

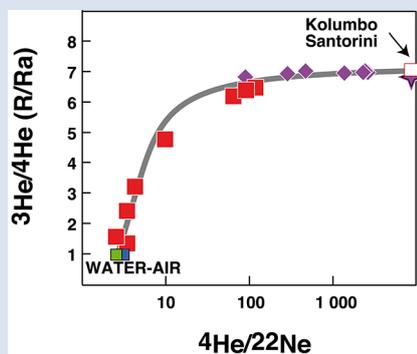
New insights into the plumbing system of Santorini using helium and carbon isotopes

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Abstract



We have analysed He, Ne and CO₂ concentrations and isotopic ratios in seawater samples collected using a ROV above hydrothermal fields and in CO₂-accumulating pools within Santorini caldera (Greece). Our results provide new insights on the plumbing and magmatic sources of this volcano, which is critical to understand and better predict its volcanic eruptions, and its relationships to nearby volcanic systems. The ³He/⁴He ratio is as high as 6.54 times the atmospheric ratio, and significantly higher than any other samples from Santorini, including the active eruptive centre of Nea Kameni (~3.6 Ra). The ³He/⁴He ratio, corrected for atmospheric helium dissolved in seawater is ~7 Ra, a value similar to that measured at the nearby Kolumbo submarine volcano crater. The fluids display typical mantle signatures never recorded before in the active centres of the island of Santorini, in which fluids and gases are contaminated at shallow depths. The helium isotopic signature suggests that the source of volatiles for these two volcanoes is similar to the MORB source instead of being the subcontinental lithospheric mantle as suggested previously.

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Introduction

Santorini is one of the most dangerous active volcanoes on Earth, and understanding its dynamics and evolution is fundamental to constrain its degassing history and associated plumbing structure. Santorini is located in the central part of the South Aegean volcanic arc, which extends 500 km from the western Saronikos Gulf up to Nisyros-Kos in the east (Fig. 1). This arc results from the subduction of the remnant ocean crust of the African plate under the Aegean microplate. The last caldera-forming eruption, the famous Minoan eruption 1627 BC (Friedrich *et al.*, 2006), was followed by several eruptions building the Palea and Nea Kameni islands within the centre of Santorini caldera (Nomikou *et al.*, 2014). Since the last volcanic eruption in 1950, a magmatic event with no surface expression occurred between 2011 and 2012. The seismic activity and surface deformation have been attributed to a ~4 km deep magmatic intrusion (Parks *et al.*, 2015). This subsurface magmatic event is supported by prior studies (Parks *et al.*, 2013; Rizzo *et al.*, 2015) that have shown C and He isotopic signals during this unrest period consistent with magmatic intrusion into the shallow plumbing system.

Earlier submarine explorations of the caldera seafloor identified several hydrothermal fields at depths of up to

~350 mbsl (Sigurdsson *et al.*, 2006; Nomikou *et al.*, 2013) (Fig. 1). Among the different sites, they observed a vent field in the north of the caldera (Caldera Hydrothermal Field), extending over ~200 x 300 m², with hundreds of mounds of variable size, ~0.1 to several m in diameter, and raising up to ~2 m above the surrounding sedimented seafloor (Fig. 1). This hydrothermal field aligns with the so-called Kolumbo line, which represents a tectonic structure in the NE favouring the transport of magmas from depths, similar to the Kameni line in the SW of the caldera. The Kolumbo line extends to the NE to the Kolumbo submarine volcano, which is the largest of 25 submarine volcanic cones sited along this fault and is located ~7 km of Santorini (Nomikou *et al.*, 2012). Trace elements and radiogenic isotopes have shown significant differences suggesting a different petrogenesis and a different mantle source between those two volcanoes (Klaver *et al.*, 2016), although, based on helium isotopes, Rizzo *et al.* (2016) suggest that the two volcanoes share the same mantle source but a different plumbing.

The ~350 m deep hydrothermal field along the NE edge of the Santorini caldera was studied in 2012 and immediately after the inflation event observed between 2011 and 2012. The Caldera 2012 cruise deployed the remotely operated vehicle (ROV) Max Rover, the submersible Thetis (both from HCMR,

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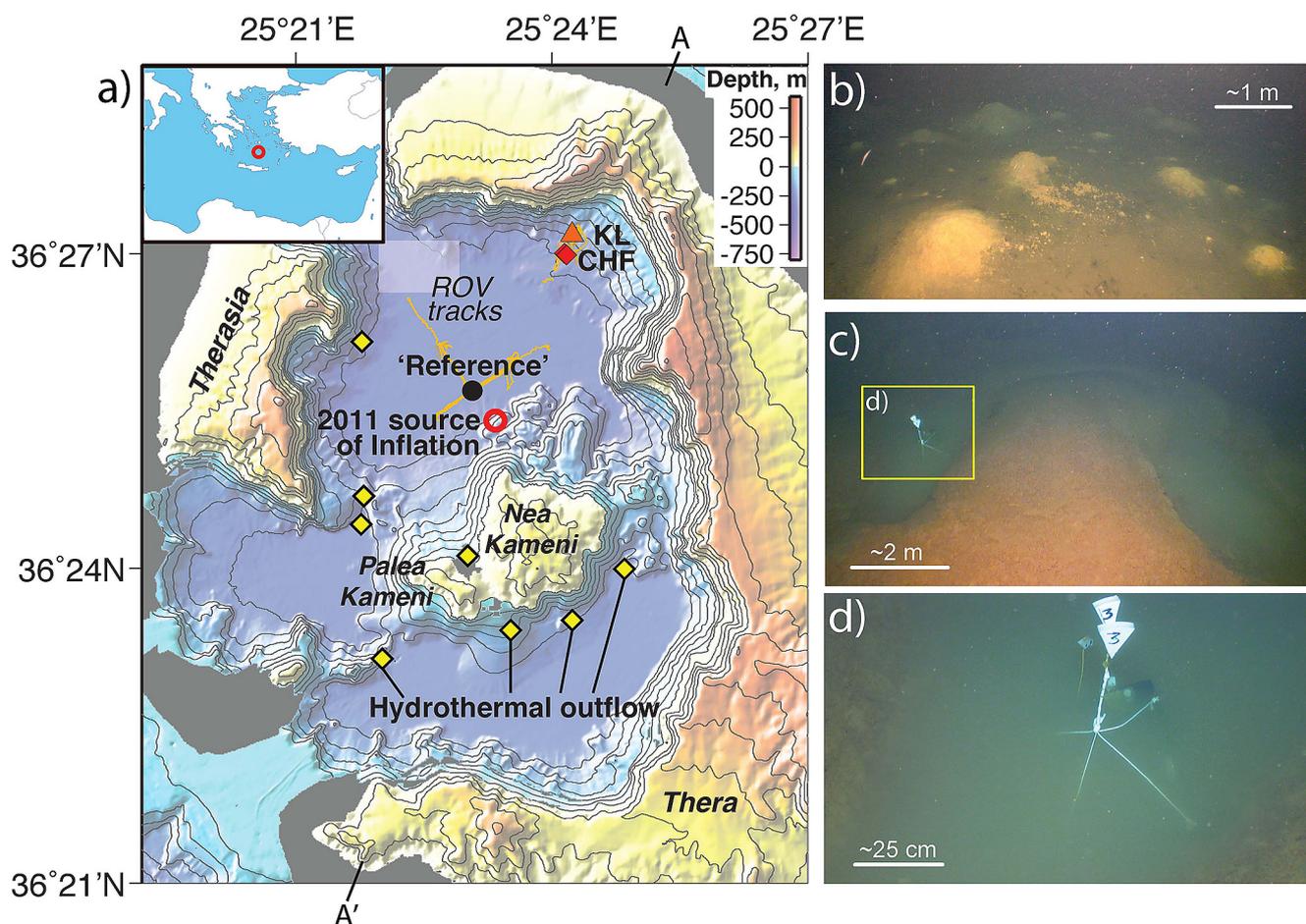


Figure 1 (a) Synthetic topographic map (Nomikou *et al.*, 2014) showing the position of hydrothermal outflow areas within the Santorin caldera. Two samples were collected at the 'Reference' site, which corresponds to near-bottom water away from hydrothermal sources and at the bottom of the northern basin of the caldera. The other samples were collected at the caldera hydrothermal field (CHF), which shows mounds of bacterial mat (b), and at the Kallisti Limnes (KL), which shows sub-sea pools with CO₂-rich fluids (Camilli *et al.*, 2015) (c and d). CHF and other hydrothermal areas throughout the caldera where observed in 2006 (Sigurdsson *et al.*, 2006). The red open circle corresponds to the Mogi source model associated with the 2011 inflation event (Newman *et al.*, 2012). A and A' indicate the ends of bathymetric profile in Figure 3.

Greece) and the autonomous underwater vehicle (AUV) Girona 500 (U. Girona, Spain). Temperatures within hydrothermal mounds, composed of an accumulation of bacterial fluff, are ~5 °C higher than those of ambient seawater (~15 °C), suggesting low temperature hydrothermal outflow at very low flux rates. During this cruise, we collected water samples above these mounds to constrain their origin using helium, neon and carbon isotopes, and off-site for reference (Fig. 1). Moreover, during this cruise, CO₂-rich pools were discovered and sampled slightly north of this hydrothermal field, at the base of the caldera wall and at shallower depths of 250 to 200 m (Camilli *et al.*, 2015) (Fig. 1).

Samples

Fluid samples were acquired with Niskin bottles fitted at the lower part of the ROV and closed by the ROV operators. The ROV also dove into and collected samples within the Kallisti Limnes, and immediately above them. At the caldera floor we recovered samples at ~1 m or less above different hydrothermal mounds. Upon ROV recovery on-board, water samples were transferred from the Niskin bottles to copper tubes sealed with pinch clamps at both ends. He and C isotope measurements were performed at IPGP a few months later.

Analytical Procedure and Results

Noble gases were extracted from water samples (standards and samples) using the analytical protocol developed by Greau (2012). Distilled water equilibrated with air is used as standard for He and Ne. Helium and neon were measured using the HELIX-SFT (ThermoFisher©) mass spectrometer sited at IPGP. CO₂ concentration and the carbon isotopic ratio were measured at IPGP's Laboratory of Stable Isotopes using their standard procedure (Assayag *et al.*, 2006).

Helium, neon, CO₂ abundances, C/³He and isotopic ratios are given in Table S-1. Concentrations of ⁴He vary between 3.8×10^{-8} and 2.2×10^{-6} cm³ STP/gH₂O. The ³He/⁴He ratio varies between 0.99 ± 0.04 Ra and 6.5 ± 0.3 Ra. The ²⁰Ne/²²Ne ratios are atmospheric within uncertainty. The ³He/⁴He ratio correlates positively with the ⁴He/²²Ne (Fig. 2) suggesting a mixing between air/seawater and a mantle-derived component. The CO₂/³He ratio varies from 1.0×10^{10} to 9.25×10^{11} . The carbon isotopic ratios vary from -0.13 ± 0.06 up to 1.06 ± 0.06 ‰ relative to the PDB standard and are negatively correlated with the ³He/⁴He ratios, suggesting also a mixture between two components (Fig. 2).

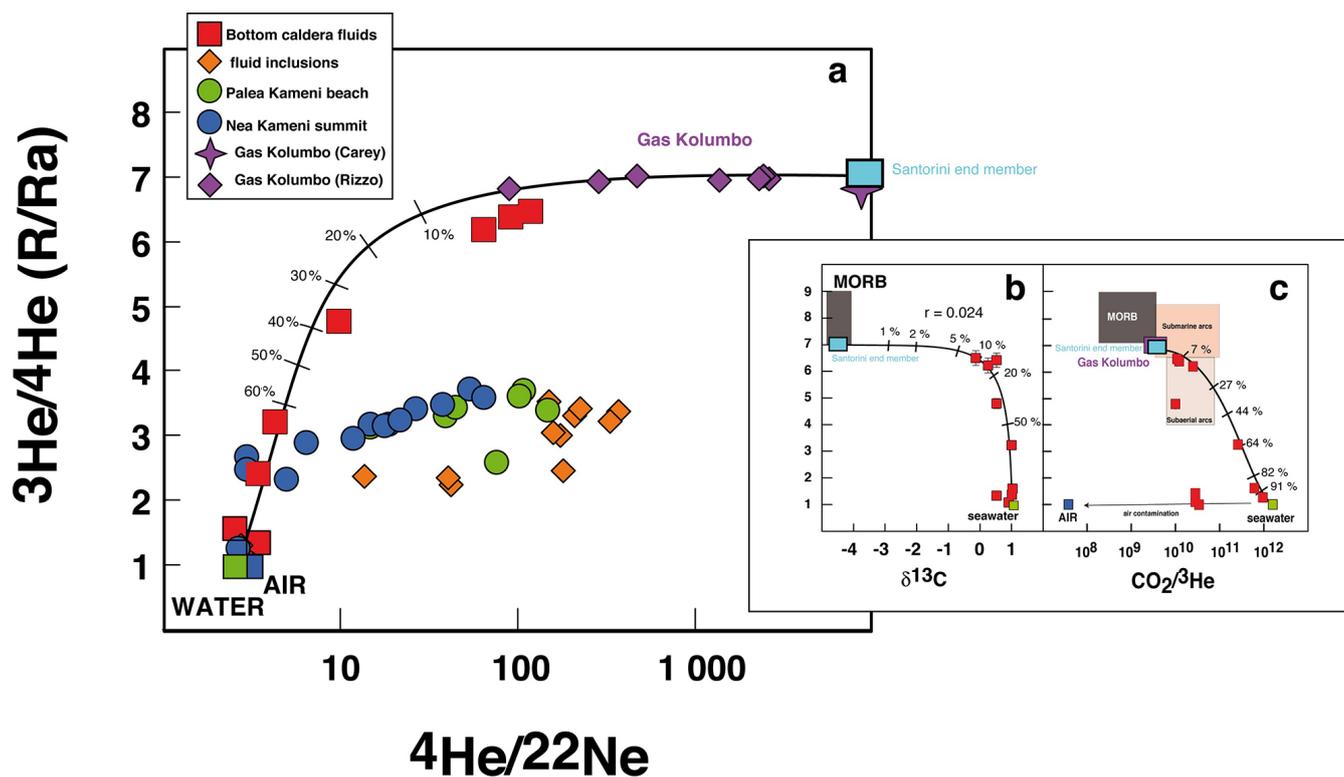


Figure 2 (a) Mixing diagram showing the $^3\text{He}/^4\text{He}$ ratio reported against $^4\text{He}/^{22}\text{Ne}$ (Ra is the helium atmospheric isotopic ratio). The mantle-derived end member has a $^3\text{He}/^4\text{He}$ ratio of ~ 7 Ra, identical to the value of the nearby Kolumbo volcano (Carey *et al.*, 2013; Rizzo *et al.*, 2016) suggesting a common mantle source. All samples from Palea or Nea Kameni (gases and fluid/melt inclusions in phenocrysts) show a different trend, with a lower $^3\text{He}/^4\text{He}$ ratio reflecting shallow crustal assimilation (Shimizu *et al.*, 2005; Rizzo *et al.*, 2015). The insert shows the $^3\text{He}/^4\text{He}$ ratio versus $\delta^{13}\text{C}$ (b) and $\text{CO}_2/^3\text{He}$ (c). The strong hyperbolic curvature of the mixing curve reported in insert (b) reflects the $(^4\text{He}/\text{CO}_2)_{\text{seawater}}/(^4\text{He}/\text{CO}_2)_{\text{MORB}}$ ratio of ~ 0.024 , explaining why the $\delta^{13}\text{C}$ does not show a mantle value whereas helium almost does. Percentages that are indicated on the mixing curves represent the fraction of seawater-derived helium.

Discussion

The He-C systematics clearly show that fluids have a magmatic origin both for the hydrothermal field with bacterial mounds and for the CO_2 pools from the Kallisti Limnes area. Indeed, a measured $^3\text{He}/^4\text{He}$ ratio as high as 6.5 ± 0.3 Ra is typical of volcanic contexts. Moreover, we can correct this measured $^3\text{He}/^4\text{He}$ ratio for the seawater-derived helium using neon, assuming it is entirely of atmospheric origin. The corrected $^3\text{He}/^4\text{He}$ ratio corresponds to the plateau value reached at high $^4\text{He}/^{22}\text{Ne}$ (>1000) in Figure 2. It is close to ~ 7 Ra, which is the same ratio measured on CO_2 -rich gas from Kolumbo submarine volcano (Carey *et al.*, 2013; Rizzo *et al.*, 2016). Carbon isotopes and the $\text{CO}_2/^3\text{He}$ ratios also confirm the mantle origin for the CO_2 and helium. The $^{13}\text{C}/^{12}\text{C} - ^3\text{He}/^4\text{He}$ diagram of Figure 2 suggests a binary mixing between seawater and a mantle-derived component, although the $\delta^{13}\text{C}$ is not reaching the mantle value of ~ -4.5 ‰ (Javoy and Pineau, 1991).

The helium isotopic ratios measured in our studied samples are less radiogenic than fluids or minerals collected on the active zone of Palea and Nea Kameni islands (Shimizu *et al.*, 2005; Rizzo *et al.*, 2015). The shallow magma chamber beneath the volcanic active centre of Santorini, is probably located at ~ 3 - 4 km depth (Fig. 3) (Parks *et al.*, 2015). The helium isotopic signature of the surface fumaroles or bubbling springs at the islands does not reach the mantle isotopic signature observed in deep hydrothermal field and CO_2 pools of the northeast flank of the caldera (Fig. 2). Therefore, the more radiogenic helium isotopic ratios measured on the fumaroles or bubbling springs from Nea Kameni cannot be considered as reflecting the mantle source and the possible presence

of recycled sediments in it, revealing instead rather shallow processes of contamination, as also suggested by Rizzo *et al.* (2016). The value of the helium isotopic ratio of both Santorini and Kolumbo volcanoes (~ 7 Ra) suggests that the source of volatiles is the asthenosphere rather than the subcontinental lithospheric mantle, which presents a more radiogenic helium isotopic ratio of 6.1 ± 0.9 than the MORB source (Gautheron and Moreira, 2002).

Although the deep magmatic origin for helium and CO_2 in the northeast hydrothermal field is clear, the flux of magmatic gases is low. At Santorini, there is no observed bubbling in this hydrothermal field, while bubbling is abundant and widespread within the nearby Kolumbo submarine volcano, at the north of the crater (Nomikou *et al.*, 2012; Carey *et al.*, 2013; Rizzo *et al.*, 2016). The Santorini hydrothermal mounds also show temperatures that are only 5 °C above ambient seawater temperature, much lower than the >100 °C measured at Kolumbo's hydrothermal outflows. These temperatures and the visual observations of the mounds and CO_2 pools, with no visual evidence of flow, indicate that the hydrothermal flux at the Caldera Field is very low. A dilution of the gas flux from the mantle is required before reaching surface. Anomalies of He and CO_2 concentrations were measured on soils onshore along the Kolumbo line (Barberi and Carapezza, 1994). Unfortunately, no isotopic composition was measured to confirm if these gases are the same. However, the location of these anomalous concentrations of He and CO_2 suggests that the mantle-derived gases we observed at the bottom of Santorini caldera extend up to the surface, following the tectonic Kolumbo line, which we therefore infer to be preferential path for degassing.



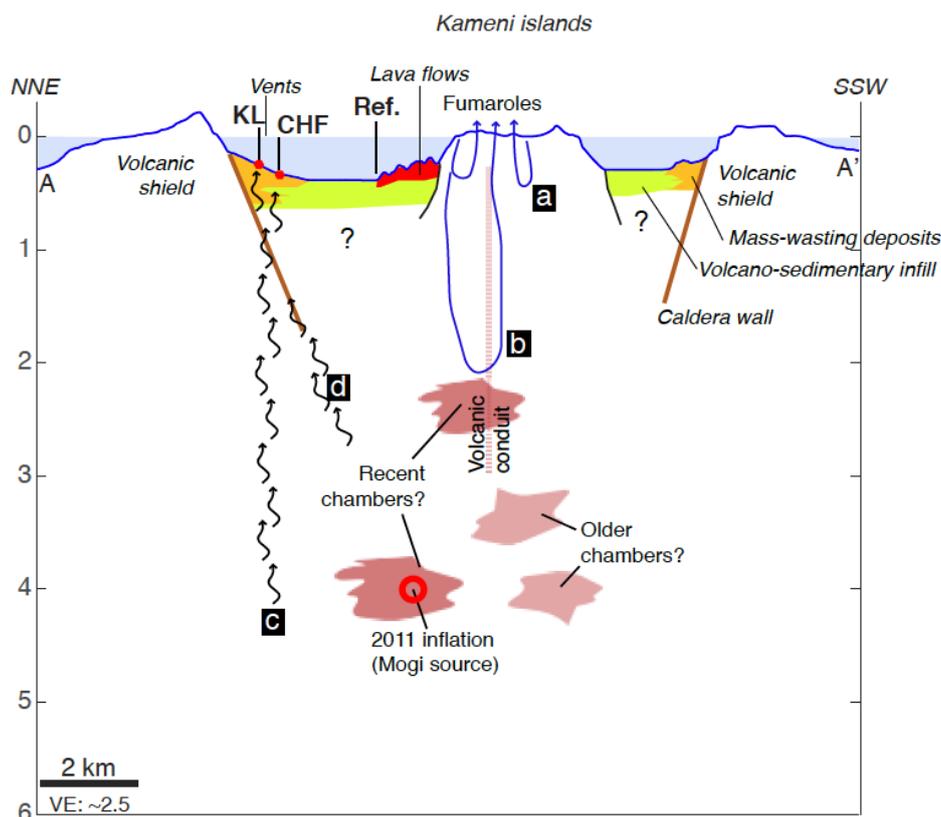


Figure 3 Possible sources and transfer of magmatic CO_2 and He within the Santorini caldera. Gases from Nea Kameni derive from a shallow reservoir, which is degassed and has assimilated crustal rocks, sampled by hydrothermal circulation (a, b). A pristine mantle signature is sampled by fluids at the Kalisti Limnes and hydrothermal areas. These fluids may either percolate through the volcanic shield and the pre-volcanic basement (c), or be supplied from a more central area and in association with recent magma chambers, if the fluids migrate along caldera walls and associated caldera faults (d).

Figure 3 summarises our vision of the different degassing processes occurring within Santorini caldera. Magmatic gases from the shallow magmatic chamber degas below Nea and Palea Kameni thanks to hydrothermal circulation, although their compositions do not reflect the mantle source. Crustal assimilation has altered these deep-seated signatures and, notwithstanding recent magma injections, the helium isotopic composition is not representative of the mantle source. A flux of magmatic CO_2 and helium is observed on the NE of the caldera, on the Kalisti Limnes and on caldera hydrothermal areas, with mantle compositions. However, the gas likely focuses along the tectonic Kolumbo line, with a very weak flux and diluted with seawater. A detailed work on the geometry, extent, and thermal structure of these vents is required to estimate this magmatic gas flux better. The helium isotopic signature is similar to the one of the Kolumbo volcano (Carey *et al.*, 2013; Rizzo *et al.*, 2016), suggesting that those two volcanoes either sample the same magmatic source for volatiles, or there are two different sources that are geochemically similar for volatiles, although they might be different for other elements (Klaver *et al.*, 2016). Moreover, this source appears similar to the MORB source instead of being the subcontinental mantle, which presents a more radiogenic helium isotopic signature (Gautheron and Moreira, 2002).

Conclusions

Using new helium and CO_2 in water collected at the bottom of the Santorini caldera, at recently discovered hydrothermal fields and nearby CO_2 -rich pools (Kallisti Limnes), we show that C and He at Santorini are mantle-derived and that the magma source of these volatiles is similar to that of the nearby

Kolumbo submarine volcano. The fluids from the submarine hydrothermal field derive directly from the deep magmatic system of Santorini without being affected by the shallow magmatic plumbing as for Nea and Palea Kameni islands. These fluids follow efficient paths to the seafloor likely along fault zones anchored deep in the volcanic arc. The helium isotopic composition shows that the mantle source of the Santorini magmatism is more likely the asthenosphere than the subcontinental lithospheric mantle.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1914>.



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