitoring at volcanoes now allows us to track activity from unrest to eruption, thus providing valuable insights into the behavior of volatiles throughout the entire sequence. In the next 10 years, the research community stands to benefit from the expansion of geochemical monitoring networks to many more active volcanoes. This, along with technical advances in instrumentation, and in particular the increasing role that unoccupied aircraft systems (UAS) and satellite-based observations are likely to play in collecting volcanic gas measurements, will provide a rich dataset for testing hypotheses and developing diagnostic tools for eruption forecasts. The use of consistent, well-documented analytical methods and ensuring free, public access to the collected data with few restrictions will be most beneficial to the advancement of volcanic gas science.

Keywords

Volcanic gases, Geochemistry, Volatiles, Volcanic eruptions

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Code availability

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Consent to participate

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CK developed the outline for this review and led the writing of the manuscript. AA and MdM assisted in the writing, provided the data for the Turrialba example, and drafted the figures. CK revised the figures. All authors revised the manuscript in preparation for submission.

Introduction

Volatiles emitted from volcanoes have had profound impact on Earth's natural environment throughout its geologic history. Volcanic gases formed the Earth's early atmosphere and oceans, and thus provided habitat for the first life forms approximately four billion years ago (Oro et al. 1990; Schaefer and Fegley 2007). Though magma is driven from great depth towards the Earth's surface by pressure and temperature gradients, it is the chemical and physical behavior of volatiles that control eruption style and provide the fuel for explosive volcanism (Oppenheimer et al. 2014; Cashman and Sparks 2013; Woods 1995). It is therefore not surprising that much can be gleaned from observations of volcanic degassing, whether they are made before, during, or after periods of unrest or eruption.

At the same time, such studies represent no easy task as volcanic degassing is extremely variable in space and time. Volatiles can diffuse through magma bodies, travel laterally along faults, exsolve and re-dissolve in magmatic or aqueous fluids, or be stored in underground reservoirs from which they can be explosively erupted into the atmosphere or leak slowly to the surface over millennia. These complexities exacerbate the development of sound strategies for representative sample collection and measurement surveys. Observations made at a single time and location must be interpreted in the context of these complex volatile source, storage, and transport mechanisms to avoid the risk of arriving at incorrect or misleading conclusions.

In this article, we take inventory of where the field of volcanic gas geochemistry resides at present. We begin with a brief review of observations and concepts that have shaped today's understanding of volatile degassing processes. We describe the measurement techniques and instrumentation that have led to these findings and give an outlook on how these tools may improve in the future. Finally, we suggest several areas of focus for the next decade that we believe to be of particular importance for improving our understanding of degassing processes and the use of volcanic gas measurements as a diagnostic tool for eruption forecasting.

The information content of volcanic gases

On 28 May 1912, A.L Day and E.S. Shepherd of the Carnegie Institute's Geophysical Laboratory had the good fortune to find a pressurized hornito vent on the floor of Kīlauea's Halemaʻumaʻu Crater while looking for an opportunity to sample volcanic gases (Day and Shepherd 1913). To the surprise of many at that time, chemical analyses of samples they collected revealed that the principal component of the high-

temperature volcanic gas was water vapor (Day and Shepherd 1913; Sutton and Elias 2014). Closer analysis of samples collected in Hawai'i and elsewhere over the next few decades revealed that the primary components of all high temperature volcanic gases are water vapor (H_2O, typically 75-98%), carbon dioxide (CO_2, 0.3-13%), sulfur dioxide (SO_2, 0.3-3%), and hydrogen sulfide (H_2S, 0.02-2%) with smaller fractions of hydrogen halides (HCl, HF, and HBr), hydrogen (H), helium (He), and reduced carbon species (carbon monoxide CO, carbonyl sulfide COS, and carbon disulfide CS_2) (Gerlach 2004; Giggenbach 1996; Textor et al. 2004; Fischer and Chiodini 2015). Trace amounts of numerous other species, mostly metals and metalloids, are emitted either as gaseous species or aerosol particles (Symonds et al. 1987; Martin et al. 2010; Mather et al. 2012; Zelenski et al. 2013; Ilyinskaya et al. 2021; Mason et al. 2021). Note that many of these species pose environmental and health hazards (see Stewart et al. 2022 in this issue for a review).

Measured as they are emitted from volcanic vents into the Earth's atmosphere, these volcanic gases have a diverse origin. Arc gases are richer in water and chlorine than those released by midocean ridge basalts (MORB) due to the incorporation of fluids delivered by subducted sediments and altered oceanic crust (Wallace 2005). In contrast, hotspot and rift volcanism produce magmas with more carbon-rich (and water-poor) compositions (Gerlach 2004, see Fig. 1). Helium in hotspot volcanic gases is typically enriched in primordial ^3He relative to MORB, unambiguously indicating deep mantle origin (Hart et al. 1992; Lupton and Craig 1975). In contrast, gases produced from volcanic systems where crustal assimilation is a dominant process are enriched in crustally-derived radiogenic ^4He (Hilton et al. 1993). Taken together with other isotopic (H, C, N, S, Ar, Ne) evidence, volcanic gases provide important information on magma generation (Chiodini et al., 2010; Fischer and Chiodini 2015).

Gas emissions can also be used to infer magma depth, which is crucial for volcano monitoring, due to the distinct solubilities of the various volatile species in melts (Giggenbach 1996). Studies of melt inclusions (MI) in erupted products show that magmas often exhibit an exsolved vapor phase by the time they reach the mid-crust (10-15 km), and that most of the exsolved vapor is initially CO_2 (Edmonds and Wallace 2017; Lowenstern 2001; Fig. 1). The solubility of H_2O is several times greater than that of CO_2 such that H_2O remains dissolved in the melt until it reaches shallower depths, typically within 5 km of the surface (Wallace et al 2015; Fig. 1). However, since H_2O is an order of magnitude more abundant than CO_2 in magma, it is the abrupt and voluminous exsolution of H_2O that provides the energy for explosive volcanism (Chiodini et al. 2016; Papale et al. 1999). The vapor-melt partitioning of sulfur is complicated due to its occurrence in different dissolved forms (S^{2-} and S^{6+}), various gaseous species (SO_2 and H_2S), and solubility

dependence on oxygen fugacity. Generally, sulfur will exsolve from the melt at depths as great as ~10 km in H_2O-rich magmas, especially in relatively cool rhyolites, while only partitioning to the gas phase at very shallow depths (100s of meters) in H_2O-poor basalts (Wallace and Edmonds, 2011). Finally, we note that, while MI studies have provided great insight into magmatic processes, the recognition that older literature MI data often significantly underestimate melt CO_2 contents (by a factor of ~2.5; Rasmussen et al. 2020) requires re-evaluation of quantitative models linking gas emissions to magma degassing depth.

Eventually, exsolved volatiles are emitted to the atmosphere as volcanic gases, and it is mostly this transition from CO_2-rich deeply sourced gas, toward H_2O-S-rich shallow exsolved gas (see degassing lines in Fig. 1), that geochemists attempt to capture when monitoring volcanoes (Aiuppa et al. 2007). However, while at open-vent volcanoes without significant hydrothermal systems high CO_2/H_2O and CO_2/S ratios unambiguously indicate deep origin and gases with relatively low CO_2/H_2O and CO_2/S have usually equilibrated at shallow depth before being released (Fig. 1), complications arise at wet volcanoes that have active hydrothermal systems. Here, magmatic gases react with groundwater, brines, hydrothermal fluids, and host rocks, greatly affecting the composition of gases emitted at the surface. Though highly complex in detail, such interactions generally add water, reduce the oxidation state of the gases (Giggenbach 1987), and often efficiently remove sulfur from the gas stream in a process known as 'scrubbing' (Symonds et al. 2001; Fig. 1). Thus, at active volcanoes with hydrothermal systems, CO_2-rich gases can reflect either deeply-derived magmatic degassing or extensive hydrothermal scrubbing (Stix and de Moor 2018; Fig. 1c). Though S behavior in magmatic-hydrothermal systems is complex and kinetically inhibited (Giggenbach 1996, 1997), abruptly decreasing H_2S/SO_2 is often associated with the transition from quiescence to eruptive activity (de Moor et al. 2016a, 2019; Fig. 2), and high frequency gas monitoring provides a promising avenue for monitoring of phreatic/phreatomagmatic systems.

Tools of the trade

For many years, volcanic gas samples were collected using evacuated glass bottles and analyzed by gas chromatography (GC) (Symonds et al. 1994). In 1975, Werner Giggenbach revolutionized direct sampling by introducing sampling bottles containing sodium hydroxide solution and an evacuated headspace (Giggenbach 1975). The solution absorbs all major volcanic gas species, thus greatly increasing sample volume and improving precision and analytical sensitivity to both the absorbed gases and the minor non-reactive gas species concentrated in the headspace of the bottle. To this day, analysis of direct gas samples still provides the most comprehensive compositional information on volcanic gas emissions and thus

elucidates important detail on volcanic and hydrothermal processes (Corazza 1986; Giggenbach and Matsuo 1991; Giggenbach et al. 2001). If a complete characterization of emissions is desired, direct gas samples can be augmented with samples collected by pumping the gas and aerosol mixture through impregnated filters which absorb acid gases and trace species for analysis in the laboratory (Finnegan et al. 1989).

Another revolution in volcanic gas geochemistry occurred approximately 15 years ago with the advent of robust continuous gas monitoring technology. Continuous gas monitoring is achieved mainly by two types of instruments: For one, Multi-GAS instruments are deployed near active craters and measure in situ major gas compositions (H_2O, CO_2, SO_2, H_2S) in air-diluted volcanic plumes using a combination of IR absorption and electrochemical sensors (Aiuppa et al. 2005; Shinohara 2005). Multi-GAS measurements primarily target major gas ratios (CO_2/SO_2, H_2S/SO_2, H_2O/CO_2.) to correct for air dilution. Secondly, differential optical absorption spectrometers (DOAS) measure the absorption of scattered solar radiation by gases (mainly SO_2) in overhead volcanic plumes (Edmonds et al. 2003; Galle et al. 2002, 2010). DOAS instruments are miniaturized successors to the highly innovative correlation spectrometers (COSPEC) developed in the 1970s which enabled volcanic SO_2 emission rates, typically given in kg/s or metric tons per day (t/d), to be measured for the first time (Moffat and Millan 1971; Millán and Hoff 1978). At volcanoes with both Multi-GAS and DOAS instruments, emission rates of all major volatile species can be derived by scaling the DOAS-derived SO_2 emission rates with the X/SO_2 ratios measured by Multi-GAS (X = H_2O, CO_2, H_2S).

Our understanding of global volcanic CO_2 fluxes has especially benefited from the combined Multi-GAS and DOAS approach (Burton et al. 2013; Fischer et al. 2019; Werner et al. 2019; Fischer and Aiuppa 2020), though situations exist where magmatic or hydrothermal CO_2 travels along faults and fractures and diffuses through soils to the surface, sometimes away from any obvious volcanic features. Such diffuse CO_2 emissions can be quantified using soil-gas surveys in which the accumulation of CO_2 in chambers placed on the ground is measured. Repeating the measurement along a grid covering the area of interest yields a total diffuse CO_2 flux from that area, a parameter that can track magma movement below (Chiodini et al. 1998; Lewicki et al. 2005; Werner et al. 2014).

Next to the DOAS measurements mentioned above, several other remote sensing techniques can provide a variety of information on volcanic degassing. In the last decade, hyperspectral imaging methods in the UV and IR have been developed that allow 2D mapping of volcanic gas plumes (Bluth et al. 2007; Kern et al. 2010; Kuhn et al. 2014; Mori and Burton 2006). Though less selective than the DOAS systems, these

172 "SO_2 cameras" provide 2D imagery at unprecedented temporal resolution (typically on the order of 1 Hz)
173 which allows direct comparison with high-resolution geophysical data and the study of syn-eruptive
174 processes occurring on short time scales (McGonigle et al. 2017; Nadeau et al. 2011, 2015; Pering et al.
175 2015; Tamburello et al. 2013). The first continuous SO_2 camera systems have been installed on volcanoes
176 in recent years (Burton et al. 2015; Delle Donne et al. 2019, 2017; Kern et al. 2015). Open-path Fourier
177 Transform Infrared Spectroscopy (FTIR) is another remote sensing technique that is sensitive not only to
178 SO_2, but also to other IR-active species such as CO_2, CO, HCl, and HF, thus allowing a nearly complete
179 plume characterization if a suitable measurement configuration and radiation source can be found
180 (Francis et al. 1998; Love et al. 1998; Oppenheimer et al. 1998).

181 Finally, satellite observations also provide information on volcanic degassing. Beginning with the
182 successful launch of the Total Ozone Mapping Spectrometer (TOMS) instrument in 1978, spectroscopic
183 data collected by satellites have provided the community with a wealth of information on global volcanic
184 degassing (Carn et al. 2003, 2015; Krueger 1983). Though not as sensitive as ground-based measurements,
185 satellites provide global coverage on an approximately daily basis and can track large gas plumes all
186 around the world. To date, satellite measurements mainly target SO_2 in the UV spectral region, with the
187 Tropospheric Monitoring Instrument (TROPOMI) currently providing daily global coverage at
188 unprecedented 3.5 x 7 km resolution (Theys et al. 2019). In certain conditions, satellite-borne IR
189 spectroscopy can also provide information on SO_2, H_2S, HCl, sulfate aerosol, ash, and possibly even CO_2,
190 though the latter is extremely challenging due to the high atmospheric background CO_2 concentration and
191 current technology will only allow quantitative CO_2 detection on rare occasions (Carn et al. 2016; Clarisse
192 et al. 2010, 2011, 2012; Johnson et al. 2020; Schwandner et al. 2017).

193 The next 10 years

194 Though volcanic gas geochemistry clearly has a long legacy including many important discoveries, the field
195 has lagged behind geophysical disciplines in terms of continuous, real-time monitoring. Whereas well-
196 monitored volcanoes have typically had geophysical networks for decades, continuous gas-geochemical
197 monitoring has only begun in earnest in the last 10-15 years. Many volcano observatories have only
198 recently gained the capacity to deploy Multi-GAS and DOAS instruments to the volcanoes they are charged
199 with monitoring. These efforts are helped by community-wide global initiatives such as the Network for
200 Observation of Volcanic and Atmospheric Change (NOVAC, https://novac-community.org; Arellano et al.
201 2021; Galle et al. 2010) and the Deep Earth Carbon Degassing (DECADE,

https://deepcarboncycle.org/home-decade; Fischer 2013; Fischer et al. 2019) initiative which aim to provide instrumentation, technical know-how, and scientific understanding of the measurement results to staff at observatories and research institutions around the world.

We expect that continuous geochemical monitoring will expand greatly in the next 10 years, motivated by the extremely promising results from volcanoes that have been instrumented or where campaign measurements were fortuitously performed at key moments. Examples include the emission of substantial precursory CO_2 at Redoubt volcano starting almost 6 months prior to its 2009 eruption (Werner et al. 2013), a marked increase in CO_2/SO_2 ratios measured by continuous Multi-GAS in the plume of Villarrica volcano one month before its paroxysmal March 2015 eruption (Aiuppa et al. 2017), the systematic increase of SO_2 flux through the crater lake of Poás volcano detected by DOAS and Multi-GAS instruments prior to phreatic eruptions (de Moor et al. 2016b, 2019), or the recently discovered increase in CO_2 emission rate that appears to precede paroxysms at Stromboli by weeks to months (Aiuppa et al 2021).

Ground-based instruments are often destroyed by eruptions, resulting in a relative paucity of syn-eruptive gas composition data. Unoccupied aircraft systems (UAS) are likely to play an important role in filling this knowledge gap and in routine volcano monitoring, as they can provide access to otherwise inaccessible gas plumes. In the past several years, numerous studies have shown that reliable measurements of plumes can be obtained by mounting miniaturized Multi-GAS or DOAS instruments on small, multi-rotor UAS (James et al. 2020; Liu et al. 2019, 2020; McGonigle et al. 2008; Mori et al. 2016; Rüdiger et al. 2021; Stix et al. 2018; de Moor et al. 2019), or by collecting samples of these plumes for later analysis in the laboratory (Rüdiger et al. 2018; Liu et al. 2020; Galle et al. 2021; Ilyinskaya et al. 2021; Mason et al. 2021). As the technology continues to evolve and regulatory hurdles are overcome, somewhat larger UAS hold even greater potential as these can carry larger, more sensitive payloads to volcanic vents from safe distances even during times of unrest (Galle et al. 2021; Syahbana et al. 2019).

Isotopic measurements of volcanic gases, traditionally the domain of specialized laboratories, have also become more applicable to monitoring. Portable high-resolution laser absorption cavity ringdown instruments can now examine carbon isotopes at sensitivities sufficient to sample dilute plumes and can sometimes even be used directly in the field (Fischer and Lopez 2016; Stix et al. 2017; Ajayi and Ayers 2021). As the frequency of isotope measurements of volcanic gases increases, new insights will be achieved on the sources and processes governing dynamic variations in gas emissions.

Gas measurements inform our understanding of volcanic systems far beyond pattern recognition and eruption forecasting. We expect that the diagnostic power of these measurements will continue to increase as experimental volcanology provides better constraints on volatile solubility and degassing processes, and as those results are used to improve degassing models. These models are key to interpreting gas measurements, as simplified interpretations are often ambiguous. For example, an increase in CO_2/SO_2 ratio could indicate deep recharge of carbon-rich magma or increasingly efficient scrubbing of sulfur by a shallow hydrothermal system. Only by considering all available geochemical parameters in a degassing model can these processes be distinguished. However, diverse hydrothermal systems and non-equilibrium (kinetic) processes will provide significant challenges to universally applicable geochemical models of volcanic degassing. Integration of robust geochemical and geophysical data streams into real-time machine learning pattern recognition algorithms is a promising approach for improved and objective eruption forecasts.

Conclusions

Our view is that volcanic gas geochemistry, after numerous recent and important developments, is now entering what could be a golden era for the field. Technological advances in instrumentation combined with an improved understanding of how volatiles behave in volcanic systems is allowing for a paradigm change in the diagnostic capability of volcanic gas monitoring, which could place these techniques on par with geophysical methods.

The degree to which this potential is realized depends on how the community can overcome a few remaining challenges. Gas monitoring instrumentation is still largely custom-built, in contrast to the commercial, off-the-shelf solutions available for seismic or geodetic monitoring. The software packages used for data analysis (e.g., RatioCalc (Tamburello 2015), Mobile DOAS (Johansson et al. 2021a), the NOVAC Program (Johansson et al. 2021b), and Pyplis (Gliß et al. 2017)) are also custom solutions developed by the volcanology community and typically lack the high degree of automation often available in commercial geophysics software, although first examples of fully automated data processing and visualization routines are now at use at some volcanoes (Delle Donne et al., 2019; Aiuppa et al., 2021). This, along with the relatively small size of the gas geochemistry community compared with other volcanology disciplines, has limited the speed and efficiency at which monitoring networks have been able to expand. Gas monitoring data and field instrumentation are also inherently at the mercy of wind patterns (i.e., plume travel direction) and at risk of destruction by eruptions, often yielding incomplete

time series data – a situation which is likely to improve markedly as gas networks improve their spatial coverage of individual volcanoes.

Also, in contrast to other volcano monitoring disciplines, the gas geochemistry community has been slow to adopt standardized, public data portals. This is largely because the field has historically been highly diverse in terms of data production methods and somewhat 'data-starved', but such portals will be needed as data volume increases over the coming years and will be especially important in allowing comparative and interdisciplinary studies of the world's active volcanoes. The EarthChem/DECADE database (https://decade.earthchem.org/), the Mapping Gas Emissions project (http://www.magadb.net/), and the NOVAC data portal (https://novac.chalmers.se/) provide important first steps in this direction.

The motivation to overcome these challenges stems from the promises that volcanic gas measurements hold: that changes in gas composition and emission rate are likely one of the first signs of unrest at many more volcanoes than we are currently aware of; that more widespread geochemical monitoring will allow us to capture such signals with increased frequency and reliability; and that coupling these gas measurements with improved volatile degassing models and increasingly sophisticated data analysis methods will lead to a significant improvement in our ability to forecast volcanic events.

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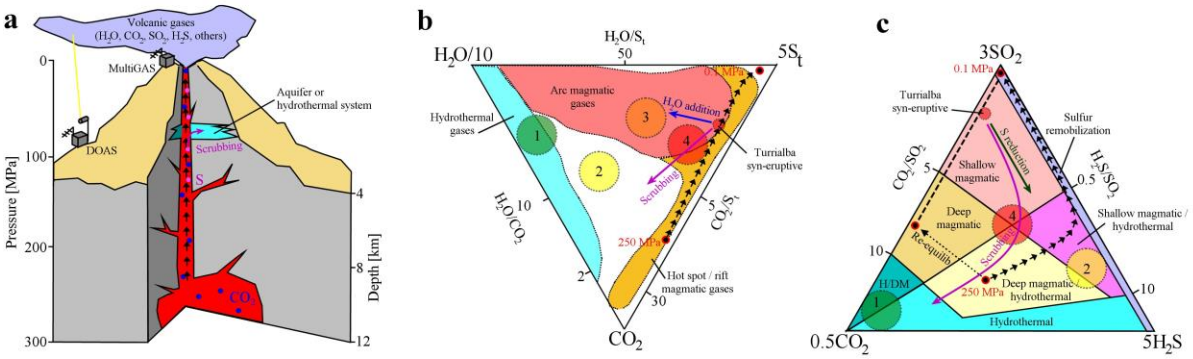
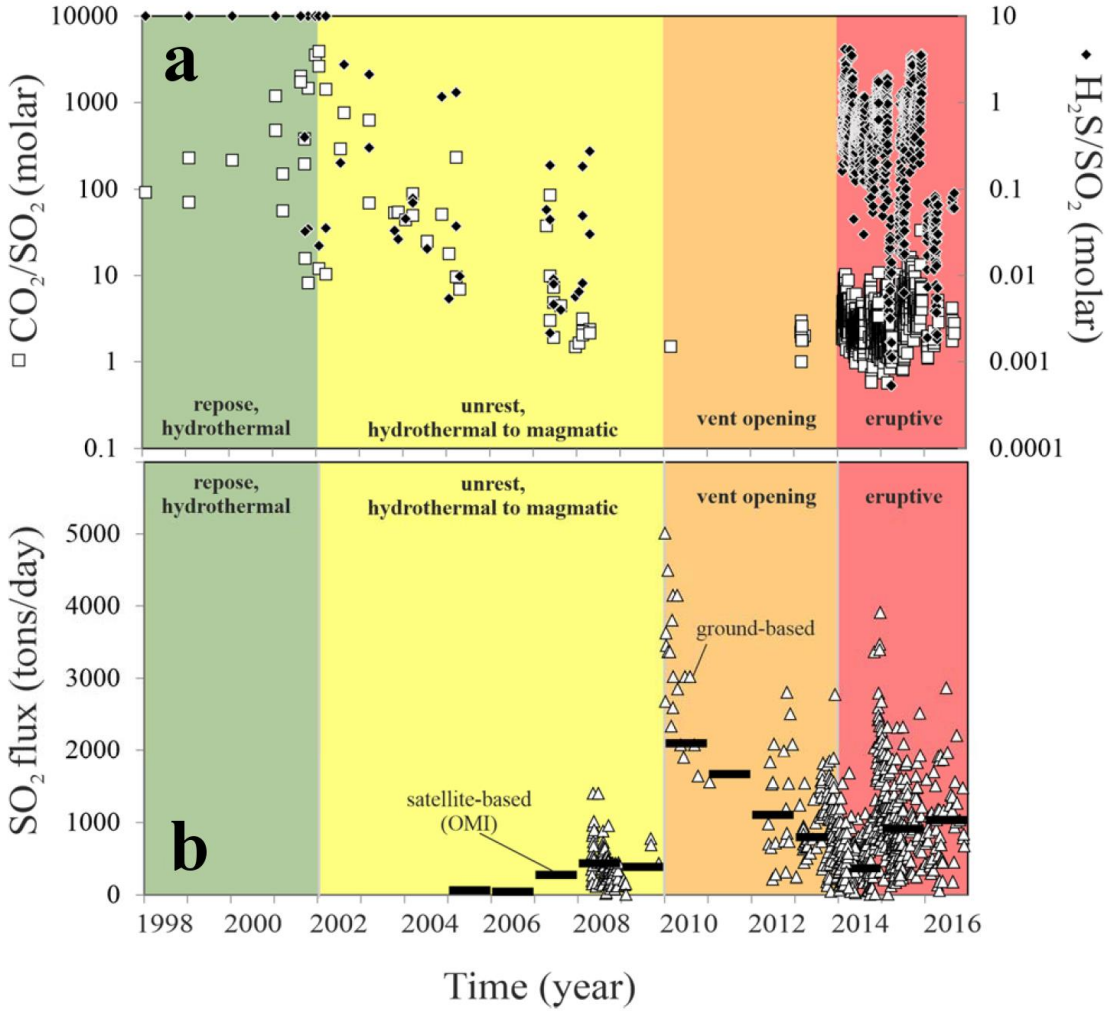


Fig. 1 Conceptual model for volatile behavior in volcanic systems. (a) Schematic cross-section of a volcano plumbing system, showing magma/gas migration pathways from a deep magma storage zone to the surface. (b) CO_2-H_2O-S_t (total sulfur) ternary diagram, showing proportions in volcanic gases (Giggenbach 1996). The compositional fields of arc and non-arc magmatic gases, and of hydrothermal gases, are from Aiuppa (2015). (c) CO_2-SO_2-H_2S ternary diagram, showing generalized compositional fields of magmatic and hydrothermal gases (modified from Stix and de Moor 2018). The field H/DM, not present in the original work of Stix and de Moor (2018), identifies an uncertain area where both hydrothermal and deep magmatic gases can plot. In (b) and (c), the dashed arrows represent the modeled composition of an exsolved volatile phase in magma ascending from approx. 10 km to the surface (see 'Model 1' in the study by de Moor et al. (2016a), for details on model initialization). The numbered circles denote the mean gas compositions measured at Turrialba during the four stages of activity from 1998 to 2016 (repose to eruption, compare Fig. 2). Syn-eruptive compositions are depicted by a small circle – these are phase 4 measurements further filtered to exclude H_2O/S_t falling outside the 90th to 10th percentile bracket to remove points likely affected by external water addition or condensation in the plume. Solid arrows originating from here describe the effects of scrubbing, addition of external (meteoric or hydrothermal) H_2O, and S reduction. The dashed line in (c) represents the gas composition that would be measured at the point of emission, after H_2S/SO_2 re-equilibrates to low values at high temperature and low pressure (de Moor et al. 2016a).



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663 **Fig. 2** Volcanic gas composition (a) and SO_2 flux (b) measured at Turrialba Volcano, Costa Rica, since 1998. Over the past two
664 decades at Turrialba, the Observatorio Vulcanológico y Sismológico de Costa Rica (OVSICORI) and international partners have
665 recorded one of the most complete continuous geochemical datasets available globally. The measurements clearly show the
666 sequence from a period of quiescence prior to 2001, when hydrothermal gases dominated emissions (Vaselli et al., 2010),
667 successively towards the magmatic unrest that has occurred since 2015 (de Moor et al. 2016a). Prior to 2001, CO_2/total sulfur (S_t)
668 ratios greater than 100 and a complete lack of SO_2 (H_2S/SO_2 depicted as equal to 10000 in Fig 2a) prevailed, indicative of purely
669 hydrothermal degassing during this period of quiescence. However, the gas signature became increasingly magmatic during 2001-
670 2010, with CO_2/S_t decreasing by two orders of magnitude and detectable, low-level SO_2 emissions beginning. The SO_2 emission
671 rate spiked sharply in 2010 with the opening of a new, high-temperature vent at the volcano's summit. From this time on, the
672 H_2S/SO_2 ratio varied over 4 orders of magnitude reflecting the ability of individual magmatic eruptions to transfer SO_2-rich gases
673 to the surface with negligible gas-water interaction. Data compiled from: Vaselli et al. (2010); Campion et al. (2012); Conde et al.
674 (2013); Aiuppa et al. (2014); Moussallam et al. (2014); Zimmer et al. (2014); de Moor et al. (2016a, 2017); Carn et al. (2017); Avard
675 et al. (2020) ; and Aiuppa (unpublished). Additional SO_2 emission rate satellite data from
676 https://so2.gsfc.nasa.gov/measures.html.