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Gas chemistry of the Dallol region of the Danakil Depression in the Afar region of the northern-most East African Rift

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ABSTRACT

A combination of noble and major gas composition and isotope geochemistry provides a window into the source of volatiles and the mechanisms of transport associated with a series of hot springs located near the Dallol volcano within the Danakil Depression along the Red Sea arm of the Afar triple junction. The helium isotopic composition of these gases range up to 11.9 times the atmospheric ratio (11.9 R/Ra), which suggests that the Afar plume interacts with the Afar depression across at least the 300 km transect from Tendaho-Gabo basin to Dallol within the Danakil Depression. The ⁴He/⁴⁰Ar* of ~14 in the mantle-rich end-member at Dallol indicates significant degassing prior to emplacement at Dallol either during basaltic dyke intrusions beneath the Danakil Depression or during the release and transport of fluids from a degassed subsolidus source in the upper mantle along high permeability fracture zones. The $CO_2/^3$ He of the magmatic end-member is ~2× higher (7.7×10⁹) and more positive δ^{13} C (CO₂) (-2.1‰) than other archetypal plumes (e.g. Hawaii, Iceland, etc.). The Dallol composition is consistent with a hypothetical model that assumes a plume-type starting composition and experiences ~92% degassing (where helium is preferentially degassed with respect to CO₂) and the addition of CO₂ from the thermal degradation of carbonate. Non-atmospheric excess N₂ with a δ^{15} N (N₂) of + 3.5 to + 4‰ dominates the Dallol volatiles and suggests interaction between mantle fluids and Proterozoic meta-sediments. By comparing and modeling the range in atmospherically (e.g. 20 Ne, 36 Ar, 84 Kr) and mantle-derived (e.g. 4 He/ 40 Ar* and CO₂/ 3 He) components in Dallol volatiles, we propose that the coherent variations in these gases result from mixing of magmatic volatiles with extremely degassed remnant fluids present within the hydrothermal reservoir.

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1. Introduction

Volatile geochemistry plays a fundamental role in constraining the source and dynamic processes that generate the fluids brought to the Earth's surface during volcanic, magmatic, and hydrothermal activity. The inert nature, low terrestrial abundance, and well characterized isotopic composition of each of the major terrestrial reservoirs of noble gases (i.e. mantle, crust, hydrosphere, and atmosphere) make these geochemical tracers exceptionally useful for evaluating the evolution of magmatic bodies, understanding the chemical heterogeneities within the mantle, as well as distinguishing the source, mixtures, and sub-surface crustal

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interactions of mantle-derived fluids (e.g. Craig and Lupton, 1976; Mamyrin and Tolstikhin, 1984; Poreda and Craig, 1989; Kurz, 1993; Lollar et al., 1997; Hilton et al., 1999; Ballentine et al., 2001; Fischer et al., 2009; Zhou et al., 2012). Paired noble gas and volatile isotope chemistry provide insights into the source, character, and mixing relationships of mantle and crustal fluids both globally and at locations along the geologically and tectonically complex East African Rift, including some areas within the Afar triple junction (i.e. Tendaho Basin) (Marty et al., 1996; Scarsi and Craig, 1996; Pik et al., 2006; Montagner et al., 2007; Fischer et al., 2009; Tassi et al., 2009; Tedesco et al., 2010; Hilton et al., 2011). Nonetheless, there is paucity of noble gas isotope and volatile geochemical data for several magmatic segments with recent historical activity, including the peculiar and picturesque Dallol hot springs in the Danakil Depression (Fig. 1).

Located in one of the most remote, inhospitable (temperatures routinely exceed 40 °C), and seldom studied locations in the world, the Dallol hot springs are an important local economic resource (i.e. rock salt, potash, manganese deposit mining and tourism),

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Fig. 1. The Afar depression and active volcanoes, near the triple junction of the actively spreading Red Sea and Gulf of Aden, and magmatically rifting Main Ethiopian Rift (MER). The Tendaho graben (containing the Ayrobera (Ay), Dubti/Tendaho (Du), and Alalobeda (Al) hot springs) is located near the triple junction along the Tendaho-Gabaad (Gabo) Discontinuity. The TGD is along-strike of the recently active Dabbahu Magmatic segment (DMS) (erupted in 2005 and 2007; Wright et al., 2006; Ayele et al., 2007) and Danakil Depression, which contains the Erta 'Ale (EA) and Dallol (DA) volcanoes and the nearby Dallol hot spring area. The ³He/⁴He ratios are shown for each hot spring-fumarole for comparison. The Red Sea brine ³He/⁴He was reported in Lupton et al. (1977).

while the associated 'boinas' (i.e. the Afari name for hot springs) are commonly necessary for human and animal drinking water consumption (Holwerda and Hutchinson, 1968). The limited amount of published data for volatile chemistry within the Erta 'Ale volcanic complex of the Danakil Depression focuses on major species (e.g. CO₂, S₂O, H₂, H₂S), acidic gases (e.g. HF, HCl), and water (H₂O) (Tazieff et al., 1972; LeGuern et al., 1975; Giggenbach and LeGuern, 1976; Oppenheimer and Francis, 1997; Sawyer et al., 2008). The Dallol hot springs offer a unique window into the interrelation between Afar plume mantle processes and the transport of volatiles to the surface within the complex geological environment of active extension and crustal formation along an active rift segment. Additionally, these data represent the first noble gas or major gas data for this active magmatic segment within this Red Sea arm of the Afar triple junction.

2. Geological setting

The East African Rift System (EARS) constitutes the classic example of active continental rifting that continues to split Africa from Arabia (e.g. Wright et al., 2006; Ebinger et al., 2008). Today, active rifting and volcanism span the distance from the Afar triple junction as far south as Mozambique (e.g. Hayward and Ebinger, 1996; Furman, 2007) (Fig. 2). The first recorded volcanism along the EARS began ~45 Ma in



Fig. 2. Evolution of δ^{13} C–CO₂, CO₂/³He, and ⁴He/⁴⁰Ar* calculated for the gas phase of degassing archetypal plume magmatic body (green box) (Poreda et al., 1992; Giggenbach and Poreda, 1993) (model following Ballentine et al., 2002). The model assumes an initial starting composition of δ^{13} C–CO₂ = $-2%_{\circ}$, CO₂/³He = 2×10^9 and bulk earth ⁴He/⁴⁰Ar* = 1.8. These end-members are within the ranges observed for other plume environments and alkaline-rich magmatic end-members. Note that even by using favorable end-member compositions the mantle gases must have degassing model cannot account for the extent of δ^{13} C–CO₂ = $4%_{\circ}$, CO₂/³He = 3×10^9 . The validity of this end-member. We also model a degassing trend for a hypothetical plume gas component that has an initial δ^{13} C–CO₂ = $+1\%_{\circ}$, CO₂/³He = 3×10^9 . The validity of this end-member. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

southern Ethiopia, while the largest volume of lava erupted further north toward Afar. The most voluminous eruptions occurred when the Ethiopian traps, still observable today as the ~2000 m high Ethiopian plateau, were emplaced as flood basalts in about 1 Myr at ~30 Ma (Ebinger and Sleep, 1998; George et al., 1998; Pik et al., 1998; Courtillot et al., 1999; Kieffer et al., 2004). The onset of the Ethiopian flood basalts at ~30 Ma is unambiguously linked to the deep mantle Afar plume, whose thermal and seismic anomalies persist to the present day (Lupton et al., 1977; Hayward and Ebinger, 1996; Marty et al., 1996; Scarsi and Craig, 1996; Bastow et al., 2005; Benoit et al., 2006a, 2006b; Pik et al., 2006). The flood basalt sequence is contemporaneous with the initiation of rifting of the southern Red Sea and is likely responsible for stimulating the seafloor spreading in the Gulf of Aden and the Red Sea (e.g. Courtillot et al., 1999; Lahitte et al., 2003; Kendall et al., 2005). The evolution of this rift is responsible for the formation of the 300-km wide Afar depression (Afar triple junction), located at the intersection of the Red Sea, Gulf of Aden, and East African Rift, throughout the last ~30 Myr (predominantly the last 10 Myr) (e.g. White and McKenzie, 1989; Hayward and Ebinger, 1996; Wright et al., 2006; Ayele et al., 2007).

During the last ~2–4 Myr, the northern Afar depression has experienced increased seismic, tectonic, and volcanic activity along localized magmatic segments that erupt dominantly basaltic volcanics

(e.g. Wright et al., 2006; Ebinger et al., 2008; Avele et al., 2009; Keir et al., 2009). While the Dabbahu magmatic segment only recently became unrestful during an unprecedented volcanic-seismic crisis along the ~60 km-long dyke intrusion that began in September of 2005, four primary magmatic segments are historically active and experience much of the Quaternary strain within the region, including the Dabbahu, Alayta, Tat 'Ale, and Erta 'Ale (e.g. Wright et al., 2006; Ayele et al., 2009; Keir et al., 2009). These magmatic segments are comprised of fissural basaltic flows, basaltic cones, and stratovolcanoes, that are similar in size, morphology, structure, emplacement depth, and spacing to each other, and to slow-spreading mid-oceanic ridge segments (i.e. Iceland) (e.g. Hayward and Ebinger, 1996; Ebinger et al., 2008). Currently, rifting occurs at rates up to ~15 mm/yr resulting in highly extended, thinned (i.e. 18 km thickening to 26 km toward the south), and variably intruded continental crust beneath the Afar region (Bastow et al., 2005; Wright et al., 2006; Ebinger et al., 2008).

Herein we focus on the Dallol hot springs of the Danakil Depression (Fig. 1), which extends predominantly NNW-SSE roughly parallel to the Red Sea rift axis and is bound by the Danakil horst (NW-SW trending), the western escarpment of the Danakil Mountains to the west, and the Tendaho-Goba' fault scarp to the east (Wright et al., 2006; Ayele et al., 2009). Importantly, the Tendaho-Goba' fault scarp discontinuity separates the zone of sub-EW extension in the EAR and the NE-SW opening of the Red Sea rift arm (e.g. Ebinger et al., 2008; Ayele et al., 2009). The Danakil Depression also contains the Erta 'Ale range and the similarly-named Erta 'Ale volcano, which typically erupts tholeiitic to alkaline basalts (Bizouard et al., 1980; Oppenheimer and Francis, 1998). Erta 'Ale is famous for its permanent and active lava lake (Barberi et al., 1973; Burgi et al., 2002), a phenomenon only observed at a few other locations globally (e.g. Mount Nyiragongo (Tedesco et al., 2010) and Mount Erebus (Calkins et al., 2008; Sims et al., 2008)).

Approximately 80 km NW of Erta 'Ale, the Dallol hot springs, are located at ~120 m below sea level in the northern portion of the Danakil Depression. Mount Dallol occurs near the center of the hot spring field with an elevation of ~ -60 m (i.e. 60 m below sea level) (Holwerda and Hutchinson, 1968; Gebresilassie et al., 2011). Along the rift margins that bound the Dallol field, exposed Neoproterozoic metavolcanic and metasedimentary basement rocks are overlain by Permian to Palaeogene shallow marine and continental sedimentary sequences including sandstone, limestone, and some minor shales that were uplifted and partially eroded prior to rifting (Holwerda and Hutchinson, 1968; Davidson et al., 1994; Gebresilassie et al., 2011). After rifting commenced and the Danakil graben was created within the Afar depression, the area received a mixture of alluvial fan deposits that covered the basin (Holwerda and Hutchinson, 1968; Davidson et al., 1994; Gebresilassie et al., 2011). Throughout the Miocene, the Danakil Depression was frequently inundated by seawater that subsequently evaporated and deposited muddy gypsum and halite salts across the basin (Holwerda and Hutchinson, 1968; Gebresilassie et al., 2011). The salt deposits in the basin likely precipitated from a large inland lake on the order of 1150 km² within the rift depression (Holwerda and Hutchinson, 1968). Over time, the repeated cycles of inundation and evaporation yielded a deposition of ~1000 m of evaporite deposits including: anhydrite-gypsum, halite, sylvite and carnallite, depending on the major anions and cations found in the deposits (Holwerda and Hutchinson, 1968; Gebresilassie et al., 2011).

Throughout the last 8–10 Myr periodic basaltic dyke intrusions sporadically puncture the evaporite deposits and are thought to produce the necessary heat to generate the hydrothermal convection cells that feed the hot springs. Despite common misconception, Mount Dallol is not a volcanic center and no observable volcanic products were found at the surface during any of three field campaigns to the area (2005–2008). Instead the formation of hot pools, such as that observed at "Black Lake" with present temperatures ~70 °C, result from a phreatic explosion related to the increasing gas pressure in a superficial hydrothermal reservoir hypothesized to

result from a dyke intrusion (Holwerda and Hutchinson, 1968). Most of the superficial products are consistent with salt evaporite deposits, and some remnants of older marine, low depth, clay-sediments (Holwerda and Hutchinson, 1968). The Dallol hot springs typically consist of circular to sub-circular ponds commonly formed by explosive vapor eruptions known as maars (Holwerda and Hutchinson, 1968; Gebresilassie et al., 2011).

Field observations show that brine fluids in the Dallol area (i.e. the "hill" characterized by several multi-color warm/hot pools) are extremely salty (>500g/L), highly acidic (i.e. pH approaching 0.5), and gas-rich (i.e. steady, vigorous bubbling of gases). The salt dome fluids and hot springs are hypothesized to result from the interaction between hot mantle fluids or basalt dyke injections with evaporite deposits at unknown depths. It is unclear if sulfur-rich gases and the low pH brine fluids provide evidence of the interaction of hot mantle fluids with the evaporites or are at least in part related directly to mantle components at depth. We hypothesize that a combination of major and trace gas compositions may provide insights into the source and history of mantle fluids and their interaction with crustal waters and evaporites.

3. Sampling and methods

3.1. Sample collection

Gas and water samples (only gases will be discussed herein) were collected from representative bubbling hot pools in the Dallol volcano area and its vicinity (Fig. 1). Gas samples were collected using an inverted HDPE funnel connected by silicone/Tygon® tubes to pre-evacuated 100 mL borosilicate flasks with a Teflon stopcock filled with 40 mL of 4 N NaOH and 0.15 M Cd(OH)₂ suspension (Giggenbach and Goguel, 1989; Montegrossi et al., 2001). The water vapor in these gas samples is fixed by the relatively low temperature of discharge and is thus not considered part of the gas composition. As a result, gas data is reported on a water-free basis. At each sampling point, two different samples were collected: one was analyzed in the laboratories of the University of Florence and INGV (Instituto Nazionale Vulcanologia Geofisica) of Naples (Italy) for the determination of the chemical composition, the carbon isotopic composition of CO₂, and the nitrogen isotopic composition of N₂; the second was used for the analysis of the isotopic ratios of noble gases (He, Ne, Kr, and Ar) at the Rare Gas Facility at the University of Rochester (USA).

3.2. Sample analysis and analytical techniques

The concentrations of N₂, O₂, H₂, and Ar were measured from the headspace using a Shimadzu 15A gas chromatograph (GC) equipped with a 10-m-long 5A molecular sieve column and a thermal conductivity detector (TCD). Hydrocarbons, including CH₄ and C₂H₆, were analyzed using a Shimadzu 14A GC equipped with a 10-m-long stainless steel column (Φ , 2 mm) packed with a Chromosorb PAW 80/100 mesh coated with a 23% SP 1700, and a flame ionization detector (FID). The carbon dioxide (CO_2) composition is determined by separating the alkaline solution from the solid precipitate by centrifugation to determine: 1) CO_2 as CO_3^{2-} by titration (Metrohm Basic Titrino) with a 0.5 N HCl solution; and 2) H₂S by first oxidizing CdS to SO_4^{2-} with H_2O_2 and then using ion chromatography (Tedesco, 1994; Montegrossi et al., 2001; Tassi et al., 2010, 2011). The analytical uncertainty for all reported data was < 5%. The carbon isotopic composition ($^{13}C/^{12}C$) of CO₂ (hereafter expressed as $\delta^{13}C-CO_2 \approx$ (per mil) V-PDB) was determined by adding ~5 mL anhydrous phosphoric acid to 2 mL of the soda solution under vacuum and allowing the emanated CO_2 to equilibrate at 25 ± 0.1 °C in a thermal bath overnight. The extracted CO₂ was then purified using liquid N₂ and N₂-trichloroethylene cryogenic traps, and analyzed using a Finnigan Delta S mass spectrometer. We used internal (Carrara and San Vincenzo marbles) and international

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(NBS18, limestone, and NBS19, carbonate) standards to estimate the external precision. The analytical precision and reproducibility were $\pm 0.05\%$ and 0.1‰, respectively (Capaccioni et al., 2011; Aguilera et al., 2012). The isotopic composition of N₂ was determined on the residual gases by coupling a GC (Agilent Technologies 6890 N) with the Finnigan Delta S MS. The GC is equipped with a molecular sieve column (MS 5 Å capillary, 30 m×0.53 mm×50 µm; He carrier gas), TCD detector and a post column switching device (Denswitch), which is able to split the column gas flow to the TCD detector and to the MS. The ion beam focuses masses 28, 29 and 30 on the three cups using a jump calibration procedure taking into account any hysteresis of the magnet. The analytical procedure allows simultaneous determination of ³⁶Ar, ⁴⁰Ar, O₂, N₂, CH₄ and δ^{15} N (Chiodini et al., 2012).

Noble gas elemental and isotopic compositions were analyzed at the University of Rochester Rare Gas Facility. Prior to gas analysis, a 77 μ cm³ air standard at STP was used to tune mass calibrations, minimize formation of doubly charged species (e.g. ⁴⁰Ar²⁺ and CO₂²⁺), and quantify isobaric interferences on neon isotopes as <3%. Ne isotopic composition was corrected by measuring [⁴⁰Ar⁺] and [CO₂⁺] and subtracting the quantified production ratio for each doubly charged species by methods reported previously (Poreda and Farley, 1992; Darrah and Poreda, in press). Other potential interferences, including HF and H₂O were similarly monitored for and corrected.

The elemental and isotopic analyses of helium (He), neon (Ne), argon (Ar), and krypton (Kr) gases were carried out on a VG 5400 mass spectrometer by methods described previously (Poreda and Farley, 1992; Darrah and Poreda, in press; Hunt et al., in press). For noble gas isotope analysis, the gas samples were purified in a high vacuum line constructed of stainless steel and Corning-1724 glass to minimize helium diffusion. Water vapor and CO_2 were cryogenically trapped at -90 °C and -195 °C, respectively. Bulk gases (N₂ and O₂) were purified by consecutive exposure to a Zr-Al getter (SAES ST-707) held at 450 °C and a SAES SORB-AC cartridge held at 250 °C then cooled to 25 °C in an activated charcoal cold finger. This was followed by the sequential trapping of Ar into an activated charcoal finger at liquid nitrogen temperatures and He and Ne into an activated charcoal cold finger at 12 K. The helium was released from the cryogenic finger at 31 K and expanded into the spectrometer and measured, followed by Ne and Ar analyses (e.g. Poreda and Farley, 1992; Darrah and Poreda, in press). He, Ne, Ar, and Kr concentrations were determined by comparison to an air standard of known volume (0.77 cm³ of air at STP) to an accuracy of \pm 3%. Average blank levels were 1×10^{-10} cm³ for ⁴He, 2×10^{-16} cm³ for ³He, and 1×10^{-11} cm³ for ²²Ne. Sample errors were propagated quadratically (square root of the sum of individual errors squared) and include sample standard deviation, mass estimation, and external precision. The 1σ variation on standards of comparable concentration was 1.5% for ⁴He and 4.5% for ³He on average, respectively.

The helium (³He/⁴He) isotope ratios (hereafter expressed as R/Ra ratios, where R is the ³He/⁴He measured ratio and Ra is the ³He/⁴He ratio of the air: 1.39×10^{-6}) (Clarke et al., 1969) were normalized to Yellowstone Park standard (MM) with ${}^{3}\text{He}/{}^{4}\text{He} = 16.5 \pm 0.1$ times the air ratio (as measured in five noble gas laboratories) using a Yellowstone Park standard ($R_{MM}/R_A = [{}^{3}He/{}^{4}He_{MM}]/[{}^{3}He/{}^{4}He_{air}]$) (Poreda and Farley, 1992). SAES-ST-101 getters reduced the HD⁺ background to ~1000 ions/s. The VG 5400 noble gas mass spectrometer is fitted with a Johnston electron multiplier with pulse counting electronics on the axial collector (Poreda and Farley, 1992). Mass resolution of 550 $(m/\Delta m)$ enabled complete baseline separation of the ³He⁺ and HD⁺ peaks. The measured ³He/⁴He ratios were corrected for the addition of air (monitoring ⁴He/²²Ne), by assuming that the fumarolic Ne is low and of atmospheric origin (Craig and Lupton, 1976; Sano and Wakita, 1988; Sano et al., 1988). Analytical error for the R/Ra determination was \leq 0.3%. Sensitivity for the Ar concentrations was about 4×10^{-4} A/Torr on the Faraday cup (resolution 200 (m/ Δ m)), while precision for the ⁴⁰Ar/³⁶Ar ratios averaged at 0.3%.

4. Results

4.1. Major gas chemistry

All samples were analyzed for their major gas abundance, the stable isotopic composition of select major gases (δ^{13} C–CO₂ and δ^{15} N–N₂), and the elemental abundance and isotopic composition of noble gases. The gas compositions are presented in Table 1, while the isotopic parameters and gas ratios are presented in Table 2. The chemical composition of dry gas (i.e. water free) in all samples is dominated by CO₂ ranging from 968,000 to 994,000 µmol/mol (i.e. 96.8 to 99.4% of the total gas sampled). Dallol gases also contain trace quantities of N₂ (from 1620 to 6500 µmol/mol), H₂S (309 to 28,400 µmol/mol), CH₄ (0.01 to 3220 $\mu mol/mol)$ and H_2 (2.8 to 10,620 $\mu mol/mol).$ Of these components, only N₂ and H₂ showed a strong (positive) correlation to each other ($r^2 = 0.79$; p<0.01), while only H₂S was correlated with $[CO_2]$ ($r^2 = -0.89$; p<0.01). Samples 2, 10, 11, and 12 form a coherent set of gases that shows relatively high H₂ (from 104 to 218 µmol/mol) and low CH₄ (from 0.0135 to 0.0513 µmol/mol) concentrations. In these samples, light hydrocarbons (C₂H₆, C₃H₈, C₃H₆, and C₆H₆) also have relatively low concentrations, with a total summed value<0.03 µmol/mol. Distinct from this pattern, samples 4 and 17 show high CH₄ and low H₂ concentrations (up to 4040 and 3.38 µmol/mol, respectively), and light hydrocarbons (as sum) up to 40 µmol/mol. These high CH₄ and low H₂ samples represent the two samples that are most distal to the Dallol volcano. Importantly, no other samples display any apparent geographic distribution with respect to Mount Dallol or discharge temperature. Sample 13 is characterized by concentrations of CH₄ (130 µmol/mol) and light hydrocarbons (with a sum of up to 3.82 µmol/mol) intermediate with respect to those of the two previous groups, and the highest H₂ concentration (10,620 µmol/mol). The oxygen concentrations are <1.32 µmol/mol in all samples except 4 and 17 (277 and 166 µmol/mol, respectively).

Because hydrothermal fluids typically interact with groundwater, the presence of atmospheric (ASW) nitrogen is common in most hydrothermal gases (e.g. Giggenbach and Poreda, 1993; Snyder et al., 2003). Often nitrogen has a partially crustal or magmatic source making it necessary to calculate the amount of nitrogen sourced from hydrothermal system from magmatic or crustal origins, commonly termed "excess nitrogen", as opposed to atmospheric contributions (Giggenbach and Poreda, 1993). Because Ar may be sourced from a combination of radiogenic, air-saturated water, and atmospheric (air contamination) contributions, we calculate excess N₂ ([N₂]_{ex}) relative to ³⁶Ar assuming all ³⁶Ar is derived from a singular source (ASW) according to Eq. (1) (e.g. Giggenbach and Poreda, 1993; Snyder et al., 2003). For consistency, [N₂]_{ex} is calculated assuming air-saturated water, keeping in mind that small amounts of entrained air can contribute to [N₂]_{ex} particularly when sampling hot springs.

$$[N_2]_{excess} = [N_2]_{measured} - \left[(N_2/Ar)_{ASW} \times \left(295.5 \times {}^{36}Ar_{measured} \right) \right] \qquad (1)$$

At Dallol, $[N_2]_{ex}$ ranges from 411 to 1454 µmol/mol. These $[N_2]_{ex}$ values account for between 7 and 74% of the total N_2 (Table 1). The $[N_2]_{ex}$ significantly positively correlates with the ${}^{4}\text{He}/{}^{20}\text{Ne}$ ($r^2 = 0.80$; p = 0.016), ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ ($r^2 = 0.92$; p = 0.002), ${}^{3}\text{He}/{}^{4}\text{He}$ ($r^2 = 0.78$; p = 0.024), ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ ($r^2 = 0.91$; p < 0.002), and $\delta^{13}\text{C-CO}_2$ ($r^2 = 0.99$; p < 0.01), and is significantly negatively correlated to $CO_2/{}^{3}\text{He}$ ($r^2 = -0.95$; p < 0.01) discussed below.

4.2. Stable isotopic composition

The stable isotopic composition of CO_2 reflects the history of inorganic and organic reactions that generate CO_2 from many potential sources (e.g. mantle-derived, thermal breakdown (i.e. decarbonation) of carbonate sediments, methanogenesis, oxidation of organic matter) (e.g. Ballentine et al., 1991; Lollar and Ballentine, 2009). At Dallol,

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l able 1 Dallol gas co	mposition. A	malyses in a w	ater free basis.	. Xg is the gas	fraction.											
Sample	Xg	CO ₂	H ₂ S	²⁰ Ne	³⁶ Ar	Ar	⁸⁴ Kr	N_2	02	CH ₄	H ₂	He	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₆ H ₆
	mol/mol	pmol/mol	hmol/mol	hmol/mol	µmol/mol	µmol/mol	µmol/mol	hmol/mol	µmol/mol	µmol/mol	µmol/mol	lom/lomu	hmol/mol	lom/lomu	µmol/mol	µmol/mol
Dallol 1		982,000		0.005	0.0215	7.056	0.0005	1188	0.5	767.6		0.2075				
Dallol 2	0.893	977,000	20,800	0.039	0.0597	18.8	0.0013	1900	0.97	0.0135	111	11.8	0.0057	0.0036	0.0013	0.0013
Dallol 4	0.916	994,000	309	0.021	0.0473	14.4	0.0015	1620	277	4040	3.38	3.35	35.2	7.0	0.0005	0.9664
Dallol 10	0.917	974,000	23,400	0.045	0.0400	13.2	0.0008	1990	0.25	0.0447	218	17.6	0.0164	0.0073	0.0053	0.0010
Dallol 11	0.988	977,000	21,500	0.024	0.0332	11.0	0.0005	1700	1.32	0.0513	104	22.0	0.0112	0.0046	0.0013	0.0010
Dallol 12	0.977	969,000	28,400	0.036	0.0382	12.8	0.0007	1990	0.25	0.0303	208	14.0	0.0091	0.0056	0.0019	0.0069
Dallol 13	0.104	981,000	1710	0.062	0.2206	65.5	0.0071	6500	0.10	130	10,620	0.42	2.29	0.72	0.3187	0.4907
Dallol 17	0.993	968,000	27,300	0.014	0.0301	9.2	0.0007	1310	166	3220	2.86	4.14	26.0	5.46	0.0005	0.7519

the δ^{13} C-CO₂ values span from -6.19 to -2.12% V-PDB, which fall within the anticipated range for both mantle-derived (-3 to -8% V-PDB) and crustal CO₂ (-8 to +2% V-PDB) (Jenden et al., 1993; Zhou et al., 2012). As a result, the δ^{13} C-CO₂ cannot uniquely distinguish the source or relative contributions of these gases. Interestingly, the δ^{13} C-CO₂ correlates strongly to 20 Ne/ 36 Ar (r^2 =0.83; p=0.041), excess N₂ (r^2 =0.99; p<0.01), 40 Ar/ 36 Ar (r^2 =0.90; p=0.015), and 4 He/ 40 Ar* (r^2 =0.81; p<0.049) described below (Figs. 5, 6). These δ^{13} C-CO₂ values correspond to a CO₂/ 3 He range from 7.1×10⁹ to 1.01×10¹¹, which negatively correlates (r^2 =-0.84; p=0.034) with the δ^{13} C-CO₂ (Table 2; Fig. 5).

Similar to the stable isotopic compositions of CO₂, stable nitrogen isotopes provide clues on the origin of N₂. All the $\delta^{15}N$ values at Dallol, standardized to air, are positive and range from 2.93 to 4.50% (Table 2; Fig. 3). The nitrogen isotopic composition of Dallol gases plots along a mixing line between thermally post-mature sediments and atmospheric components (ASW and/or AIR) without resolvable contributions from typically MORB-type N₂ ($\sim -4\%$) (Fig. 3) (e.g. Snyder et al., 2003). This trajectory indicates that N₂ is sourced from thermally post-mature sediments (potentially from Proterozoic mobile belt sediments deposited in the basin) without significant contributions from typical MORB-type components (e.g. Snyder et al., 2003). The timing of N₂ incorporation into mantle-derived fluids from sedimentary inputs (e.g. interaction of mantle fluids with crustal materials during emplacement or entrainment of N₂ into the mantle prior to the release of mantle-derived fluids) at Dallol is unclear. However, the consistently non-atmospheric nature of $\delta^{15}N$ in Dallol gases does suggest that N2 was likely incorporated before interaction with the aqueous system (Fig. 3).

4.3. Noble gases

The helium (range from 0.20 to 22.0 µmol/mol), neon (0.006 to 0.069 µmol/mol), argon (9.2 to 65.5 µmol/mol), and krypton (0.001 to 0.012 µmol/mol) concentrations in Dallol gases are displayed in Table 1. Because magmatic gases have a paucity of neon relative to the atmosphere, the ⁴He/²⁰Ne serves as a sensitive proxy by which to distinguish contributions sourced in the mantle or crust (i.e. He) from those entrained during interaction with groundwater (e.g. ²⁰Ne) (Craig and Lupton, 1976; Sano and Wakita, 1988; Sano et al., 1988). The measured ⁴He/²⁰Ne ratios at Dallol range from 12.4 to 684.5 (Table 2; Fig. 6). These values greatly exceed (by 40-2000 times) the ⁴He/²⁰Ne expected for atmospheric gases dissolved in groundwater (0.288) indicating negligible atmospheric helium in Dallol gases (Craig et al., 1963, 1978; Weiss, 1971b; Zhou et al., 2012). Because Dallol gases are dominated by atmospheric (ASW) neon, the neon isotopic compositions for the two measured samples with the highest ⁴He/²⁰Ne (samples 11 and 12) are not resolvable from atmospheric ratios (samples 11 and 12: ${}^{20}Ne/{}^{22}Ne = 9.88$ and 9.78 and ²¹Ne/²²Ne 0.0291 and 0.0289, respectively). The isotopic composition of atmospheric gases ²⁰Ne/³⁶Ar and ⁸⁴Kr/³⁶Ar, entrained into groundwater by Henry's law partitioning during groundwater recharge, vary from 0.23 to 1.13 and 0.015 to 0.032, respectively (Table 2; Fig. 6).

The isotopic composition of helium is often useful for distinguishing gases derived from a MORB-type or plume mantle (7–30 Ra), subcontinental lithosphere (~6 Ra), and crust (i.e. ~0.01 Ra) (e.g. Poreda et al., 1986; Jenden et al., 1988; Lollar et al., 1994; Ballentine et al., 2001; Zhou et al., 2012). The helium isotopic composition for Dallol ranges from 10.9 to 11.9 Ra, where $Ra = R_{Air}$ and $R_{Air} = 1.39 \times 10^{-6}$ (Clarke et al., 1969; Mamyrin and Tolstikhin, 1984) and indicates a significant mantle signature controlled by the degree of primordial helium trapped in the mantle since the accretion of the Earth (Lupton and Craig, 1976). These values exceed typical MORB-type compositions and are consistent with contributions from mantle plume materials (e.g. Craig and Lupton, 1976). Because radiogenic ⁴⁰Ar, is produced by the decay

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Table 2

	Ar/N_2	C_1/C_2	C_1/C_3	⁴ He/ ²⁰ Ne	²⁰ Ne/ ³⁶ Ar	⁸⁴ Kr/ ³⁶ Ar	R/Ra	⁴⁰ Ar/ ³⁶ Ar	$^{4}\text{He}/^{40}\text{Ar}^{*}$	N_2 excess	$\rm CO_2/^3He$	CH ₄ / ³ He	$\rm CO_2/^{36}Ar$	$\delta^{15} N$	$\delta^{13}C$
Dallol 1	0.0070			25.6	0.231	0.025	11.0	328	0.2	376	1.01E+11	1.42E+09	6.49E+07		
Dallol 2	0.0099	2.4	3.7	304.5	0.656	0.021	11.7	315	10.3	1043	8.64E+09	1.19E + 02	1.63E+07	3.06	
Dallol 4	0.0089	114.8	576.9	137.2	0.448	0.032	11.9	304	6.9	967	4.27E+10	1.74E + 08	2.11E+07	2.93	-4.22
Dallol 10	0.0067	2.7	6.1	381.7	1.132	0.019	11.9	330	12.8	1352	7.11E+09	3.26E+02	2.43E+07	4.01	-2.88
Dallol 11	0.0065	4.6	11.1	684.5	0.722	0.015	11.4	331	14.0	1254	7.81E+09	4.10E + 02	3.06E+07	4.5	-2.69
Dallol 12	0.0065	3.3	5.4	408.9	0.949	0.018	11.6	335	10.0	1454	7.17E+09	2.24E + 02	2.52E + 07	4.18	-2.12
Dallol 13	0.0101	57.0	181.0	12.4	0.281	0.032	10.9	297	2.5	411	8.47E+10	1.12E + 07	4.43E+06	2.97	-6.19
Dallol 17	0.0069	123.7	588.8	103.0	0.468	0.022	11.5	304	5.7	952	4.91E+10	1.63E+08	3.44E+07	4.18	-4.23

of potassium (i.e. 40 K) within the mantle it also provides a marker for mantle gas contributions. The argon isotopic compositions (40 Ar/ 36 Ar) at Dallol range from 297 to 335 (Table 2; Fig. 2). By using the atmospheric ratio of 40 Ar/ 36 Ar (295.5), excess argon (40 Ar*) (a combination of 40 Ar from radiogenic production in the crust and mantle) can be calculated by subtracting the atmospheric value from the measured value in Eq. (2).

$${}^{40}\text{Ar}* = \left({}^{40}\text{Ar}/{}^{36}\text{Ar}\right)_{\text{measured}} - 295.5 \times {}^{36}\text{Ar}_{\text{measured}}$$
(2)

The corresponding ratios of ⁴He and ⁴⁰Ar^{*} can provide sensitive tracers for relative amount of degassing that has occurred prior to the release of fluids from the mantle and/or their migration (e.g. Poreda et al., 1992, 1993; Lollar et al., 1997; Winckler et al., 2001; Ballentine and Lollar, 2002; Ballentine et al., 2002; Tedesco et al., 2010; Hunt et al., in press). At Dallol, the ⁴He/⁴⁰Ar^{*} ranges from 0.2 to 14 (Table 2; Fig. 2).



We hypothesize that the upper end-member (~14) results from the highly degassed nature of mantle fluids that feed Dallol hot springs, rather than from any large variations of the time-integrated K/U ratio in the mantle source.

5. Discussion

The Dallol bubbling gases provide valuable information about the source, transport, and interaction of mantle volatiles within a kinematically active rift segment of the Afar depression. The Dallol area is particularly interesting because it is located in the northwestern part of the Afar depression in an area with rift propagation consistent with the orientation of the Red Sea rift system. The Red Sea rift system represents one arm of the Afar triple junction that includes



Fig. 3. (Top) Ar/N₂ vs. δ^{15} N–N₂: Dallol gases plot along a mixing line consistent with inputs form thermally post-mature sediments and atmospheric components (ASW and/or AIR) without resolvable contributions from typically MORB-type N₂ (~-4‰). Thus, we hypothesize that the nitrogen was incorporated into the mantle fluids prior to interaction with groundwater because nearly all of the N₂ in this system is non-atmospheric in origin. (Bottom) CH₄/N₂ vs. δ^{15} N–N₂: The nitrogen isotopic composition shows no correlation with any shallow level hydrothermal generation of nitrogen or methane. Both high and low (essentially zero) methane springs have non-atmospheric nitrogen.

Fig. 4. With the exception of one sample, the majority $\text{CO}_2/^3\text{He}$ and $[\text{N}_2]$ (predominantly non-atmospheric) values correlate with atmospherically derived [²⁰Ne]. This trend has previously been interpreted as an indication that groundwater plays a fundamental role in controlling the $\text{CO}_2/^3\text{He}$ and indicates pre-mixture of mantle-derived and aqueous fluids in low temperature carbon dioxide fields (Gilfillan et al., 2009; Zhou et al., 2012). Similarly, we hypothesize that the $\text{CO}_2/^3\text{He}$ is altered by interaction with crustal water. However, unlike recent investigations (e.g., Zhou et al., 2012) the highest $\text{CO}_2/^3\text{He}$ does not represent the original emplaced fluid. Instead, samples with the highest [²⁰Ne] and lowest $\text{CO}_2/^3\text{He}$ correspond to the mantle-derived fluids at Dallol.

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Fig. 5. Gas components plotted against $CO_2/^3$ He. Because the inferred mantle end-member has the lowest $CO_2/^3$ He, we interpret elevated $CO_2/^3$ He as a proxy for degassing where ³He is preferentially lost to CO_2 (discussed further in Figs. 6, 7). The trends fix the end-member CO_2 isotopic composition at -2.1%, which is similar to but slightly heavier than other high temperature mantle plume environments (e.g. Hawaii, Iceland, Yellowstone) and may be the result of carbonate addition. The end-member ${}^{4}\text{He}/{}^{40}\text{Ar}^*$ is significantly higher than typical plume environments or the nearby actively spreading Red Sea rift axis brines (Lupton et al., 1977; Winckler et al., 2001) and has only been observed in lavas that have undergone substantial degassing wherein Ar degasses preferentially to helium reflecting the lower solubility of Ar in basaltic melts.

nascent transition from continental to ocean rifting (i.e. closer to the triple junction; located approximately within the Tendaho graben), a relatively young ocean spreading center (last 4–5 Myr; ~15–20° N), and an established and actively spreading center (above 20–23° N, northwest of the current study area) (e.g. Winckler et al., 2001). In addition, the Dallol hot spring gases provide a unique perspective into the mechanisms involved in the transfer of mantle-derived volatiles to the hydrothermal reservoir and from the hydrothermal reservoir to hot springs at the surface.

5.1. Gas source identification

Dallol gases display elevated helium isotopic ratios (up to 11.9 Ra) that unambiguously resolve significant contributions of primordial gases from the Earth's mantle (e.g. Craig and Lupton, 1976; Lupton and Craig, 1976; Mamyrin and Tolstikhin, 1984). Because the mantle-rich end-member described above exceeds the helium isotopic composition of typical MORB-type components (7–9 Ra), we interpret these values as evidence for contributions from a deep mantle, plume-sourced

a) 0.08 b) 12.0 Dallol 11.8 0.06 11.6 ⁵He/⁴He (Ra) ⁸⁴Kr/³⁶Ar 0.04 11.4 11.2 0.02 11.0 Dallol 0.00 10.8 0.8 0.0 02 04 0.6 10 12 0.2 0.0 0.4 0.6 0.8 1.0 1.2 20 Ne/36 Ar ²⁰Ne/³⁶Ar C) d) 1600 14 1400 12 [N₂] _{excess} (µmol/mol) 1200 10 ⁴He/⁴⁰Ar* 1000 8 6 800 4 600 Dallol 2 Dallol 400 0 0.2 0.0 0.4 0.6 0.8 1.0 1.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 20Ne/36Ar 20 Ne/36 Ar e) f) 2e+11 0 Dallol -2 2e+1 8¹³C-CO, CO./³He -4 -6 5e+10 -8 Dallol -10 0.0 02 04 0.6 0.8 1.0 12 0.0 0.2 0.4 0.6 0.8 1.0 12 ²⁰Ne/³⁶Ar ²⁰Ne/³⁶Ar Degassing Mixing

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Fig. 6. The Dallol hot springs exhibit a large range in 20 Ne/ 36 Ar ratios from 1.15 (5× ASW) to near air-saturated water of 0.2 (ASW: gray shaded area represents approximate anticipated range). Because of the differing aqueous solubilities of these two gases (Weiss, 1971a, 1971b), their relative ratio provides a sensitive tracer for kinetic gas loss and mixing. Panel (a) shows the atmospheric gas composition. We assume that the highest measured 3 He/ 4 He (i.e. 11.9Ra) and 4 He/ 20 Ne (i.e. ~410) from a common original gas source can be reasonably considered as the mantle end-member composition. Using this premise, the hydrothermal end-member for the Dallol gases derived from the mantle source have the highest 3 He/ 4 He = 11.9 and 20 Ne/ 36 Ar = 1.15 and lowest CO₂/ 3 He. The solid cyan and dashed pink lines represent: 1) a hypothesized 2-component mixture between the Dallol mantle end-member and a highly degassed remnant brine and 2) a solubility partitioning degassing model, respectively (as discussed in Section 5.2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

component likely associated with the Afar plume (e.g. Craig and Lupton, 1976; Mamyrin and Tolstikhin, 1984). These observed helium isotopic ratios are consistent with those measured near the Afar triple junction (11.8 Ra) within the kinematically active Tendaho-Gabo rift segment (Craig, 1977; Darrah et al., 2008), but higher than the MORB-type values observed in brines at actively rifting Red Sea spreading centers (i.e. ~9.0 Ra) (e.g. Lupton et al., 1977; Winckler et al., 2001). At present, it is unclear if the "plume" contributions observed at Dallol relate to its spatial proximity to the Afar trip junction or its relative immaturity along the nascent tip of the southeastern segment of the Red Sea rift that has only transitioned from continental

to oceanic rifting in the last 2–4 Myr. The similarity in the helium isotopic composition between Dallol and the Tendaho Basin likely indicates that the Afar plume interacts and sources the volatiles across at least the 290 km traverse between these two locations; a relationship that does not extend to the active spreading centers in the central segment of the Red Sea rift.

Dallol

In addition to helium isotopes, other noble gas and isotopic parameters provide information on the source and movement of fluids from the mantle within this region. For example, by comparing ⁴He to other radiogenic noble gases ⁴⁰Ar (Steiger and Jager, 1977), one can gain additional insights into the source and progression of magmatic

degassing (e.g. Sarda and Moreira, 2002) and the migration of fluids within and from the mantle (Poreda and Craig, 1992; Poreda et al., 1992, 1993). Similarly, paired $CO_2/{}^{3}$ He and δ^{13} C–CO₂ provide information about the chemistry of magmatic sources, the entrainment of crustal sediments, and the various sources of carbon (e.g. Tedesco, 1994; Moreira et al., 1996; Dixon et al., 1997; Dixon and Clague, 2001; Snyder et al., 2001; Tedesco et al., 2010). Based on the complete gas chemistry, we make the assumption that the samples with the most primordial helium isotopic composition (up to ~11.88 R_{Air}), non-atmospheric 4 He/ 20 Ne (up to ~430), greatest [N₂]_{ex} (~1200 to 1400), and highest reservoir temperatures up to ~310 °C (as inferred from gas-steam ratios $CO_2/^{36}Ar$ (~3.4×10⁷)) represent the mantle-derived fluid endmember (consistent with other lines of evidence discussed below) (Table 2) (Craig and Lupton, 1976; Poreda et al., 1992; Giggenbach and Poreda, 1993). These samples have the lowest observed $CO_2/{}^{3}He$ (~7.1 to 7.8×10^9), heaviest δ^{13} C-CO₂ = ~ -2.1 to -2.9‰, and the most non-atmospheric (ASW) 20 Ne/ 36 Ar (up to ~1.13) (Tables 1, 2; Figs. 2, 5, 6). We attempt to understand the evolution of this end-member that feeds Dallol in order to evaluate its implications within the context of other archetypal plumes around the world.

The end-member ⁴He/⁴⁰Ar^{*} values at Dallol greatly exceed current mantle production ratios ~3.7 (calculated on the basis of measured (U+Th)/K in the MORB) and the "bulk earth" values of ~1.8 (calculated at 4.5 Ga) (Jochum et al., 1983) (Fig. 2). Because the ⁴He and ⁴⁰Ar (and hence the ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$) composition of fumarolic gases is strongly dependent upon the introduction of gaseous components from the degassing melt the large difference in solubility between helium and argon in silicate melts (helium is $4 \times$ more soluble: Dymond and Hogan, 1978; Lux, 1987; Poreda et al., 1993; Dixon and Stolper, 1995; Dixon et al., 1995, 1997), may dramatically alter the ⁴He/⁴⁰Ar^{*} that ultimately enters the fumarolic system at Dallol. The ⁴He/⁴⁰Ar* values well above bulk-earth values (1.8) typically observed in plume environments (e.g. Jochum et al., 1983) and those observed in the nearby Red Sea rift axis basin (i.e. 2.1) (Winckler et al., 2001) indicate significant degassing of mantle-derived fluids before emplacement at Dallol. This trend toward increasing ⁴He/⁴⁰Ar* is quite rare and has only been observed in lavas that have undergone substantial degassing as opposed to gas loss from the aqueous systems that produce decreasing ⁴He/⁴⁰Ar^{*} ratios (Dymond and Hogan, 1978; Poreda et al., 1993; Dixon et al., 1997; Tedesco et al., 2010).

Similar to the ⁴He/⁴⁰Ar^{*}, the Dallol fluids CO₂/³He (~7.7×10⁹) show significant mantle-derived contributions, that are consistent with the Afar deep mantle plume, but are significantly elevated as compared to other well defined mantle plumes (e.g. Hawaii (CO₂/³He: 4×10⁹), Iceland (CO₂/³He: 3.3×10⁹)) (e.g. Poreda et al., 1992; Giggenbach and Poreda, 1993) and especially MORB (CO₂/³He: 2.1×10⁹) (Marty and Jambon, 1987). In addition, the Dallol end-member δ^{13} C-CO₂ appears to be ~ -2.15‰. This composition may in part relate to its generation from a more CO₂-rich partially degassed alkaline-rich basalt commonly present in the Afar and other locations along the East African Rift (Lux, 1987; Dixon and Stolper, 1995; Dixon et al., 1997, 1995; Dixon and Clague, 2001; Tedesco et al., 2010) or contribution from a carbonate source of carbon dioxide.

To investigate the potential for degassing to account for the observed mantle-derived end-member at Dallol, we perform a simple Rayleigh fractionation model for the evolution of mantle-derived components as shown previously (e.g. Ballentine et al., 2002). Our model assumes an initial plume composition of $CO_2/^{3}He (2-4 \times 10^{9})$, $\delta^{13}C-CO_2 (-2 \text{ to } -4\%)$, and $^{4}He/^{40}Ar^*$ (1.8) consistent with ranges observed in previous work (e.g. Marty and Jambon, 1987; Poreda and Arnorsson, 1992; Poreda et al., 1992; Giggenbach and Poreda, 1993; Hilton et al., 1999, 2011). For simplicity, we show the model calculations for the end-member that are most favorable to the compositions observed at Dallol (i.e. $\delta^{13}C-CO_2 = -2\%$). The fractionation factors for $CO_2/^{3}He$ are assumed to be 2.5 (i.e. CO_2 is 2.5 × more soluble than helium in magmas with decreasing silica (SiO₂) content), $δ^{13}$ C-CO₂ = -2.0‰ or α = 1.002, and ⁴He/⁴⁰Ar^{*} = 0.25 (helium is 4× less soluble) based on prior magmatic solubility observations for alkali-rich basaltic magmas similar to those observed at the Afar plume (Lux, 1987; Poreda et al., 1992; Dixon and Stolper, 1995; Dixon et al., 1997; Dixon and Clague, 2001). Because the ⁴He/⁴⁰Ar^{*} is the least affected by the magmatic chemistry of the hypothesized basaltic melt, we first evaluate the modeled ⁴He/⁴⁰Ar^{*} results (Fig. 2). The modeled ⁴He/⁴⁰Ar^{*} approaches the observed Dallol mantle-derived end-member (~14) at a value consistent with the degassing of an archetypal plume to approximately 92% (Fig. 2). This model is consistent with our assertion that the mantle-derived end-member that feeds Dallol is strongly degassed before interaction with the hypothesized hydrothermal reservoir.

We envision three possible scenarios that may account for the degassed mantle-sourced volatiles present at Dallol: 1) volatiles are sourced locally from localized dyke intrusions, similar to those associated with rifting that have a component of plume sourced magma (Wright et al., 2006; Ebinger et al., 2008; Keir et al., 2009); 2) volatiles are sourced locally and ascend vertically from the plume head (either with magmatic fluids, during steady state degassing, or decompressive melting) that extends across the Afar depression and released in areas with active extension (active rift segments), which has degassed over the last ~30 Myr; or 3) volatiles are sourced from the partially degassed material that is channeled laterally ~290 km northwest from the center of Afar plume at the Afar triple junction (Tendaho-Gabo rift segment) along a rift channel that underplates the continental lithosphere beneath Afar and is subsequently released in the Dallol area similar to the processes observed at other locations where mantle plumes and active rifts interact (e.g. Easter Microplate and Reykjanes Ridge) (Poreda and Craig, 1992; Poreda et al., 1993). The available dataset does not allow us to uniquely identify which of these scenarios regulate the degassing signal observed at Dallol. However, Scenario 3, the plume channel hypothesis, has merit if the Afar plume is similar to other mantle plume-spreading center geometries (i.e. Reykjanes Ridge-Iceland and Easter Hotspot-Microplate). Most plumes also exist for long periods of time (e.g. Iceland and Hawaii hot spots have been active for at least ~65 and 81 Myr, respectively) and produce a complex eruptive history that has active post-erosional volcanism occurring hundreds of kilometers away from the plume center (e.g. North Arch volcanic field: Dixon et al., 1997). Based on the available dataset, each of these mechanisms warrants further consideration. These hypotheses are testable by evaluating fumarole chemistry along this and other rift segments to determine if a geospatially coherent set of gas variations exist from the plume head (Tendaho-Gabo basin) to Dallol.

Our model calculations suggest that some of the elevated $\text{CO}_2/^3\text{He}$ may relate to the evolution of the strongly degassed mantle-derived component as inferred from the ${}^4\text{He}/{}^40\text{Ar}^*$ noted above. However, at Dallol even the mantle-derived end-member gases have $\sim 1.5 \times$ higher $\text{CO}_2/{}^3\text{He}$ than the modeled values anticipated based on the ${}^4\text{He}/{}^{40}\text{Ar}^*$ ratio (i.e. a proxy less susceptible to variability in mantle composition (MORB-type vs. alkaline-enriched)). Additionally, compositional differences (i.e. the alkali-rich nature of plume-type volcanism) may also account for some of this increase, but it does not explain why the end-member $\text{CO}_2/{}^3\text{He}$ found in Dallol is $> 2 \times$ that of the archetypal plumes of Hawaii and Iceland. This suggests the potential for an additional source of CO_2 .

The δ^{13} C–CO₂ can often differentiate the origin of a gas (e.g. mantle degassing versus oxidation of organic matter), but is not always applicable in hydrothermal systems because of the non-ambiguous nature of potential mantle and crustal δ^{13} C–CO₂ inputs (e.g. mantle – 3 to – 8‰ and crustal +2 to –8‰) (Schoell, 1983; Whiticar et al., 1986; Jenden et al., 1993; Lollar et al., 1997). A closer examination of δ^{13} C–CO₂ of Dallol gases indicates a heavier composition than the other plumes (–2‰ vs. – 3 to –4‰ (e.g. Poreda et al., 1992; Giggenbach and Poreda, 1993)). We note that these observations are reversed to the modeled evolution for the mantle reservoir that feeds Dallol (i.e. δ^{13} C–CO₂ decreases during

degassing from a magma; Fig. 2). Thus, we hypothesize that an exogenous source of CO₂ with enriched δ^{13} C–CO₂ likely contributes to these volatiles. The observed elevated CO₂/³He and δ^{13} C–CO₂ are consistent with CO₂ inputs from thermal decarbonation of detrital carbonates (e.g. Lollar et al., 1997; Tassi et al., 2010; Aguilera et al., 2012; Zhou et al., 2012) that may result from assimilation of Proterozoic carbonates similar to those exposed in the Danakil horst (Gebresilassie et al., 2011). We design a hypothetical degassing model that starts with an archetypal plume that includes inputs from carbonates with enriched δ^{13} C–CO₂ (Fig. 2). This hypothetical model includes initial δ^{13} C–CO₂ = +1% and CO₂/³He = 3×10^9 . While the validity of our hypothesized end-member is arbitrary, it does account for the CO₂/³He and δ^{13} C–CO₂ end-member at Dallol and is consistent with the degassed ⁴He/⁴⁰Ar* composition (Fig. 2).

This proposed addition of crustal gases is supported by nonatmospheric N_2 abundance and isotopic composition (Fig. 3). The N_2 composition of all Dallol gas emanations is significantly above the air-saturated water (ASW) and atmospheric concentrations (Table 2, Fig. 3). This nitrogen excess $([N_2]_{ex})$ suggests an additional source of nitrogen from either primary mantle fluids that have entrained mature crustal sediments or water-rock interactions of mantle-derived fluids with shallower crustal materials (Snyder et al., 2003; Fischer et al., 2005). We compare the nitrogen isotopic composition ($\delta^{15}N-N_2$) compared to Ar/N₂ (Table 2, Fig. 3). The δ^{15} N–N₂ indicates that all of the Dallol hot springs emit gases consistent with thermally mature sediments that have minimal inputs from atmospheric or typical mantletype (MORB = ~ -3.5 to -4%) N₂ (e.g. Snyder et al., 2003). Even the samples that have experienced substantial gas loss (discussed below) are dominated by nitrogen from thermally post-mature sediments (Fig. 3). Interestingly, this isotopic trajectory suggests that the N₂ in the Dallol gases likely represents a mixture with thermally post-mature crustal sediments typically observed in other settings such as hydrothermal systems associated with subduction zones (e.g. Momotombo, Nicaragua and Lastarria, Central Andean Volcanic Complex: Snyder et al., 2003; Aguilera et al., 2012). Subduction zone and Dallol gases both contain heavy N, high $CO_2/{}^{3}$ He with a carbonate isotopic input (i.e. heavier δ^{13} C–CO₂). The Dallol fluids do contain considerable [N₂]_{ex} (~ 1.4×10^3 on average), but not to the extent observed in subduction zone lavas (($[N_2]_{ex}$ at Momotombo: ~40×10³ and Lastarria: 13×10³) Snyder et al., 2003; Aguilera et al., 2012), which we anticipate relates to the lower contributions of meta-sedimentary nitrogen in this rift basin in addition to potentially different hydrodynamic conditions and transport processes feeding the Dallol hot springs. We suggest that the interaction of mantle-derived fluids with Proterozoic metasediments deposited previously in the inland lake in the Danakil Depression is responsible for the [N2]excess observed at Dallol. Similar interactions between mantle-derived fluids and meta-sediments may also account for a small, but detectable addition of CO₂ from carbonate clasts.

Unlike N₂, in the Dallol bubbling springs, the abundance of hydrocarbons is highly variable. Two samples have percentage level methane and an abundance ratio to higher hydrocarbons (e.g. C_1/C_2) consistent with thermogenic hydrocarbon production ($C_1/C_2 = ~115-125$) (Schoell, 1980, 1988), while the other samples have hydrocarbon at near background levels (Table 1). The relative abundance of N₂ and CH₄ shows no correlation with the δ^{15} N–N₂ indicating a different source for each gas. For example, both springs with both high and low (essentially zero) [CH₄] have uniform non-atmospheric δ^{15} N–N₂ and high [N₂]_{ex}.

5.2. Gas-water interactions

In order to understand the mechanisms involved in the transfer of magmatic volatiles to the hydrothermal reservoir and from the hydrothermal reservoir to hot springs at the surface, it is essential to understand both mantle-derived components and their interaction with fluids sourced within the crust. Recently, Gilfillan et al. (2008, 2009)

and Zhou et al. (2012) demonstrated the applicability of paired noble gas, carbon dioxide, and stable carbon isotopes for understanding the interactions and sub-surface processes that alter the composition of gases within a crustally emplaced CO₂ reservoir and meteoric water. Atmospherically derived noble gases (e.g. ²⁰Ne, ³⁶Ar, ⁸⁴Kr) can provide insights into the mechanisms of interaction of mantle fluids with crustal fluids. Because both ²⁰Ne and ³⁶Ar have a dominantly atmospheric (air-saturated water) source and differing aqueous solubilities (Ne less soluble than Ar), gas loss and/or mixing with an ASW-dominated low temperature fluid will generate lower ²⁰Ne/³⁶Ar ratios that approach ASW values (e.g. ~0.156).

Previous work examining the role of groundwater in altering the composition of mantle-derived gases demonstrates the utility of comparing mantle and atmospheric-derived crustal components (Ballentine and Holland, 2008; Gilfillan et al., 2008, 2009; Zhou et al., 2012). By examining the Dallol data within this framework, we identify a strong correlation between $CO_2/{}^{3}$ He vs. 20 Ne (Fig. 4) and a consistent correlation between various mantle-derived components and [²⁰Ne] (e.g. ⁴He vs. ²⁰Ne and N₂ vs. ²⁰Ne) and the ²⁰Ne/³⁶Ar ratio (e.g. $CO_2/^3$ He or ⁴He/⁴⁰Ar^{*} vs. ²⁰Ne/³⁶Ar) (Figs. 4, 6). These strong linear correlations indicate that: 1) both mantle and atmospherically-derived components are pre-mixed prior to alteration from degassing or mixing in hydrothermal waters and 2) that groundwater plays an important role in modulating the relative distribution of mantle (and/or crustal) and atmosphericderived components after the interaction with mantle-derived fluids; a scenario consistent with previous work in other CO₂ dominated systems (e.g. Ballentine and Lollar, 2002; Gilfillan et al., 2008, 2009; Zhou et al., 2012). One important contrast to prior work, is the mechanism of interaction with groundwater that controls the distribution of carbon dioxide by preferential extraction of less soluble components (e.g. ³He or ²⁰Ne) from groundwater and subsequent (re-)dissolution of the more soluble components (e.g. CO₂ and ³⁶Ar) into relatively low temperature groundwater (Gilfillan et al., 2008, 2009; Zhou et al., 2012). This process follows the emplacement of CO₂-rich fluid (highest $CO_2/^3$ He observed in the system) into the crust. As the CO_2 -rich fluid migrates through under-saturated zones "water washing" preferentially dissolves CO_2 decreasing the original $CO_2/{}^{3}He$. In contrast, at Dallol the mantle-derived CO₂-rich fluid end-member emplaced in the crust appear to have the lowest $CO_2/{}^3He$ that subsequently increases as preferential loss of the less soluble components from the hydrothermal aqueous reservoir occurs.

One important observation is the non-ASW ²⁰Ne/³⁶Ar in the Dallol hot spring mantle-derived end-member. Dallol gases range from approximately air-saturated water (ASW) (~0.23) up to 1.1 (Fig. 6, Table 2) with the most "pure" mantle-derived end-member in the highest ²⁰Ne/³⁶Ar. To examine the ²⁰Ne/³⁶Ar end-member, a recently developed GGS-R model (i.e. Gilfillan et al., 2008, 2009; Zhou et al., 2012) is applied to evaluate the atmospheric derived components (i.e. ²⁰Ne/³⁶Ar and ⁸⁴Kr/³⁶Ar). At Dallol, these proxies are completely atmospherically derived and sensitive to phase partitioning, so it is useful to first evaluate their composition at Dallol in order to understand the interactions that occur with crustal water. Previous modeling (i.e. Gilfillan et al., 2008, 2009; Zhou et al., 2012) suggests that the observed 20 Ne/ 36 Ar (up to 1.1) in the fluids of the mantle end-member cannot be accounted for by a simple single or multiple-stage groundwater degassing model, but requires a multiplestage groundwater gas-phase stripping and (re-)dissolution model (GGS-R). Additionally, the conceptualization of this model fits the geological setting at Dallol in which there is a continuous percolation of a mantle-derived CO₂-rich gas phase through an aqueous system. In theory, as the CO₂-rich fluid percolates through groundwater it extracts dissolved gas components (according to solubility) from groundwater by partitioning them into the migrating gas phase (i.e. stripping) that later re-dissolves soluble components back into groundwater as the physical conditions change (e.g. pressure increases, flux decreases, etc.) (e.g. Gilfillan et al., 2008, 2009; Zhou et al., 2012). In hydrothermal systems such as Dallol, this re-dissolution potentially may occur as steam

cools during interaction with cooler waters at shallower depths. One major drawback to this proposed mechanism of CO₂-rich fluid interaction is the fact that fumarolic and hydrothermal systems, such as Dallol, may interact above the boiling temperature. In this scenario, the entire system may flash to steam (as is inferred by the $CO_2/^{36}Ar$) and may fractionate atmospheric gases in a non-equilibrium manner or by "bulk-stripping" in which all atmospheric gases are lost independent of solubility. Additionally, we cannot completely discount the potential that the elevated $^{20}Ne/^{36}Ar$ (~1.1) may be intrinsic to the initial mantle-derived component (values up to 0.5 to 1.6 in mantle components) (e.g. Poreda and Farley, 1992; Farley and Poreda, 1993).

Similar to previous work, this process is modeled as an open system Rayleigh fractionation process using the conditions specific to Dallol (field parameters, measured end-member components, etc.). The fractionation model assumes that all neon is atmospheric (ASW) (Table 2; Fig. 7; Craig and Lupton, 1976; Sano and Wakita, 1988; Sano et al., 1988). For the Dallol area, we assume initial end-member compositions as shown in Tables 1 and 2 and Fig. 5. Atmospheric solubility components are assumed as follow throughout: zero salinity at recharge, equilibrated at 15 °C, recharged at sea level. Under these conditions, the initial 20 Ne/ 36 Ar = 0.151. Although



Fig. 7. The Dallol hot springs exhibit a large range in ²⁰Ne/³⁶Ar ratios (Fig. 6) from near ASW (0.156) to 1.15, which can be explained as either gas loss or mixing. Because He and Ne have similar solubilities in aqueous fluids, the ⁴He/²⁰Ne vs. ²⁰Ne/³⁶Ar ratio provides a sensitive proxy for addressing the degassing versus mixing scenarios. Dallol data better fits a mixing (solid cyan line) trend that intercepts at approximately zero [⁴He] at ASW composition (as opposed to degassing model (dashed pink line)). We suggest that mixing may occur between a somewhat recent mantle-sourced end-member and a highly degassed residual brine (i.e. that has already preferentially lost less soluble gases). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the reservoir depth at which mantle-derived and aqueous fluids interact for Dallol is unknown, an estimated depth of ~2000 m (below the halite aquitard), is assumed with approximate temperature conditions at 200 °C, and ~1 M NaCl. From these conditions, we calculate the solubility coefficients, Henry's law constants, and fugacity and activity coefficients consistent with previous work (Gilfillan et al., 2008, 2009; Zhou et al., 2012; and references therein). These parameters yield dimensionless Henry's law values for He=47.6, Ne=52.0, Ar=37.5, Kr=32.4, CO₂=3.01, and the δ^{13} C-CO₂ fractionation factor is assumed to be $\alpha = 1.002$. The plot of ⁸⁴Kr/³⁶Ar vs. ²⁰Ne/³⁶Ar shows a strong fit for the atmospheric derived gases. Assuming all neon is atmospheric, the observed ²⁰Ne/³⁶Ar is indicative of a multiple-stage stripping as CO₂-rich fluids percolate through the shallower aqueous fluids and then partially re-dissolve.

Comparing the composition of various mantle fluid components to the atmospheric noble gas composition (i.e. 20 Ne/ 36 Ar) allows one to differentiate the signature of shallow processes from those intrinsic to mantle signatures. This data will potentially improve the understanding of mantle-derived end-member (i.e. $CO_2/^3$ He, δ^{13} C- CO_2 , $[N_2]_{ex}$) and suggest the mechanism(s) responsible for the variations observed in the current sample set (Figs. 4, 6, 7). We envision several hypotheses to account for the observed data range including: Scenario 1: crustal emplacement of fluids that have experienced variable degassing at depth; Scenario 2: a solubility controlled degassing process, or Scenario 3: mixing in the shallow aquifer.

Dallol gases exhibit coherent variations between mantle-derived and atmospheric components. The correlation in $CO_2/{}^{3}$ He vs. 20 Ne, 4 He vs. 20 Ne, N₂ vs. 20 Ne, $CO_2/{}^{3}$ He vs. 20 Ne/ 36 Ar, and 4 He/ 40 Ar* vs. 20 Ne/ 36 Ar can only be explained by pre-mixture of mantle-derived and atmospheric components before fractionation or mixing (e.g. Ballentine and Lollar, 2002; Gilfillan et al., 2009; Zhou et al., 2012). This pre-mixture is inconsistent with Scenario 1.

To test the remaining two hypothetical scenarios, we construct two models: a) Scenario 2 utilizes a gas fractionation model (using analogous conditions and an open system Rayleigh fractionation similar to the GGS-R model used above, but in the opposite direction; lighter gases are lost from the system) and b) Scenario 3 utilizes a mixing model that assumes the same starting composition as the GGS-R model and mixes through a groundwater devoid of less soluble mantle-derived components (i.e. ⁴He) (potentially that has already degassed) and with an ASW composition of ²⁰Ne, ³⁶Ar, ⁸⁴Kr and [CO₂] at saturation. The GGS-R model assumes the continuous percolation of a mantle-derived CO₂ phase that extracts dissolved gas components from groundwater and partitions into the migrating gas phase (i.e. stripping). For the Dallol area, we assume initial conditions according to our derived mantle end-member (Tables 1, 2) and ASW composition for ²⁰Ne, ³⁶Ar, and ⁸⁴Kr.

The comparison of the solubility fractionation degassing model and mixing models provides insight into the remaining two scenarios. Because He and Ne are inert noble gases with similar solubilities in aqueous fluids, that are sourced from different fluids (⁴He from the mantle (or crust) and ²⁰Ne from ASW), their relative proportions provide a sensitive proxy for addressing the degassing versus mixing scenarios (Weiss, 1971a, 1971b; Gilfillan et al., 2009; Lollar and Ballentine, 2009). For example, degassing that alters the ²⁰Ne/³⁶Ar by a factor of ~4 (observed change) would lead to a change in the ${}^{4}\text{He}/{}^{20}\text{Ne}$ of < 50% (model shown in Fig. 7). By comparison, highly degassed remnant fluids should be devoid of mantle-derived helium and have an initial composition of ${}^{4}\text{He}/{}^{20}\text{Ne}$ that approaches 0 at ASW ${}^{20}\text{Ne}/{}^{36}\text{Ar} =$ ~0.150. In all cases, the Dallol data appear to more accurately fit a straight mixing line model as opposed to the Rayleigh fractionation curve (Figs. 4, 5, 7), specifically for the ⁴He/²⁰Ne (Fig. 7). Fig. 7 shows that for the lowest 20 Ne/ 36 Ar samples, the 4 He/ 20 Ne and 4 He/ 36 Ar are approximately $100 \times$ lower than the mantle-derived end-member and extrapolate through zero at ASW compositions (20 Ne/ 36 Ar = ~0.150). Therefore, we suggest that the proposed mixing model between the

mantle-derived end-member and highly degassed remnant fluid (Scenario 3) better characterizes the observations at Dallol. Although it should be noted that the proposed mixing model has the obvious limitation of effectively testing the validity of our own empirically devised hypothesis, it does overall provide a better fit than an open system degassing model.

5.3. Potential implications for the Dallol hydrothermal system

Based on the observations of the source and crustal fluid interactions discussed above, we briefly describe a conceptual model for the interactions between mantle fluids, crustal sediments, and sub-surface fluids (i.e. brine) within the Dallol region. Fig. 8 is a schematic representation of the volatile transfer mechanism at Dallol. In this scenario, partially degassed (as identified by the ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ discussed above) mantle fluids, even potentially basaltic magmas, first interact with Proterozoic metasediments and extract thermally post-mature sedimentary N and potentially C from the detrital sediments. Because several episodes of dyke intrusion and hydrothermal activity have been observed elsewhere in the Afar depression (e.g. Dabbahu magmatic segment), we prefer a model in which dyke intrusion drives hydrothermal activity (Wright et al., 2006; Ebinger et al., 2008; Ayele et al., 2009; Keir et al., 2009). As the magma (or other mantle-derived fluids) is emplaced within the Danakil Depression, a CO₂ dominated gas exsolves entraining N₂ and noble gases within the nucleated carbon dioxide bubbles creating a pre-mixed fluid that is eventually altered by interactions with the aqueous system. Finally, the CO₂-rich mantle-derived gas mixes with a hydrothermal reservoir that has a previously degassed character as inferred by the low ⁴He/²⁰Ne, ⁴He/³⁶Ar, ²⁰Ne/³⁶Ar and elevated $CO_2/{}^{3}He$ (schematic in Fig. 8) at an undetermined depth in the shallow crust. The mechanism responsible for the formation of the highly elevated ²⁰Ne/³⁶Ar in the inferred mantle-rich end-member likely results from the transport of the magmatic-rich end-member gas components through an aqueous fluid that enriches the less soluble noble gases in the migratory gas phase (i.e. liquid phase partitioning). The scenario is similar to the groundwater gas stripping-re(dissolution) model proposed previously (e.g. Ballentine and Holland, 2008; Gilfillan et al., 2009; Lollar and Ballentine, 2009; Zhou et al., 2012). However, some contribution intrinsic to the mantle-derived volatiles or interaction with deeper meta-sediments, etc. cannot be entirely excluded. Clearly the paired application of major and trace gas geochemistry in combination with more sophisticated numerical modeling is required to test the hypothesized model for Dallol as well as the interaction of CO₂-rich fluids in other hy-drothermal systems.

6. Conclusion

The helium isotopic composition (~11.9 Ra) and ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ (up to 14) suggests that a partially degassed Afar plume end-member sources the volatiles emitted within the Dallol area of the Danakil Depression. The tectonophysical implications of this data suggest that the Afar plume interacts across at least the 300 km transect from the Tendaho-Gabo basin (i.e. Afar triple junction) to at least the Danakil Depression, while MORB-like helium isotopes characterize the gas chemistry of the nearby actively spreading center along the Red Sea rift axis. The $CO_2/{}^{3}$ He of the magmatic end-member is broadly consistent with the alkali-rich composition of Afar (Erta 'Ale-type volcanism) and other plume environments (e.g. Hawaii, Iceland, etc.), although Dallol has $\sim 2 \times$ higher CO₂/³He (7.7×10^9) and more positive $\delta^{13}C$ (CO₂) (-2.1‰) which suggests a possible admixture of carbonate-derived CO₂. As mantle-derived fluids (e.g. basaltic melts), migrate through the crust, they interact with Proterozoic meta-sediments to produce significant quantities of nonatmospheric excess N₂, and potentially some carbonate-derived CO₂ that is emitted in the Dallol hot springs. By comparing the range in atmospherically and mantle-derived components using simple numerical modeling, we determine that coherent variations result from mixing of



Fig. 8. A schematic representation of the suggested model for the volatile transfer mechanisms and interaction at the Dallol hydrothermal system. We suggest that a partially degassed basaltic magma or migrated high temperature fluids sourced from the mantle (as identified by the ${}^{4}\text{He}/{}^{40}\text{Ar}^*$) first interacts with Proterozoic meta-sediments and extracts thermally post-mature sedimentary N and potentially C (from carbonate sediments). As the magma or other fluid is emplaced within the Danakil Depression, a CO₂ dominated gas mixes with a hydrothermal reservoir present in the shallow crust. Finally, the relatively recently emplaced CO₂-rich volatiles mix with a remnant hydrothermal reservoir that has a highly degassed character as inferred by the low ${}^{4}\text{He}/{}^{36}\text{Ar}$, ${}^{20}\text{Ne}/{}^{36}\text{Ar}$ and elevated CO₂/ ${}^{3}\text{He}$.

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mantle-derived volatiles with an extremely degassed remnant fluid present in the hydrothermal reservoir that feeds the Dallol hot springs.

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