



Evidence for Zn isotopic fractionation at Merapi volcano

Jean-Paul Toutain^{a,*}, Jeroen Sonke^a, Marguerite Munoz^a, Anthony Nonell^{a,b}, Mireille Polvé^a, Jérôme Viers^a, Rémy Freydisier^a, Francesco Sortino^c, Jean-Louis Joron^d, Sri Sumarti^e

^a Observatoire Midi-Pyrénées, Laboratoire des Mécanismes et Transferts en Géologie, CNRS/IRD/Université Paul Sabatier Toulouse 3, 14 av. Edouard Belin, 31400 Toulouse, France

^b Laboratoire d'analyses nucléaires isotopiques et élémentaires, DEN/DPC/SECR/LANIE, Commissariat à l'Energie Atomique/Saclay, 91191 Gif-sur-Yvette cedex, France

^c Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, V. Ugo la Malfa, 153, 90146 Palermo, Italy

^d Laboratoire Pierre Sue, Commissariat à l'Energie Atomique/Saclay, 91191 Gif-sur-Yvette cedex, France

^e DVGHM, Jalan Cendana, 15, Yogyakarta, Indonesia

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ABSTRACT

Fumarolic gases, rocks and condensate samples from Merapi volcano (Indonesia) have been analyzed by multiple collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) for their Zn isotopic compositions. The variation observed, expressed as $\delta^{66}\text{Zn}$ ($\delta^{66}\text{Zn} = [({}^{66}\text{Zn}/{}^{64}\text{Zn})_{\text{sample}}/({}^{66}\text{Zn}/{}^{64}\text{Zn})_{\text{MC 3-049L}} - 1] \cdot 10^3$), ranges from +0.05‰ to +1.68‰. The overall reproducibility was found to be better than 0.10‰ (2SD). The $\delta^{66}\text{Zn}$ of andesitic rock samples are homogeneous with a mean value of +0.24‰, which is comparable to previously reported basalt data. $\delta^{66}\text{Zn}$ in the Woro fumarolic field are ranging from +0.05‰ to +0.85‰ and +1.48‰ to +1.68‰ in fumarolic gases and condensates respectively. Upon cooling from 590 to 297 °C, gaseous Zn concentrations decrease and become increasingly enriched in the lighter Zn isotopes, while the condensates become increasingly enriched in the heavier isotopes. Gas and condensate isotopic compositions can be explained with a Rayleigh condensation model with temperature dependent isotope fractionation factor, $\alpha_{(\text{solid/vapor})}$. Over the 574 °C to 297 °C range of observations, $1000 \ln(\alpha_{\text{solid/vapor}}) = C_1 + C_2/T + C_3/T^2$ (with $C_1 = 0$, $C_2 = -0.88 \times 10^3$, $C_3 = 1.00 \times 10^6$ and T in degrees Kelvin), which corresponds to $\alpha_{(\text{solid/vapor})}$ of 1.00033 to 1.00153 respectively at the indicated temperatures.

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1. Introduction

Our understanding of the geological, environmental and cosmochemical cycling of transition and other non-traditional elements has evolved significantly through stable isotope studies using multiple-collector inductively coupled plasma-mass spectrometers (MC-ICP-MS) (Johnson et al., 2004). Among the responsible fractionation processes, partial evaporation and/or condensation reactions have been shown to generate large mass-dependent isotopic fractionation for Mg (Young et al., 2002), Cd (Wombacher et al., 2003, 2004) and even Hg (Brönsted and von Hevesy, 1920; Estrade et al., 2007). Such observations underscore the potential role of volcanic degassing on isotopic fractionation and its traceability in the global cycling of elements. For example Rehkämper (Rehkämper et al., 2007) suggest that the TI isotopic signature of the oceans is strongly affected by post-degassing volcanic inputs.

Actively degassing volcanoes therefore should be relevant sites to test and quantify the existence of isotopic fractionation of volatile

metals in magmatic environment. Few passively degassing volcanoes allow access to both high temperature, weakly evolved magmatic gases and their secondary phases (low temperature gases, aerosols, solid deposits) that are produced by the fractional condensation of the gases upon cooling (Bernard, 1985; Quisefit et al., 1989; Toutain et al., 1990). Merapi is one of the main passively degassing volcanoes on Earth and allows nearly continuous and easy access to high temperature gases.

The aim of this study was to explore evaporation/condensation-induced Zn isotopic variations upon large temperature gradients in high temperature magmatic environments. We have investigated andesitic rocks, fumarolic gases and condensate deposits as a function of temperature. Zn was chosen because of its significant concentrations in magmas and its volatile character that generally result in Zn enrichment of fumarolic gases, aerosols, condensates and incrustations at many active volcanoes (Symonds et al., 1987; Taran et al., 1995; Toutain et al., 2003). Zinc has five stable isotopes with masses 64, 66, 67, 68 and 70 and average abundances 48.63%, 27.90%, 4.10%, 18.75% and 0.62%, respectively (Rosman and Taylor, 1998). Zinc is weakly redox sensitive due to its dominant oxidation state (+2), which helps to restrict the possible causes of isotopic variations (Albarede, 2004). Reliable chemical separation and instrumental procedures have been

* Corresponding author.

E-mail address: toutain@lmtg.obs-mip.fr (J.-P. Toutain).

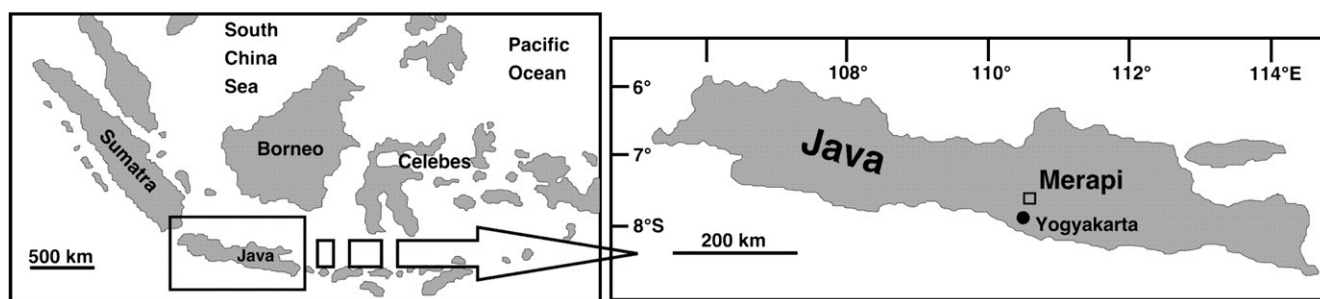


Fig. 1. Geographic location of Merapi volcano (Indonesia).

developed for Zn isotopic analysis (Maréchal et al., 1999). Limited equilibrium isotopic fractionation (0.5‰ per amu) has been observed during low temperature aquatic adsorption processes (Pokrovsky et al., 2005; Gelibert et al., 2006). Larger fractionation up to 0.8‰ per amu has been observed upon intermediate (<400 °C) temperature hydrothermal deposition (Mason et al., 2005; Wilkinson et al., 2005; John et al., 2008) and biological uptake and recycling (Weiss et al., 2005; Viers et al., 2007; Weiss et al., 2007). No theoretical studies have been undertaken so far, yet limited high temperature studies on lunar soils and basalts (Moynier et al., 2006), and on industrial refining (Sivry et al., submitted for publication; Sonke et al., in press) point at the importance of kinetic isotope fractionation during evaporation/condensation processes. The most recent review of Zn isotopic data is by (Cloquet et al., 2008).

2. Magmatic gases and condensates at merapi

Merapi (2965 m a.s.l) is an andesitic stratovolcano located in central Java (Fig. 1). High temperature gases (up to 900 °C) are continuously emitted from the two main fumarolic fields: Gendol, and Woro (Le Guern and Bernard, 1982; Symonds et al., 1987). Historical eruptions, hazard evaluation and volcanic processes are reviewed in (Voight et al., 2000a). Recent eruptive activity is characterized by successive formation and collapse of an andesitic dome (Ratdomopurbo and Poupinet, 2000; Voight et al., 2000b) generating lava and pyroclastic flows. Early data on high temperature gases and condensate phases are available (Le Guern and Bernard, 1982; Bernard, 1985; Symonds et al., 1987; Symonds, 1993). The gas phase is mainly composed of H₂O and CO₂ with minor amounts of H₂S, SO₂, HCl, HF, trace gases and metal species originated mainly from shallow magma degassing at 915 °C (Symonds et al., 1987). Thermodynamic calculations indicate that metals (including Zn) are mainly transported as chloride species in the gas phase. Silica tube condensates, which are more representative of naturally condensing species in the ground than incrustations sampled at the vents were also collected at Merapi (Le Guern and Bernard, 1982; Bernard, 1985; Symonds et al., 1987; Symonds, 1993). A summary of the mineral phases identified is presented in Table 1. In these solid deposits, Zn was detected as an enriched minor element in hercinitite, K–Ca sulfate, acmite, aphtitalite and Na–K–Fe sulfate. A specific Zn compound (ZnS_(S)) was identified at temperature around 300–600 °C, which is in accord with thermodynamic modeling (Symonds et al., 1987). A Zn sulphate mineral (Zn₃(SO₄)(Cl,OH)₄) was also identified at lower T°C in the 1984 silica tube, probably as the result of more oxidizing conditions due to atmospheric contamination.

3. Sample collection

3.1. Gas samples

Eight fumarolic gases were collected at Woro fumarolic field in 2001–2002. The gases were channeled through a silica tube to a

condenser constituted of an acetone-cooler and a glass reception flask (Chevrier and Le Guern, 1982). In order to insure a continuous flow of gas, a weak and constant depression was applied with a hand-pump allowing the fast condensation of water, acid gases and associated trace elements. Three fumaroles were also sampled during the same periods by using NH₄OH bottles. These are 600 ml quartz flasks, pre-washed with double distilled HNO₃ and 4 N ultra-pure NH₄OH, partially filled with 100 cc of Merck ultra-pure NH₄OH and then put under vacuum. This new sampling technique derived from Giggensbach (1975) allows the complete collection of gas into a closed system (Sortino et al., 2006). Gas condensates and NH₄OH samples were stored in double distilled HNO₃ pre-washed PP bottles before laboratory treatment.

Table 1

Summary of sublimates phases collected in silica tubes at Merapi volcano in 1978–1980 (Bernard, 1985; Le Guern and Bernard, 1982) and in 1984 (Symonds, 1993; Symonds et al., 1987)

Sampling date	Mineral phase	Composition	Enriched minor elements	Temperature (°C)
1978–1980 Silica tubes				
	Magnetic	Fe ₃ O ₄		900–600
	Hercynite	FeAl ₂ O ₄	Mn,Zn	900–600
	Cristoballite	SiO ₂		900–600
	Acmit	NaFeSi ₂ O ₆		650–600
	Molybdenite	MoS ₂	Re	650–550
	Wolframite	(Fe,Mn)WO ₄		630–600
	Halite	NaCl		630–330
	Sylvite	KCl		630–300
	Pyrite	FeS ₂		550–300
	Sphalerite	ZnS	Cd,Fe	550–300
	Galena	Pbs	Bi,Sn	450–150
	Pb–Bi–sulfide	PbBi ₂ S ₂ (?)	Sn	450–150
	Pb–NH ₄ chloride	NH ₄ Pb ₂ Cl ₅	Br,Tl	300–150
	Salamoniac	NH ₄ Cl	Br	250–150
	Sulfur	S	As, I, Te, Se	150–100
1984 Silica tubes				
	Cristoballite	SiO ₂		Around 800°C
	Magnetite	Fe ₃ O ₄	Al,Ti	
	K–Ca Sulfate	K–Ca(SO ₄) ₂	Cu, Zn,Cl	
	Acmite	NaFeSi ₂ O ₆	Cl,K,Cu,Zn,Pb	
	Halite	NaCl		
	Sylvite	KCl		
	Pyrite	FeS ₂		
	Wollastonite	CaSiO ₃	Cl,Al	
	Sphalerite	Zn	Cd,Fe	
	Aphtitalite	(Na,K) ₃ Na ₂ (SO ₄) ₂	Cu,Zn,Cl	
	Galena	PbS	Sn	
	Cs–K Sulfate	?		
	Pb–K chloride	PbKCl ₃		
	Na–K–Fe Sulfate	(Na,K) ₂ Fe(SO ₄)(Cl) ₂	Cu,Zn	
	Zn Sulfate	Zn ₃ (SO ₄)(Cl,OH) ₄		
	K–Pb Sulfate	K ₂ Pb(SO ₄) ₂		
	K–Zn Sulfate	K ₂ Zn(SO ₄)(Cl) ₃		Around 450°C

Mineral phases are listed in the order observed in the silica tubes (from highest to lowest temperature).

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