Enhanced weathering in the seabed: rapid olivine dissolution and iron sulfide formation in submarine volcanic ash

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Abstract. In basaltic volcanic ash recovered from a seamount at 3000 m water depth we discovered marcasite and pyrite precipitation within cavities that formed by partial to complete dissolution of olivine. In places, these cavities are reminiscent of negative crystal shapes, elsewhere they apparently continue along cracks. In strong contrast, adjacent volcanic glass shows little, if any, evidence for dissolution. The FeS2 precipitates were commonly found to be conjoined and planar aggregates, occurring in the center of the voids. Their maximum volume fraction in relation to the void space as determined by 2D and 3D imaging techniques corresponds to the amount of iron released by olivine dissolution. Almost all occurrences of FeS2 precipitation are related to Cr-spinel
inclusions in the former olivine. We propose that rapid olivine dissolution was initiated
by reduced, H₂S-bearing fluids at olivine grain boundaries or surfaces exposed by cracks.
Many of these cracks are connected to spinel grains, where the iron liberated from olivine
is mineralized as FeS₂, initially facilitated by heterogeneous nucleation. Subsequent
pyrite and/or marcasite precipitation occurred as overgrowth on existing FeS₂ aggregates.
The particular chemical environment of low-pH, hydrogen sulfide-bearing fluids may
have enhanced olivine dissolution by (i) keeping Fe in solution and (ii) sequestering
important quantities of Fe as FeS₂. The in-situ oxidation of ferrous Fe and precipitation of
ferric hydroxides at the olivine surface commonly observed in oxic environments was
obviously impeded. It would have slowed down olivine dissolution to rates more similar
to the dissolution of basaltic glass. We have no direct indication that the process of rapid
olivine dissolution was aided by subseafloor life. However, the presence of fibrous
structures with small sulfide particles could indicate a late colonization of sulfate-
reducing bacteria that may add an additional path of iron fixation.

**Keywords:** Olivine, pyrite, marcasite, seamount, Canary Islands, dissolution, alteration,
X-ray microscopy

**INTRODUCTION**

Iron sulfide formation pathways are commonly linked to the degradation of organic
matter (see Roberts, 2015, and references therein). Examples include macroscopic iron
sulfide nodules as remineralization of large-scale sedimentary organic matter fragments
(Jiang et al., 2001), or formation of microscopic iron sulfide aggregates formed by
remineralization of organic matter within microfossil chambers (Passier et al., 1997;
Sulfidic environments, iron-bearing detrital minerals undergo drastic alteration (see review of Roberts, 2015): hydrogen sulfide, which in many near-surface geochemical environments is a byproduct of bacterial sulfate reduction or anaerobic oxidation of methane, reacts with $\text{Fe}^{2+}$ released from detrital minerals by dissolution to form iron sulfide minerals (mackinawite, greigite, and pyrite). It is not uncommon that marcasite ($\text{FeS}_2$, orthorhombic) or pyrite ($\text{FeS}_2$, cubic) replace greigite ($\text{Fe}_3\text{S}_4$, cubic) and mackinawite ($\text{(Fe,Ni)}_{1+x}\text{S}$ ($x = 0-0.07$), tetragonal) when an excess of $\text{H}_2\text{S}$ is present (Hunger and Benning, 2007; Posfai et al., 1998; Roberts, 2015).

To our knowledge, the presence of sulfides connected with intense dissolution of olivine in a submarine volcanic setting has not been described so far. It is unclear, if this is a consequence of sparse sampling or of limited preservation of the appropriate boundary conditions for sulfide formation / conservation in this particular geological setting.

This communication seeks to unravel the formation of a striking reaction texture of $\text{FeS}_2$ within cavities in olivine phenocrysts, observed in glassy basaltic tephra from a seamount near the Canary Islands, Spain. While many of these cavities are reminiscent of negative shapes of their crystal host, elsewhere these voids appear to continue and broaden along cracks. Notably, the delicate $\text{FeS}_2$ precipitates hardly extend into the surrounding matrix of volcanic glass. We employ 2D and 3D spectroscopic methods to decipher mineral compositions and growth relations, and thermodynamic/kinetic computations to elucidate potential conditions and mechanisms of this reaction texture. Finally, we assess whether a microbial contribution to this process of olivine dissolution and iron sulfide formation is essential at all.
GEOLOGICAL SETTING

The samples were recovered from Henry Seamount, a Cretaceous volcanic edifice 40 km southeast of El Hierro island, rising \( \sim 700 \) m above \( \sim 3700 \) m deep ocean floor (Fig. 1) (Gee et al., 2001; Klügel et al., 2011). The seamount was investigated and sampled during R/V Meteor cruises M66/1 and M146, which provided evidence for Pleistocene to present hydrothermal fluid circulation in the summit region. This evidence includes locally dense coverage by shells from vesicomyid clams, occurrence of authigenic barite, and localization of sites of weak fluid venting (Klügel et al., 2011; Klügel et al., 2020). Most clams belong to the genus *Abyssogena southwardae*, which live in symbiosis with sulfide-oxidizing bacteria and are mostly buried in \( \text{H}_2\text{S} \)-rich sediment at hydrothermal vents and cold seeps (Krylova et al., 2010). Overall, the summit area of the seamount is variably covered by pelagic sediment.

Some samples from the top of the seamount contain heterolithologic basaltic tephra and dispersed basaltic rock fragments, suggesting rejuvenated volcanic activity (Klügel et al., 2020). The tephra occurrences are commonly associated with clam shells, and basaltic ash from one sample released \( \text{H}_2\text{S} \) during recovery on-board. The samples investigated here represent the dominant lithology of an ash layer overlain by 10-13 cm of pelagic sediment, recovered by gravity coring at 3145 m water depth; similar observations were also made in ash samples from two other sites. A detailed description of this core (sample 22841-1) and the other samples is given in Klügel et al. (2018).
Detailed fabric inspections of single fragments were performed on a field emission scanning electron microscope (SEM) Zeiss SUPRA 40 with a Bruker EDS-detector XFlash 6|30 operated at 15 kV. Mineral analyses and fabric inspections of polished thin sections of stray samples were performed on a Cameca SX-100 electron probe microanalyzer (EPMA) at the Department of Geosciences, University of Bremen. Olivine was analyzed with 15 kV / 30 nA, spinel with 15 kV / 15 nA, and sulfide with 20 kV / 20 nA, using a focused beam in all cases. Calibrations used natural minerals from the Smithsonian Institution (Jarosewich et al., 1980), in-house standards, and pure elements (Ni, Co); the built-in PAP correction was applied for data reduction. Analytical precision and accuracy were controlled by regular analyses of Smithsonian reference standards along with the samples (see Table 1 for average olivine, spinel and sulfide analyses, and Table S1-3 in supplementary online material for individual analyses).

Stokes Raman spectra were collected at different locations of the polished section of sample 22841. The spectra were recorded on a LabRam ARAMIS (Horiba Jobin Yvon) Micro-Raman spectrometer equipped with a laser working at 633 nm and less than 20 mW output. The use of a 50x objective (Olympus) with a numerical aperture of 0.75 provides a focus spot of about 1 µm diameter when closing the confocal hole to 200 µm. By usage of a neutral density filter (setting D1, 90% reduction) the laser power on the sample surface was estimated to be about 0.33 mW. Raman spectra were collected in the range between 100 cm⁻¹ and 1000 cm⁻¹ with a spectral resolution of approximately 2 cm⁻¹ using a grating of 1800 grooves/mm and a thermoelectrically cooled CCD detector.
The Rayleigh position and the linearity of the spectrometer were calibrated against the silicon signal and the emission lines of a neon lamp, respectively.

For 3D X-ray microscopy (XRM), two particles (olivine single grain: sample 22841-1A-SG; olivine multiple grains aggregate: 22841-1A-MGA) were glued by nail polish onto the tip of a graphite pencil mine. Both particles were scanned in 360° rotation scans conducted with the 3D X-ray microscope ZEISS Xradia 520 system of the MAPEX Center for Materials and Processes, University of Bremen, Germany. Particle 22841-1A-SG was scanned in overview mode with 1.30 µm per voxel and a beam energy of 90 kV and an energy flux of 89 µA (and ZEISS filter LE3), and a smaller volume of interest (VOI) of this sample was scanned with 0.36 µm per voxel (90 kV, 89 µA, filter LE3). Particle 22841-1A-MGA was scanned in overview mode with 2.44 µm per voxel (60 kV, 83 µA, filter LE3), and a smaller VOI was scanned with 0.78 µm per voxel (80 kV, 88 µA, filter LE3). Correction of ring artefacts and reconstruction of the spatial information on the linear attenuation coefficient in the samples was done using the ZEISS Reconstructor software. For each particle, an image volume of ca. 1000 x 1000 x 1000 voxels was available. All subsequent processing of volume data (e.g., rendering, filtering the raw data, segmentation, surface generation, 3D quantitative image analysis of iron sulfide volume fractions) was done using Avizo 2019 (FEI). For visualization of volume reconstructions and single slices, the Avizo filter module RekursiveExponential was used in 3D mode; for quantitative 3D image analyses of void and iron sulfide volume, prior to segmentation and binarization, this step was followed by a Non-LocalMeans filtering in 3D mode. Avizo module AmbientOcclusion was chosen to discriminate cavities inside
volcanic ash particles from the surrounding region (Titschack et al., 2018). Avizo was also used to determine the volume fractions of iron sulfide in 2D electron microprobe BSE images.

In the reaction path modeling, volcanic glass, olivine, and organic carbon were reacted with seawater at 5°C using Geochemist’s Workbench 7.0 (Bethke, 1996). The system had 1 kg of seawater, 10 g of glass, 2 g of olivine, and 0.1 g of organic carbon. This high water-to-rock ratio was chosen to reflect the porous nature of the tephra layer in the shallow seabed. Graphite represents organic carbon, while fayalite represents olivine in the model. The reaction rates were assumed to be slowest for glass ($10^{-16}$ mol cm$^{-2}$s$^{-1}$), fastest for organic carbon ($5 \times 10^{-13}$ mol cm$^{-2}$s$^{-1}$) and intermediate for olivine ($10^{-15}$ mol cm$^{-2}$s$^{-1}$). These rates are reflecting experimental constraints on the reaction rates of olivine and basaltic glass at neutral pH (Oelkers et al., 2018; Oelkers and Gislason, 2001). We used rates lower than the ones measured at 25°C to account for the lower temperature (5°C). Empirical observations of breakdown rates of moderately old (100-1000 yrs) organic matter in seafloor sediments (Middelburg, 1989) was used to approximate graphite dissolution rate in the model. Thermodynamic data of minerals and aqueous species are from SUPCRT92 [Johnson et al. (1992) with updates from Wolery and Jove-Colon (2004)]. The thermodynamic properties of the volcanic glass were computed using a polyhedral approach for the average composition of sample 22841-1A (Klügel et al., 2020). Gibbs energies, entropies, volumes, and Maier-Kelly coefficients of the constituent oxides were taken from Helgeson et al. (1978) and updates in Wolery and Jove-Colon (2004). Equilibrium constants for dissolution reactions of the model glass
composition were computed using aqueous species data from SUPCRT92 (Johnson et al., 1992) for a pressure of 25 MPa.

RESULTS

Petrography and microfabric on the grain scale

The ash particles investigated here consist of fresh glass of alkali basaltic composition with olivine phenocrysts (termed ash type 1 in Klügel et al., 2020). Olivine is euhedral to subhedral, up to 2 mm in size, and occurs isolated or in clusters. The crystals show a narrow compositional range of $\text{Fo}_{79.5-82.6}$ (average $\text{Fo}_{81.5})$, 0.23-0.39 wt% CaO, 0.18-0.31 wt% NiO, and no systematic zonation (Table 1). They contain inclusions of spinel with $\text{Cr#} = \text{molar Cr/(Cr+Al)}$ of 0.45–0.53, $\text{Mg#} = \text{molar Mg/(Mg+Fe}^{2+})$ of 0.39–0.50, and $\text{Fe}^{3+}/\text{Fe}^{tot}$ of 0.40-0.45 (Table 1); occasional spinel microphenocrysts in the glass, and within iron sulfide precipitates, have similar compositions. By using the glass analyses in Klügel et al. (2020) and the $\text{Fe}^{2+}$-Mg partition coefficient between olivine and melt after Toplis (2005), we obtain a melt $\text{Fe}^{3+}/\text{Fe}^{tot}$ ratio of 0.34.

Many olivine phenocrysts show pronounced development of iron sulfide within cavities inside the crystals (Figs. 2b and c). In places, these cavities are reminiscent of negative crystal shapes (Fig. 3a and b), elsewhere they apparently continue along cracks. Similar sulfide formation, albeit far less common and less intense, is found along cracks in some clinopyroxene phenocrysts in lithologically different ash fragments (Fig. 2a).

Where cavities meet both olivine and host glass, SEM investigations revealed very limited dissolution features of the glass (Fig. 3b and c). In some cases, cavities clearly
discernible as negative shapes of olivine crystals are entirely devoid of olivine material (Fig. 4a, c). Even in these cavities, iron sulfide precipitation does not appear to be irregular, but organized in relation to initial cracks or microfissures in the former olivine host.

Microprobe analyses of the sulfides (Table 1) indicate FeS$_2$ stoichiometry with some Fe replaced by Ni (0.35-0.87 wt%) and Mn (0.39-1.84 wt%). The serrate characteristic of many sulfide crystal shapes in SEM images (Fig. 3) clearly point to marcasite, forming conjoined, planar aggregates with a bead chain aspect in profile. Within olivine crystals affected only by incipient dissolution, FeS$_2$ aggregates can be observed in the center of narrow voids in relation to initial cracks or microfissures (Fig. 4b). Inside larger dissolution cavities in olivine, or where olivine was completely dissolved, FeS$_2$ precipitation is also organized as chains or planar aggregates, and does not occur deliberately anywhere on a free olivine or glass surface (Figs. 3-4, Fig. 5). In places, where aggregates of several olivine grains are surrounded by glass matrix (Fig. 4a and b), XRM reveals that cavities in these associated grains may be multiply connected and form a complex pore network (Fig. S1, supplementary online material).

The baseline-corrected and normalized Raman spectra of FeS$_2$ analyzed at selected locations of the polished thin section are displayed over the 200 to 600 cm$^{-1}$ spectral range in Fig. 6. Following Vogt et al. (1983) and Lutz and Müller (1991), and considering the measured spectral resolution, the assignment of Raman bands to symmetry modes for pyrite (Py) and marcasite (Mrc) has been made as follows: 324 cm$^{-1}$ (combined $A_g^{\text{Mrc}}$, $B_{2g}^{\text{Mrc}}$, and $B_{3g}^{\text{Mrc}}$), 343 cm$^{-1}$ ($E_g^{\text{Py}}$), 350 cm$^{-1}$ ($T_{g}^{\text{Py}}$), 378 (combined $A_g^{\text{Py}}$ and $T_{g}^{\text{Py}}$), 388 cm$^{-1}$ ($A_g^{\text{Mrc}}$), 398 cm$^{-1}$ ($B_{1g}^{\text{Mrc}}$), 430 cm$^{-1}$ ($T_{g}^{\text{Py}}$), 448 cm$^{-1}$ ($B_{1g}^{\text{Mrc}}$). The integrated area
under the bands at about 324 cm\(^{-1}\) and 343 cm\(^{-1}\), respectively, was used to distinguish between pyrite and marcasite. Moreover, considering that their differential Raman scattering cross sections are similar, a quantitative approach has been performed.

The Raman spectra reveal the presence of both pyrite and marcasite in most of the analyzed locations (Fig. 6, fit results are given in Table 2). Pure pyrite spectra were observed in at least two locations (G1-11 and G1-14, Fig. 6b and c, respectively). A pure marcasite phase was not identified within the investigated locations of the grains. However, at G2-01 (Fig. 6d) shows that the location is comprised of about 97% marcasite along with a minor (3%) pyrite phase fraction.

**Relation between cavity volume and iron sulfide content**

Cavities completely filled with iron sulfide were not observed in any olivine. By means of 2D (derived from BSE images, Fig. 7a-e) and 3D (derived from reconstructed XRM image volumes, Fig. 7f) quantitative digital image analysis, iron sulfide contents in voids within olivine single crystals were found to range between 17.4 area\% and 24.0 area\%, and between 18.1 and 19.4 vol\%. XRM analysis of the second sample (supplementary Fig. S1), an aggregate consisting of several attached olivine grains surrounded by a glass matrix, revealed an uneven distribution of iron sulfide precipitation. The volume fraction of iron sulfide in the largest void, extending over six olivine crystals, reached only 4.2 vol\% (Fig. 7g\(_1\)). In comparison, a high-resolution scan of a region within the same aggregate reveals a degree of iron sulfide void filling of 10.1 vol\% (Fig. 7g\(_2\)). Altogether, the iron sulfide precipitation in the pore space of the olivine
grain aggregate is substantially less than what was observed in voids within olivine single crystals hosted in other particles (see Table 3).

Fabric relation of iron sulfide and spinel

Whereas olivine is largely affected by dissolution processes, the host glass shows only minor etch pits and spinel exhibits no indication of dissolution. Spinel occurring within the volcanic glass or in olivine material unaffected by dissolution mostly exhibits euhedral to subhedral morphology (Fig. 8a). Likewise, spinel situated within cavities displays the very same morphology, and is mostly overgrown by the iron sulfide precipitates (Fig. 4a, Fig. 5b, Fig. 8, and supplementary Fig. S3). Moreover, detailed observations of some sites visible in Figs. 4a, 8b, and S3 indicate that iron sulfide growth was not initiated as alteration of spinel rims to sulfide, but by overgrowth on the existing spinel surface.

Further potential nucleation sites of small sulfide particles

High-resolution 3D X-ray microscopy imaging (Fig. 8b) shows that small sulfide particles (1-2 µm) are also observed along and/or within filamentous stalks connecting cavity-centered, aligned sulfide aggregates of up to 20-60 µm diameter, analogous to the strand of a bead chain. The XRM image material (0.36 µm voxel size, compare scale information in Fig. 8b) depicts these stalks to be less X-ray attenuating than the volcanic glass, and more similar to void space. As the particles investigated by 3D X-ray microscopy were neither cut nor ground and hence did not suffer any stress during
sample preparation, the filamentous stalks could be preserved within the well-protected pore space inside the gravity core material in a desiccated manner. It is possible that these structures represent organic material; however, further investigations by e.g. Raman spectrometry cannot be carried out due to the inaccessibility of the interior of this particular ash particle.

**DISCUSSION**

**Chemical environment for olivine dissolution and iron sulfide formation**

Abundant FeS$_2$ precipitation within cavities created by olivine dissolution indicates the availability of reactive iron (likely derived from olivine dissolution) and sulfide in solution. Indeed, evidence of hydrogen sulfide at the sample sites is twofold: (i) the perception of hydrogen sulfide smell during sample recovery; and (ii) the spatial association of the samples to shells of vesicomyid clams on the top sediment layer. All known species of the genus *Abyssogena* have been observed in sulfide-rich habitats at hydrothermal vents and cold seeps (Krylova et al., 2010). Typically, *Abyssogena* live half-buried in the sediments, where the anterior part of the clam with the extendable foot has access to hydrogen sulfide.

Notably, the microfabric of FeS$_2$ precipitation within cavities resembling negative olivine crystal shapes indicates conditions of enhanced olivine dissolution. In contrast, volcanic glass adjacent to the olivine crystals was nearly unaffected by dissolution processes. Generally, basalt glass is observed to dissolve slightly more slowly (ca. $10^{-12}$ mol cm$^{-2}$ s$^{-1}$ at pH 3, and ca. $10^{-15}$ mol cm$^{-2}$ s$^{-1}$ at pH 6) (Flaathen et al., 2010; Gislason...
and Oelkers, 2003; Oelkers and Gislason, 2001) than olivine (ca. $10^{-12}$ mol cm$^{-2}$ s$^{-1}$ at pH 3, and ca. $10^{-14}$ mol cm$^{-2}$ s$^{-1}$ at pH 6) (Oelkers et al., 2018; Rimstidt et al., 2012) at 25°C and under oxic conditions. In contrast, the chemical environment of reducing, low-pH, sulfide-bearing fluids may enhance olivine dissolution by keeping Fe in solution and sequestering important quantities of Fe as FeS$_2$. Under these conditions in-situ oxidation of ferrous Fe and precipitation of ferric hydroxides at the olivine surface are impeded. These two processes may lower olivine reactivity and cause inhibition of olivine dissolution under oxic conditions (Gerrits et al., 2020). Similarly, experimental simulations by Wiggering et al. (1992) showed that subaqueous weathering under a CO$_2$-rich, H$_2$S-bearing, hypothetical Archean atmosphere was much more intense than under today's conditions: in this acidic environment, ferrous iron released by dissolution remained in solution. The effect of the addition of H$_2$S to fluids on silicate dissolution has been explored by Stefánsson et al. (2011) to simulate sequestration of H$_2$S into wastewater to be reinjected into the geothermal system Hellisheidi, Iceland. Their reaction path modelling showed that the accompanying decrease in pH resulted in undersaturation of Al-bearing silicates, but supersaturation with respect to sulfides.

As elements other than Fe were removed during olivine dissolution, the question arises whether the Fe in the precipitated FeS$_2$ was inherited entirely from the dissolved olivine material. A simple mass balance shows that complete fixation of Fe should result in ca. 20 vol% FeS$_2$ filling of the cavity created by olivine dissolution (Fo$_{81.5}$). Analyses of BSE images revealed iron sulfide fillings between 17.4 and 24.0 percent by area (Fig. 7a-e, and Table 3), and analyses of two cavities inside an olivine single crystal using reconstructed XRM scans yielded 18.1 and 19.4 volume percent, respectively. These
results suggest that dissolution of olivine has provided all iron necessary for iron sulfide formation nearly in-situ inside olivine cavities (Fig. 7f). Notwithstanding, a highly-connected cavity spanning over several grouped olivine crystals exhibits far less than maximum iron sulfide fixation: Figure 7g depicts low 4.2 vol% iron sulfide precipitation within the entire pore network, increasing to 10.1 vol% within a restricted region. Apparently, not all Fe deliberated from dissolved olivine was fixated by iron sulfide precipitation.

Although the serrate crystal shapes of the iron sulfides point to marcasite precipitation from solution, the coincident presence of pyrite in most places (Fig. 6) indicates a more complex FeS₂ fixation history. Locally, pyrite makes up a very high phase fraction in the Raman spectra of the analyzed spots. While we could not find a systematic relation between marcasite/pyrite ratios and petrographic features such as void size or crack width, our data suggest that domains with high proportions of pyrite are co-located with spinel (e.g., G-13 and G-14, Fig. 6c). In some locations concomitant red/blue-shift of the frequencies has been observed for both phases irrespective of their proportion. For instance, whereas the fitted frequencies at G1-11 correspond to those observed by Vogt et al. (1983), a general blue shift has been identified at G1-14 (see supplementary Fig. S2). The corresponding higher frequencies with broader line shape at G1-14 in general can be explained by slightly different unit cell dimensions and, rather likely when considering the geochemical environment of our investigated samples, by a spread in the distribution of degree of crystallinity and average crystallite size. Of note, Bryant et al. (2017) suggested that red shift of band positions can be associated with laser-induced heating during Raman investigations, and that variations in the ratios of band intensities can arise
due to differing crystallographic orientations of the Raman locations with respect to the laser’s dominant polarization plane.

Can the observation of co-existing pyrite and marcasite be related to phase transformations induced by Raman laser heating? Xi et al. (2019) discussed such thermal transformation, and found that the minimum laser power for these reactions to occur is 2.87 mW (see their Fig. 6 and related text). In contrast, our Raman investigations were carried out with a substantially reduced the laser power on the sample surface of about 0.33 mW (by usage of a neutral density filter, see methods section). Moreover, during the measurements, we could not observe any change of either intensity of a given band or appearance/disappearance of any band. For these reasons we can exclude transformation induced by laser heating during our Raman analyses. However, variable proportions of Mrc and Py in the sulfide aggregates of the present study could be related to marcasite to pyrite transformation at hydrothermal conditions. In a recent study of an interface-coupled dissolution-reprecipitation reaction involving pyrrhotite, Yao et al. (2021) observed that Mrc to Py transformation in small particles (< 100 nm) can occur within a few months at 210 °C, a pH of 1, and a high sulfide saturation index. Although we do not know how these conditions relate to those of our study, the experiments of Yao et al. (2021) suggest that post-crystallization transformation of marcasite to pyrite may have contributed to the variable Mrc and Py proportions observed by us.

Commonly, marcasite is associated with iron sulfide formation at lower pH than estimated for pyrite formation (recently summarized in (Yao et al., 2021; Yao et al., 2020)). Precipitation of marcasite from hydrothermal solutions has been observed in experimental studies at pH values of 5 or lower (Murowchick and Barnes, 1986;
Schoonen and Barnes, 1991). However, in more complex experimental environments or natural systems, inhomogeneities can catalyze heterogeneous nucleation: Qian et al. (2011) suggested that a coupled dissolution-reprecipitation reaction can have marcasite replace pyrrhotite at low sulfide activity of the fluid and does not require low pH. These authors also found that marcasite formed only on pyrrhotite grains, not on other parts of their experimental autoclaves, which suggests an epitaxial nucleation at an incipient reaction stage. Significant in respect to the iron sulfide microfabric relations observed in this study, experiments of Schoonen and Barnes (1991) indicate that, in acidic solutions below 100 °C, nucleation of FeS$_2$ is actually inhibited, although growth of existing marcasite and pyrite is possible under these conditions.

The microfabric of conjoined, variably intergrown crystals (Barbee et al., 2020; Welsch et al., 2012) constituting the iron sulfide aggregates of our study suggests an increased reaction affinity ($\Delta G_r$), at least during early growth of the center layer (Figs. 3, 7, and 8). This is in conspicuous contrast to the absence of nucleation sites of FeS$_2$ on volcanic glass. Thus, the presence and intergrowth of two different iron sulfide modifications does not necessarily reflect changes of boundary conditions such as temperature or pH value. It is also unlikely to reflect transformation of the one modification into the other, as we have discussed above. It could however indicate a formation pathway that successfully overcame hindered nucleation. Pyrite may have grown in the first place, and subsequent fixation of FeS$_2$ may have occurred as marcasite precipitation, producing the serrate shapes observed. Potential indications of this growth sequence are (i) the higher pyrite fraction in mixed iron sulfide analyses near spinel (which is located prevalently in the center of the precipitates), and (ii) the serrate,
marcasite-like shape of the outer parts of the iron sulfide precipitates (presumably fixated later than the interior parts).

Control on the sites of iron sulfide precipitation

Our observation that FeS$_2$ precipitation is completely lacking at the surfaces of volcanic glass and dissolving olivine evidently corroborates the finding of Schoonen and Barnes (1991) that the rate of homogeneous FeS$_2$ nucleation is negligible in acidic solutions. Instead, we observe that iron sulfide precipitation at an incipient stage is inevitably linked to the presence of spinel inclusions in olivine (Figs. 4a, and 8, and S3). In particular, Fig. 8b$_4$ exemplarily depicts a stage of incipient growth of iron sulfide on spinel. Regarding the inventory of available sites for heterogeneous FeS$_2$ nucleation, spinel surfaces apparently provide the preferred opportunity for heterogeneous nucleation, since olivine is dissolving, and volcanic glass is obviously not favoring iron sulfide precipitation. The latter observation is particularly important, as it demonstrates the requirement of a pre-existing crystal structure for heterogeneous nucleation of iron sulfide to occur.

The idea of heterogeneous nucleation of marcasite is corroborated by the experimental results of Qian et al. (2011) who reported epitaxial marcasite nucleation exclusively on pyrrhotite grains and not on other parts of their autoclaves. Furthermore, we show that FeS$_2$ precipitation has occurred dominantly where a spinel surface is connected to a cavity within dissolved olivine. After heterogeneous nucleation on spinel grains has occurred, iron sulfide can grow under conditions at which rates of homogeneous nucleation are still low. If spinel surfaces are critical to the nucleation of iron sulfide, then
a relationship between the abundance of both phases may be expected. Indeed, we found that regions with minor spinel exposed at olivine dissolution surfaces within the interconnected pore space of the olivine aggregates show less FeS$_2$ precipitation (see Fig. S1).

These interpretations are in accordance with the results of 3D X-ray microscopy (Figs. 8 and S3), which unveiled nucleation sites on spinel, development of cavities around spinel grains near the olivine dissolution surface, and the organization of FeS$_2$ aggregates with spinel crystals enclosed therein. Raman spectroscopy showed that FeS$_2$ occurrences close to spinel grains are dominated by pyrite. This supports our earlier notion that iron sulfide formation initially proceeds via heterogeneous growth of pyrite on spinel (both of cubic symmetry), joined by marcasite precipitation in later stages. Heterogeneous FeS$_2$ nucleation may occur directly on the spinel surface. It is conceivable that an alternative iron sulfide formation pathway occurs via thin layers of greigite (Fe$_3$S$_4$; the thio-spinel of iron), a phase not uncommon to submarine iron sulfide formation in a sedimentary setting (Rickard, 2012; Roberts, 2015). In this case, greigite rather than FeS$_2$ may have been the phase to grow initially on the spinel surface, providing opportunity for subsequent nucleation of pyrite. However, we did not detect any greigite by our EPMA or Raman investigations at the resolution used. At this point, we cannot resolve by which mechanisms heterogeneous nucleation actually occurred, and whether epitaxial growth played a major role.

**Thermodynamic/kinetic constraints concerning formation pathway and timing**
We conducted reaction path model calculations to determine if the formation of pyrite or marcasite is plausible in a system in which seawater interacts with basaltic glass, olivine, and organic carbon. The results in Fig. 10 show that pyrite is indeed expected to be the dominant secondary mineral in the early stages of evolution. Celadonite and smectite clay are predicted to form later in the sequence as the pool of solutes is more strongly affected by elements released by (slow) glass dissolution. When the organic carbon is oxidized and the reducing power for sulfate reduction is exhausted in the model, pyrite formation slows and eventually gives way to the formation of goethite and clay. In the mature stages of alteration, clay, oxide, and carbonate dominate the predicted assemblage of secondary minerals. This is consistent with what is observed in altered basalts from the ocean crust (e.g., Alt, 1995). Of particular importance in the modeling results is the episode between 100 and 10,000 years, during which pyrite is predicted to dominate the secondary mineral assemblage (Fig. 10). The assumption of reaction rates decreasing in the order of organic carbon, olivine, and glass is critical for the model to predict the abundant pyrite formation in the first couple of thousands of years. The model predicts organic carbon to become oxidized by sulfate, which is turned to sulfide. Iron is released from olivine dissolution, which is faster than the dissolution of glass by roughly an order of magnitude (Oelkers et al., 2018; Oelkers and Gislason, 2001). Iron then reacts with sulfide from bacterial sulfate reduction to form pyrite (or marcasite). Distinguishing between the two FeS$_2$ polymorphs in the model does not make any difference. Marcasite is predicted to form when pyrite formation is suppressed in the model, and its abundance curve is undistinguishable from that of pyrite in Fig. 10.
The absolute reaction rates are poorly constrained, but our assumed factors of 10 and 500 by which the dissolution of olivine and reaction of organic carbon, respectively, is faster than glass dissolution are reasonable. Organic carbon reaction kinetics in the diagenetic system is controlled by microbial metabolism, as the reduced carbon is the electron donor in the catabolic reaction that uses sulfate as terminal electron acceptor. By as of yet unidentified mechanisms, the metabolic products of microbial sulfate reduction may enhance the difference in dissolution rates between olivine and volcanic glass. The more accelerated olivine dissolution is relative to the rate of basalt glass dissolution, the more pronounced is the dominance of pyrite in the secondary mineral assemblage in the incipient alteration stage, before clay-oxide-carbonate alteration eventually takes over. The mechanisms behind this enhanced weathering of olivine in the sulfate-reduction zone need to be examined and may involve microbially produced chelators that help solubilize the iron.

The predicted period for dominant pyrite formation between 100 and 10,000 years is consistent with a presumably young age of the fresh volcanic ash samples here studied. Precise age dates are lacking, but the spatial association between ash and clam shell fields led Klügel et al. (2020) to hypothesize that hydrothermal circulation and consequent colonization by vesicomyid Abyssogena clams were initiated by one or more pulses of volcanic activity. The age of the ash may thus be close to the radiocarbon ages of clam shells, which are in the range of a few ka to <20 ka (Klügel et al., 2011; Klügel et al., 2020). This age range would be consistent with a sediment coverage of the ash by <13 cm in the gravity core (Fig. 1b), and <20 cm in nearby grab samples, if a sedimentation rate of <7 cm/ka (Gee et al., 2001) is assumed.
Conceptual model for iron sulfide formation

A most striking feature of the observed dissolution-precipitation reaction is that the iron sulfide fillings are organized in a bead chain aspect and are centered in the cavities (Figs. 7 and 8). Here we present a conceptual model for iron sulfide formation from rapidly dissolving olivine (Fig. 9).

The key features are intracrystalline cracks within the olivine crystals, along which low-pH, H$_2$S-bearing fluids could percolate (Fig. 9b). These cracks appear to develop preferentially around spinel (see Welsch et al., 2012, their figure 11), likely during the submarine eruption event or during magma ascent and decompression as a result of different elastic properties and thermal expansion of spinel and host olivine. Facilitated by high solubility of Fe$^{2+}$ in the reduced fluids, rapid olivine dissolution proceeds at grain boundaries and at surfaces exposed by the cracks. By heterogeneous nucleation of FeS$_2$ on spinel grains, pyrite and possibly marcasite precipitation can begin within very thin fissures at an early stage of dissolution once Fe$^{2+}$ is available (Fig. 9c-d). Continued olivine dissolution enlarges these cracks forming cavities, and continued nucleation and growth of pyrite and/or marcasite form aggregates centered within the growing gaps. A cartoon representation of the chemical environment for rapid olivine dissolution and iron sulfide formation is presented in Fig. 9a.

Possible role of microbial interactions for olivine dissolution and/or FeS$_2$ precipitation
Although there are many studies that report microbial or fungial mediation of mineral dissolution reactions (Gerrits et al., 2020; Thiel et al., 2019; Welch and Banfield, 2002), the process of rapid olivine dissolution was not necessarily directly mediated by subseafloor life. The observation of smooth dissolution surfaces with negative crystal shapes point to a crystallographic-mineralogical control rather than microbe-aided olivine dissolution. Whereas microbial reduction of sulfate to sulfide may have produced the reducing environment required for the dissolution, an abiotic sulfide source from depth is also possible (Klügel et al., 2020).

The precipitation of iron sulfide aggregates investigated in this study may well be understood by epitaxial nucleation related to spinel and continued iron sulfide precipitation from low-pH and H$_2$S-bearing fluids (Fig. 9). When microbes exert crystallochemical control over the nucleation and growth of the mineral particles, distinctly different particle morphologies and narrow size distributions can develop (Bazylinski and Frankel, 2003). For instance, magnetotactic bacteria intracellularly produce greigite particles in the size range of 100 nm (Heywood et al., 1991; Posfai et al., 1998) that are aligned in μm-sized multiple chains, and extracellular biomineralization of greigite was reported by Gorlas et al. (2018). Furthermore, biomineralization producing extracellular, filamentous structures (Chan et al., 2011; Emerson et al., 2007; Hallbeck and Pedersen, 1991; Vigliaturo et al., 2020) has been linked to Fe(III)-rich filaments observed in the geological record (Alt, 1988; Hofmann et al., 2008; Little et al., 2004; Slack et al., 2007). Therefore, in the rock studied here, late colonization of sulfate-reducing bacteria may eventually have added a further path of iron fixation (Figs. 8b and
9e): fibrous structures with small sulfide particles in extracellular stalks could well contribute as nuclei for later iron sulfide growth sites.

Implications

Under sulfidic conditions, dissolution of olivine at the seafloor can be rapid and greatly exceed glass dissolution rates. These conditions can be due to microbial respiration of seawater sulfate to sulfide in marine sediments, or to influx of hydrothermally sourced (abiotic) sulfide. The sulfide-bearing fluids enhance olivine dissolution by preventing the formation of hydrous ferric oxide layers and sequestering iron as FeS$_2$.

An important prerequisite of the effective fixation of Fe as iron sulfide may be the opportunity of heterogeneous nucleation. There is no evidence for homogenous nucleation of FeS$_2$. Instead, initial pyrite precipitation was facilitated by heterogeneous nucleation on spinel grains exposed to the void space. Subsequent removal of Fe from solution occurred exclusively by pyrite and marcasite precipitation as overgrowth on existing iron sulfide aggregates.

The delicate structures of FeS$_2$ within voids created by olivine dissolution have not been described before. They may represent a transient feature in seafloor alteration, as progressive dissolution of volcanic glass causes the formation of Fe-oxyhydroxides and clay minerals (iddingsitization), which is the commonly observed alteration feature in seafloor basalts. The filling of former olivine voids by these later alteration phases and/or
carbonates may obscure the earlier formed iron sulfides, making them a comparatively rare observation.

ACKNOWLEDGMENTS

W.A.K. and W.B. are grateful for funding by DFG Reinhart Koselleck Project [grant no. BA 1605/10-1], and AK acknowledges funding of the Henry Seamount research by DFG (grant KL1313/18-1). We gratefully acknowledge the reviews of Benjamin Malvoisin and an unknown reviewer.
Figure Captions

Figure 1. (a) Location map of El Hierro island and Henry Seamount, made with GeoMapApp (Ryan et al., 2009); inset shows the Canary Islands. (b) Gravity core sample GeoB22841-1 taken from the summit of the seamount. It contains coarse basaltic ash investigated here, overlain by marine sediment.

Figure 2. Volcanic ash particles embedded in thin section (plane polarized light). (a) Survey of the different lithologies occurring in the volcanic ash layer. Several particles contain olivine or pyroxene crystals that exhibit sulfide-filled cavities. (b) Sulfide-filled cavity in volcanic glass where the former olivine has completely vanished. (c) Particle with olivines displaying tubular cavities, others exhibiting dissolution features at rims or end faces.

Figure 3. Iron sulfide mineralization in dissolution-induced cavities in olivine (SEM). (a) Cavity resembles negative olivine crystal shape, with iron sulfide mineralization as conjoined, planar aggregates. (b) In contrast to olivine (right side), volcanic glass displays only slightly corroded surfaces with small etch pits. (c) Iron sulfide growth (serrate marcasite and euhedral spinel) on volcanic glass surface.

Figure 4. BSE images from a thin section depicts iron sulfide precipitation (white) inside cavities created by olivine dissolution. Key: Pl, plagioclase; Ol, olivine; Spl, spinel. (a) Even in cavities completely devoid of olivine, iron sulfide precipitation is organized in
conjoined aggregates, forming a bead chain aspect in profile. (b) Mineralization in the center of a tubular void in an olivine crystal. (c) Iron sulfide precipitation does not occur deliberately, and is minor or lacking on volcanic glass surfaces (neither on dissolving olivine). It does occur on some spinel surfaces, as can be seen in (a).

Figure 5. Occurrence and connectivity of voids inside a volcanic ash particle (3D X-ray microscopy, XRM). (a₁,₂) Visualization of pore space (blue) in the volume reconstruction of an ash particle consisting of a single olivine grain and glass matrix attached. Note that this sample was analyzed with SEM in Fig. 3a. (b₁,₂,₃). Reconstructed slices at different levels, displaying the bead chain aspect of iron sulfide mineralization and the location of these structures aligned in the center of the cavities. Note the occurrence of spinel in these aggregates. (c) Location of a high-resolution scan inside this particle (see Fig. 8a, b). Please compare also supplementary figure S1.

Figure 6. Raman spectra at selected locations on the polished thin section. (a) In most of the analyzed locations, the baseline-corrected and normalized spectra reveal the presence of both pyrite and marcasite in varying proportions. In some locations concomitant red/blue-shift of the frequencies has been observed for both phases irrespective of their proportions, which we explain in terms of slightly different average crystallite sizes. Colored letters A, B, E and T with indices indicate Raman vibrational modes for pyrite and marcasite (colored vertical bars); see text for details. (b)-(d) BSE image with locations G1-01 to G1-12 (b), G1-13 to G1-16 (c), and G2-01 to G2-03, respectively. Phase proportions are indicated by pie charts.
**Figure 7.** 2D and 3D quantitative image analysis of iron sulfide precipitation (yellow) inside cavities (blue) created by olivine dissolution. (a)-(e) 2D analyses of selected cavities using BSE images. (f1,2) and (g1,2) 3D analyses of selected cavities using reconstructed XRM scans.

**Figure 8.** Results from high-resolution XRM scans showing microfabric of olivine dissolution and FeS$_2$ precipitation processes, with particular consideration of spinel occurrence. Key: Spl, spinel; Sf, sulfide. (a) Semitransparent rendering of olivine (green) and iron sulfide reveals presence of spinel inside the FeS$_2$ precipitates (a1, a4). a2: Opaque rendering of this layer highlights the serrate characteristic of iron sulfide in this particular piece (see also Fig. 3a). a3: 3D view of a olivine dissolution surface, encompassing the iron sulfide mineralization. Note the tiny bridges that in places connect the sulfide layer with the retreated olivine dissolution surface. (b) Reconstructed image slices of the volume of interest in (a) unveil sulfide growth features, such as nucleation sites both on spinel and filamentous structures, development of cavities around spinel grains near the olivine dissolution surface, the organization of iron sulfide aggregates, and spinel crystals enclosed therein. For localization of the high-resolution scan please refer to Fig. 5. Please compare also supplementary figure S3.

**Figure 9.** Conceptual model for rapid olivine dissolution and iron sulfide formation. (a) Cartoon representation of the chemical environment for rapid olivine dissolution and iron sulfide formation. Widespread occurrence of shells of vesicomyid clams (genus...
Abyssogena) at the sampling site indicate the presence of sulfide-rich fluids. (b-e) Iron sulfide formation involves: (b) development of cracks in olivine, preferentially around spinel, (c) infiltration of reducing sulfide-bearing solutions and initiation of olivine dissolution, (d) heterogeneous nucleation of FeS$_2$ preferably as pyrite on spinel and continued growth of FeS$_2$ aggregates. (e) Eventually, colonization of sulfate-reducing bacteria may add an additional path for microbial iron fixation.

**Figure 10.** Results of a reaction path model calculation showing the possible timing of pyrite (or marcasite) formation. See text for model details.

**Supplementary figures:** S1, S2, S3.
Table Captions

Table 1. Average olivine, spinel and sulfide analyses of the investigated samples. See also Table S1-3 in supplementary online material for individual analyses.

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<th>CaO</th>
<th>NiO</th>
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<th>Fo%</th>
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afu per 3 cat.

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Table 2: Raman fit frequencies (±0.1 cm⁻¹) and their assignments for the respective symmetry species obtained from the deconvoluted spectra of FeS₂ at selected locations of the polished thin sections as labeled in Fig. 6. The symmetry species of the pyrite (Py) and marcasite (Mrc) are given.

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<th>T_g(Py)</th>
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Table 3. Percentage of iron sulfide content in relation to the hosting cavity.

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<td>XRM</td>
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<td>over multiple olivines</td>
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<td>Close-up of the above</td>
<td>10.1</td>
<td>XRM</td>
<td>g₂</td>
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Abbreviations: Ol - olivine, BSE - back-scattered image (2D quantitative image analysis), XRM - 3D X-ray microscopy (3D quantitative image analysis).

Tables (Supplementary files):

- Table S1: Olivine analyses.
- Table S2: Spinel analyses.
- Table S3: Sulfide analyses.
REFERENCES CITED


Figure 1
Figure 3
Figure 4
Figure 5

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 6
**Figure 7**

- **a**: 24.00 area% FeS$_2$
- **b**: 17.4 area% FeS$_2$
- **c**: 19.9 area% FeS$_2$
- **d**: 20.8 area% FeS$_2$
- **e**: 18.0 area% FeS$_2$
- **f**: 19.4 vol.% FeS$_2$
- **f$_1$**: 18.1 vol.% FeS$_2$
- **g**: Volume of hi-res scan
- **g$_1$**: 3D model of the largest void. Width of this void ca. 2.2 mm
- **g$_2$**: Hi-res scan: width 677 µm
Figure 8
Figure 9
Figure 10