INVESTIGATING LAVA BALLOON FORMATION: NEW EXPLORATION OF THE 1993 SUBMARINE VENT SITE AT SOCORRO ISLAND, MEXICO

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ABSTRACT

The third of five known lava balloon eruptions occurred January 1993 to March 1994 west of Socorro Island, Mexico. Large highly-vesicular basaltic scoria rose to the sea surface in pulses. Buoyant samples were collected and studied, but the submarine vent was never precisely located. New multibeam mapping and remotely operated vehicle exploration in 2017 by E/V Nautilus located and sampled the 1993 vent site, a volcaniclastic cone at 250 m depth with pillow lava and large scoria blocks. An active, low-temperature hydrothermal system (0.2°C above ambient) with white filamentous bacteria and yellow microbial mats occurs over the roughly 4000 m² vent area. SEM imagery of fine-grained volcaniclastic sediment shows a dominance of vesicular clasts and bubble wall shards with some Limu o Pele and Pele’s hair. Some pillow tubes exhibit large interior gas cavities and expansion into vertical hornito-like structures. Observed volcanic facies at the vent site indicate that both effusive (pillow lava) and explosive (scoria, volcanic ash) activity occurred simultaneously during the 1993 submarine eruption. The generation of giant buoyant scoria was likely caused by episodic formation of a scoriaceous plug at the vent site that would fail periodically resulting in pulses of scoria being discharged. A subset of the erupted scoria was buoyant enough to reach the sea surface, the rest accumulated close to the vent. The great abundance of fine grained volcaniclastic material suggests simultaneous explosive activity likely driven mainly by primary volatile degassing. The petrogenesis and volatile degassing of magma erupted as buoyant basaltic scoria from this eruption were investigated by electron microprobe for major elements, LA-ICP-MS for trace elements, and FTIR for volatiles.
Similar to the alkaline basalts from nearby Socorro and San Benedicto Islands, recently collected seafloor samples from the 1993 Socorro submarine eruption contain 48.5-48.7 wt.% SiO$_2$ and 5.1-5.5 wt.% Na$_2$O+K$_2$O. Seafloor Socorro samples are trachybasalts, matching the buoyant clasts (collected in the first 6 months of the eruption). Buoyant scoria from early in the eruption are more evolved (e.g., lower MgO) than late stage scoria collected from the seafloor. Mineral-melt evolution models indicate that fractional crystallization of a common parent magma explains shifts in major and trace elements from evolved early stage (buoyant) samples to the more primitive late stage (seafloor) clasts. Trace element patterns of the most primitive basalts have features in common with Petit spots (e.g. positive Sr and Zr anomalies [Hirano et al., 2006]), suggestive of commonalities between these different intra-plate magmatic systems. Olivine-hosted melt inclusions reveal extreme CO$_2$-oversaturation in the melt with highs of 3929 ppm CO$_2$ and 0.73 wt.% H$_2$O. Volatile modeling of seafloor samples provides tentative evidence that the magma sourcing the 1993 eruption shifted from an open system degassing regime to a closed system once the magma entered a staging zone at a pressure of about 3 kbar (9-10 km). The 1993 Socorro eruptive material was sourced from a fairly homogenous parental melt with a possible shift in magma staging depths from 5 km to 9 km throughout this year-long submarine eruption.
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PREFACE

The following thesis was written in manuscript format outlined by the American Geophysical Union (AGU) and the Geochemical Society for their electronic journal *Geochemistry, Geophysics, Geosystems* (G-Cubed). This manuscript has not been published, but we have plans to submit it to G-Cubed in the coming year. Preliminary interpretations from this study were presented as a poster (V51F-0160) at the 2018 AGU Fall Meeting in the *What Can Pyroclasts Tell Us?* session (Volcanology, Geochemistry and Petrology section).
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MANUSCRIPT

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INVESTIGATING LAVA BALLOON FORMATION: NEW EXPLORATION OF THE 1993 SUBMARINE VENT SITE AT SOCORRO ISLAND, MEXICO

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1. Introduction

Submarine eruptions are rarely observed, and those that have been documented tend to be in deep water (>500m) [e.g. Chadwick et al., 2008; Fox et al., 2001; Haymon et al., 1993; or see Rubin et al., 2012]. Despite its role in ocean island formation and potential hazards to nearby coastal communities and marine life, shallow submarine volcanism (<400 m depth) remains poorly understood from the perspective of eruptive behaviors and mechanisms.

Remotely operated vehicle (ROV) or other robotic submersible exploration [e.g. Nomikou et al., 2012; Embley et al., 2006; Chadwick et al., 1997; Haymon et al., 1993; Perfit et al., 198] provides in situ imagery of submarine vent sites, allowing for detailed investigation of facies types, their distribution, and general morphology of the vent for precisely targeted sampling efforts. Other principal methods for interpreting both shallow and deep submarine volcanic events include dredging [e.g. Davis et al., 1995; Colantoni et al., 1981; Fornari et al., 1979; Moore and Fiske, 1969; Palmer, 1964] and field observations of uplifted sequences [e.g. Goto and Tsuchiya, 2004; Busby-Spera, 1984; de Rosen-Spence et al., 1980; Cas, 1978; Dimroth et al., 1978]. Examination of a vent site following a submarine eruption provides an opportunity to investigate volcanic products and processes, but commonly lacks critical information about the temporal evolution of eruptive sequences.

The formation of lava balloons (i.e. large, basaltic, highly vesicular floating scoria) from shallow (<400 m) submarine volcanoes is an unusual and rarely observed style of explosive volcanism (Figure 1a). The 1993 Socorro submarine eruption in Mexico [Siebe
et al., 1995] is one of only five known lava balloon-forming events, all of which occurred in shallow water settings. The four other known locations are: El Hierro, Canary Islands, Spain, 2011-2012 [Somoza et al., 2017; Carracedo et al., 2012; Troll et al., 2012], Serreta Ridge, Terceira Island, Azores, 1998-2001 [Madureira et al., 2017; Kueppers et al., 2012; Gaspar et al., 2003], Foerstner volcano, Pantelleria Island, Italy, 1891 [Conte et al., 2014; Kelly et al., 2014; Washington, 1909; Butler, 1892], and Hawai‘i, USA, 1877 [Moore et al., 1985]. While these five eruptions share fundamental similarities, each event is distinct in several ways. Strombolian style activity [Kelley et al., 2014], fragmentation in an energetic pyroclastic plume [Somoza et al., 2017], fire fountaining [Siebe et al., 1995], and the rise of gas bubbles in lava lakes [Kueppers et al., 2012] represent the diverse spectrum of processes that have thus far been proposed for this unique eruption type.

Three out of the five lava balloon vent sites have been precisely located, explored, mapped, and documented [e.g. Somoza et al., 2017; Kelly et al., 2014; Kueppers et al., 2012]. These lava balloon eruptions are excellent examples of shallow submarine volcanism that provide useful eruption timelines based on the appearance of floating scoria on the sea surface.

During the Socorro eruption (January 1993 - March 1994), samples were retrieved from the sea surface, but little was known about the vent characteristics or its precise location. Recent ROV exploration of the 1993 submarine eruption site west of Socorro Island, Mexico, during cruise NA092 on the E/V Nautilus provides new information and samples from this historic lava balloon-forming event [Carey et al., 2018]. Here, we present new integrated volcanological and geochemical analyses
focused on the morphology of the vent site, distribution of volcanic products, magmatic composition and pre-eruption volatile content of the 1993 Socorro magma. These results and the 1993 sea surface observations [Siebe et al., 1995] inform a model for the volcanic processes that occurred during this submarine eruption, which we assess in the context of proposed mechanisms from similar events. We also consider the origins of the basalt feeding this eruption and outline a tentative path or conduit that the pre-eruptive magma followed.
2. Location, Geologic Setting, and Characteristics of the Socorro 1993 Eruption

The 1993 submarine eruption occurred about 3 km west of Socorro Island, a shield volcano in Mexico’s Revillagigedo Archipelago (Figure 1). This set of four islands—Socorro, Clarion, San Benedicto, and Roca Partida—is located at the north end of the Mathematician Ridge, and west of the East Pacific Rise (Figure 1). The Mathematician Ridge is a failed spreading center that was active about 6.5 to 3.15 Ma B.P. A major plate reorganization in this region resulted in the translation of mid-ocean spreading eastward to the currently active East Pacific Rise [Mammerickx et al., 1982; Sclater et al., 1971]. The Revillagigedo islands are emergent members of several seamounts within the Mathematician Ridge region. Historical eruptions occurred on the eastern islands, but the ages of islands further west are unknown. These centers represent alkaline magmatism associated with a failed mid-ocean ridge spreading center [Bohrson and Reid, 1997, 1995; Batiza and Vanko, 1985]. The Revillagigedo region (Socorro, Clarion, San Benedicto) is noteworthy for hosting the only known peralkaline, silicic volcanic centers in the Pacific basin.

At 120 km² (exposed land surface) Socorro is the largest island rising up from a depth of about 3000 m to a maximum elevation of 1050 m at the summit of Mt. Evermann. A basal radius of 24 km yields a volume of about 2500 km³ for the bulk Socorro edifice (Figure 1c; Siebe et al., 1995). Currently there are active fumaroles on Mt. Evermann.

Acoustic signals associated with the 1993 Socorro submarine eruption were first detected by SOFAR (SOund Fixing And Ranging) hydrophones in the Pacific on January
19, 1993 [McCreery et al., 1993; Siebe et al., 1995]. Small vapor columns and numerous floating, hissing rocks were observed starting on January 29, 1993 (Figure 1a; Siebe et al., 1995). Siebe et al. [1995] collected buoyant scoria and reticulite at the sea surface using nets for the first six months of the eruption from January 31, 1993 to July 1993.

Small implosions from thermal contraction fractured the blocks and caused them to fill with water and sink after about 15 minutes on the sea surface [Siebe et al., 1995]. Two distinct regions (~100 m apart) with intermittent pulses of lava balloons were seen during helicopter observations [Siebe et al., 1995]. From January 1993 to April 1994, floating lava balloons appeared in irregular pulses covering an area of about 6000 m² [Siebe et al., 1995]. Buoyant scoria was not observed near Socorro after April 1994.
3. Mapping and Seafloor Sampling Methods

Bathymetric mapping of the Revillagigedo region was conducted during cruises NA089 and NA092 of the E/V Nautilus using a Kongsberg EM302 multibeam system [Raineault et al., 2018]. ROV explorations in 2017 during cruise NA092 (dive H1662) investigated the region west of Socorro Island where floating scoria were observed in 1993. Dive H1662 explored a series of cones and ridges west of Socorro, in search of lava balloon remnants or other signs of a recent vent site (Figure 2). Dive H1662 lasted for 23 hours on November 10-11, 2017 with a maximum depth of 529 m and an average depth of 289 m.

Dive H1662 conducted ultrahigh-resolution mapping using a BlueView 1350 kHz 90° multibeam echosounder mounted to ROV Hercules at an altitude of about 5-10 m above the seafloor. This survey also collected stereo imagery that formed the foundation of an ultrahigh-resolution 3D model of the vent site (created with COLMAP 3.6, Figure 3). Structure-from-Motion (SfM) photogrammetric imaging techniques, which employ feature detection between all overlapping images to calculate both 3D positions of objects and the pose and trajectories of the cameras, generated the model.

ROV Hercules suction sampler and a grab tool (Kraft Predator Force Feedback Manipulator) collected a variety of samples including tephra, several glassy and weathered lava balloons, and small scoria blocks throughout the H1662 dive region (Table 1). We rinsed, dried, and described the 13 geologic samples from dive H1662 in the E/V Nautilus wet lab.
4. Sample Preparation and Analytical Techniques

4.1 Petrology and Geochemistry

We conducted geochemical analyses of matrix glasses, melt inclusions, and phenocrysts using a variety of micro-analytical techniques. We determined major elements with the Cameca SX-100 electron microprobe at Brown University and trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using the Thermo Electron Corporation X Series II ICP-MS with New Wave Research UP-213 Nd-YAG Laser Ablation System at the University of Rhode Island Graduate School of Oceanography. We determined dissolved volatiles (H₂O, CO₂) in glasses by Fourier transform infrared spectroscopy (FTIR) using the Thermo Nicolet i550 FTIR spectrometer with Continuum microscope at the University of Rhode Island Graduate School of Oceanography. We used X-ray absorption near edge structure spectroscopy (XANES) at Argonne National Laboratory to determine the ratio of ferric to total iron (Fe³⁺/ΣFe).

Appendix A includes detailed methodologies for all analytical techniques, sample preparation, and data corrections.

4.2 Volcanology

During dive H1662, we performed ultrahigh-resolution mapping. We utilized both ultrahigh and high-resolution mapping data to characterize the morphology of the submarine region west of Socorro. Using a custom Matlab image tagging program [Adam Soule, pers. comm.], we analyzed ROV video stills and seafloor imagery from H1662. This analysis generated bathymetric feature and facies density maps. We used the Macropod focal-stacking system (Macroscopic Solutions Focal Stacking System with
a Canon EOS 6D Mark II) at the Rhode Island School of Design Nature Laboratory to capture high-definition images of micro-structures in geological samples. We documented volcaniclastic particle morphologies with scanning electron microscopy (SEM) using the JEOL JSM-5900LV at the University of Rhode Island Kirk Engineering Laboratory. We evaluated large format (3” x 5”) thin sections (prepared by Burnham Petrographic LLC) for petrographic analysis. Appendix A includes detailed methodologies for volcanological analytical techniques.
5. ROV observations

Multibeam mapping of the region west of Socorro Island reveals an elliptical set of ridges and coalesced cones in the region where lava balloon samples appeared on the sea surface in 1993-1994. ROV explorations in 2017 targeted these ridges and cones in a clockwise direction around the ellipse, to identify similar lava balloon morphologies or signs of a recent vent site on the seafloor (Figure 2). Dive H1662 began northwest of the ellipse at a depth of 529 m. In this area, the seafloor consists of a fan of unconsolidated volcanic sand, and the ROV collected a sample of this material (NA092-001) before proceeding to the north ridge.

5.1 North Ridge

The north ridge is a smooth 430 m n-shaped arcuate ridge (Figure 2). ROV Hercules collected samples NA092-002 through -005 along the central peak of the ridge at a depth of about 272 m. Samples from north ridge include highly vesicular, basaltic scoria fragments, varying from glassy to slightly weathered, with large internal gas cavities (Table 1). Although samples from this region appear similar to those expected from a lava balloon eruption, there were no signs of a distinct vent site along this ridge.

5.2 East Cones

The east cones region consists of two prominent volcaniclastic cones and several other smaller cones (Figure 2). The northern prominent cone is south of a small ridge (300 m) that apparently consists of a series of small coalesced cones, while the southern cone is east of another smaller cone. ROV Hercules collected sample NA092-007, highly vesicular scoria, just west of the area between these two primary cones. NA092-007 has
a typical lava balloon morphology, highly vesicular rim with large inner gas cavity, but it is the most weathered sample collected on dive H1662. This region was similar to the north ridge in that there were large and small scoria as well as volcanic sand present but no signs of a recent vent site. We did not explore the less-prominent ridges and cones in the southern half of the ellipse due to dive time limitations.

5.3 West Ridge and 1993 Vent Site

Two linear chains of three coalesced cones, one running roughly NE-SW and the other NW-SE, comprises the arcuate west ridge region, which extends for about 690 m with similar seafloor morphology and volcanic lithologies (Figure 2).

ROV Hercules explored the entire west ridge starting at the southern end. The first peak explored in the west ridge was strikingly different from previously explored peaks and ridges as it hosted a low-temperature hydrothermal system (0.2°C above ambient) colonized with abundant white filamentous bacteria and yellow microbial mats over the roughly 4000 m² summit area (Figure 3). ROV Hercules collected one glassy, highly vesicular scoria sample (NA092-008) in the hydrothermal area. There were more glassy scoria samples (NA092-010) and abundant volcanic sand present along the northern portion of the west ridge, but the hydrothermally active region was distinctly limited to the first peak in the west ridge.

Upon further exploration of the hydrothermal region, we identified a variety of morphologies including highly vesicular glassy scoria, pillow lavas, pillow tubes, and hornitos (Figure 4). Due to its hydrothermal activity, diverse volcanic morphologies, and proximity to the 1993 buoyant sample coordinates, this peak on the southern end of the
west ridge is likely the main Socorro submarine vent site that produced basaltic balloons in 1993-1994.

Siebe et al. [1995] observed two distinct clusters of buoyant scoria on the sea surface in 1993 trending in the ENE direction. We observed glassy pillow rinds, scoria, and some hornitos (although less abundant) along the northern portion of the west ridge, trending NE. It is possible that the secondary cluster of buoyant clasts observed in 1993 was sourced from one of the northern cones in the west ridge region (Figure 2).

The hydrothermally active 1993 vent site consists of a range of volcanic facies abundant with microbial communities. Through sampling and video observations, we defined the principal volcanic facies and determined the extent of the hydrothermally active region at the vent by identifying the microbial mat coverage. The yellow microbial mats are abundant around the periphery of the vent site, with distinct transitions to dark volcanic tephra along the flanks of the cone.

We determined the abundance and distribution of the different volcanic facies by examining imagery from the ultrahigh-resolution survey (Figure 3). A total of 3828 images were captured systematically along the 25 survey lines and analyzed for the presence of large scoria, small scoria, hornitos, pillow lobes, pillow tubes, white bacteria, yellow bacteria, volcanic sand, and ripples (Table 2).

Small and large scoria are present throughout the vent site survey, with the exception of a small region west of the summit with more abundant volcanic sand and ripples (Figure 5). Volcanic sand is ubiquitous throughout the vent survey particularly in the northern and central survey areas (Figure 5). An elongate pillow tube (at least 10 m)
extends along the summit of the cone on the eastern edge of the survey (Figure 5).

Pillow lobes are most abundant in the region around the elongate pillow tubes at the cone summit. A large vertical hornito-like structure amidst several pillow lobes provides evidence of a rootless vent on the southern flank (Figure 4). Overall, angular vesicular scoria and abundant tephra make up the primary volcanic facies of the vent, while pillow lava and hornitos are less common (Figure 5).
6. Morphological and Textural Characteristics of Volcanic Products

Prior to this study, buoyant scoria or lava balloons collected at the sea surface during the eruption were the only samples accessible for geochemical and textural analysis of the 1993 eruptive products. Siebe et al. [1995] observed buoyant scoria fragments on the sea surface for the first 7 months of the eruption. Beginning in July 1993 through at least February 1994, about 25-50% of the visible surface products were isolated floating reticulite, representing the first submarine documentation of basaltic reticulite [Siebe et al., 1995]. The mineralogy of these samples did not vary throughout the first 7 months of the eruption, and they had similar chemical compositions to the dredged trachybasalts from the surrounding region [Moore, 1970].

Seafloor samples collected by ROV from the presumed 1993 vent site in November 2017 include a range of volcanic products: glassy tephra varying in size from ash to lapilli, glassy scoria (lava balloons; although buoyancy during eruption is unknown) and glassy pillow rims (Figure 4). The recently recovered seafloor scoria contain internal zones of reticulite. There may be isolated reticulite blocks on the seafloor, but we were unable to recover many attempted samples due to the extreme fragility of all basaltic material. Samples collected on the seafloor at the vent site in 2017 likely represent end-stage eruptive products (1994 or later) stratigraphically above sunken buoyant lava balloons. Samples collected from the vent site exhibit a range of textures demonstrating a variety of effusive and explosive eruptive styles.
6.1 Vesicular Scoria (Lava Balloons)

Vesicular scoria fragments contain several elongate, large internal gas cavities (>20 cm), numerous small vesicles, and smooth bubble walls. Bubbles in thin sections vary in shape, size, and population density. Sample NA092-012 exhibits the clearest bubble gradients of all scoria. Starting at the quenched, light brown striated glassy crust (Figure 6), a band of elongate coalesced bubbles, mostly elliptical in shape, borders a glassy zone divided by large coalesced hemispherical bubbles (Figure 6). The next zone moving inward towards the core contains circular bubbles of varying sizes with relatively uniform population density (Figure 6). This transitions into reticulitic inner cavities where vesicularity is so high that bubbles coalesce and leave only thin glass selvages in the interstitial spaces between bubbles (Figure 6d). The only zone with notable microlites is this transition from large coalesced bubbles to reticulite.

Sample NA092-016 exhibits similar textures with banding and zonations defined by the presence of hemispherical coalesced vesicles, changes in bubble population density, and significant microlites within the inner transition zone.

6.2 Pillow Lobes and Tubes

Pillow lobes and elongate pillow tubes are primarily at the summit of the vent site and the rootless vent (Figure 4). They have round, smooth glassy rims with abundant vesicles and striations typical of pillow lava extrusion. Unlike the angular scoria, pillow rims appeared to have fairly uniform vesicularity from crust to interior. The quenched rim was poorly preserved in the thin section for pillow sample NA092-010, but exhibits bubbles shaped as rounded ellipses with the long axis parallel to the
crust (Figure 7). Moving inward, the bubbles are more circular in a zone with significant microlites (Figure 7). Bubbles return to elongate ellipses but with their long axis trending perpendicular to the crust (Figure 7). In this interior zone there are some larger elongate coalesced regions, although coalesced vesicles are distinct in shape from the hemispherical coalescence observed in the angular scoria (NA092-012 and NA092-016; Figure 6). In contrast to typical deep-sea pillow lavas, those at the Socorro vent site were extremely friable despite their rigid appearance. Attempts to sample the pillow exteriors with the ROV often resulted in rapid disintegration even with the lowest values of touch feedback on the manipulator arm.

6.3 Hornito Lavas

The hornito (about 0.5-1 m in height and width) on the side flank of the vent region contained several vertical glassy structures. The outer crust of the hornitos is glassy, thick, and far less friable than the nearby scoria and pillows (Figure 8). The interior is filled with rounded lava mounds that appear to have refilled the structure following collapse or detachment of vesiculated lava. Multiple layers of orange oxidized rinds appear to outline and divide the hornito rim. Sampling was not successful.

6.4 Volcanic Ash and Lapilli

ROV Hercules collected glassy volcanic tephra throughout the vent region during dive H1662. Vent site samples NA092-013 and NA092-014 exhibit a variety of textures (Figure 9). The majority of grains consist of highly vesicular glassy shards with well-developed bubble outlines. Less common are fragments of Pele’s hair and primitive reticulite (Figure 10) in the interstitial spaces between long elliptical vesicles, on the
order of 0.2 mm to 0.4 mm in diameter (Figure 9). Pipe vesicles and highly vesicular shards have bubble diameters of 10 µm to 0.2 mm (Figure 9). Thin bubble wall fragments are also present in the shape of Limu o Pele morphologies (Figure 9).
7. Geochemical and Volatile Results

7.1 Major Element Geochemistry

The recently recovered seafloor samples at Socorro are trachybasalts, mostly matching the buoyant samples collected in 1993 (Figure 11). Generally, the Socorro submarine samples are at the mafic end of the trend defined by the regional alkaline lavas (Figure 11; Bohrson and Reid, 1999). The Mg# (molar ratio of Mg/[Mg+Fe]) of matrix glass samples from H1662 ranges from 0.46 (NA092-004) to 0.52 (NA092-010). Matrix glass major elements from dive H1662 are included in Table 3.

7.2 Trace and Rare Earth Element Geochemistry

For all H1662 matrix glasses, the rare earth elements (REEs) tend to follow a sloped pattern demonstrating enrichments in the lighter REEs relative to chondrite (Figure 12). Samples collected on the north ridge (NA092-002 through NA092-005, Figure 12) are more mafic with smooth REE patterns (i.e., no Eu-anomaly) and overall lower REE abundances relative to the other Socorro submarine samples, although the slopes of the REE patterns are similar (La/Yb range from 8.2 to 10.7). The west ridge samples (NA092-008 through NA092-016, Figure 12) and those from the sea-surface (SOC-1 and SOC-4, Figure 12) have similar REE abundances and patterns.

In other incompatible elements, H1662 glasses (normalized to NMORB) tend to be enriched (Figure 13; Appendix Table B1). The same general regional groupings of samples noted in the REE patterns tend to appear on a NMORB-normalized trace element diagram as well, although more distinctions are evident. Samples from the north ridge are the least enriched overall in the less incompatible trace elements but
tightly cluster with the other regional samples in the highly incompatible elements (e.g. Cs, Ba, U). The buoyant samples have lower Rb, Cs, and Ba than any of the seafloor samples. Some seafloor samples have positive spikes in Pb and Sr. All seafloor and buoyant clasts, with the exception of one buoyant lava balloon (SOC), exhibit a dip in U. Olivine phenocrysts (hosting melt inclusions) had Cr$_2$O$_3$ contents ranging from 0.02-0.03 wt.% and NiO ranging from 0.16-0.25 wt.%. (Table 3).

7.3 Volatile Contents of Melt Inclusions and Glasses

Melt inclusions from the Socorro submarine eruption are volatile-rich (Figure 14). After post-entrapment crystallization (PEC) and vapor bubble (VB) corrections (see Appendix A for details), melt inclusion H$_2$O content ranged from 0.56 to 0.73 wt.% and CO$_2$ ranged from 320 ppm to 3929 ppm (Table 3). Matrix glasses from NA092-014 and NA092-016 have lower volatile contents in comparison to melt inclusions from the same samples. Matrix glass H$_2$O content ranged from 0.22 to 0.35 wt.% and CO$_2$ ranged from 38 ppm to 225 ppm (Table 3; Figure 14). Given a calculated magma temperature of 1185°C (olivine-liquid; Putirka, 2007; Médard and Grove, 2007), and pressure of 27 bars (hydrostatic pressure of the eruption vent), the erupted lava was volatile-oversaturated at the conditions of eruption (dashed line in Figure 14).

Melt inclusions from the NA092 submarine Socorro samples have the highest CO$_2$ content yet reported for Socorro scoria samples from the 1993 eruption (buoyant and submarine). Buoyant Socorro scoria are also typically richer in H$_2$O, reaching values up to ~1 wt.% (Figure 14; Balcanoff, 2016). By contrast, melt inclusions from Foerstner volcano (Pantelleria) lava balloons are even higher in H$_2$O, reaching values up to about
1.1 wt.%, but contain substantially lower CO₂ contents (<2000 ppm; Figure 14; *Balcanoff*, 2016). Melt inclusions from the Terceira (Azores) lava balloons [*Kueppers et al.*, 2012] have the highest H₂O contents measured for lava balloon eruptions (1.18 wt.%), but they are not as rich in CO₂ (190-1500 ppm CO₂) as the Socorro suite (38-3929 ppm CO₂; Figure 14). Note that volatiles measured from buoyant Socorro samples by Balcanoff [2016] represent minima for the 1993 buoyant lava balloons because that study did not perform VB corrections (Appendix A for details). Despite the differences between individual lava balloon eruptions, these events are, in general, significantly richer in volatiles relative to MORB [*Le Voyer et al.*, 2019]. Tucker et al. [2019], however, recently constrained the CO₂ contents of parental magmas for several Hawaiian volcanoes in the range of 3900 to 10,000 ppm CO₂. Thus, the Socorro high of 3929 ppm CO₂ is actually in the lower range of Pacific ocean island basalts (OIBs).
8. Interpretations

8.1 Eruption Mechanism on the Seafloor

A variety of proposed eruption mechanisms may produce lava balloons, but generally, they form when the bulk density of mafic magma including its gas bubbles is less than seawater [Siebe et al., 1995; Kueppers et al., 2012; Kelley et al., 2014; Somoza et al., 2017]. Quenching of the outer crust helps contain the internal gas bubbles and allows balloons to rise up to the sea surface. Once in contact with air at low pressure they degas further, and the gas cavities eventually breach and become waterlogged. Then the broken, water-logged lava balloons sink back to the seafloor, usually on the timescale of a few minutes to hours.

At Socorro, the variety of volcanic facies at the vent (pillow morphologies, volcanic tephra, scoria, and hornitos) suggest a combination of effusive and explosive activity. In addition, eyewitness accounts report that the arrival of buoyant scoria at the sea surface occurred in a series of distinct pulses, suggesting a periodic expulsion of buoyant scoria. We propose that the eruptive activity at Socorro cycled among at least three stages to create pulses of buoyant scoria at the sea surface and produce the spectrum of eruptive products observed at the vent site.

The Socorro vent site consists of a primary vent at the bathymetric high point (251 m), with at least one secondary vent (260 m) at the same site on the southern west ridge (Figures 2). The primary vent, consisting of pillow tubes and extremely fragile pillow lobes amongst abundant scoria and volcanic sand, is likely the main source of the pulsatory releases of buoyant clasts to the sea surface (Figure 5). The abundant volcanic
sand is indicative of a highly explosive component to the eruption, while the presence of pillow morphologies suggests a more effusive eruptive style. Volcanic tephra from the vent site exhibit micro-morphologies representing violent bursting of bubbles (thin glass sheets, i.e., Limu o Pele; Figure 9) likely due to exsolution of primary volatiles from the magma.

During stage one, simultaneous effusive and explosive activity builds a clastic cone of interbedded lavas and tephra (Figure 15). The explosive activity is not vigorous enough to produce a convective, tephra-laden plume that reaches at the sea surface. Rubin et al. [2012] observed an example of this type of activity, although located at deeper depths, at West Mata volcano in the Tonga Arc where low intensity Strombolian-like explosions occurred at the same time as pillow lava formation.

Accumulation of highly vesicular pillow lavas and tephra at the vent may have led to stage two, where a temporary plug impeded the further extrusion of magma (Figure 15). Within this plug, there were likely sections of highly vesicular, buoyant pillow lavas that could not freely ascend because of denser, adjacent lobes of pillow lava or overlying tephra deposits. Some emplaced pillow lobes observed at the vent summit were aligned almost vertically with a broken glassy carapace exposing a hollow interior. Siebe et al. [1995] suggested that gas-rich sections of pillow flows may have detached to form lava balloons, although it’s difficult to envision how this mechanism alone could account for the highly episodic arrival of scoria at the sea surface.

Pressure beneath a vent plug, either from continued extrusion of magma or build-up of exsolved volatiles, may have led to failure and disruption of the plug,
generating a pulse of fragmented, highly-vesicular scoria, some of which contained sufficient gas fractions to rise to the sea surface (Figure 15). With time, the scoria became water-logged and sank back to the seafloor. Many of the large isolated scoria at the vent have aligned striations similar to those commonly observed on the surfaces of pillow lava tubes (Figure 16). This suggests that the balloons likely represent the disruption of highly vesicular pillow lavas and were not produced by fragmentation of magma within some type of highly energetic convective eruption plume. Following failure of the temporary plug, a combination of explosive and effusive activity resumed and reset the system towards another cycle of vent blockage and eventual failure. Some of the pulsatory nature of the eruption may also be linked to unsteady discharge of magma, but there are insufficient observations to quantitatively assess this possibility.

The secondary vent (Figure 5) on the southern flank of the vent site includes a region with pillow lobes and a large hornito-like structure (Figure 8). In subaerial regimes, hornitos form from the spattering of lava due to exsolution of gases or from the release of heated water within [Jurado-Chichay et al., 1996]. Somoza et al. [2017] observed similar hornitos at the El Hierro lava balloon eruption in 2011-2012. Yellow microbial orifices highlighted small lateral degassing vents on the deeper (118 m) hornitos from the El Hierro balloon eruption [Somoza et al., 2017]. Similar facies at the Socorro flank hornito appear as yellow holes and bands punctuated by microbial life (Figure 8). The internal structure of the Socorro hornito exhibits large smooth internal bubble walls and partitioned zones of bubble accumulation (Figure 8).
Somoza et al. [2017] concluded that spattered semifluid lava produced the El Hierro hornitos, a late-stage eruptive process. The onset of the Socorro hornito may also be associated with end-stage processes. Alternatively, the Socorro hornitos may represent the local development of buoyant zones where the vesicularity of pillow lava lobes causes them to rise up. This phenomenon, where the bulk density of magma plus gas bubbles is less than the surrounding environment (water) prior to fragmentation, can never be obtained in the subaerial environment and is likely to lead to novel eruptive behavior in the submarine realm [e.g. Friedman et al., 2012; Rotella et al., 2013].

8.2 Volcanic System Below the Seafloor and Origins of Basalt

The transition from explosive to effusive activity during a single eruptive phase is known to be linked to a variety of magmatic properties and processes including gas loss, conduit geometry, and magma viscosity [Cassidy et al., 2018]. Magma ascent rate, related to conduit geometry, controls gas loss, which is tied to degassing behavior. Degassing behaviors associated with different degassing regimes or systems (opened vs. closed) are essential to assessing the controls on various eruptive styles.

Potential degassing regimes modeled by measured volatiles can constrain magma storage and ascent and the evolution of the magmatic system throughout the eruption (i.e. buoyant early stage samples vs. seafloor late-stage samples). Recent volatile studies of the buoyant Socorro (early stage) samples led Balcanoff [2016] to a combined open and closed system scenario for the 1993 eruption. Early stage Socorro volatile trends appear to first undergo open system behavior with CO$_2$ >3500 ppm and
H₂O > 0.8 wt.% \cite{Balcanoff, 2016}. At around 1800 bars (~5 km), Balcanoff \cite{2016} suggests a shift to a range of possible closed system regimes (5% to 20% exsolved gas). The possible 20% primary gas content in such a closed system regime would require a ponding of degassed volatiles at depth.

Volatile evolution throughout the eruptive sequence, inferred from differences between early stage volatile measurements made by Balcanoff \cite{2016} relative to those of the present study, may provide clues to changing eruptive styles \cite{Stock et al., 2016; Cassidy et al., 2018}. We modelled degassing pathways and isobars based on the highest CO₂ content (3929 ppm; Table 3) from the seafloor Socorro samples in VOLATILECALC \cite{Newman and Lowenstern, 2002}. Similar to the early stage volatile data (Figure 17), the volatiles from H1662 vent samples tentatively follow an open system regime until reaching a pressure of 3300 bars (~10 km). A fully closed system regime is highly unlikely for the Socorro eruption, hence the closed system models fitting volatile data for this degassing style require unrealistically high degrees of exsolved gas (40-80%; Figure 17). Due to the limited analyzed melt inclusions from NA092 samples, all conclusions drawn from volatile models are highly tentative and represent permissible scenarios that explain a small number of data points.

The depth at which the Socorro system appears to shift from open to closed system degassing regimes may be the result of uncertainty in isobaric modeling, but it also may suggest changing depths of a magma staging zone throughout the eruptive sequence. SiO₂ content of buoyant clasts was lower in comparison to those collected on the seafloor, such that two sets of isobars (modeled using SiO₂ low of 44.5 wt.% and
high of 49.4 wt.%) were necessary to explain the data. These demonstrate the impact SiO$_2$ has on volatile solubility (bold vs. narrow isobars in Figure 17). CO$_2$ solubility varies as a function of metal cation proportions for a given SiO$_2$ content in a melt [Spera and Bergman, 1980]. Dixon [1997] parameterized the compositional dependence of CO$_2$ solubility on melt depolymerization and the potential cations available to react with carbonate. Thus, melts with the same volatile content and fractions can reach vapor saturation at lower pressures due to higher CO$_2$ solubility at lower SiO$_2$ content [Dixon, 1997].

Investigating the evolved nature of the erupted material from the 1993 Socorro eruption is valuable to understand the implications of volatile solubility and depth modeling which is related to major element compositions. A unique aspect of Revillagigedo volcanism at large is its evolved magmas, and the composition of Socorro Island, above sea level, is mostly peralkaline siliceous rocks [Bohrson and Reid, 1995]. Investigating the possible tectono-magmatic controls on the development of evolved peralkaline siliceous magmas is essential context for determining the origins of the gas-rich magma that erupted in 1993. In comparing other global silicic peralkaline volcanic centers, Bohrson and Reid [1997] identified three common conditions for the formation of these evolved magmas: a mildly extensional tectonic setting, a shallow magma reservoir, and parental magmas that are transitional to mildly alkalic basalt. Socorro is associated with a recently abandoned mid-ocean ridge segment that is consistent with the extensional tectonic setting condition.
Early stage erupted material (average Mg# 0.40; Balcanoff, 2016) is generally more evolved than late stage erupted material (average Mg# 0.48; 1993 vent site samples, present study). Both major and trace element variations demonstrate the effects of fractional crystallization on the 1993 erupted magma. Using the most mafic vent site sample (NA092-011) as the starting parental melt for the 1993 Socorro eruption, we modeled a liquid line of descent (Figure 18) using Petrolog3 [Danyushevsky and Plechov, 2011].

Fractional crystallization of olivine and plagioclase from a common parental magma explains the difference between the late stage seafloor vent samples (present study) to the early stage buoyant samples [Balcanoff, 2016] (Figure 18). Late stage, less-evolved samples start with higher MgO than early stage evolved samples, highlighting the crystallization of olivine. TiO$_2$ increases from about 3 wt.% in the late stage samples to about 4 wt.% in the early stage samples, indicating incompatible behavior and the absence of a mineral phase (e.g., magnetite) that would remove TiO$_2$ from the melt (Figure 18). Al$_2$O$_3$ shifts from about 16 wt.% in the late stage samples to about 14 wt.% in the early stage samples, indicating plagioclase crystallizing in the melt (Figure 18). The near negligible shift of CaO/Al$_2$O$_3$ (mostly flat) emphasizes that Al was incorporated into plagioclase faster than Ca into clinopyroxene (Figure 18), which fits with petrographic data that show an absence of clinopyroxene. Fractional crystallization of olivine and plagioclase thus explains the major element variations throughout the eruptive sequence, indicating a likely homogenous parental melt. Major elements from the submarine vent site (buoyant and seafloor) also fit within the window of variations for
subaerial Socorro Island data [Bohrson and Reid, 1995] suggesting that the regional eruptive material at Socorro may be sourced from a similar parental melt.

Trace elements in Socorro glasses have features (Ba, Pb, Sr, Zr peaks) similar to patterns of petit spot basalts (Figure 13; Hirano et al., 2006). The most mafic samples from the 1993 vent, in particular, have trace element signatures that are most likely mantle-derived, and the observation of common anomalies with other intraplate volcanic systems [e.g. Hirano et al., 2006] suggests some common source or process that links them. The absence of a Sr peak for the buoyant, evolved material, compared to the notable peak in Sr for seafloor parental material (Figure 13), could indicate the assimilation of a plagioclase-rich lithology during magmatic evolution, or it could arise from fractional crystallization. To test between these models, we calculated a liquid line of descent (LLD) for MgO vs. Sr/Nd (Figure 19) using the trace element partitioning features of Petrolog3. The modeled LLD on Figure 19 further demonstrates the importance of fractional crystallization in the 1993 magmatic system, as the Sr/Nd ratio decreases steadily with MgO consistent with preferential removal of Sr by plagioclase from a common parental magma. Overall, the more primitive material (H1662 samples) has trace element patterns with features similar to petit spot basalts [Hirano et al., 2006], and all 1993 Socorro material fits within the range of subaerial Socorro Island basalts [Bohrson and Reid, 1995] (Figure 19).

Volatile solubility models (Figure 17) suggest that magma reached a staging area at about 5 km in the early stage when the melt was less mafic (measured from buoyant clasts) and this may have shifted to 10 km in the later eruptive stages when the melt
was more mafic (NA092 seafloor samples). Once entering the staging zone, a closed system model better describes the degassing feedback of the regime leading to increased explosive potential [Cassidy et al., 2018].

Negative feedbacks are known to occur in open system degassing scenarios. When volatiles decouple from the melt, exsolved volatiles can accumulate in a chamber or staging zone beginning a closed system cycle. Volatile exsolution in a closed system increases the buoyancy of the magma, which may lead to over-pressure and faster ascent [Cashman, 2004]. For both early [Balcanoff, 2016] and (tentative) late stage Socorro volatile data, the magma maintained constant CO$_2$ (~1700 ppm) at depth in the respective staging zones (Figure 17). Open system volatile loss (esp. CO$_2$-rich vapor) deeper in the system would deliver CO$_2$ gas that could flux a shallower staged magma with CO$_2$-rich vapor, driving a decrease in H$_2$O and a slight increase in CO$_2$ contents, moving along an isobar (Figure 17).

Siebe et al. [1995] noted that the earlier floating scoria at Socorro tended to have a less vesiculated outer carapace than the later reticulitic samples. The buoyant products initially observed at Socorro did not contain reticulite, but beginning in July 1993 through February 1994, roughly 25-50% of floating scoria at Socorro contained reticulite. Siebe et al. [1995] concluded that the lack of vesicle sorting and the presence of ‘lava foam’ (i.e. reticulite) in many samples suggests that the magma had not been stored in a chamber (or stalled at a boundary) for very long, and thus the erupted magma retained most of its original gas inventory. The Socorro magma staging area may
have shifted deeper and stored magma for less time later in the eruption, such that
bubble coalescence was not possible.

The crustal thickness at Socorro is poorly constrained with models indicating a
possible range of about 2-7 km [Dick et al., 2003; Laske et al., 2013]. The Mathematician
Ridge stopped spreading about 3.5 Ma, yielding a minimum seafloor age of about 4.5
Ma (3.5 Ma + 1 Ma seafloor at time of spreading), translating to a lithospheric thickness
at Socorro of about 20 km, assuming the total thickness is the sum of the volcano relief
(4 km) plus the normal crustal thickness (2-7 km) plus three times the volcano relief,
giving a lithospheric range of 18-23 km [Robert Pockalny, pers. comm]. Thus, the early
staking zone (modeled at about 5 km) would likely have been in the crust (Figure 20).
This earlier and shallower staging area in the crust may be at a lithologic boundary (i.e.,
a transition zone between pillows, dykes, or gabbros). Magma from later in the eruption
(modeled at about 10 km) may have stalled in the upper mantle (Figure 20), possibly at
the Moho in a manner similar to magma underplating [Cox, 1993]. Due to the highly
variable crustal and lithospheric thicknesses, in addition to the tentative volatile
modelling, the shifting magma staging zone and the degassing interpretations represent
exploratory hypotheses.
9. Conclusion

This study utilized ultrahigh-resolution bathymetric surveys, video footage, seafloor imagery, geochemical and textural analyses of recently collected samples to investigate the volcanic processes and construct an eruption and plume model for this unusual lava balloon-forming event. Our exploration has led to the discovery of the vent site for the 1993 submarine eruption and definition of the volcanic facies produced during the event. Observed volcanic facies at the vent site indicate that both effusive (pillow lava) and explosive (scoria, volcanic ash) activity occurred simultaneously during the 1993 submarine eruption. We found that the generation of giant buoyant scoria was likely caused by episodic formation of a scoriaceous plug at the vent site that failed periodically resulting in pulses of scoria being discharged. A subset of the erupted scoria was buoyant enough to reach the sea surface, and the rest accumulated close to the vent. Volatile data reveal that an open system degassing regime likely shifted to closed system degassing once the magma entered a staging zone, which may have shifted depths throughout the eruption. Major and trace element variations are explained by fractional crystallization processes with the seafloor (H1662) late stage material representing the parental melt and the buoyant early stage material being more evolved. Tentative volatile modeling indicates the staging zone depth shifted from 5 km during the early stage to 10 km in the late stage.

Although mechanisms responsible for eruptions that generate giant buoyant scoria are diverse, there are notable similarities across all lava balloon events including: shallow vent depth (200-400 m), high volatile content, magmatic composition (alkaline
basalts) and geotectonic environment (oceanic island hotspots). Recognition of this type of scoria facies in ancient sequences can thus be used to infer paleoenvironmental conditions and geotectonic setting.
Figure 1. (a) Steaming floating scoria, or lava balloons, from the 1993 submarine eruption west of Socorro Island before sinking [Photo: Mystique]. (b) The Revillagigedo Archipelago islands (red circles) relative to the major geotectonic boundaries in the eastern Pacific [Figure made with GeoMapApp 3.6.8; Ryan et al., 2009]. (c) Socorro Island and new multibeam bathymetry of the vent area west of Socorro (5 m grid, left depth legend) and the surrounding region (30 m grid, right depth legend) collected during cruise NA089 and NA092.
Figure 2. Bathymetric map of the 1993 vent region west of Socorro Island with sample locations (red circles) and H1662 dive track (grey line). Map is labeled with abbreviated sample numbers without the cruise ID (e.g. 1 is sample NA092-001). Shaded ellipses identify the three primary sample regions - west ridge, north ridge, and east cones.
Figure 3. (a) Perspective view of the multibeam bathymetry map of the area west of Socorro Island, showing the track of ROV Hercules dive H1662. Inset shows the extent of the 1993 vent ultrahigh-resolution ROV survey region. (b) 3D image reconstruction in plan view of the ultrahigh-resolution vent survey (same orientation as inset in (a)) showing abundant white and yellow microbial mats surrounding basaltic scoria. Inset image highlights the stark boundary between different microbial mats.
**Figure 4.** Primary volcanic facies of the 1993 submarine vent site. (a) Angular vesicular scoria colonized by yellow and white microbial mats from ongoing low-temperature hydrothermal activity at the vent. (b) Pillow lobes and tubes at the vent site summit. (c) Hornito structures were present at the summit and the side flank of the vent. (d) Volcanic sand and coarse tephra were present throughout the vent site and vent region.
Figure 5. Distribution maps of different volcanic facies at the 1993 vent site determined by visual examination of images from the ultrahigh-resolution survey area. Sample locations are represented by the black diamonds and the scale bar at the top of (b) applies to all three panes. (a) Map of small and large scoria locations. (b) Map of pillow lava, hornito, and presence of ripples. (c) Map of volcanic sand distribution based on seafloor coverage (%).
Figure 6. Thin section scan of sample NA092-012 (width of scan is about 10 cm). General zones of similar vesicularity and texture divide up the distinct bubble gradient. (a) Quenched crust (top right inset is a composite image from the top of the crust); (b) hemispherical coalesced vesicle zone; (c) smaller circular vesicle zone (center right inset is a composite image of this zone); (d) transition zone into reticulitic interior with microlites (bottom right inset is a composite image from this zone). All composite images were collected and stacked using the Macropod system.
Figure 7. Thin section scan of sample NA092-010 (width of scan is about 10 cm). (a) Elliptical bubble zone just below quenched crust (trending horizontal); (b) circular bubbles and microlite-rich zone; (c) elliptical bubble zone with coalesced vesicles (trending vertical). Inset composite image of NA092-010 cross-section collected and stacked using the Macropod system.
Figure 8. Hornito structure on the side flank of the 1993 vent site. Right inset shows the glassy rind exposed from attempted sampling efforts. Top left scale applies for both images.
Figure 9. Scanning electron micrographs of volcanic ash and lapilli from the 1993 vent site. (a) Pele's hair formation (NA092-014); (b) pipe vesicle and vesicular shard (NA092-013); (c) Limu o Pele (NA092-013). Scale bar in top right of (c) applies for all micrographs.
Figure 10. Fragile light brown reticulite formed within the interior of large scoria (NA092-012). The network of glass filaments outlines vesicles that range in size from <0.5mm to >2mm in diameter.
Figure 11. Plot of silica vs. total alkalis ($\text{Na}_2\text{O}+\text{K}_2\text{O}$) for recently recovered H1662 Socorro seafloor scoria, 1993 Socorro buoyant scoria [Balcanoff, 2016; Siebe et al., 1995] and regional subaerial samples from Socorro Island and San Benedicto Island [Bohrson and Reid, 1999].
Figure 12. Chondrite-normalized [Nakamura, 1974] rare earth element compositions for recently recovered basaltic scoria, tephra, and pillows from H1662. Measured compositions from thin sections (SOC 1 and SOC 4) of samples collected on the sea-surface in 1993 are included for comparison.
Figure 13. NMORB-normalized [Sun and McDonough, 1989] trace element compositions for recently recovered basaltic scoria, tephra, and pillows from H1662. Measured compositions from thin sections (SOC 1 and SOC 4) of samples collected on the seafloor in 1993 are included for comparison. Petit spot basalt pattern shown for comparison [Hirano et al., 2006].
Figure 14. Volatile contents of 1993 Socorro submarine and buoyant scoria. Comparative data from the Pantelleria lava balloons [Balcanoff, 2016], Terceira lava balloons [Kueppers et al., 2012], MORB field [Le Voyer et al., 2019; field bounds determined by 1-sigma from the mode], and Hawaiian OIB field [Sides et al., 2014 and Tucker et al., 2019]. Dashed isobaric solubility bar calculated in VOLATILECALC [Newman and Lowenstern, 2002] demonstrates volatile saturation in the basalt melt at vent depth (27 bars, ~270 m depth) with a calculated magma temperature of 1185°C based on NA092-014 [olivine-liquid thermometer calculation Putirka, 2007, and Médard and Grove, 2007].
Figure 15. Mechanism for the 1993 Socorro submarine eruption exhibiting a three-stage cycle of simultaneous effusive and explosive activity. (a) Numerous small explosions generating abundant coarse tephra, small highly vesicular scoria, pillow lobes. (b) Built up scoria and pillows at the primary vent form a plug stopping the release of further eruptive products (on the order of hours). (c) accumulated pressure and material below the plug cause a sudden rupture resulting in a pulse of large highly buoyant scoria. With a cleared vent orifice, the cycle will continue on to stage (a).
Figure 16. Pillow tube formation at the 1993 Socorro submarine vent site exhibiting the ribbed striated pillow textures on lobes, tubes, and scoria. (a) Elongate pillow tube at vent summit. (b) Pillow lobes with striated crust and highly vesicular margins. (c) Disjointed pillow tube with vesicular striated crust. (d) Elongate pillow lobes with ribbed striated crust. (e) NA092-016 scoria sample with striated crust similar to pillow morphologies.
Figure 17. Volatile degassing paths (dashed lines) include an open system model, closed system models with varying degrees of exsolved gas (5%, 25%, 75%), and closed system models for a possible second stage (5%, 25%). Two sets of isobars are presented to demonstrate the significance that SiO$_2$ content plays in calculating pressure: the bolder (left labeled) isobars were calculated with the highest SiO$_2$ content of NA092 Socorro samples (49.4 wt.%) while the narrow (right labeled) isobars were calculated with the lowest SiO$_2$ content of buoyant Socorro samples [44.5 wt.%; Balcanoff, 2016]. Calculations for degassing pathways and isobars performed in VOLATILECALC [Newman and Lowenstern, 2002].
Figure 18. (caption on next page)
Figure 18. Major element variation diagrams of Socorro submarine regional and vent samples, 1993 buoyant Socorro scoria, and subaerial Socorro Island basalts highlighting fractional crystallization of olivine, (a) magnetite, (b) plagioclase, and (c) the absence of clinopyroxene crystallization. Legend applies for all plots. *Liquid line of descent modelled in Petrolog3 [Danyushevsky and Plechov, 2011] with the following input parameters: NA092-11 as starting parental melt, 3.2 kb pressure, fO$_2$=QFM, mineral-melt solution model of Danyushevsky et al. [2001], forced to an olivine-plagioclase cotectic lattice strain model from Blundy and Wood [2001] to calculate plagioclase/melt partitioning for Sr, plagioclase/melt D=0.069 for Nd [Philpotts and Schnetzler, 1970], olivine/melt D=0.0023 for Nd [Fujimaki et al., 1984], olivine/melt D=0.02 for Sr [Villemant et al., 1981], D values determined specifically for alkali basalt.
Figure 19. MgO vs. Sr/Nd highlighting the fractionation of olivine and plagioclase in the 1993 Socorro eruptive sequence. *Liquid line of descent modelled in Petrolog3 [Danyushevsky and Plechov, 2011], see Figure 18 caption for input parameters.
Figure 20. Possible plume model for the 1993 Socorro submarine eruption featuring magma ascent through two staging zones. The early erupted material (buoyant, more evolved) would be sourced from the 5 km staging zone, while the later erupted material (seafloor collected, more primitive) would be directly sourced from the deeper 10 km staging zone. The conduit may have changed shapes throughout the eruption and cleared a path for the deeper parental magma to move through the crust without being stalled. Plume model not to scale.
Table 1. Geologic sample descriptions and locations for seafloor samples collected during dive H1662 in the 1993 submarine vent region.

| Sample ID | Latitude  | Longitude | Depth [m] | Region              | Description                                                                 |
|-----------|-----------|-----------|-----------|---------------------|-----------------------------------------------------------------------------|
| NA092-001 | 18.8013   | -111.0810 | 526       | dive start (fan)    | Coarse glassy volcanic tephra                                               |
| NA092-002 | 18.8001   | -111.0743 | 272       | north ridge         | Coarse glassy basalt scoria fragments with some primitive reticulite       |
| NA092-003 | 18.8001   | -111.0743 | 272       | north ridge         | Coarse glassy volcanic tephra                                               |
| NA092-004 | 18.8001   | -111.0743 | 273       | north ridge         | Glassy highly vesicular scoriaceous basalt (~18 cm); seawater quench surface preserved, internal gas cavities 2.5 cm, reticulite on inner slice wall |
| NA092-005 | 18.8001   | -111.0743 | 272       | north ridge         | Slightly weathered basalt scoria (~25 cm); large internal glassy gas cavities <10 cm diameter |
| NA092-007 | 18.7940   | -111.0689 | 306       | east cones          | Moderately weathered basalt scoria (~25 cm); highly elongated gas cavities <10 cm, some red-orange oxidized staining on exterior |
| NA092-008 | 18.7918   | -111.0789 | 247       | west ridge/vent site| Glassy basaltic highly friable scoria fragments; large internal gas cavities <3 cm |
| NA092-010 | 18.7942   | -111.0785 | 257       | west ridge          | Glassy pillow rim ~4 cm thick; consistent bubble size and density across rim cross section |
| NA092-011 | 18.7916   | -111.0791 | 252       | west ridge/vent site| Glassy vesicular small basalt scoria (5-16 cm); interior gas cavities 3 cm, smooth bubble walls |
| NA092-012 | 18.7917   | -111.0792 | 250       | west ridge/vent site| Glassy vesicular basalt scoria blocks; internal gas cavities 8 cm, light brown reticulite |
| NA092-013 | 18.7918   | -111.0793 | 254       | west ridge/vent site| Coarse glassy volcanic tephra mixed with some bacterial mats                |
| NA092-014 | 18.7916   | -111.0792 | 252       | west ridge/vent site| Glassy basaltic scoria (16 cm); internal gas cavities 4 cm, smooth glassy bubble walls |
| NA092-015 | 18.7917   | -111.0791 | 251       | west ridge/vent site| Glassy vesicular balloon 24 cm and several smaller fragments (2-6 cm) of scoria; seawater contact preserved, smooth bubble walls, a lot of reticulite |
| NA092-016 | 18.7916   | -111.0791 | 251       | west ridge/vent site| Glassy large basaltic scoria blocks; large (10 cm) interior gas pockets with smooth glassy interior, stratified exterior surface |
Table 2. Image analysis results of attribution occurrence and vent coverage from the ultrahigh-resolution vent survey images.

| Attribute                  | Images with Occurrence | Vent Coverage (%) |
|----------------------------|------------------------|-------------------|
| Large Scoria               | 3002                   | 78.4              |
| Small Scoria               | 3645                   | 95.2              |
| Hornito                    | 16                     | 0.4               |
| Pillow Lobe                | 225                    | 5.9               |
| Pillow Tube                | 20                     | 0.5               |
| White Bacteria (0-20%)     | 1267                   | 33.1              |
| White Bacteria (20-60%)    | 2275                   | 59.4              |
| White Bacteria (60-100%)   | 50                     | 1.3               |
| Yellow Bacteria (0-20%)    | 710                    | 18.5              |
| Yellow Bacteria (20-60%)   | 871                    | 22.8              |
| Yellow Bacteria (60-100%)  | 5                      | 0.1               |
| Volcanic Sand (0-20%)      | 1102                   | 28.8              |
| Volcanic Sand (20-60%)     | 2652                   | 69.3              |
| Volcanic Sand (60-100%)    | 67                     | 1.8               |
| Ripples                    | 224                    | 5.9               |
Table 3. Major element compositions of matrix glass and olivine-hosted melt inclusions and volatile data from seafloor scoria collected at the Socorro vent during dive H1662.

| Sample | Major Element Compositions (wt%) | Volatile Data | PFC correction | REE correction |
|--------|---------------------------------|--------------|---------------|---------------|
|        | SiO₂ | Al₂O₃ | FeO | MgO | CaO | Na₂O | K₂O | P₂O₅ | Cl | F | PC | REE |
|        |      |      |     |     |     |      |     |      |   |   |    |     |
| 

* Glass volatile data obtained from matrix glass of a scavenged melt inclusion in MA
* REE calculated using equations: REE = 1000*mass% in melt sample * melt density / (1000 - melt density)
* Scavenged major data for rims and cores were corrected, as the rim values were used for all inclusions to correct for PFC
* All corrections performed using glass data (with PFC, melt has temperatures of 1050°C, glass density of 2.6 g/cm³)
APPENDIX

Appendix A. Detailed methodologies

A.1 Electron microprobe analytical techniques

Quantitative analysis of basaltic glass chips, mounted on 1 inch round epoxy holders, was performed on the Brown University Cameca SX-100 electron microprobe to determine major element compositions (SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, MgO, CaO, Na$_2$O, K$_2$O, MnO, P$_2$O$_5$, SO$_2$). Operating conditions of the instrument consisted of 15 kV voltage, 10 nA current and a 20 micron diameter, and a defocused beam. Counting times were 30 seconds for on peak, and half that time for backgrounds, for all elements except Na, which was counted for 20 seconds. The data were calculated using the PAP correction procedures [Pouchou and Pichoir, 1991]. One-sigma standard deviations are <1% for major elements and 4–9% for minor elements. Standards used for the basaltic glass analysis included USGS AGV-2 andesite glass (Si); USGS BIR-1G Iceland basalt glass (Al, Ca); synthetic Fo$_{97}$ forsterite, University of Rhode Island (Mg); Rockport, Massachusetts fayalite, NMNH 85,276 (Fe); Amelia albite, (Na); rhodonite, AMNH 104738 (Mn); Purdue University (Na); synthetic orthoclase OR-1, AMNH (K); synthetic rutile, Brown University, (Ti); Berlineite, synthetic, AMNH G. Harlow (P); and Peru pyrite, Brown University (S). The electron microprobe is equipped with extra-large diffracting crystals (LTAP, LLIF, LPET) that generate roughly five times the count rate of standard-sized diffracting crystals. Extra-large crystals were used in the analysis of Mg, Mn, Fe, Ti, Na, P and S. Standard-sized crystals were used for Si, Al, Ca and K. Na, K and S were analyzed using a loss routine to account for any volatilization of the elements under the beam. USGS
Columbia River basalt BCR-2G and the Smithsonian A99 glass were used as secondary reference standards and values are reported in Table B2.

A.2 LA-ICP-MS analytical techniques

Trace and minor elements (Li, Be, Sc, V, Cr, Co, Ni, Cu, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U, Yb, Zn, Zr, K2O, TiO2) were determined by LA-ICP-MS (Thermo Electron Corporation X Series II with New Wave Research UP-213 Laser Ablation System) at the University of Rhode Island Graduate School of Oceanography. Analyses were conducted using a 10 Hz repeat rate, 80µm spot size, and 75% energy output. Reduction methods follow Lytle et al. [2012]. Eight natural glass standards from the USGS (BCR-2g, BHVO-2g, BIR-1g; Kelley et al., 2003) and the Max Plank Institute (GOR132-G, StHls-G, T1-G, ML3B-G, KL2-G; Jochum et al., 2006) were used to make calibration curves for all elements to an r^2 > 0.99. Each glass chip was analyzed in triplicate. See Figure B2 for an example LA-ICP-MS time-resolved data spectrum.

A.3 XANES analytical techniques

X-ray absorption near edge structure (XANES; at Argonne National Laboratory) spectroscopy was performed on newly collected glass from dive H1662. Analyses were performed on sample NA092-011 (glassy balloon), which had the highest MgO content (5.8 wt. %) out of all vent samples (ranging from 5.4 to 5.8 wt. % MgO). We prepared a doubly-polished glass wafer from the glassy rim of this sample. XANES data were collected during session 2018_1 at beamline 13-ID-E of the Advanced Photon Source, Argonne National Laboratory, using methods presented by Cottrell et al. (2009), but
adopting the updated calibration of Zhang et al. (2018), which accounts for the effects of recoil-free fraction on the Mössbauer spectra used to independently characterize the XANES reference glasses for Fe$^{3+}/\Sigma$Fe ratios. We further used measures recommended by Cottrell et al. (2018) to minimize the effects of radiation-induced Fe oxidation on hydrous basalt glasses by working with a defocused 25x25 µm beam and attenuating the incident photon flux with Al foil to 1.1E9 ph/s, giving a flux density at the sample surface of 1.7E6 ph/s/µm$^2$.

A.4 Melt inclusion sample preparation and FTIR analytical techniques

Olivine phenocrysts were extracted from newly collected samples from dive H1662. Crystals with melt inclusions containing no more than one vapor bubble and no evidence of secondary mineralization were selected and prepared as double-polished wafers for FTIR spectroscopy at the University of Rhode Island Graduate School of Oceanography Thermo Scientific Nicolet iS50 spectrometer coupled with a Continuum IR microscope. A total of 4 melt inclusions hosted in olivine crystals ranging from Fo$_{80-82}$ were analyzed from samples NA092-014 (3) and NA092-016 (1). Three spectra per inclusion were collected with a wavenumber resolution of 512 scans at 1 cm$^{-1}$. Dissolved H$_2$O and CO$_2$ concentrations were then determined using the Beer-Lambert Law (where absorbance is proportional to the composition of the glass) using absorption coefficients (3550 cm$^{-1}$ for total H$_2$O; 1515 and 1430 cm$^{-1}$ for CO$_3^{2-}$) calculated from the major element composition [Dixon et al., 1995; Luhr, 2001]. We used a molar absorptivity of 63 L/mol•cm for H$_2$O and 375 L/mol•cm for CO$_2$. FTIR analytical methods follow those from Kelley and Cottrell [2012].
In general, olivine phenocrysts in NA092 seafloor basaltic scoria were small (50-200 µm) and contained small, often elongate, glass inclusions (many <10 um). The sizes and shapes of these melt inclusions presented a challenge for sample preparation and FTIR measurements. Successful preparation and analysis were achieved for <10% of attempts. Successfully analyzed melt inclusions were among the largest preserved, ranging from about 50 x 60 um to 50 x 163 um (photomicrographs of inclusions in Appendix Table B3 and dimensions reported in Table 3). Measuring volatiles in matrix glasses was also challenging due to the extremely vesicular nature of the matrix. Zones with more pools of glass that appeared less vesicular and aphyric in thin section were targeted for FTIR preparation. See Figure B3 for example FTIR data spectrum.

A.5 Post-entrainment corrections to major element and volatile data in melt inclusions

Post-entrainment crystallization (PEC) and vapor bubble (VB; also called shrinkage bubbles) corrections were performed to account for known post-entrainment modification effects on the major element compositions and measured CO$_2$ concentrations in melt inclusions [e.g. Moore et al., 2015; Maclennan, 2017]. We calculated the equilibrium olivine composition using K$_D$=0.3 (with XANES determined Fe$^{3+}$/ΣFe = 0.143) and then added olivine back in 0.01% increments to the melt inclusion composition until reaching equilibrium with the host Fo content [methods from Kelley and Cottrell, 2012]. PEC corrections ranged from 1.9 to 5.2% olivine added back.

Exsolved volatiles in the VBs were calculated and added to the PEC-corrected dissolved volatiles in the melt inclusions in order to determine the total CO$_2$ and H$_2$O concentrations of the glass prior to volatile loss to the bubble. CO$_2$ partitioned into the
VB is equal to the volume of the VB (φ) times the ratio of the volumetric CO₂ vapor density (ρᵥ) to the melt density (ρₘ) [where exsolved CO₂ in bubble = φ(ρᵥ/ρₘ), e.g. Tucker et al., 2019]. VBs were assumed to be spheroids within ellipsoidal melt inclusions. VB volume was calculated from optically measured axes of VBs and inclusions via photomicrographs of pre-polished grains (Appendix Table B3). The volumetric CO₂ vapor density was calculated using the ideal gas law (n=PV/RT) with a glass transition temperature for trachybasalts of 700°C [Di Genova et al., 2014] and an average glass density of 2.7 g/cm³ calculated from major element composition using the Dixon et al. [1995] method. Saturation pressures and mole fractions of CO₂ and H₂O (mixed vapor) were calculated in VOLATILECALC [Newman and Lowenstern, 2002]. The PEC correction method was performed a second time post-VB correction to determine the final total volatile content of the melt inclusions.

A.6 Imaging, image analysis and microscopy analytical techniques

Forward-looking imagery was collected systematically every 5 seconds throughout dive H1662 by the MISO (Woods Hole Oceanographic Institution Multidisciplinary Instrumentation in Support of Oceanography Facility) GoPro system mounted to ROV Hercules. Down-looking imagery was also systematically collected during the ultrahigh-resolution mapping survey every 3 seconds using the Roman stereo-still camera.

Adam Soule developed an adjustable Graphical User Interface (GUI) which pulls images from a dive directory and allows the user to characterize various attributes present in individual images. The categories of attributes selected for analysis of H1662
imagery include: morphology (large scoria, small scoria, hornito, pillow lobe, pillow tube), microbial mat presence (white bacteria at 0-20%, 20-60%, or 60-100% cover; yellow bacteria at 0-20%, 20-60%, or 60-100% cover), volcanic sand cover (at 0-20%, 20-60%, or 60-100%), and sediment cover (at 0-20%, 20-60%, or 60-100%). We performed image analyses on both sets of imagery, the full-dive GoPro suite (Table B4) and the stereo-stills from the ultrahigh-resolution survey (Table 2). A single user characterized all dive imagery to minimize user interpretation variation. We calculated the total attribute presence for both sets of image analyses. We performed spatial analysis of attribute presence through timecoded locations of analyzed images, and we generated layered attribute maps in Fledermaus.

We performed qualitative imaging of basaltic scoria and reticulite at the Rhode Island School of Design Nature Laboratory using a Macroscopic Solutions Focal Stacking System. Camera used was a Canon EOS 6D Mark II with a Macro Twin Lite MT26-EXRT Flash. Zerene Stacker software was used to align and stack 66 photos per composite image using both PMax and DMap techniques.

We characterized particle morphologies of volcanic sediment from the vent site (NA092-013 and NA092-014) using scanning electron microscopy (SEM; JEOL JSM-5900LV at the University of Rhode Island Kirk Engineering Laboratory). SEM run conditions varied based on particle size from: vacuum 24-27, spot size of 37-42, magnification 80-300, and accelerating voltage set at 20.
Appendix B. Supplemental data

Figures

**Figure B1.** Petrographic images of glass chips used for FTIR volatile analysis for comparison with melt inclusion data.
Figure B2. Time-resolved LA-ICP-MS example spectrum for run 1/3 on sample NA092-001. Select masses (\(^{26}\)Mg, \(^{27}\)Al, \(^{39}\)K, \(^{47}\)Ti, \(^{57}\)Fe) are exhibited on plot to demonstrate the homogeneity of the glass sample with minimal decay over time. Region between pink vertical bars indicates the signal used in the measurement (PkLow to PkHigh). Background signal (between BgLow and BgHigh), while laser is turning on, is used in data reduction which is subtracted from the peak signal. Washout data (right of PkHigh) was not used in data reduction.
Figure B3. FTIR example spectrum for sample NA092-014-ML03 (Socorro CO₂ high of 3900 ppm) with noticeable H₂O peak at 3530 cm⁻¹.
Table B1. Trace and rare earth element LA-ICP-MS data from all H1662 submarine glasses and from two sea surface samples collected near Socorro in 1993 (SOC 1 and 4).

Note that each datum is an average of 3 or 4 measured points on a glass chip.
### Table B2. Reference standards for electron microprobe analyses of matrix glasses and melt inclusions.

| (time)   | BCR for matrix glass (1/17/18) | BCR for matrix glass (1/18/18) | BCR for matrix glass (1/18/18) | A99 for melt inclusions (3/13/19) |
|----------|---------------------------------|---------------------------------|---------------------------------|-----------------------------------|
|          | 16:13                           | 16:17                           | 22:49                           | 22:53                             | 22:58                             | 8:57                             | 9:02                             |
| SiO₂     | 54.49                           | 54.53                           | 54.43                           | 54.51                             | 54.45                             | 50.95                            | 50.88                            |
| TiO₂     | 2.28                            | 2.26                            | 2.29                            | 2.26                             | 2.28                             | 4.09                            | 4.16                            |
| Al₂O₃    | 13.45                           | 13.51                           | 13.45                           | 13.38                             | 13.42                             | 12.46                           | 12.43                            |
| FeO      | 12.51                           | 12.29                           | 12.41                           | 12.44                             | 12.37                             | 13.36                           | 13.45                            |
| MnO      | 0.18                            | 0.19                            | 0.16                            | 0.25                             | 0.16                             | 0.23                            | 0.22                            |
| MgO      | 3.72                            | 3.58                            | 3.58                            | 3.67                             | 3.55                             | 5.12                            | 5.08                            |
| CaO      | 7.03                            | 7.1                             | 7.02                            | 7.11                             | 7.08                             | 9.31                            | 9.37                            |
| Na₂O     | 3.27                            | 3.2                             | 3.24                            | 3.33                             | 3.24                             | 2.58                            | 2.74                            |
| K₂O      | 1.74                            | 1.72                            | 1.72                            | 1.75                             | 1.77                             | 0.82                            | 0.8                             |
| P₂O₅     | 0.37                            | 0.38                            | 0.37                            | 0.41                             | 0.38                             | 0.38                            | 0.37                            |
| SO₂      | 0                               | 0                               | 0                               | 0.01                             | 0                                | 0.03                            | 0                               |
| Total    | 99.04                           | 98.76                           | 98.67                           | 99.12                             | 98.7                             | 99.34                           | 99.52                            |
| Cl       | -                               | -                               | -                               | -                                | -                                | 0.02                            | 0.02                            |
Table B3. Petrographic images for olivine-hosted melt inclusions from highly vesicular basaltic scoria collected on dive H1662.

| Sample   | Inclusion | Pre-Polish Photo | Photo (PPL) | Melt Inclusion Wafer Thickness (cm) |
|----------|-----------|------------------|-------------|-----------------------------------|
| NA093-014| ML03      | ![Image](image1)  | ![Image](image2) | 0.0045                            |
| NA093-014| ML04g     | ![Image](image3)  | ![Image](image4) | 0.0044                            |
| NA093-014| ML08      | ![Image](image5)  | ![Image](image6) | 0.0047                            |
| NA093-014| ML10      | ![Image](image7)  | ![Image](image8) | 0.0049                            |
| NA093-016| ML05      | ![Image](image9)  | ![Image](image10) | 0.0048                            |
Table B4. Image analysis results of attribution occurrence and H1662 full dive coverage from full dive GoPro image suite.

| Attribute               | Images with Occurrence | Dive Coverage (%) |
|-------------------------|------------------------|-------------------|
| Large Scoria            | 2711                   | 42.5              |
| Small Scoria            | 5407                   | 84.7              |
| Hornito                 | 116                    | 1.8               |
| Pillow Lobe             | 659                    | 10.3              |
| Pillow Tube             | 253                    | 4.0               |
| White Bacteria (0-20%)  | 954                    | 14.9              |
| White Bacteria (20-60%) | 1120                   | 17.5              |
| White Bacteria (60-100%)| 1                      | 0.0               |
| Yellow Bacteria (0-20%) | 1899                   | 29.7              |
| Yellow Bacteria (20-60%)| 256                    | 4.0               |
| Yellow Bacteria (60-100%)| 7                      | 0.1               |
| Volcanic Sand (0-20%)   | 3565                   | 55.8              |
| Volcanic Sand (20-60%)  | 1653                   | 25.9              |
| Volcanic Sand (60-100%) | 81                     | 1.3               |
| Sediment (0-5%)         | 650                    | 10.2              |
| Sediment (5-25%)        | 1714                   | 26.8              |
| Sediment (25-50%)       | 2281                   | 35.7              |
| Sediment (50-75%)       | 962                    | 15.1              |
| Sediment (75-100%)      | 584                    | 9.1               |
| Ripples                 | 139                    | 2.2               |

Note that 6384 images were analyzed of the total 13770 images captured. About 54% of total images could not be analyzed because the vehicle was in transit or the frame was too blurry.
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