



# Hydrothermal Activity at a Cretaceous Seamount, Canary Archipelago, Caused by Rejuvenated Volcanism

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## OPEN ACCESS

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### Specialty section:

This article was submitted to  
Deep-Sea Environments and Ecology,  
a section of the journal  
Frontiers in Marine Science

**Received:** 17 July 2020

**Accepted:** 29 October 2020

**Published:** 26 November 2020

### Citation:

Klügel A, Villinger H, Römer M,  
Kaul N, Krastel S, Lenz K-F and  
Wintersteller P (2020) Hydrothermal  
Activity at a Cretaceous Seamount,  
Canary Archipelago, Caused by  
Rejuvenated Volcanism.  
*Front. Mar. Sci.* 7:584571.  
doi: 10.3389/fmars.2020.584571

Our knowledge of venting at intraplate seamounts is limited. Almost nothing is known about past hydrothermal activity at seamounts, because indicators are soon blanketed by sediment. This study provides evidence for temporary hydrothermal circulation at Henry Seamount, a re-activated Cretaceous volcano near El Hierro island, close to the current locus of the Canary Island hotspot. In the summit area at around 3000–3200 m water depth, we found areas with dense coverage by shell fragments from vesicomid clams, a few living chemosymbiotic bivalves, and evidence for sites of weak fluid venting. Our observations suggest pulses of hydrothermal activity since some thousands or tens of thousands years, which is now waning. We also recovered glassy heterolithic tephra and dispersed basaltic rock fragments from the summit area. Their freshness suggests eruption during the Pleistocene to Holocene, implying minor rejuvenated volcanism at Henry Seamount probably related to the nearby Canary hotspot. Heat flow values determined on the surrounding seafloor ( $49 \pm 7$  mW/m<sup>2</sup>) are close to the expected background for conductively cooled 155 Ma old crust; the proximity to the hotspot did not result in elevated basal heat flow. A weak increase in heat flow toward the southwestern seamount flank likely reflects recent local fluid circulation. We propose that hydrothermal circulation at Henry Seamount was, and still is, driven by heat pulses from weak rejuvenated volcanic activity. Our results suggest that even single eruptions at submarine intraplate volcanoes may give rise to ephemeral hydrothermal systems and generate potentially habitable environments.

**Keywords:** seamount, heatflow, hydrothermal activity, Atlantic, vesicomid clams, Canary Islands

## INTRODUCTION

The seafloor is scattered with hundreds of thousands of volcanic seamounts of > 100 m elevation that occur in all parts of the ocean plates (Wessel, 2001; Hillier and Watts, 2007). During their different evolutionary stages, seamounts interact in various ways with the ocean (Staudigel and Clague, 2010). One particular and globally relevant interaction is hydrothermal circulation through seamounts, which extracts significant lithospheric heat and promotes chemical exchange between

crust and ocean (Villinger et al., 2002, 2017; Harris et al., 2004; Fisher and Wheat, 2010). At volcanically inactive seamounts, low-temperature hydrothermal circulation can be driven by heat from the cooling lithosphere in conjunction with topographic gradients and basement outcrops (Fisher et al., 2003; Harris et al., 2004; Fisher and Wheat, 2010). At volcanically active seamounts, vigorous hydrothermal activity can be driven by magmatic heat sources at comparatively shallow levels, which is common at arc settings (Butterfield, 2000; de Ronde and Stucker, 2015; Caratori Tontini et al., 2019) but also at some intraplate volcanoes. Examples are very rare, however, and are mostly confined to active systems (Sakai et al., 1987; Staudigel et al., 2004; German et al., 2020) with few exceptions (Medialdea et al., 2017).

Little is known, however, about ephemeral hydrothermal circulation at the many intraplate seamounts and small volcanic cones that erupt only rarely, or are monogenetic. At low magma supply rates these volcanoes should not have a shallow magma reservoir as a heat source for sustained hydrothermal activity (Clague and Dixon, 2000). A single submarine eruption can result in residual hydrothermal activity due to cooling and degassing (Santana-Casiano et al., 2016), but duration and implications of such activity remain to be explored. What is the thermal footprint of temporary fluid circulation on the seafloor? Can fluid circulation persist long enough for chemoautotrophic communities to develop, and are these common occurrences? These questions are difficult to address, largely because few deep-sea volcanoes have been thoroughly explored. Moreover, traces of previous hydrothermal activity are quickly buried by sediment, and any precipitated sulfide minerals and structures from hydrothermal flow will quickly oxidize and collapse. Any such discovery is rare. In this study, we provide evidence for waning Holocene hydrothermal activity at a Cretaceous seamount located near the Canary Islands that was likely caused by a small pulse of rejuvenated volcanism.

## GEOLOGICAL BACKGROUND

The Canary Islands are part of an intraplate hotspot chain offshore NW Africa, with decreasing ages of seamounts and volcanic islands from east to west (Figure 1A). El Hierro, situated on ~155 Ma old ocean crust, is the youngest island along the chain (1.1 Ma; Guillou et al., 1996) and is located near the present Canary hotspot (Geldmacher et al., 2005). The only historic eruption of El Hierro was submarine and occurred between 2011 and 2012 a few kilometers off the island's southern tip, with the shallowest peak shoaling to 89 m below sea level (Martí et al., 2013; Rivera et al., 2013). The new volcanic cone shows evidence for waning hydrothermal activity, given mostly by the expulsion of fluids rich in magmatic CO<sub>2</sub> (Santana-Casiano et al., 2016).

Henry Seamount, located 40 km southeast of El Hierro, is a volcanic edifice that rises ~700 m above ~3700 m deep ocean floor (Gee et al., 2001; Figure 1B). A reconnaissance dredging campaign over the seamount in 2005 yielded trachytic rocks that were dated by the <sup>40</sup>Ar/<sup>39</sup>Ar method at 126 Ma, a barite block overgrown by a coral with a radiocarbon age of 41 ka, and shell fragments from vesicomid clams, two of which gave

radiocarbon ages of 3.4 and 18.6 ka, respectively (Klügel et al., 2011). Many trachyte fragments were barite-metasomatized. On the basis of these observations, these authors could show that Henry Seamount is an extinct early Cretaceous age volcano that is unrelated to the Canary hotspot (cf. Geldmacher et al., 2005) but shows low-temperature hydrothermal activity of Holocene age. They suggested that seawater infiltrated through basement outcrops of El Hierro's submarine flank, migrated and became heated within the oceanic crust to finally discharge at Henry Seamount. To test this hypothesis, we explored the seamount and the surrounding area in 2018 during R/V METEOR cruise M146 by high-resolution reflection seismics, heat flow determinations using a 6 m long probe, high-resolution hydroacoustic mapping with an autonomous underwater vehicle (AUV), TV-sled surveys, and sediment sampling with a gravity corer and a Van Veen grab.

## METHODS

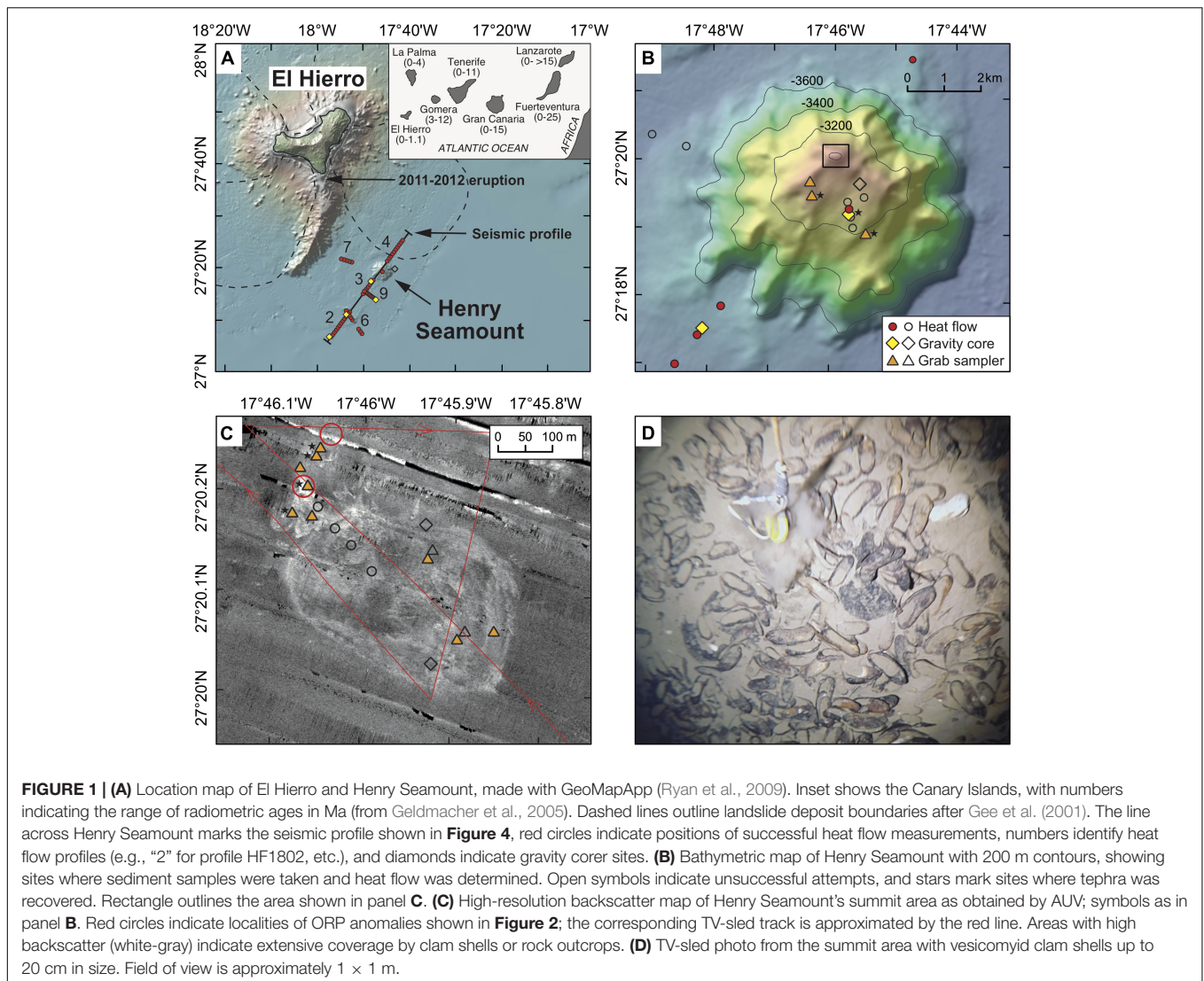
A description of the shipborne methods is given in Klügel and Shipboard Scientific Party (2018), and is summarized in the **Supplementary Material**.

Compositions of glasses from tephra and lava fragments were determined using a Cameca SX-100 electron microprobe (EMP) at the Department of Geosciences, University of Bremen. Glass was analyzed for major elements, S and Cl with an acceleration voltage of 15 kV, beam current of 40 nA, and a defocused beam of 15 μm diameter. Peak counting times were 60 s for sulfur and chlorine and 10 s for most other elements; background counting times were half as long. Minerals and glasses from the Smithsonian Institution (Jarosewich et al., 1980) were used for calibration. Sulfur was calibrated using pyrite because peak analyses indicated similar maxima positions for sulfides, basaltic glass standards and samples, hence a predominance of S<sup>2-</sup> speciation. Between two and seven EMP analyses were averaged for each glass sample. Analytical quality was monitored by repeated analyses of the glass standards VG-2 and VG-A99 (Smithsonian) and BHVO-2G and BCR-2G (USGS; Jochum et al., 2005) along with the samples. Precision of sulfur analyses was 3.5% for a concentration around 1400 ppm (VG-2), and 18% for a concentration around 150 ppm (VG-A99).

## RESULTS

### Seafloor Observations

A major discovery of cruise M146 was the widespread occurrence of dead vesicomid clams in the summit area and the flanks of Henry Seamount. Locally, the seafloor is completely covered with shells, such that their distribution is very recognizable as prominent backscatter on high-resolution hydroacoustic maps (Figures 1C,D). Most clam shells belong to the genus *Abyssogena southwardae*, resembling those previously dredged at the seamount (Klügel et al., 2011). These clams live in symbiosis with sulfide-oxidizing bacteria at hydrothermal vents and cold seeps at >2980 water depth (Krylova et al., 2010), and have thus far not been reported elsewhere from the Canary Archipelago.

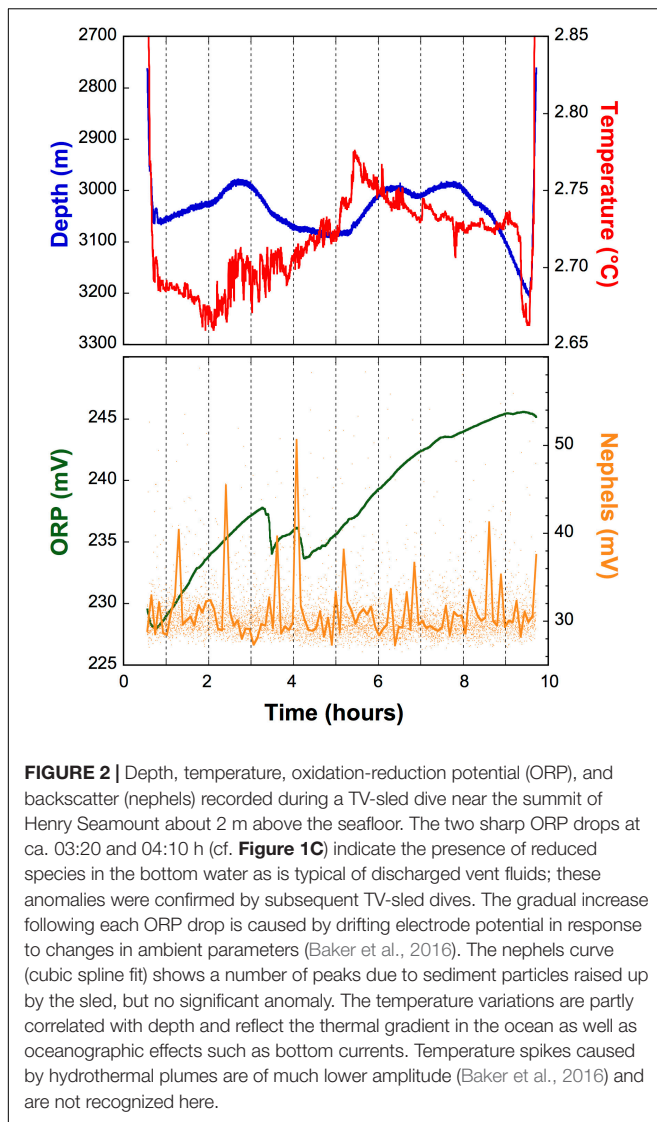


*A. southwardae* has a wide distribution in the Atlantic including the Logatchev hydrothermal vent area, the Vema Fracture Zone, the Wideawake hydrothermal field, off Barbados, and offshore Virginia (Krylova et al., 2010). Preliminary radiocarbon ages for some of the recovered shells from Henry Seamount are consistent with the age range previously reported (Klügel et al., 2011). Many of the shells have a black coating of presumably manganese oxides, which is additional evidence that these vesicomid communities are long dead. Living clams were not observed by the TV-sled, but grab samples showed some small-sized (<1 cm) chemosymbiotic thyasirid bivalves of the genus *Ochetoctena tomasi* with preserved inner soft tissues, which appear to have been alive prior to sampling (Krylova, personal communication). In the vicinity of some shell fields, the MAPRs on the TV-sled repeatedly recorded significant negative oxidation-reduction potential (ORP) anomalies a few meters above the seafloor (**Figure 2**). These anomalies are sensitive indicators for discharge of fluids with reduced chemical species (de Ronde et al., 2014; Baker et al., 2016), and indicate that hydrothermal flow at Henry

Seamount is still ongoing. Associated thermal anomalies are lacking, probably because their amplitude is too small as to be observed (cf. Baker et al., 2016).

## Basaltic Samples

Six grab samples and one gravity core from the Henry Seamount summit area (**Figures 1B,C**) recovered basaltic tephra (heterolithic coarse ash to small lapilli) and some dispersed basaltic rock fragments up to 4 cm in size. The tephra seems to be widespread on the plateau, with sample localities up to 2 km apart. It was covered by up to ~20 cm of pelagic sediment, and in some samples was weakly cemented. The mixture of different lithologies suggests that it has been reworked. Several tephra and rock fragment lithologies can be distinguished based on matrix and phenocryst assemblages. Glassy fragments with fresh sideromelane are prevalent; a few samples show incipient alteration on rims or cracks. Vesicularity varies from zero to about 50%; most vesicles are <1 mm in size. The dominant tephra lithology, denoted as ash type 1, consists of vesicular



**FIGURE 2** | Depth, temperature, oxidation-reduction potential (ORP), and backscatter (nephels) recorded during a TV-sled dive near the summit of Henry Seamount about 2 m above the seafloor. The two sharp ORP drops at ca. 03:20 and 04:10 h (cf. **Figure 1C**) indicate the presence of reduced species in the bottom water as is typical of discharged vent fluids; these anomalies were confirmed by subsequent TV-sled dives. The gradual increase following each ORP drop is caused by drifting electrode potential in response to changes in ambient parameters (Baker et al., 2016). The nephels curve (cubic spline fit) shows a number of peaks due to sediment particles raised up by the sled, but no significant anomaly. The temperature variations are partly correlated with depth and reflect the thermal gradient in the ocean as well as oceanographic effects such as bottom currents. Temperature spikes caused by hydrothermal plumes are of much lower amplitude (Baker et al., 2016) and are not recognized here.

sideromelane fragments with olivine phenocrysts  $\pm$  plagioclase and rare clinopyroxene microlites (**Figure 3A**). Most fragments are angular and equant; flat bubble wall fragments similar to limu o Pele are rare. Type 1 and other glassy ash fragments closely resemble pyroclasts from deep-sea strombolian or hawaiian eruptions of volatile-rich magma (Clague et al., 2003; Eissen et al., 2003; Davis and Clague, 2006). By contrast, microlite-rich angular ash particles and larger rock fragments with flow texture appear to be derived from submarine lava flows.

The samples are dominantly alkalic to transitional basalts with major element compositions similar to subaerial and submarine whole-rock samples from El Hierro (**Figure 3B**). The sulfur contents of matrix and interstitial glasses from Henry Seamount (250–960 ppm) overlap with the range for glasses from submarine El Hierro samples (430–1480 ppm) but barely grade into that for subaerial glasses (<290 ppm). Glasses from ash type 1 consistently have the highest sulfur and lowest alkali and phosphorus contents of all Henry Seamount samples (**Figure 3**).

## Heat Flow and Seismic Data

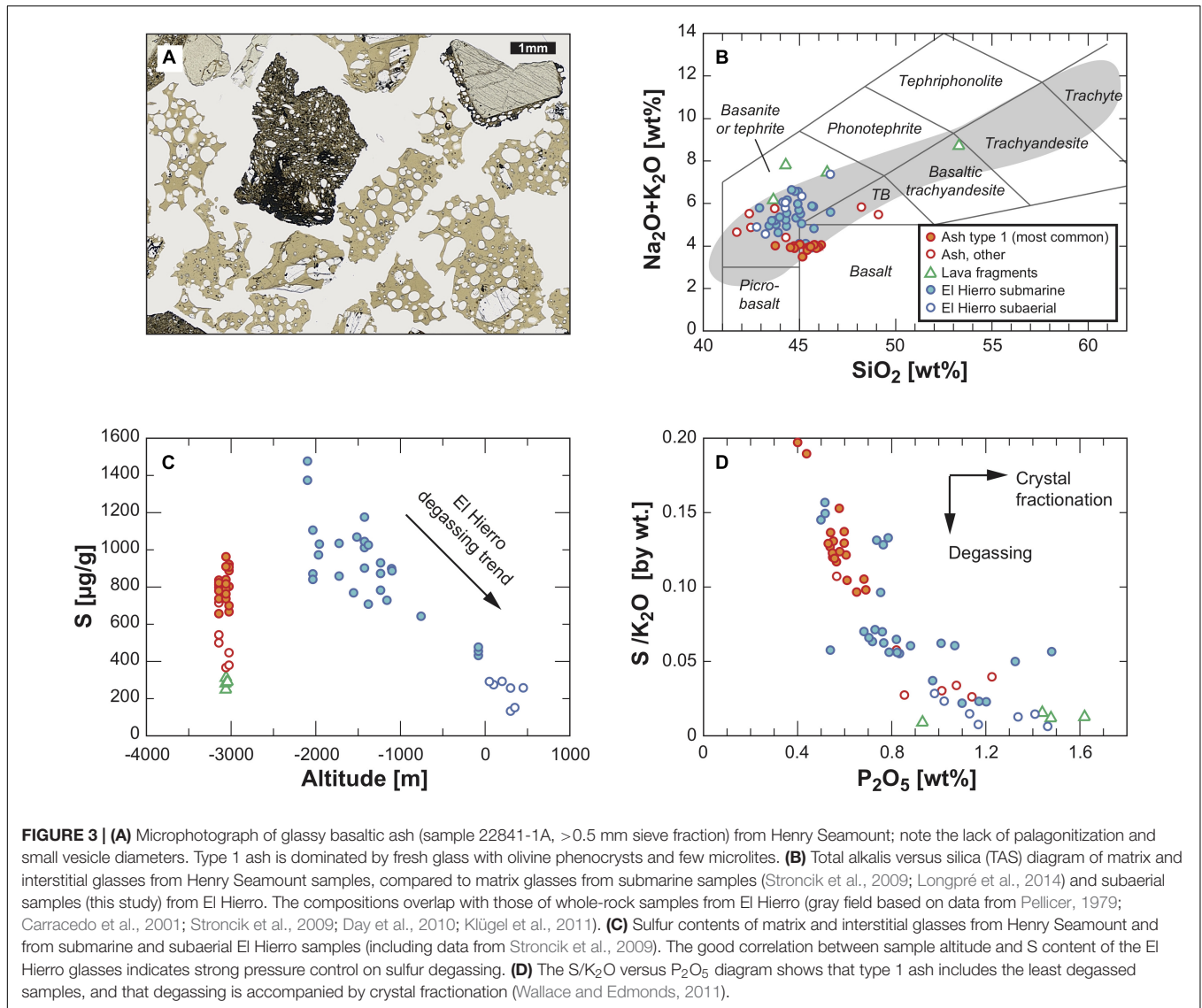
In order to establish the hydrogeological regime around Henry Seamount, we determined the heat flow distribution along lines co-located with seismic profiles, using a 6-m-long heat probe penetrating the sediment (**Figure 1A**). With one exception, all heat flow values are between 35 and 65 mW/m<sup>2</sup> with an average of  $49 \pm 7$  mW/m<sup>2</sup> ( $\pm 1$  sigma), close to the value of 53 mW/m<sup>2</sup> predicted by conductive cooling of 155 Ma crust (Hasterok, 2013). Thus, there is no increased basal heat flow despite the proximity to the Canary hotspot. The highest value of 83 mW/m<sup>2</sup> was obtained at the summit region of Henry Seamount, where only one successful measurement could be achieved (**Figure 4B**). This value is subject to some uncertainty because the heat probe penetrated the sediment by only 2.5 m, thus the heat flow may be affected by local variation in sediment thickness, or erosional events. Conversely, purely conductive heat flow should decrease on top of a topographic high because isotherms would be spaced farther apart (Harris et al., 2004; **Figure 4C**). We cautiously suggest, therefore, that the elevated heat flow at the summit is real and that is related to the inferred hydrothermal activity.

A 50 km long SW-NE seismic and heat flow traverse across Henry Seamount (**Figure 4**) shows some heat flow variations, but no robust trend indicative of fluid recharge or discharge comparable to other hydrothermally active seamounts (Fisher and Harris, 2010). The most noticeable patterns is a weak gradual increase in heat flow toward the southwestern base of the seamount over a 5 km distance (**Figure 4B**). Overall, the seismic section reveals different sediment structures SW and NE of Henry Seamount, which is reflected in the heat flow patterns as well. For example, most heat flow values in the well-stratified sediments to the SW are slightly below the predicted value of 53 mW/m<sup>2</sup>, whereas those to the NE are systematically higher (**Figure 4B**). In the SW, locally elevated heat flow values coincide with zones of seismic amplitude blanking (**Figure 4A**), i.e., reduction of the amplitude of seismic reflections caused, e.g., by the presence of gas hydrates (Lee and Dillon, 2001). A prominent blanking zone 10 km southwest of the seamount summit shows upward bending of adjacent reflectors, resembling doming linked to deeper magmatic intrusions and related hydrothermal activity (Berndt et al., 2016; Medialdea et al., 2017). This feature seems to be rather old because the overlying reflectors are not bent; it is also not accompanied by a heat flow anomaly (**Figure 4B**). The sediments to the NE of the seamount are characterized by strong reflectors in the upper 100 ms two-way travel time (TWT) with a hummocky surface, underlain by an almost transparent seismic unit (**Figure 4A**). This is indicative of mass transport deposits, and coincides with the extent of the >175 ka San Andres slump identified by Gee et al. (2001; **Figure 1A**).

## DISCUSSION

### Origin of Basaltic Samples

The recovery of fresh basaltic samples on a Cretaceous volcano raises the question whether this material originates from Henry Seamount itself, or from an adjacent volcano, with El Hierro

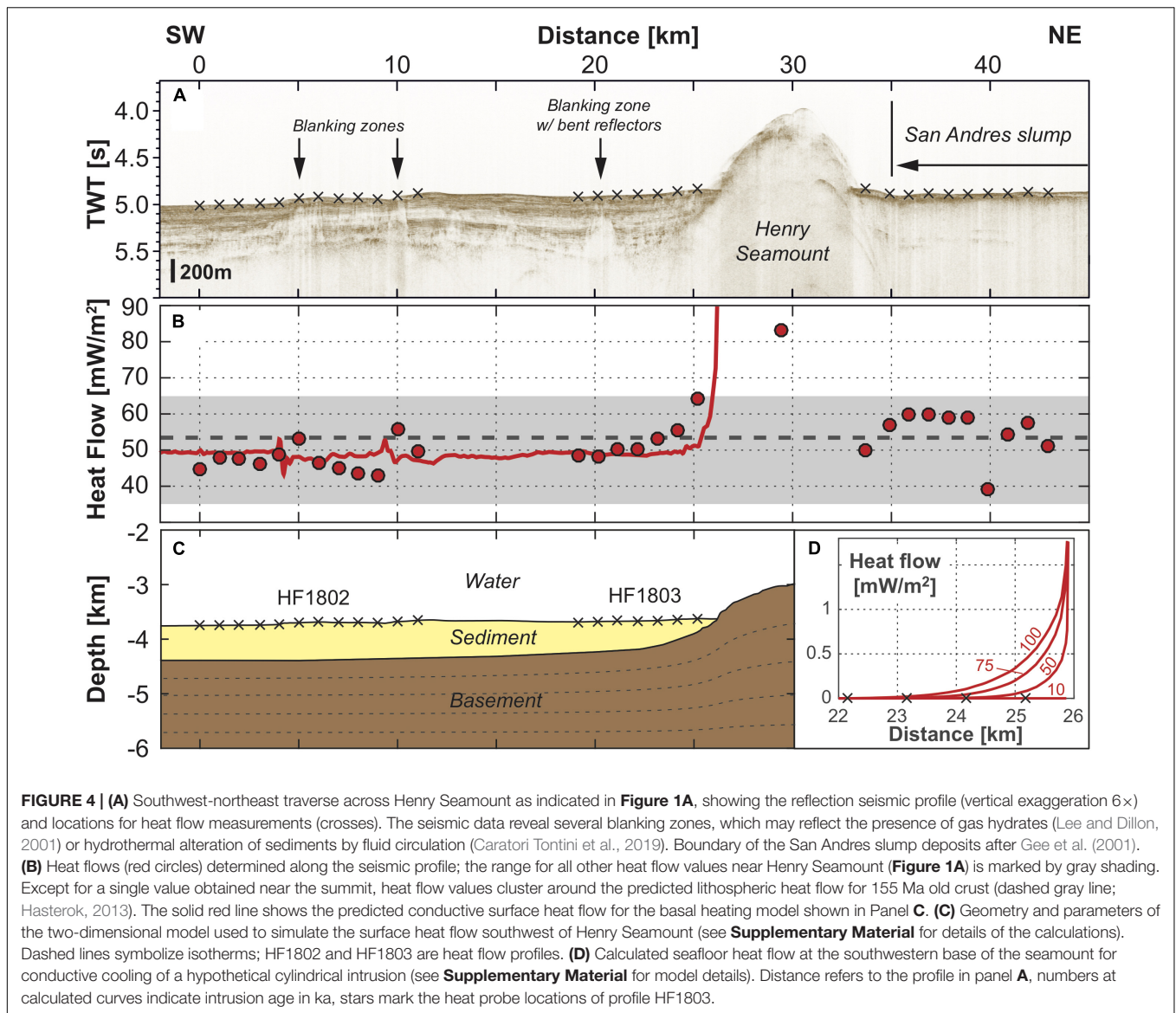


being the only plausible source. For type 1 ash, an origin from El Hierro is unlikely for two main reasons. Firstly, the ash layer was found only on top of Henry Seamount but not in gravity cores in its vicinity (Figure 1), as would be expected if the ash represented a fallout or a mass flow deposit from El Hierro. Secondly, sulfur concentrations in type 1 ash glass are significantly higher than in subaerial or shallow submarine glasses from El Hierro. Sulfur contents strongly depend on melt degassing (Wallace and Edmonds, 2011), and for El Hierro correlate well with eruption depth (Figure 3C). Although S concentrations in Henry Seamount samples are below the El Hierro trend, which extrapolates to >1600 ppm at 3000 m depth, a plot of S/K<sub>2</sub>O versus K<sub>2</sub>O or P<sub>2</sub>O<sub>5</sub> shows that type 1 ash glass is actually the least degassed, consistent with a deep submarine origin (Figure 3D). This plot discriminates between crystal fractionation and degassing processes, because S, K, and P are incompatible and maintain their ratios during mantle melting and crystallization (Wallace and Edmonds, 2011).

In contrast to type 1 ash, other basaltic samples from Henry Seamount appear to be more degassed than expected for a 3000 m water depth (Figures 3C,D). Glassy lava fragments have S and S/K<sub>2</sub>O values similar to subaerial samples, which however does not rule out a submarine origin (cf. Davis et al., 1991). If derived from El Hierro, it is not clear how the dense fragments could have been transported to the top of Henry Seamount. Relocation by submarine mass flows appears unlikely. El Hierro's last giant flank collapse toward the southeast occurred at ca. 145 ka (Gee et al., 2001), thus the presence of fresh fragments >600 m above the adjacent seafloor can hardly be reconciled with this event.

## Evidence for Rejuvenated Volcanism

The combined data strongly suggest that type 1 ash, and probably most other basaltic samples as well, originated from Henry Seamount. The age of the samples is not known, but the freshness of the glass and very limited vesicle fillings clearly exclude a genetic relation to the 126 Ma trachytes from



the seamount (Klügel et al., 2011). By comparison to 0.12–0.65 Ma glassy mid-ocean ridge basalts that show incipient palagonitization (Schramm et al., 2005), the unpalagonitized glassy samples are likely contemporaneous with the subaerial volcanic activity at El Hierro (<1.1 Ma; Guillou et al., 1996). The samples could be as young as the spatially associated clam shells and hydrothermal precipitates, i.e., a few ka to some tens of ka (Klügel et al., 2011). This would be consistent with <20 cm sediment coverage of ash observed in gravity core and grab samples, assuming a sedimentation rate of <7 cm/ka (Gee et al., 2001). In any case, the presence of fresh type 1 ash on top of Henry Seamount provides compelling evidence for one or more relatively recent eruptions of this otherwise Cretaceous volcano.

The limited recovery of ash in grab samples suggests one or more explosive low-volume eruptions, which may have produced a small vent with some tephra and little or no lava, rather

than a significant volcanic cone. Such low-volume deposits can be difficult to identify in the bathymetric data or by TV-sled, in particular when draped by sediment, or covered by benthic communities. This may explain why our bathymetric data do not indicate an obvious crater or volcanic cone. Despite the limited eruption volume inferred, the difficulty of sediment penetration by gravity core and heat probe in the summit region (**Figure 1C**) suggests that the sandy ash layer has considerable thickness in some places.

The cause for rejuvenated volcanism may be related to the large extent of the melting anomaly beneath the Canary hotspot combined with plate motion (Geldmacher et al., 2005). That is, considering that there was Holocene volcanic activity across the entire archipelago, from Lanzarote in the east to the youngest islands La Palma and El Hierro in the west, there is little reason why one or more eruptions should not occur 40 km southeast of El Hierro. Some of the magma

produced at the active end of the hotspot chain, which is not far from Henry Seamount, may have passed through a lithospheric region that was modified by the Cretaceous volcanism. Metasomatized mantle and mechanically weak zones may have focused further magma ascent, which eventually led to eruption just at the former volcano.

## Heat Flow Modeling

We now turn our attention as to what caused the observed heat flow to increase by  $16 \text{ mW/m}^2$  toward the southwestern base of Henry Seamount (**Figure 4B**). Plausible scenarios include (i) decreasing sediment thickness and thermal refraction, (ii) cooling of a magmatic intrusion within the seamount, or (iii) advective heat transport by hydrothermal circulation. To assess the influence of sediment thinning close to the seamount (i), we set up a steady-state conductive finite element model with axial symmetry and the seamount center as midpoint (**Figure 4C**); see the **Supplementary Material** for details of the calculations. The modeled surface heat flow is almost constant along the profile, and sharply increases toward the seamount flank (**Figure 4B**). However, the observed heat flow increase near the flank is well above the predicted increase for any realistic values of the model parameters. This shows that the thinning of the sediments cannot account for our observations and therefore, another heat source must be involved.

A second numerical simulation tested if conductive cooling of a hypothetical vertical intrusion in the center of the seamount could produce the observed heat flow increase (ii). We chose a vertical cylindrical intrusive body with a diameter of 100 m and initial temperature of  $1200^\circ\text{C}$ , extending from the top of the seamount downward (see **Supplementary Material**). This intrusion shape is not meant to imitate a natural basaltic intrusion, which would likely be a dike or sill of  $<100 \text{ m}$  thickness, but rather to illustrate the thermal effect of an extreme scenario. The model results show that in this case the increase in surface heat flow at the closest heat probe location would reach only  $0.4 \text{ mW/m}^2$  after 100 ka, well below the observed increase of  $16 \text{ mW/m}^2$  (**Figure 4D**). It would be far less for a meter-thick basaltic dike. A significant increase in surface heat flow would result only if an intrusion were located close to the measured profile, which is not supported by our observations, or if advective heat transport played a major role.

## Driver for Hydrothermal Activity

The results of our modeling suggest that the observed heat flow increase near the SW base of Henry Seamount cannot be explained by conductive cooling alone, but requires advective heat transport by hydrothermal circulation [model (iii) of above]. Compared to other hydrothermally active seamounts (Fisher and Harris, 2010), the heat flow increase is of small magnitude and lateral extent. This suggests a relatively recent origin and/or transient nature of hydrothermal circulation, with the sediments not having adapted to the thermal change at deeper levels. What is the driver for this flow? If the circulation represented ridge flank flow that is purely driven by seamount

relief and basal heat from the cooling lithosphere (Harris et al., 2004; Fisher and Wheat, 2010), then it should have lasted for a long time and still persist, as there is no obvious reason for flow rates to decrease. This would not explain why the chemosynthetic communities are mostly extinct and manifested as shell graveyards, and why obtained ages for all samples related to hydrothermal activity are  $<41 \text{ ka}$  (Klügel et al., 2011). Long-term basal heat from the nearby Canary hotspot cannot play a role for the same reason; in addition, our data do not show increased basal heat flow (**Figure 4B**). It is possible that relief-driven circulation plays a subordinate role at Henry Seamount, but its relative effect cannot be assessed from our limited data.

Our heat flow data and observed manifestations of hydrothermal discharge at the top of Henry Seamount are best explained by a scenario involving ephemeral periods of hydrothermal circulation. We propose that circulation was initiated, and is still driven, by weak pulses of rejuvenated volcanic activity that also produced the basaltic samples. The initial hydrothermal fluids probably were hot and sulfide-bearing, providing habitats for sulfur-oxidizing metabolisms and vesicomysids at the discharge sites. The decay of magmatic heat soon resulted in waning hydrothermal flow and extinction of the chemosynthetic communities; eventually a new magmatic event brought another heat pulse and renewed hydrothermalism. An ephemeral character of hydrothermal flow at Henry Seamount could also explain the low amount of hydrothermal deposits observed; thus far only local barite precipitates were found (Klügel et al., 2011). Considering the presumably low erupted volume at Henry Seamount and overall similarity to El Hierro lavas, the existence of a crustal magma reservoir is highly unlikely (cf. Klügel et al., 2015), hence, the magmatic heat must have been delivered from the volcanic deposits and/or a shallow dike. This scenario has some resemblance to the weak diffuse hydrothermal activity observed at the Lilliput field, southern Mid-Atlantic Ridge, which is thought to have resulted from a single diking event (Haase et al., 2009).

If the development of hydrothermal circulation and chemosynthetic communities at Henry Seamount was indeed a consequence of single magmatic pulses, then similar scenarios might be envisaged for many other volcanic seamounts in the deep ocean basins. Whether they are monogenetic or form by a succession of eruptions over a long period of time, each eruption has the potential to drive ephemeral hydrothermal activity (e.g., Medialdea et al., 2017; German et al., 2020), which may provide habitats for chemosynthetic communities. The same holds for the submarine flanks of volcanic islands that are often scattered with presumably monogenetic volcanic cones (e.g., Santana-Casiano et al., 2016). Detection of short-lived hydrothermal circulation is challenging, however, because the response of surface heat flow is weak and the sites may become increasingly blanketed by sediment after cessation of activity. Moreover, deep-sea chemosynthetic communities are not well preserved in the geological record (Krylova et al., 2010). As exploration of the deep sea is still very limited, Henry Seamount may be a rare example of a common feature rather than a special case.

## DATA AVAILABILITY STATEMENT

Readers can access our data on the Pangaea data base (<https://doi.pangaea.de/10.1594/PANGAEA.913552>), and the report of cruise M146 is available at [https://doi.org/10.2312/cr\\_m146](https://doi.org/10.2312/cr_m146).

## AUTHOR CONTRIBUTIONS

AK, HV, SK, and MR conceived the project. AK investigated the tephra samples and wrote most of the text. HV and NK collected and processed the heat flow data. SK and KFL collected and processed the seismic data. PW and MR collected and processed the multibeam data. All authors were actively involved in the discussion, interpretation of the data, and preparation of the manuscript.

## FUNDING

Our research was funded by the Deutsche Forschungsgemeinschaft (DFG, grant KL1313/18-1), and MR was funded by the DFG under Germany's Excellence Strategy – EXC-2077 – 390741603.

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## ACKNOWLEDGMENTS

We are grateful to Captain R. Hammacher, the crew and the shipboard scientific party of METEOR cruise M146 for excellent work, and the Leitstelle Deutsche Forschungsschiffe for overall support. We thank C. Hübscher (University of Hamburg) for kindly loaning us a sparkler array on short notice, S. Walker for providing MAPRs and advice, and G. Bohrmann and E. Krylova for helpful discussions. The constructive comments by R. Harris, C. de Ronde, and the reviewers are appreciated and improved the manuscript.

## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmars.2020.584571/full#supplementary-material>

**Supplementary Text |** Methods and parameters for the numerical modeling, and shipborne methods.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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