

PROCESSES CONTROLLING WATER ISOTOPIC COMPOSITION AND CHLORINE CONTENT IN VOLCANIC GASES

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Water is a predominant component of volatiles in magmas and volcanic gases; its content in volcanic gases with rare exceptions varies usually within 80-98 mol%. As a rule, gases from subduction zone volcanoes are more water-rich than gases from rift and hot spot zones. This is maybe the only reliable difference in the major species chemistry between these, so-called “andesitic” and “basaltic” gases according to terminology of Giggenbach. The following terminology will be used herein for gases from volcanoes of different tectonic setting: “A” (Andesitic) gases – from andesitic and more acidic passively degassing volcanoes of subduction zones. “AB” gases (Arc-Basaltic) – from calc-alkaline subduction-type basaltic volcanoes. “B” (Basaltic) gases - from intraplate (rift and hot spot) basaltic volcanoes.

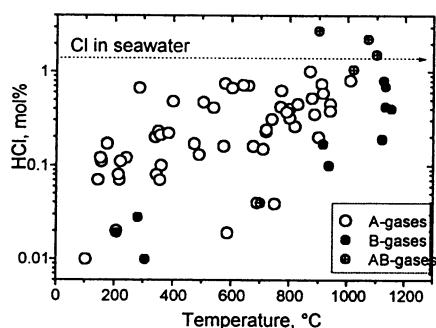


Fig. 1 Correlation between HCl-content sampling temperature for volcanic gases:

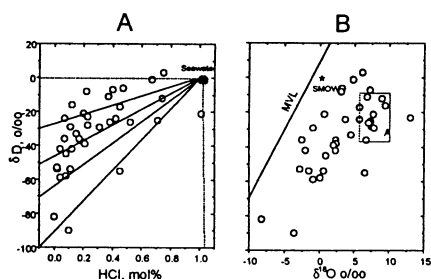


Fig. 2 δ D-HCl correlations and Craig plot for A-gases:

Condensates of high-temperature volcanic gases are strongly acidic, sometimes with a negative pH. Their metal content, especially Na, is low, usually less than 100 ppm in total, which nearly corresponds to the saturated-in-NaCl water vapor at low pressure (Pitzer and Pabalan, 1986). In particular, it means that the main Cl-bearing specie in volcanic gases is HCl, not metal chlorides. The HCl concentration in the highest-temperature A- and some B-gases sometimes close to 1 mol% with the most probable range of 0.4-0.7 mol%. Therefore, it is a problem to explain the almost complete exchange of cations by hydrogen from the evolved seawater or alkali Cl-rich brines, which should be formed under P-T conditions on the melt-fluid interface. Moreover, in contrast to S and C content, why is the Cl content in volcanic gases strongly limited?

CHLORINE CONTENT AND ISOTOPIC COMPOSITION OF VOLCANIC VAPORS

General trends

Chlorine is the only component of volcanic gases showing general geochemical trends at least for A gases. Correlation between HCl content and sampling temperature for A-gases is shown in Fig.1. The overall trend of having more Cl in a gas with higher temperature is well expressed.

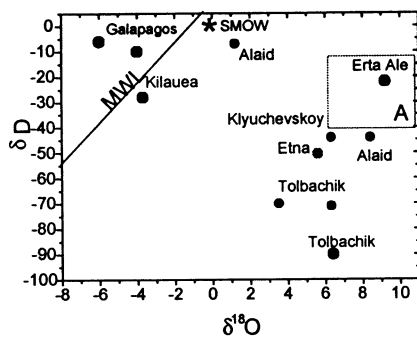


Fig. 3 Craig plot for AB- and B-gases

High-temperature gases with a low Cl-content are always diluted by meteoric water as follows from Fig. 2A where δD -values of volcanic vapors are plotted vs the Cl content for A-gases only. The Cl-concentrations higher than 1 mol% (seawater value) were practically not determined in fumarolic fluids from passively degassing volcanoes. The overall trend of the water isotopic composition for A-gases (Fig.2B) was already discussed in Taran et al.(1989) and Giggenbach (1992), where the area "A" (andesitic waters) was suggested to correspond to isotopic composition of a mixture of water dissolved

in the mantle (MORB-type) and water released from the oceanic slab, with more than 80% of subducted, and thus altered, seawater.

In contrast to the obvious trend for A-vapors, a few available isotopic data for gases from basaltic volcanoes, B-gases from spreading zones and hot spots or AB-gases of subduction zones, do not show any trends (Fig. 3). Therefore, at least for B and AB-gases, non-arc- and arc-type, we still do not have an appropriate isotopic signature for the magmatic end member.

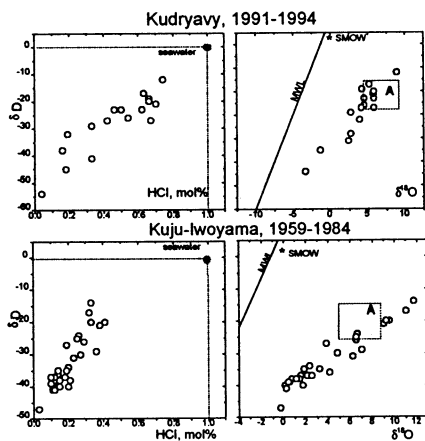


Fig. 4 Positive δD -HCl correlation and a mixing trend on the Craig plot for Kudryavy and Kuju volcanoes

Positive δD -Cl correlations (Fig. 4)

The next two examples demonstrate "right" trends of the vapor isotopic compositions and of Cl- δD correlations. Data for Kudryavy volcano (Taran et al., 1995) are the result of mixing between Cl-free meteoric water and Cl-enriched end member with δD and Cl values close to seawater. The highest δD and Cl values correspond to the highest temperatures of fumaroles (up to 940°C). The same, correlations are obvious for Kuju volcano, Kyushu Island (Mizutani et al., 1986). However, "magmatic" end member has here a significantly lower Cl-content, at least for this set of data obtained for fumaroles below 500°C

Negative δD -Cl correlation (Fig5).

Two subduction-type volcanoes - Vulcano, Italy, and Colima, Mexico display a negative δD -Cl trend.

Vulcano is a small island belonging to Eolian Archipelago in Mediterranean Sea, and Colima is a large and very active stratovolcano of the Mexican Volcanic Belt. Most probably, the observed trend for Vulcano relates to a complex process of mixing and evaporation of a hydrothermal brine of marine origin, thermal and shallow waters of meteoric origin, leaching of deep-seated precipitates, etc. (Chiodini et al., 1995) The most intriguing

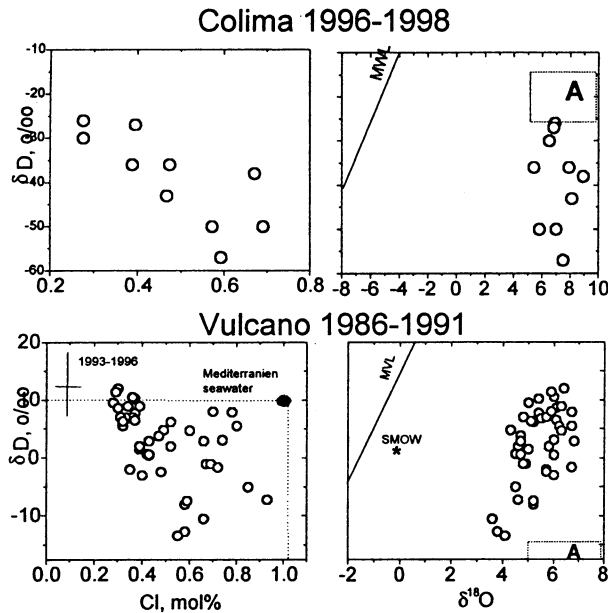


Fig. 5 A negative δD -HCl trend and Craig plots for Colima and Vulcano

evidence here is that one of the end members has δD -values close to the Mediterranean seawater, but significantly depleted in Cl. The other end member, on the contrary, has the Cl-content closer to the seawater value, but significantly depleted in D. In the case of Colima volcano the observed trend is most probably related to the shallow magma degassing. This is the only reasonable explanation for a negative δD -Cl correlation for the 800°C fumarole.

High- and medium-temperature volcanic vapors with a predominant meteoric or seawater source

The next examples demonstrate that even very hot volcanic gas vents may discharge vapors with very low fraction of magmatic component. Hot fumaroles (600-800°C) of Augustine volcano discharge vapor of mixed meteoric-seawater origin (Fig. 6). The “contamination” of volcanic gases by seawater is better seen at White Island (data from Stewart and Hulston, 1975 and the 4th Volcanic Gas Workshop, Giggenbach and Matsuo, 1991). Vapors from White Island, with δD between -17 and -25‰ and $\delta^{18}O$ = +6 to +7‰ (within the “subduction-type” isotopic range) contain ≤ 0.3 mol% of HCl.

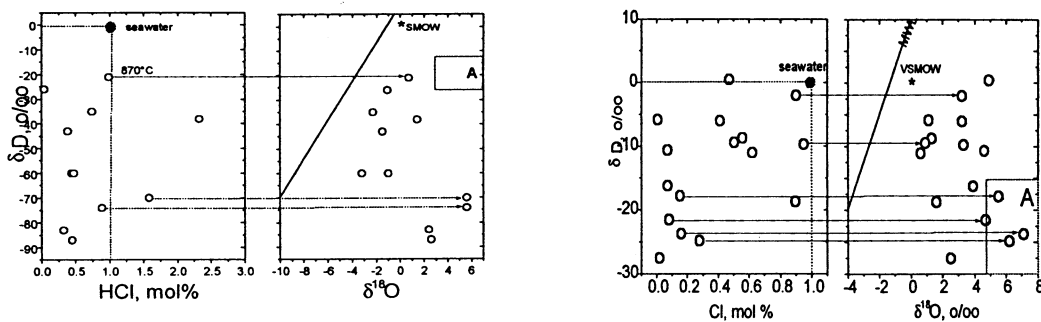


Fig. 6. δD -HCl correlation and Craig plot for Augustine and White Island volcanoes. Data from Symonds et al., 1990 and Stewart and Hulston, 1974.

MAGMA DEGASSING THROUGH VOLCANOES

Magmatic gases can be released close to the surface from a magma column (conduit) with convecting magma rising from a deep magma chamber, like in models of Kazahaya et al. (1994) and Stevenson and Blake (1998). Lava lakes (Kilauea, Erta Ale, Erebus, etc.) are the open-to-the-surface tops of such convective cells. Two volcanoes, Satsuma-Iwojima and Kudryavy, with strong and permanent fumaroles near 900°C might be examples of "buried" temporary lava lakes covered by a relatively thin cap of country rocks.

The source of gases may be also the material of a crystallizing extrusion or a lava plug; this is probably the case for Showashinzan, Avacha and Colima volcanoes. Such a fractured lava plug or an extrusion with volume between 10^7 and 10^8 m³, like at Colima volcano after the 1976 eruption can cool, crystallize and release excess of volatiles at low pressure by the Rayleigh mechanism during a long enough period of time. The Showashinzan dome and Colima volcano show such degassing and dilution trends in gas and water isotopic composition over time.

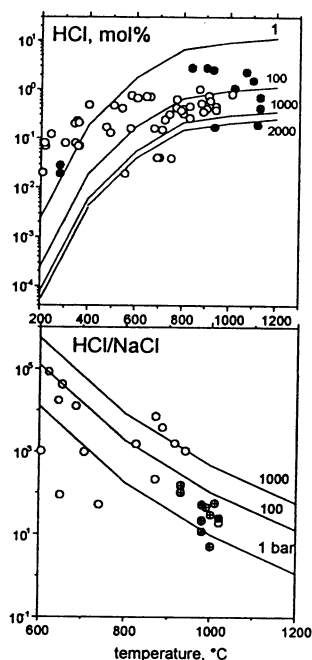
The source of volcanic gases may be the cooling and crystallizing or hot and convecting magma body at a considerable depth, the magma body being connected with the surface by fractures in permeable country rocks, like in the model of Stevenson (1993). An important feature of this mechanism is that "the most of decompression to atmospheric pressure occurs as the gas escape across the magma/country rock boundary" (Stevenson, 1993). In other words, the vertical pressure gradient in the conduit should be much below lithostatic and even hydrostatic, and thus most of the fumarolic conduit is in the P-T region of the "dry" halite (NaCl-melt)-H₂O system. One more important sequence from this mechanism is that the interface between a conduit with lower pressure gradient and saturated with water country rocks with hydrostatic pressure gradient may work like a "pump", involving ground water of different origin (cold, hydrothermal, seawater) in volcanic gas.

POSSIBLE MECHANISM OF THE HCl BUFFERING IN VOLCANIC GASES

In the case of the fluid flow from a pressure on the order of kilobars to the surface, the Cl-bearing aqueous fluid exsolved from the magmatic melt must experience a considerable evolution including the brine-vapor separation and precipitation of Cl-salts at lower pressure. This evolution leads to an "acidic" volcanic gas at the surface with the HCl concentration up to several wt% and gaseous alkali chloride concentrations at the level of saturation (a few tens of ppm) at high, >700°C, temperatures. This problem was already raised by Ryabchikov (1975) and Shinohara (1992) and refers to the strongly pressure dependent hydrolysis equilibrium of alkali chlorides, or in particular, to hydrolysis of NaCl.

The concentration of 1 mol% equal to ~2 wt% of Cl or ~3.5 wt % of NaCl. This value corresponds to the equilibrium solubility of NaCl in vapor at pressures above 1 kbar at magmatic temperatures (Bodnar et al., 1985; Pitzer and Pabalan, 1989). This amount of NaCl should be almost completely transferred to HCl before reaching the surface. It may be suggested that high-temperature volcanic gases with 0.4-0.7 mol% of HCl are either (1) originated from shallow magmas where the alkali (and iron?) chloride hydrolysis equilibrium is shifted to the right and the important Cl-bearing dissolved specie becomes HCl^o, or (2) if the pressure in the fumarolic conduit remains much below the lithostatic pressure until a considerable depth (Stevenson, 1993), the main mechanism controlling HCl concentration can be reactions between H₂O-vapor, the precipitated halite and alumino-silicate matrix

Fig. 7 Calculated and measured HCl-concentrations and HCl/NaCl ratios in high-temperature volcanic gases. Crossed circles – data for Tolbachik volcano



In this case concentrations of HCl in vapor equilibrated with albite and CaO-Al₂O₃-SiO₂ minerals can be calculated on a much simpler thermodynamic basis than in the presence of alkali-chloride brine (Chiodini et al., 1993). Results of the modelling are shown in Fig. 7, where calculated HCl concentrations and HCl/NaCl ratios in the vapor phase in equilibrium with a mineral assemblage containing halite (NaCl-melt), albite, anorthite, grossular, quartz and andalusite at different pressures from 1 to 2000 bar are compared with field data. Position of data points is reasonable, but of course, there is only qualitative, rather than quantitative correspondence, since real systems are much more compositionally, thermodynamically and dynamically complex. But it seems that the buffering of the HCl content by “dry” hydrolysis of alkali chlorides is an appropriate mechanism explaining the observing limits in Cl concentrations of volcanic gases. One of the important consequences of such buffering is that for the A-type volcanic vapors with “magmatic” isotopic signature ($\delta D=20\pm 5\%$, $\delta^{18}O=7\pm 2\%$) the lower Cl-content should correspond to higher pressure of the “last” hydrolysis equilibrium.

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