Io: The role of sulfide droplet nucleation in Pele-type volcanism. Steven M. Battaglia¹, ¹Department of Geology and Environmental Geosciences, Northern Illinois University, Davis Hall 312, Normal Rd., DeKalb, IL, 60115 (email: battagls1@gmail.com).

Introduction: Io has high-temperature volcanism occurring over its entire surface as a result of asthenospheric melting that is driven by a tidal resonance between Jupiter's satellites Europa, Ganymede, and Io. Volcanically derived sulfurous compounds resurface the satellite at a high rate [1] suggesting a vertical cycling of Io's lithosphere [2-3] whereby interior melting produces volcanic activity at the surface while burial from volcanism recycles the crust and sulfurous compounds to the satellite's interior. A suggested source for the excess sulfur (i.e. sulfur concentrations above the solubility of sulfur) on Io's surface is an insoluble sulfide phase derived from the assimilated crustal sulfurous compounds [4]. The sulfide phase that segregates from Io's reducing magmas is expected to degas vaporous sulfur to Io's surface (and contribute to the resurfacing of the satellite) before gravitationally settling to the bottom of the magma reservoir. Here, the nucleation of sulfide droplets is modeled for the silicate melts in Pele's magma supply.

Pele Hotspot: Pele is a vigorously volcanically active patera (i.e. hotspot) that has been evident from observations of the volcano during spacecraft imaging [5-6]. Temperature estimates of Pele's caldera surface from spectral analysis are persistently above 1300 K [7-8]. Evidence of continuous volcanic activity and high surface magma temperatures at Pele's patera suggest a steady supply of fresh, gas-rich, magma towards the surface to supply Pele's lava lake. Although ultramafic magmas cannot be ruled out for ionian melts [9], a high-temperature basaltic composition that replenishes Pele's lava lake is assumed here.

Sulfide Droplet Formation: In terrestrial volcanism, sulfide liquids segregate from reducing magmatic silicate melts from the oversaturation of sulfur concentration within the silicate liquid [10]. The nucleated sulfide droplets have a higher density than the silicate melt and vertically sink in the reservoir before accumulating at the bottom of the magma body, where disseminated sulfide ore deposits could be observed [11].

On Io, and likely similar to the Earth, much of the sulfur in the primordial mantle was likely extracted from an early magma ocean along with siderophile elements during core formation [12]. Sulfur dissolved in ionian magmas is probably a result of the combination of magmatic sulfur inherited from silicate melts of

the now-depleted silicate mantle and the assimilation of sulfur from the ionian crust [3-4].

Since natural basaltic glasses are assumed to nucleate sulfide droplets upon magma ascent [13] and Pele's magma supply in Io's reducing lithosphere has a limit to dissolved sulfur concentrations comparable to terrestrial MORBs [4], it is assumed here that silicate melts in Pele's patera do nucleate sulfide droplets during cooling and substantial fractionation in Io's crust.

Model: It is currently not possible to determine sulfide nucleation as a function of temperature and sulfur concentration in a silicate melt [14]. Since sulfide globules are known to exist in MORBs, a method for estimating sulfide nucleation is to assume that droplets form at a fixed degree of supersaturation (i.e. oversaturation of sulfur in the silicate melt) [15].

The nucleation of a sulfide droplet in Pele's magma supply is dependent on three factors: (i) the sulfur solubility, (ii) degree of sulfur supersaturation, and (iii) number density of sulfide nuclei upon saturation. The sulfide concentration (C_{sat}) dependent on the sulfur solubility (S) in the silicate melt can be expressed as [14]:

$$C_{\text{sat}} = S \exp\left[2\sigma V_{\text{sul}} / (aRT)\right], \tag{1}$$

where σ is the interface tension between the sulfide and silicate melt, V_{sul} is the molar volume of sulfide melt, *R* is the universal gas constant, *T* is the silicate melt temperature, and *a* is the sulfide droplet radius upon reaching saturation and is expressed as [15]:

$$a = 2\sigma V_{\rm sul} / [RT \ln(1+x)], \qquad (2)$$

where *x* is the degree of supersaturation of sulfur in the silicate melt.

Model calculations were carried out for *a* at nucleation in Pele's magmas that is dependent on *x* (Fig. 1) using Eq. 2, and C_{sat} in Pele's magmas that is dependent on *S* and the estimated *a* (Fig. 2) using Eq. 1. The solubility of sulfur *S* for Pele's magmas has been previously modeled [4] and is used here for a uniform basaltic magma composition and constant density (2800 kg m⁻³). The variables σ (0.5 N m⁻¹), V_{sul} (21.7 × 10⁻⁶ m³ mol⁻¹), and sulfide number density (10⁷) are assumed constant in the model calculations and are expected to not appreciably effect the results. **Discussion:** At a constant T in the silicate melt, a decreases with increasing x. This implies that for a small x, the necessary T for nucleation is higher. For large x, magmas may nucleate at a lower T to reach an equilibrium state between the silicate melt and sulfide droplets. Oversaturation of sulfur indicates that at a high x sulfide droplets undergo rapid growth and at a small x sulfide droplets undergo steady growth.

The gravitational settling velocity (i.e. vertical descent) and settling distance (i.e. depth descent following nucleation) varies depending on x in the silicate melt [15]. For small x, a is large at nucleation from steady growth and both settling velocity and distance is large, whereas for large x, a is small at nucleation from rapid growth and both settling velocity and distance are small. This is consistent with Stokes' Law.

At a constant pressure in Io's crust, S is difficult to achieve with an increase in x. For decreasing pressure, x decreases and proves more difficult for a silicate melt to reach saturation. It is easier to nucleate sulfide deposits upon saturation at greater depths than near surface depths in Io's lithosphere.

It is inferred that there must be continuous magma supply and convection to the near-surface regions of Io's surface including Pele's magma supply. Pele's continuous supply of magma suggests vertical displacement of negatively buoyant material that replaces degassed melt with fresh, gas-rich melt. Nucleated sulfide droplets are more dense than the silicate melt and are likely replaced by ascending melts. Since gravitational settling velocity and distance are likely to increase as droplets undergo growth at greater depths in Io's crust, Pele's magmas must be supplied from a large, stable magma source for steady sulfide droplet growth and high gravitational settling to displace old magma from near surface reservoirs. This is consistent with implications that were made from Galileo and Cassini imaging observations a decade ago [5].

Pele-type plumes (other than Pele) have been detected on Io [6-9]. Plume observations have not been as consistent as the continuous replenishment of lava to Pele's patera. From the work here, it is inferred that short-lived Pele-type plumes are characterized by high magma ascent in Io's lithosphere that rapidly nucleate sulfide droplets and withstand low gravitational settling dynamics. The non-consistent high-temperature eruptions may be a result from an unstable or small magma source underlying the patera that cannot replenish fresh gas-rich magma at similar durations as Pele's magma supply. Pele's patera is therefore speculated to have the largest and most robust magma source on Io to continuously feed the active lava lake and plume observed at the surface.



Fig. 1: Supersaturation effects on the critical radius of nucleated sulfide droplets for T=1200 K (green line), 1400 K (blue line), and 1600 K (magenta line).



Fig. 2: Pressure and supersaturation effects on sulfur solubility limits under sulfide-saturated conditions for Pele's magma (T=1440K) in Io's upper crust (10 km) calculated for degrees of supersaturation x = 0.00 (blue line), 0.05 (yellow line), and 0.10 (red line).

References: [1] Shahnas et al. (2013), *Icarus, 225*, 15-27. [2] Carr et al. (1998), *Icarus, 135*, 146-165. [3] Leone et al. (2011), *Icarus, 211*, 623-635. [4] Battaglia et al. (2014), *Icarus, 235*, 123-129. [5] Radebaugh et al. (2004), *Icarus, 169*, 65-79. [6] Spencer et al. (2007), *Science, 318*, 240-243. [7] Howell and Lopes (2011), *Icarus, 213*, 593-607. [8] Rathbun et al. (2014), *Icarus, 231*, 261-272. [9] Veeder et al. (2015), *Icarus, 245*, 379-410. [10] Ripley and Li (2013), *Econ. Geol., 108*, 45-58. [11] Simon and Ripley (2011), *Rev. Min. Geochem., 73*, 513-578. [12] Rubie et al. (2011), *Earth & Planet. Sci. Lett., 301*, 31-42. [13] Patten et al. (2013), *Chem. Geol., 358*, 170-188. [14] Zhang (2008), Geochemical Kinetics, *Princeton Univ. Press.* [15] Zhang (2015), *Chem. Geol., 391*, 56-73.