Anomalous Behavior of Zirconium and Hafnium in Volcanic Fumarolic Fluids

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Key Points:

- Subchondritic to chondritic Zr/Hf values inversely related to temperature occur in fumaroles fed by pristine magmatic fluids
- Superchondritic Zr/Hf values occur in fumaroles fed by hydrothermally contaminated volcanic fluids
- These pieces of evidence agree with the different volatility of Zr and Hf halides in magmatic gas and Zr and Hf speciation in hydrothermal fluids

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Anomalous Behavior of Zirconium and Hafnium in Volcanic Fumarolic Fluids

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Abstract The Zirconium and Hafnium concentrations in worldwide fumaroles fed by magmatic fluids reveal that the Zr/Hf ratio is inversely related to the temperature of emission. Lower Zr/Hf ratio values below the chondritic signature are found in fluids having the highest temperature while super-chondritic Zr/Hf ratio values are found in lower temperatures. Sub-chondritic values of the Zr/Hf ratio may be related to larger volatility of Hf-chloride gas species with respect to Zr-Cl gas species, while super-chondritic ratios may correspond to fluid-rock processes resulting from cooling of uprising magmatic fluids. We propose that sub-chondritic Zr/Hf ratio values in fumaroles associated with high temperature may be an appropriate marker of fast magmatic rising representing a new sensitive tool for volcanic risks strategies.

Plain Language Summary Understanding volcanoes dynamics is critical in evaluating volcanic risks and fundamental for the Earth system comprehension. The behavior of trace elements and their isotopes in fumaroles can be explored for evaluating imminent volcanic actions. Because of large crystal-chemical similarities of Zr and Hf in rocks and minerals, the Zr-Hf ratio is nearly constant to 36.6 ± 2.9 in meteorites and primitive rocks ("chondritic" reference.) We found that fumarole fluids at 1060°C–1084°C have sub-chondritic Zr/Hf signature (Zr/Hf between 24 and 29) when fast degassing of magma occurs while, fumarole fluids of lower temperature have super-chondritic or chondritic Zr/Hf values according to the intensity of rock-fluid interaction processes. The Zr/Hf ratio of fumarole fluids can be used as a new tool for volcanic risk evaluation as possible tracer of fast magmatic arriving.

1. Introduction

Fumaroles release natural fluids at the surface of volcanic areas allowing indirect investigations of melt transfer in volcanic plumbing systems. When magma rises, the composition of associated gas may change because of processes of magma degassing, temperature decreasing, fluids-rock exchanges, and shallow fluid mixing (Oppenheimer et al., 2014; Paonita et al., 2012). Variations in the volcanic gas composition may provide an understanding of quiescence to unrest transition announcing the arrival of potential volcanic events (Aiuppa et al., 2007; Oppenheimer et al., 2014; Paonita et al., 2016). Zirconium and hafnium are twin refractory trace elements with chemical coherence during magma crystallization reflecting the same ionic charge and almost the same radius (Niu, 2012; Shannon, 1976). They have a constant ratio in chondrites (the more abundant meteorites) corresponding to the so-called constant "chondritic" value of 36.6 ± 2.9 (Bau, 1996; Censi, Inguaggiato, et al., 2017; Censi et al., 2020; Jochum et al., 1986). Chondritic Zr/Hf values are often observed in pristine magmatic rocks. Zr/Hf values far from the chondritic range have been observed in hydrothermally altered rock (Iveson et al., 2018; Tiepolo et al., 2003) and in evolving peraluminous granites (Irber, 1999). Hydrothermal fluids usually show super-chondritic Zr/Hf values (Censi et al., 2015; Censi, Raso, et al., 2017; Inguaggiato et al., 2015, 2016) because hydrolysis shares differently Zr and Hf aqueous complexes enhancing absorption of Hf onto surfaces of neogenic minerals (Byrne, 2002; Shikina et al., 2018). Zirconium and hafnium concentrations in magmatic fluids have been measured in condensates from fumarole fluids between 100°C and about 1,100°C (Taran et al., 1992, 1995, 2018; Garofalo, 2006; van Hinsenberg et al., 2015; Zelenski & Bortnikova, 2005; Zelenski et al., 2013, 2014). Obtained results showed an almost similar Zr and Hf behavior apparently refractory during the magmatic degassing (Zelenski et al., 2013, 2021).

Table 1
Analyzed Zr and Hf Concentrations and Calculated Standard Deviations on Five Fractions of NASS-6 Standard Reference Seawater (Canadian National Research Council) Compared With Values Measured in the Previous Studies (Censi et al., 2020; Raso et al., 2013)

	Reference*		This study						
	Raso et al. (2013)	Censi et al. (2020)	NASS-6.1	NASS-6.2	NASS-6.3	NASS-6.4	NASS-6.5	Mean	$\pm\sigma$
ng l^{-1}									
Hf	0.89 ± 0.02	0.7 ± 0.12	0.77	0.84	0.87	0.77	0.82	0.81	0.05
Zr	23 ± 3	22.0 ± 1.5	22.9	22.7	23.0	22.8	23.3	22.9	0.21
Zr/Hf	25.6	31.0	29.8	27.1	26.3	29.7	28.3	28.2	1.57

Note. Data are given in ng l^{-1}.

Here, we have explored the Zr/Hf signature of deep fluid transported to the Earth's surface through the "volcanic plumbing system" (Burchardt, 2018), analyzing the amount of zirconium and hafnium of volcanic fumaroles in a wide range of temperature, composition, and tectonic settings.

2. Materials and Methods

The temperature of fumaroles is measured immediately before gas sampling using a type-K thermocouple. Volcanic gases are sampled using a quartz tube put into the fumarole as much as possible joined to a consecutive double-walled (Dewar) quartz tube coming out of the fumarole. The double-walled quartz tube is used to reduce the thermal exchange between fumarole fluids and atmosphere avoiding the condensation of fumarole fluids along the tube wall before the condensed. The Dewar quartz tube is joined to the condenser flask filled with the NH_4OH 4N solution (Sortino et al., 2006). In the condenser, water vapor, and other acid species react with the ammonia solution providing the best collection of fumarole fluids and condensates of reasonable quality (Zelenski et al., 2014). Concentrations of Zr and Hf are analyzed from a 100-ml aliquot of the collected condensate, filtered (through Millipore™ membranes with 0.22 µm porosity), and then transferred to a polytetrafluoroethylene (PTFE) vessel. The vessel is placed on a hot plate (about 50°C) for removing any NH_4OH trace and concentrating the remaining fraction to 5 ml final volume. Finally, 500 µl of a 10% HNO_3 solution are added before ICP-MS (Agilent 7500cc) analysis. Each solution is measured three times and ICP-MS analyses are carried out with a classical external calibration approach using ^{205} Tl solution (1 µg l^{-1}) as internal standard to compensate for any signal instability. The ICP-MS is equipped with a Micromist™ nebulizer, a Scott spray chamber, a three-channel peristaltic pump, an autosampler, and an octupole reaction system to remove any spectral interference. The lab treatment of studied samples is carried out in a laminar flow clean bench to minimize contamination while all sampling materials were previously cleaned with high purity grade reagents (Baker Ultrex II®). All plasticware used during sampling collection and treatment are cleaned with a 1:10 high purity HNO_3 hot solution.

To recognize if the collection procedure of fumarole condensates may involve Zr and Hf chemical exchanges between fumarole fluid and sampling tubes, we analyzed five aliquots (0.5 L each) of NASS-6 standard reference seawater (distributed by the National Research Council of Canada). These were boiled in the lab and the resulting vapor was transferred to a condenser flask using the same quartz tube previously used for collection of fumarole fluids. Condensate NASS-6 aliquots were put in a hot plate to remove any trace of NH_4OH. Successively, solution pH was regulated to 8 adding HNO_3 (2M) solution. Finally, we added an excess of $FeCl_3$ (1%) solution to induce precipitation of solid $Fe(OH)_3$. Zr and Hf were removed from the solution during $Fe(OH)_3$ deposition. This newly formed solid was collected by membrane filter (Millipore™ manifold filter diameter 47 mm, pore size 0.45 µm) and then dissolved in HCl (3M) solution. The later solution was diluted and analyzed by ICP-MS with an external calibration procedure (Raso et al., 2013). Results were compared to references (Censi et al., 2020; Raso et al., 2013) as reported in Table 1.

The used method for collecting fumarole fluids is widely exploited and considered among the best available (Zelenski et al., 2014). Nevertheless, two alkaline condensates from Bocca Grande fumarole (Phlegrean Fields)

Table 2
Temperature, Sampling Time, Zr, Hf Concentrations and Zr/Hf Weight Ratio Measured in Two Alkaline Condensates From the Bocca Grande Fumarole (164°C) in Phlegrean Fields

Phlegrean Fields – Bocca Grande fumarole 06.14.2013						
Time	10:25	12:30	10:25	12:30	10:25	12:30
ng l^{-1}						
	Hf		Zr		Zr/Hf	
	6,383	6,519	294,056	293,039	46.1	44.9
Mean	6,451		293,548		45.5	
±s	96		719		0.79	
T °C			164			

Note. Mean values are those reported in Table 3 with asterisks.

were collected June 14, 2013 at 10:25 and 12:40, respectively and analyzed to assess the reproducibility of the overall procedure. Related analyses are reported in Table 2.

Analyses of HCl, HF, and CO_2, by ionic chromatography (Dionex OnGuard® II H Cartridge), were carried out from a 5-ml aliquot of the alkaline condensate solution. The remaining volatile gas fraction, passing through the solution and accumulated in the vacuum head-space of the flask, was analyzed for He, H_2, O_2, N_2, CO, CH_4 by gas chromatography (PerkinElmer Clarus 500).

All the tubes forming the sampling line from the fumarole to the condenser flask were previously prewashed and left overnight in 30% HNO_3 and afterward 4 N NH_4OH ultrapure solutions.

3. Data

Fumaroles investigated in this study occur worldwide (Figure 1) and have variable chemical composition and temperature according to the different geodynamic domains. Table 2 shows the gas composition and concentration of Zr and Hf of the corresponding condensates (see methods for sampling and analytical determinations). We tentatively distinguished between low-medium temperature fumaroles ranging between 82 and 421°C from high-temperature fumaroles spanning between 430°C and 1084°C.

Low-medium temperature fumaroles occur at Vulcano (Aeolian Islands), Phlegrean Fields, Tenerife (Canary Islands), and Fogo (Capo Verde Islands), where fluids were sampled between 2012 and 2014 (Table 3). High-temperature fumaroles located in Pallas, Kudryavy, Mutnovsky and Tolbachik (Russia), Erta-Ale (Ethiopia), Kawah Ijen (Indonesia), and Momotombo (Central America) volcanoes were sampled between 1990 and 2016 (Garofalo, 2006; Taran et al., 1995, 2018; van Hinsberg et al., 2015; Zelenski & Bortnikova, 2005; Zelenski et al., 2013, 2014).

4. Results and Discussion

The distribution of the Zr/Hf ratio as a function of the HF/HCl ratio in alkaline condensate solutions is reported in Figure 2. We found that below 430°C (Figure 2a), Phlegrean Fields, Fogo Tenerife, and Vulcano Group 1 fumaroles have Zr/Hf ratio close to the chondritic value without clear relation with to HF/HCl ratio. In fumarole of Vulcano Group 2, the Zr/Hf ratios have variable super-chondritic values increasing as the HFl/HCl ratio

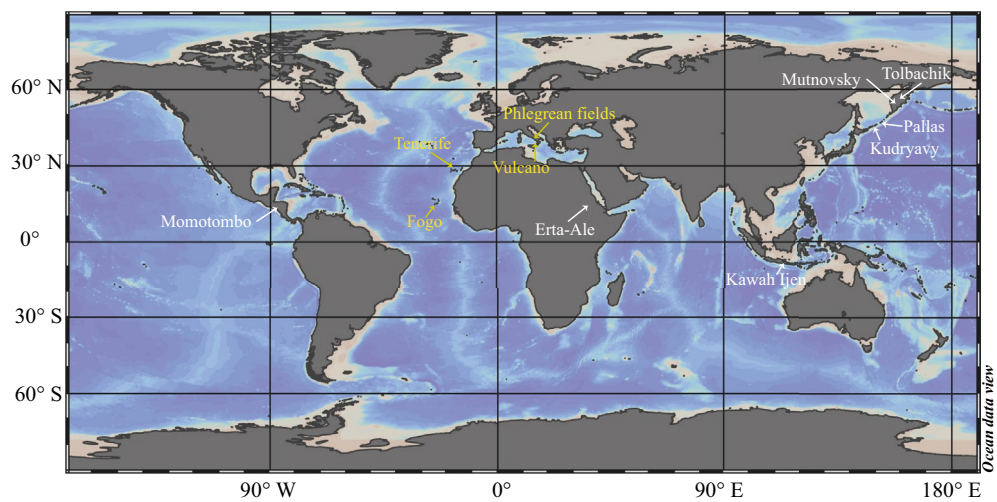

Figure 1. Location of studied fumaroles (in yellow) and those compared from references (in white). The map is redrawn from Ocean Data View™ software (Schlitzer, 2015).

Table 3

*Temperature, Sampling Date, HF, HCl, Hf, Zr Concentrations and Derived Zr/Hf Weight Ratio Measured in Alkaline Condensates From Studied Fumaroles or Reported From Previous Studies (See References). bld: Below the Detection Limit, nd: Not Determined, *: Mean Values Assessed From Two Analyzed Condensates Collected the Same Day at 10:25 and 12:40 Reported in Table 2*

Volcanic system	*T* °C	Sampling date mm.dd.yyyy	HF mmol mol-1	HCl	HF/HCl	Hf µg l-1	Zr	Zr/Hf	References
Fumaroles fed by magmatic fluids									
Vulcano Island (Group 1)	421	10.24.2013	0.14	2.54	0.06	9.3	288	31	This study
	261	10.24.2013	0.07	1.30	0.05	7.7	266	34	
	421	09.06.2013	0.09	0.63	0.14	28.3	1,099	39	
	351	03.01.2013	0.26	2.41	0.11	47.5	1,846	39	
	254	08.05.2013	0.22	2.56	0.08	2.2	99	46	
	242	03.01.2013	0.21	3.53	0.06	41.0	2,115	52	
Phlegrean Fields	164	05.16.2013	0.01	0.18	0.08	0.4	20	50	
	164	06.14.2013	0.02	0.25	0.08	6.5*	293*	45*	
	145	06.14.2013	0.01	0.17	0.05	6.1	303	49	
Fogo Island	199	03.22.2014	0.07	0.30	0.24	7.7	320	42	
	266	03.22.2014	*bld*	0.15	*nd*	14.7	571	39	
	285	03.22.2014	*bld*	0.16	*nd*	11.2	409	37	
Tenerife Island	82	03.12.2014	0.01	0.13	0.06	7.6	367	48	
Erta Ale	1,084		6.10	4.40	0.72	0.4	10	29	Zelenski et al. (2013)
Tolbachik	1,060		13.70	5.00	0.36	0.9	21	24	Zelenski et al. (2014)
Pallas	720		5.10	1.60	0.31	4.9	64	13	Taran et al. (2018)
	656		4.63	0.91	0.20	1.1	60	55	
Momotombo	776		168.70	12.84	0.08	5.9	117	20	Garofalo (2006)
	761		246.48	30.53	0.12	0.1	3	35	
	759		219.80	26.11	0.12	0.7	20	28	
	616		225.92	25.79	0.11	0.1	2	23	
	614		198.59	20.79	0.10	0.2	7	30	
	600		229.66	18.16	0.08	0.1	2	33	
	478		3.16	0.00	0.02	0.2	7	31	
Kawah Ijen	490		0.47	0.07	0.15	0.5	20	40	van Hinsberg et al. (2015)
	420		0.90	0.02	0.02	0.8	31	39	
Fumaroles fed by mixed magmatic and shallow (meteoric/hydrothermal) fluids									
Vulcano Island (Group 2)	251	10.24.2013	0.14	0.42	0.33	9.9	640	65	This study
	377	09.06.2013	0.44	1.59	0.28	2.7	202	74	
	374	03.01.2013	0.40	1.61	0.25	4.4	392	89	
	265	03.01.2013	0.40	0.51	0.78	2.2	257	119	
	378	10.24.2013	0.36	1.08	0.33	2.6	244	94	
	365	03.01.2013	0.47	0.54	0.88	1.4	228	163	
	416	08.02.2013	0.92	2.09	0.44	5.1	574	112	
Mutnovsky	507		3.40	3.64	1.07	0.9	55	61	Zelenski and Bortnikova (2005)
	450		4.59	0.84	0.18	1.5	92	61	
	410		3.85	0.80	0.21	0.7	56	80	

Table 3
Continued

Fumaroles fed by magmatic fluids									
		Sampling date	HF	HCl		Hf	Zr		
Volcanic system	*T* °C	mm.dd.yyyy	mmol mol-1		HF/HCl	µg l-1		Zr/Hf	References
Kudryavy	940		241.69	8.63	0.04	10.0	980	98	Taran et al. (1995)
	825		361.97	26.84	0.07	16.0	1,280	80	
	605		58.31	5.53	0.09	7.0	650	93	
	535		382.54	24.21	0.06	15.0	1,200	80	

raises. Above 430°C (Figure 2b), fumaroles from Erta-Ale, Tolbachik, Pallas, and Kawah Ijen have sub-chondritic or chondritic values irrespective of the HF/HCl ratio while in Kudryavy and Mutnovsky, Zr/Hf ratios are super-chondritic for a quite constant HF/HCl ratio below 0.2. Given HCl and HF are the main possible metal transport in fumarole media, our findings indicate that at lower temperatures, the sub-chondritic Zr/Hf values are not related to the HCl/HF ratio, while super-chondritic ratios are positively related to HF/HCl ratio. At higher temperature, however, super-chondritic Zr/Hf ratios are found independent of the HF/HCl ratio.

Figure 3 shows that the Zr/Hf ratio is inversely related to the temperature when fumaroles have sub-chondritic signature as in Momotombo, Pallas, Erta-Ale, and Tolbachik systems. Chondritic Zr/Hf values are in Kawah Ijen, Vulcano (Group-1), and Fogo fumaroles while slightly super-chondritic values are in Vulcano (Group-1), Phlegrean Fields, and Tenerife fumaroles. Fluids from Erta-Ale and Tolbachik have a higher temperature close to 1050, corresponding to magma degassing directly from visible fresh fractures and lava-lakes (Zelenski et al., 2013). The identified sub-chondritic signature of the Zr/Hf ratio at the highest temperatures indicates that here Hf is partitioned into the fumarolic gas relative to Zr. The degassing of magma could reflect possible larger volatility of Hf-bearing species compared to Zr gaseous species. Recent results of experimental Zr and Hf separation from mixed melted salts reveal that $HfCl_4$ gas species are significantly more volatile compared to $ZrCl_4$ gas species (Xu et al., 2016). We propose that the observed fractionation in Tolbachik and Erta-Ale fumaroles can result from the strong affinity of Hf toward Cl-compared to Zr toward Cl^- in agreement with different acid-base properties of these two metal ions (Shikina et al., 2015).

However, even if Zr-Hf fractionation through the magmatic degassing generates sub-chondritic Zr/Hf values, possible extensive interactions between Zr-depleted uprising volcanic fluids and pristine magmatic rocks of chondritic signature may progressively enhance the Zr/Hf ratio of fluids (Agashev et al., 2008; Yaxley et al., 1998). Furthermore, interactions between uprising magmatic fluids and host-rocks generate progressive fluid cooling with possible volatility changing that may destabilize Zr and Hf gaseous complex-ions (Larsen, 1970; Pastor, 1999; Pershina et al., 2002; Postma et al., 2015, 2017; Shikina et al., 2015; Xiao et al., 2014; Xu et al., 2016). These two processes may explain variations of the linear of Zr/Hf temperature trend tentatively displayed in dished line (1) of Figure 3.

Our results also show that super-chondritic Zr/Hf ratios of fumarole fluids may not be simply related to temperature as in Kudryavy, Mutnovsky, and Vulcano Group 2. Previous investigations indicated that Vulcano Group 2 fumaroles are fed by mixing between magmatic gas and hydrothermal vapor (Nuccio et al., 1999; Nuccio & Paonita, 2001). Similarly, Kudryavy and Mutnovsky fumaroles may result from mixing between hot magmatic fluids and meteoric waters (Taran et al., 1992, 1995, 2018). Mixing between magmatic and shallow meteoric/hydrothermal fluids can be represented by hyperbolic trends (Langmuir et al., 1978). We estimate a possible end-member representative of Zr/Hf and temperature conditions of magmatic fluids by Zr/Hf ratio and temperature measured in Erta-Ale and Tolbachik fumaroles. This end-member can be connected by two hyperbolas to two different end-members EM1 and EM2 corresponding to the variation of Zr/Hf ratios of hot hydrothermal fluids corresponding to several aquifers from volcanic areas (Censi et al., 2015; Censi, Raso, et al., 2017; Inguaggiato et al., 2015, 2016; Sasmaz et al., 2021; Zuddas et al., 2018). Consequently, the grey area of Figure 3 corresponds to Vulcano (Group-2), Kudryavy, and Mutnovsky fumaroles generated by variable mixing proportion between magmatic and shallow meteoric/hydrothermal fluids.

The results of this study broaden our knowledge of the geochemical behavior of Zr and Hf through natural unexplored volcanic degassing fluids underlining a different behavior between Hf and Zr in gaseous halides.

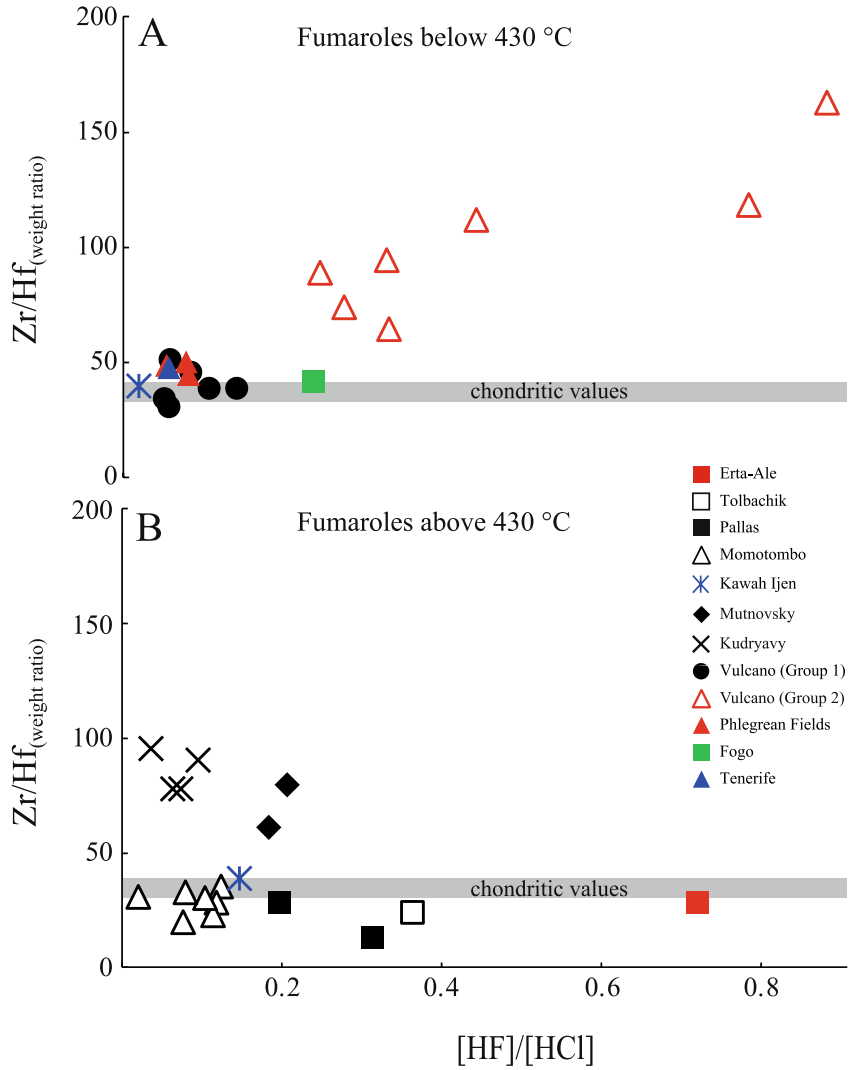

Figure 2. Zr/Hf ratio and HF/HCl concentrations measured in alkaline condensates collected from Vulcano, Phlegrean Fields, Fogo, Tenerife fumaroles compared with data from Erta-Ale (Zelenski et al., 2013), Tolbachik (Zelenski et al., 2013), Pallas (Taran et al., 2018), Momotombo (Garofalo, 2006), Kawah Ijen (van Hinsberg et al., 2015), Kudryavy (Taran et al., 1995) and Mutnovsky (Zelenski & Bortnikova, 2005). Fluids are discriminated according to the fumarole temperature below 430°C (a) and above 430°C (b). At Vulcano, fumaroles are differentiated in Group-1 fluids with Zr/Hf values unrelated to the HF/HCl ratio and Group-2 fluids where Zr/Hf values progressively increase with HF/HCl ratio. The error bar on Zr/Hf values corresponding to ±0.8 units (Table 2) falls within the size of the symbol.

Fundamentally, the difference between Zr and Hf, "twin" elements, is related to the fully occupied *4f* orbital driving "softer" Hf behavior compared to Zr (Pearson, 2005). This property is explicit in gas geochemical reactions of fumaroles as Hf softness involves larger volatility of its halides, while in aqueous fluids Hf softness enhances the hydrolysis of Hf aqueous complexes and surface reactivity. In rock minerals, the fully occupied *4f* Hf orbital results in very similar Zr and Hf ionic radii. Accordingly, a coherent behavior of Zr and Hf is observed during the mineral crystallization (Bau, 1996; Jochum et al., 1986; Nebel et al., 2010; Pfänder et al., 2007). Likewise, chondrite formation results from condensation of the primordial nebula at different temperatures fractionating Zr and Hf as a function of the volatilities (Lodders et al., 2009; Patzer et al., 2010), explaining the large geochemical coherence of Zr and Hf and different reactivity by *4f* electron occupancy of hafnium atomic structure.

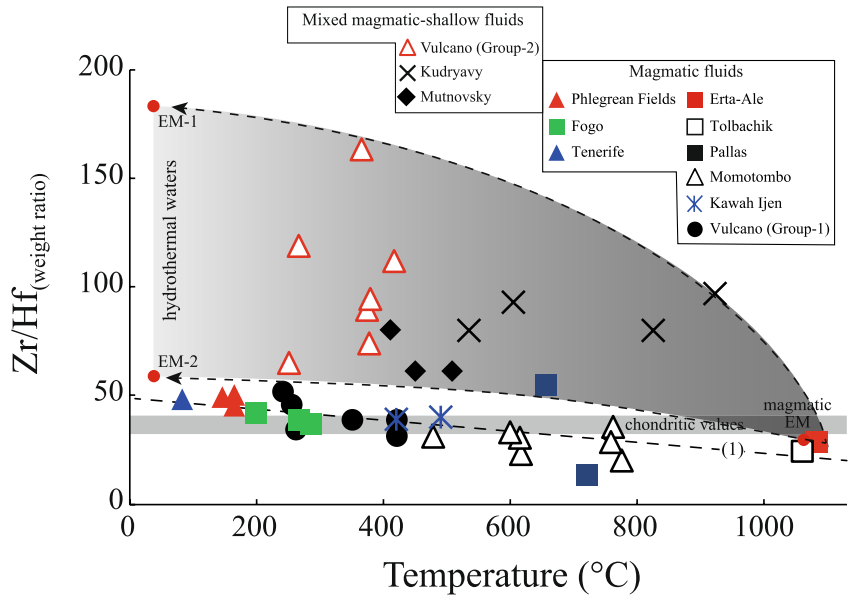

Figure 3. Zr/Hf ratio as a function of fumarole temperature. Fluids collected from fumaroles fed by magmatic fluids at Phlegrean Fields, Fogo, Tenerife, Vulcano (Group-1), Erta-Ale (Zelenski et al., 2013), Tolbachik (Zelenski et al., 2013), Pallas (Taran et al., 2018), Momotombo (Garofalo, 2006) and Kawah Ijen (van Hinsberg et al., 2015) show Zr/Hf values inversely correlated with the temperature. Fluids collected from fumaroles fed by magmatic fluids mixed with other fluids originated from shallow meteoric/hydrothermal at Vulcano (Group-2), Kudryavy (Taran et al., 1995) and Mutnovsky (Zelenski & Bortnikova, 2005) show super-chondritic Zr/Hf values unrelated to the temperature. These points fall falling along with hyperbolic arrays (dotted red curves). These arrays depict possible mixing paths between a magmatic end-member (EM) and some hydrothermal end-members (EM-1, EM-2, EM-3, and EM-4). The dotted black line (1) is the best fit of Zr/Hf versus temperature values in fumaroles fed by magmatic fluids. The equation is: $y = -0.025x + 48.6$ ($r = 0.68$; $r_{xy} > r_{2.5\%}$). The error bar on Zr/Hf values corresponding to ±0.8 units (Table 2) falls within the size of the symbols.

5. Conclusions

The significant temperature rise of a fumarole system always represents an indicator of the energy flux resulting from magma chamber to the Earth's surface. If fumaroles are mainly fed by the magmatic gas, the temperature should be coupled with the decrease of the Zr/Hf ratio in fumarole as depicted through the observed Zr/Hf versus temperature relationship. We evidenced that more Zr/Hf ratio is sub-chondritic, closer fluids are to the magma degassing magma indicating possible vicinity of magma chamber. The results of this observational study reveal that the Zr/Hf ratio of fumarole fluids is a promising indicator for establishing volcanic risk strategies.

Data Availability Statement

The geochemical data set obtained through this study was uploaded to the Earthchem FAIR aligned repository (www.earthchem.org) and will be available for download at the EarthChem Library. The required link to the data set is: Censi et al. (2021). Zr, Hf, and gas concentrations in volcanic fumarole fluids, Version 1.0. Interdisciplinary Earth Data Alliance (IEDA). https://doi.org/10.26022/IEDA/112026. Accessed 17 June 2021.

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References

Agashev, A. M., Pokhilenko, N. P., Takazawa, E., McDonald, J. A., Vavilov, M. A., Watanabe, T., & Sobolev, N. V. (2008). Primary melting sequence of a deep (N250 km) lithospheric mantle as recorded in the geochemistry of kimberlite–carbonatite assemblages, Snap Lake dyke system, Canada. *Chemical Geology*, *255*, 317–328. https://doi.org/10.1016/j.chemgeo.2008.07.003

Aiuppa, A., Moretti, R., Federico, C., Giudice, G., Gurrieri, S., Liuzzo, M., et al. (2007). Forecasting Etna eruption by real time evaluation of volcanic gas composition. *Geology*, *35*, 1115–1118. https://doi.org/10.1130/g24149a.1

Bau, M. (1996). Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology*, *123*, 323–333. https://doi.org/10.1007/s004100050159

Burchardt, S. (2018). Synthesis on the state-of-the-art and future directions in the research on volcanic and igneous plumbing systems. In *Volcanic and igneous plumbing systems* (pp. 323–333). https://doi.org/10.1016/b978-0-12-809749-6.00012-1

Byrne, R. H. (2002). Inorganic speciation of dissolved elements in seawater: The influence of pH on concentration ratios. *Geochemical Transactions*, *3*, 11–16. https://doi.org/10.1186/1467-4866-3-11

Censi, P., Cangemi, M., Brusca, L., Madonia, P., Saiano, F., & Zuddas, P. (2015). The behavior of rare-earth elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats. *Gondwana Research*, *27*, 209–215. https://doi.org/10.1016/j.gr.2013.09.014

Censi, P., Inguaggiato, C., Chiavetta, S., Schembri, C., Sposito, F., CensiZuddas, V. P., & Zuddas, P. (2017). The behaviour of zirconium, hafnium and rare earth elements during the crystallisation of halite and other salt minerals. *Chemical Geology*, *453*, 80–91. https://doi.org/10.1016/j.chemgeo.2017.02.003

Censi, P., Raso, M., Yechieli, Y., Ginat, H., Saiano, F., Zuddas, P., et al. (2017). Geochemistry of Zr, Hf, and REE in a wide spectrum of Eh and water composition: The case of Dead Sea Fault system (Israel). *Geochemistry, Geophysics, Geosystems*, *18*, 844–857. https://doi.org/10.1002/2016gc006704

Censi, P., Sirota, I., Zuddas, P., Lensky, N., Merli, M., Saiano, F., et al. (2020). Trace element fractionation through halite crystallisation. Geochemical mechanisms and environmental implications. *The Science of the Total Environment*, *723*. https://doi.org/10.1016/j.scitotenv.2020.137926

Censi, P., Sortino, F., Falcone, E. E., Censi, V., & Piazzese, D. (2021). Zr, Hf and gas concentrations in volcanic fumarole fluids, Version 1.0. *Interdisciplinary Earth Data Alliance (IEDA)*. https://doi.org/10.26022/IEDA/112026

Garofalo, K. (2006). *Origin, composition and evolution of fumarolic fluids of subduction zone volcanoes in Nicaragua*, p. 86. (PhD thesis). Christian-Albrechts-Universität zu Kiel (Germany).

Inguaggiato, C., Censi, P., Zuddas, P., D'Alessandro, W., Brusca, L., Pecoraino, G., & Bellomo, S. (2016). Zirconium-hafnium and rare earth element signatures discriminating the effect of atmospheric fallout from hydrothermal input in volcanic lake water. *Chemical Geology*, *433*, 1–11. https://doi.org/10.1016/j.chemgeo.2016.04.002

Inguaggiato, C., Censi, P., Zuddas, P., Londono, J. M., Chacon, Z., Alzate, D., et al. (2015). Geochemistry of REE, Zr and Hf in a wide range of pH and water composition: The Nevado del Ruiz volcano-hydrothermal system (Colombia). *Chemical Geology*, *417*, 125–133. https://doi.org/10.1016/j.chemgeo.2015.09.025

Irber, W. (1999). The lanthanide tetrad effect and its correlation with K/Rb, Eu/Eu*, Sr/Eu, Y/Ho, and Zr/Hf of evolving peraluminous granite suites. *Geochimica et Cosmochimica Acta*, *63*, 489–508. https://doi.org/10.1016/s0016-7037(99)00027-7

Iveson, A. A., Rowe, M. C., Webster, J. D., & Neili, O. K. (2018). Amphibole-, clinopyroxene- and plagioclase melt partitioning of trace and economic metals in halogen-bearing rhyodacitic melts. *Journal of Petrology*, *59*, 1579–1604. https://doi.org/10.1093/petrology/egy072

Jochum, K. P., Seufert, H. M., Spettel, B., & Palme, H. (1986). The solar-system abundances of Nb, Ta, and Y, and the relative abundances of refractory lithophile elements in differentiated planetary bodies. *Geochimica et Cosmochimica Acta*, *50*, 1173–1183. https://doi.org/10.1016/0016-7037(86)90400-x

Langmuir, C. H., Vocke, R. D., Hanson, G. N., & Hart, S. R. (1978). A general mixing equation with applications to Icelandic basalts. *Earth and Planetary Science Letters*, *37*, 380-392.

Larsen, E. M. (1970). Zirconium and hafnium chemistry. *Advances in Inorganic Chemistry and Radiochemistry*, *13*(C), 1–133. https://doi.org/10.1016/s0065-2792(08)60335-0

Lodders, K., Palme, H., & Gail, H.-P. (2009). Abundances of the elements in the solar system. In J. E. Trumper (Ed.), *Landolt-Bornstein, new series, astronomy and astrophysics* (pp. 560–598). Springer Verlag.

Nebel, O., van Westrenen, W., Vroon, P. Z., Wille, M., & Raith, M. M. (2010). Deep mantle storage of the Earth's missing niobium in late-stage residual melts from a magma ocean. *Geochimica et Cosmochimica Acta*, *74*, 4392–4404. https://doi.org/10.1016/j.gca.2010.04.061

Niu, Y. (2012). Earth processes cause Zr-Hf and Nb-Ta fractionations, but why and how? *RSC Advances*, *2*, 3587–3591. https://doi.org/10.1039/c2ra00384h

Nuccio, P. M., & Paonita, A. (2001). Magmatic degassing of multicomponent vapors and assessment of magma depth: Application to Vulcano island (Italy). *Earth and Planetary Science Letters*, *193*, 467–481. https://doi.org/10.1016/s0012-821x(01)00512-x

Nuccio, P. M., Paonita, A., & Sortino, F. (1999). Geochemical modelling of mixing between magmatic and hydrothermal gases: The case of Vulcano Island, Italy. *Earth and Planetary Science Letters*, *167*, 321–333. https://doi.org/10.1016/s0012-821x(99)00037-0

Oppenheimer, C., Fischer, T. P., & Scaillet, B. (2014). Volcanic degassing: Process and impact. In H. H. Holland, & K. K. Turekian (Eds.), *Treatise on geochemistry* (Vol. 4, pp. 111–179). https://doi.org/10.1016/b978-0-08-095975-7.00304-1

Paonita, A., Caracausi, A., Iacono-Marziano, G., Martelli, M., & Rizzo, A. (2012). Geochemical evidence for mixing between fluids exsolved at different depths in the magmatic system of Mt Etna (Italy). *Geochimica et Cosmochimica Acta*, *84*, 380–394. https://doi.org/10.1016/j.gca.2012.01.028

Paonita, A., Caracausi, A., Martelli, M., & Rizzo, A. L. (2016). Temporal variations of helium isotopes in volcanic gases quantify pre-eruptive refill and pressurization in magma reservoirs: The Mount Etna case. *Geology*, *44*, 499–502. https://doi.org/10.1130/g37807.1

Pastor, R. C. (1999). Crystal growth of metal fluorides for CO_2 laser operation I. The necessity of the RAP approach. *Journal of Crystal Growth*, *200*, 510–514. https://doi.org/10.1016/s0022-0248(98)01260-3

Patzer, A., Pack, A., & Gerdes, A. (2010). Zirconium and hafnium in meteorites. *Meteoritics & Planetary Science*, *45*, 1136–1151. https://doi.org/10.1111/j.1945-5100.2010.01076.x

Pearson, R. G. (2005). *Chemical hardness* (p. 198). Wiley-VCH.

Pershina, V., Trubert, D., Le Naour, C., & Kratz, J. V. (2002). Theoretical predictions of hydrolysis and complex formation of group-4 elements Zr, Hf and Rf in HF and HCl solutions. *Radiochimica Acta*, *90*, 869–877. https://doi.org/10.1524/ract.2002.90.12_2002.869

Pfänder, J. A., Münker, C., Stracke, A., & Mezger, K. (2007). Nb/Ta and Zr/Hf in ocean island basalts—Implications for crust–mantle differentiation and the fate of niobium. *Earth and Planetary Science Letters*, *254*, 158–172.

Postma, C. J., Lubbe, S. J., & Crouse, P. L. (2017). Selective sublimation/desublimation separation of ZrF_4/HfF_4. *Journal of the Southern African Institute of Mining and Metallurgy*, *117*, 939–946. https://doi.org/10.17159/2411-9717/2017/v117n10a3

Postma, C. J., Niemand, H. F., & Crouse, P. L. (2015). A theoretical approach to the sublimation separation of zirconium and hafnium in the tetrafluoride form. *Journal of the Southern African Institute of Mining and Metallurgy*, *115*, 961–965.

Raso, M., Censi, P., & Saiano, F. (2013). Simultaneous determinations of zirconium, hafnium, yttrium and lanthanides in seawater according to a co-precipitation technique onto iron-hydroxide. *Talanta*, *116*, 1085–1090. https://doi.org/10.1016/j.talanta.2013.08.019

Sasmaz, A., Zuddas, P., Cangemi, M., Piazzese, D., Ozek, G., Venturi, M., & Censi, P. (2021). Zirconium and hafnium fractionation and distribution of Rare Earth Elements in neutral–alkaline waters: Case study of Lake Van hydrothermal system, Turkey. *Journal of Geochemical Exploration*, *226*, 106784. https://doi.org/10.1016/j.gexplo.2021.106784

Schlitzer, R. (2015). *Ocean data view*. Retrieved from http://odv.awi.de

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, *32*, 751–767. https://doi.org/10.1107/s0567739476001551

Shikina, N. D., Tagirov, B. R., Bychkova, Y. V., & Volchenkova, V. A. (2018). Hydrolysis and complex formation of Zr and Hf in aqueous solutions of $HClO_4$, HCl, and NaOH in equilibrium with baddeleyite (Zr and Hf)O_2(cr) at 250°C. *Russian Journal of Physical Chemistry*, *92*, 2159–2164. https://doi.org/10.1134/s0036024418110377

Shikina, N. D., Tagirov, B. R., Volchenkova, V. A., & Bychkova, Y. V. (2015). Zr/Hf ratio in supercritical chloride fluids: Experimental study of zirconium and hafnium complexation at 450°C and 0.6–1 kbar. *Petrology*, *23*, 93–101. https://doi.org/10.1134/s086959111501004x

Sortino, F., Nonell, A., Toutain, J. P., Munoz, M., Valladon, M., & Volpicelli, G. (2006). A new method for sampling fumarolic gases: Analysis of major, minor and metallic trace elements with ammonia solutions. *Journal of Volcanology and Geothermal Research*, *158*, 244–256. https://doi.org/10.1016/j.jvolgeores.2006.05.005

Taran, Y. A., Hedenquist, J. W., Korzhinsky, M. A., Tkachenko, S. I., & Shmulovich, K. I. (1995). Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. *Geochimica et Cosmochimica Acta*, *59*, 1749–1761. https://doi.org/10.1016/0016-7037(95)00079-f

Taran, Y. A., Pilipenko, V. P., RozhkovVakin, A. M. E. A., & Vakin, E. A. (1992). A geochemical model for fumaroles of the Mutnovsky volcano, Kamchatka, USSR. *Journal of Volcanology and Geothermal Research*, *49*, 269–283. https://doi.org/10.1016/0377-0273(92)90018-9

Taran, Y. A., Zelenski, M., Chaplygin, I., Malik, N., Campion, R., Inguaggiato, S., et al. (2018). Gas emission from volcanoes of the Kuril island arc (NW Pacific): Geochemistry and fluxes. *Geochemistry, Geophysics, Geosystems*, *19*, 1859–1880. https://doi.org/10.1029/2018GC007477

Tiepolo, M., Zanetti, A., Oberti, R., Brumm, R., Foley, S., & Vannucci, R. (2003). Trace-element partitioning between synthetic potassic-richterites and silicate melts, and contrasts with the partitioning behaviour of pargasites and kaersutites. *European Journal of Mineralogy*, *15*, 329–340. https://doi.org/10.1127/0935-1221/2003/0015-0329

van Hinsberg, V., Vigouroux, N., Palmer, S., Berlo, K., Maur, G., Williams-Jones, A., et al. (2015). Element flux to the environment of the passively degassing crater lake-hosting Kawah Ijen volcano, Indonesia, and implications for estimates of the global volcanic flux. In T. Ohba, B. Capaccioni, & C. Caudron (Eds.), *Geochemistry and geophysics of active volcanic lakes* (Vol. 437, pp. 437–534). Geological Society, London, Special Publications. https://doi.org/10.1144/SP437.2

Xiao, Y., van Sandwijk, A., Yang, Y., & Langing, V. (2014). New routes for the production of reactor grade zirconium. In M. Guane-Escard, & G. M. Haarberg (Eds.), *Molten salts chemistry and technology*. John Wiley & Sons, Ltd.

Xu, L., Xiao, Y., van Sandwijk, A., Zhao, Z., Li, J., Xu, Q., & Yang, Y. (2016). Zirconium and hafnium separation with molten salt extraction in Sn–Cu–Zr–Hf and Cu–Zr–Hf alloy systems. *Separation Science and Technology*, *51*, 1664–1674. https://doi.org/10.1080/01496395.2016.1170852

Yaxley, G. M., Green, D. H., & Kamenetsky, V. (1998). Carbonatite metasomatism in the Southeastern Australian lithosphere. *Journal of Petrology*, *39*, 1917–1930. https://doi.org/10.1093/petroj/39.11-12.1917

Zelenski, M., & Bortnikova, S. (2005). Sublimate speciation at Mutnovsky volcano, Kamchatka. *European Journal of Mineralogy*, *17*, 107–118. https://doi.org/10.1127/0935-1221/2005/0017-107

Zelenski, M., Malik, N., & Taran, Y. (2014). Emissions of trace elements during the 2012-2013 effusive eruption of Tolbachik volcano, Kamchatka: Enrichment factors, partition coefficients and aerosol contribution. *Journal of Volcanology and Geothermal Research*, *285*, 136–149. https://doi.org/10.1016/j.jvolgeores.2014.08.007

Zelenski, M., Simakin, A., Taran, Y., Kamenetsky, V. S., & Malik, N. (2021). Partitioning of elements between high-temperature, low-density aqueous fluid and silicate melt as derived from volcanic gas geochemistry. *Geochimica et Cosmochimica Acta*, *295*, 112–134. https://doi.org/10.1016/j.gca.2020.12.011

Zelenski, M. E., Fischer, T. P., de Moor, M. J., Marty, B., Zimmermann, L., Ayalew, D., et al. (2013). Trace elements in the gas emissions from the Erta Ale volcano, Afar, Ethiopia. *Chemical Geology*, *357*, 95–116. https://doi.org/10.1016/j.chemgeo.2013.08.022

Zuddas, P., Censi, P., Inguaggiato, C., & Sposito, F. (2018). The behaviour of zirconium and hafnium during water-rock interaction. *Applied Geochemistry*, *94*, 46–52. https://doi.org/10.1016/j.apgeochem.2018.05.006