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THE ORIGIN OF HYDROTHERMAL AND OTHER GASES IN THE KENYA RIFT VALLEY

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Abstract: The Kenya Rift Valley (KRV) is part of a major continental rift system from which much outgassing is presently occurring. Previous research on gases in the KRV has tended to concentrate on their geothermal implications; the present paper is an attempt to broaden the interpretation by consideration of new data including helium and carbon isotope analyses from a wide cross-section of sites. In order to do this, gases have been divided into categories dependent on origin. N_2 and noble gases are for the most part atmospherically derived, although their relative concentrations may be altered from ASW ratios by various physical processes. Reduced carbon (CH, and homologues) appears to be exclusively derived from the shallow crust, with thermogenic $\delta^{13}\text{C}$ values averaging -25 % PDB for CH_4 . H_2 is likely also to be crustally formed. CO₂, generally a dominant constituent, has a narrow δ^{13} C range averaging -3.7 % PDB, and is likely to be derived with little modification from the upper mantle. Consideration of the ratio $C/^{3}$ He supports this view in most cases. Sulphur probably also originates there. Ratios of $^{3}\text{He}/^{4}\text{He}$ reach a MORB-like maximum of 8.0 R/R_A and provide the best indication of an upper mantle source of gases beneath the KRV. A correlation between 3 He/ 4 He and the hydrocarbon parameter log(C $_{1}/\Sigma C_{2-4}$) appears to be primarily The highest ${}^{3}\text{He}/{}^{4}\text{He}$ ratios in spring waters are temperature-related. associated with basalts, perhaps because of the leaching of basalt glasses. There may be a structural control on ${}^{3}\text{He}/{}^{4}\text{He}$ ratios in the KRV as a whole.

INTRODUCTION

The Kenya Rift Valley is part of the extensive East African Rift System, which "defines a diffuse plate boundary within Africa and is often regarded as an example of the early stage of continental breakup" (Daly et al, 1989). The term Kenya Rift Valley (KRV) is used here to denote the Gregory and Turkana rift zones, plus the Nyanza rift unit (ROSENDAHL, 1987). In terms of geography, coverage in this paper extends from the Suswa volcano in the south to Lake Turkana in the north and from the Mt Kenya area in the east to Lake Victoria in the west (Fig 1).

The KRV is part of the East African Rift System and is a good example of a major continental rift structure, with a typical width of 60-80 km and a depth of about 1 km. The KRV is situated on a broad domal uplift with a thin (20-35 km) crust which abruptly thickens beyond the rift margins (ACHAUER et al, 1992). The rifting process has resulted in extensive Tertiary to Quaternary volcanism. Considerable outgassing is presently taking place and has probably been doing so in one form or another for at least 20 Ma (BAILEY, 1980). In contrast to the largely non-volcanic Western Rift, stretching from Uganda in the north to Malawi in the south, the Eastern Rift is characterised by numerous late-Quaternary eruptive centres which are generally situated on or close to the rift axis. Only Oldoinyo Lengai in northern Tanzania is currently active, but many eruptive centres are dormant and support convective hydrothermal systems. The KRV forms about one-third of the Eastern Rift. Outgassing in the KRV occurs via fumaroles (steam jets) on the volcanic centres, and also by emissions from dry boreholes and seeps within the KRV proper and beyond.

Documentation of this activity commenced with detailed geological survey work in the 1950s and 60s (MASON, 1967; MCCALL, 1967), and the gases themselves have been studied from the time geothermal exploration commenced in the 1970s. These studies (GLOVER, 1972; ARMANNSSON, 1987; GEOTERMICA ITALIANA, 1987) have been mostly concerned with the assessment of subsurface temperatures and flowpaths in connection with prospective geothermal development. A more comprehensive isotopic study of gases in the KRV was started with the British Geological Survey's regional geothermal exploration work in the southern and northern parts of the KRV (ALLEN et al, 1989; ALLEN and DARLING, 1992).

This contribution presents a detailed study of gases from the KRV including carbon and helium isotope ratios and noble gas concentrations in gas and water samples. The aim is to gain further insights into the nature and mechanisms of outgassing in this part of the Rift System in the belief that these may have applicability to a broad range of geological and related topics.

SAMPLING AND ANALYSIS

Samples of gas were taken from a variety of natural sources. An inverted conical funnel immersed in water was used for springs while a clay seal was used for fumaroles and gas seeps. Details of these methods are provided in DARLING and TALBOT (1991). Additional samples from geothermal, water and dry wells were collected direct from the wellhead thus minimising the risk of air contamination.

Aliquots intended for major gas analysis (CO_2 , H_2S , H_2 , N_2 , O_2 , CH_4 and higher hydrocarbons, on an H_2O -free basis) were collected into glass vessels, which were either unmodified, or evacuated and containing a 40 percent NaOH solution

to absorb CO_2 and H_2S . Samples for noble gas analysis (He, Ne, Ar, Kr and Xe) were collected into tubes of annealed copper which were sealed by swage clamps.

Analysis of major gases was carried out at BGS Wallingford by standard techniques of chromatography and titrimetry. Carbon stable isotope ratios of CO_2 and CH_4 (after oxidation to CO_2 by CuO at 850°C) were measured on a VG-602E mass spectrometer. Noble gas abundances were analysed at Bath University on an Kratos MS-10S mass spectrometer, while helium isotope ratios were measured at the University of Cambridge on a VG-3000 mass spectrometer using the procedures of HOOKER et al (1985).

RESULTS

General

Locations for which a range of analytical results are available are shown in Fig. 1. Abundances of major gases together with carbon isotope ratios of CO_2 and CH_4 were obtained for a majority of these sites and are reported in Table 1. Gas concentrations are reported in mole percent while isotope ratios are reported in the following form:

$$\delta^{13}C = [(R_{sample}/R_{std}) - 1] \times 10^3$$

where R_{sample} is the ${}^{13}C/{}^{12}C$ ratio of the sample (CO₂ or CH₄) and R_{std} is the ${}^{13}C/{}^{12}C$ ratio of the PDB standard. Reproducibility of $\delta^{13}C$ analysis including sampling and preparation steps is estimated to be within ± 0.2 % for CO₂ and ± 0.5 % for CH₄.

Noble gas samples were taken from a smaller number of representative sites in the southern part of the KRV (Table 2) and were determined to a precision of $\pm 1\%$. Reproducibility of N₂/Ar averaged at $\pm 2\%$. Helium isotope ratios are presented in Table 3 in the form of sample ratio, corrected on the basis of Ne content for atmospheric contamination, relative to the ratio in air according to the following equations:

 $R/R_{A} = [(R_{M}/R_{A})X - 1]/(X - 1)$

where $R_A = {}^{3}He/{}^{4}He$ in the atmosphere $R_M = {}^{3}He/{}^{4}He$ measured in the sample $X = [(He/Ne)_{sample} \ \beta Ne]/[(He/Ne)_{air} \ \beta He]$

The terms BNe and BHe refer to the Bunsen solubility coefficients for He and Ne at appropriate temperature and pressure. For gas phase samples the B terms were not used. Reproducibilities for measurements of 3 He/ 4 He and He/Ne were $\pm 1\%$ and $\pm 10\%$ respectively.

Nitrogen, Oxygen and Argon

Fumaroles in the KRV are not generally very vigorous features and in addition are not always easy to sample. The presence of O_2 represents atmospheric contamination at a late stage either by near-surface entrainment from air which has penetrated porous rock, or conceivably from dissolved air in shallow perched water bodies. While some N_2 is also due to contamination at or near the point of sampling, there are cases where there is clearly an original component in the emanating gases, though this is likely to be ultimately derived from the atmosphere also. When the ratios N_2/Ar and ${}^{40}Ar/{}^{36}Ar$ (Table 2) are plotted against each other (Fig 2) most samples reveal evidence of air equilibration with water ($N_2/Ar \sim 40$). Samples with higher ratios indicate at least a component of direct air contamination not involving solution processes. However, all of these samples are dispersed along a trend coincident with the ${}^{40}Ar/{}^{36}Ar$ ratio of air, except for the Nyanza Rift sample from Bala (K53) which has a higher value. This particular case is presumed to be due to excess Ar produced by radiogenic decay of ${}^{40}K$; the ${}^{40}Ar/{}^{36}Ar$ ratio of 846 is some three times higher than the atmospheric value of 296 (Fig 2).

Carbon Dioxide, Methane and Higher Alkanes

Oxidised carbon is represented by CO_2 and the chemically equilibrated forms of HCO_3^- and $(CO_3)^{2^-}$. When atmospheric contamination (as indicated by the amount of O_2) is low or absent, CO_2 is almost always by far the most abundant fumarolic gas (on a steam-free basis) with concentrations often in excess of 90%. Highly consistent $\delta^{13}C-CO_2$ values were obtained from 32 fumaroles, wells and seeps (Table 1), with an average of -3.7% and a standard deviation of 1.1%, though with a total range from -1.7 to -7.1%. These comparatively consistent results were not produced solely from recently-active centres; examples from Bala (K53, Miocene carbonatite), Kureswa (K256, a travertinedepositing area west of the Rift proper), the Kerita CO_2 well (K237, on the eastern Rift shoulder) and from mofettes at Meru (K503 on the eastern flanks of Mt Kenya some 130 km from the KRV) all fall within a restricted range.

Reduced carbon is represented by CH_4 and higher alkanes sometimes detectable up to C_6H_{14} , plus benzene (C_6H_6), though only C_2 to C_4 are reported here. Even in the least air-contaminated fumaroles, CH_4 is rarely present at more than

1% by volume of the gas phase, with the accompanying higher homologues always a factor of 10^2 or 10^3 lower in concentration (see Table 1). No alkene compounds were detected.

Results of δ^{13} C-CH₄ analysis are given in Table 1. As with CO₂ these are quite consistent (28 sites, average -25.2‰, standard deviation 3.4‰, range -18.3 to -31.8‰), despite the variety of site types from which samples were collected.

Hydrogen and Hydrogen Sulphide

Hydrogen and H₂S concentrations are generally lower in fumarolic gases of the KRV than is typical of other hydrothermal systems. This is probably mainly due to the often considerable depth of geothermal reservoirs in the rather arid KRV, which allows abundant scope for these gases to react with wallrock or become oxidised during passage to the surface. This is demonstrated by a comparison of gas analyses from the Olkaria well (OW-n) and fumarole (OF-n) averages in Table 1. The fumarole gases are depleted in H_2 and H_2S compared to the deep fluids which are brought rapidly to the surface by the geothermal wells. Gas chromatographic analysis of some of the more sulphur-rich gas samples was undertaken to test for forms other than H_2S such as COS and CS_2 . These could not be detected at ppm level in the total gas, implying that there is little or no reaction between the S and carbon phases. The few $\mathrm{H_2}$ isotope analyses available (not reported here) are, at $\delta^2 H$ values of around -500 %, consistent with high temperature equilibrium between $\rm H_2$ and $\rm H_2O$ (ARNASON, 1977).

Neon, Krypton and Xenon

The noble gases Ne, Kr and Xe are normally almost wholly derived from the atmosphere. Table 2 gives analyses for waters and gases of the southern KRV. The results, where they indicate that samples have not re-equilibrated with air at or near the point of discharge, may be used to infer various physical processes.

A plot of Xe versus Kr for wells and springs (Fig 3) demonstrates that most waters appear to have suffered little modification (confirming other geochemical indicators) and have in at least half the cases retained ratios reflecting their recharge temperatures (which in the case of sites like K96 are likely to be at considerable altitude, though perhaps not quite as cool as the plot suggests: however, if there is 'excess' gas it is unlikely to be due to air contamination on the evidence of Fig 4). Other sites such as K35 and K118 show evidence of the Xe/Kr ratio tending to sampling temperatures or even, in the case of K100, having re-equilibrated at a higher temperature than this. Site K124 is a borehole with high CO_2 and He to which outflow from the Eburru geothermal field probably contributes (ARUSEI, 1992), and this may be a factor behind the anomalous Xe/Kr ratio.

Information about free gases is obtained from a log plot of Ne vs Kr (Fig 4). Some fumaroles (K126 and 127) show ratios close to that of air, suggesting air entrapment or contamination which is confirmed by the analyses in Table 1 (the position of K128 on the plot is more problematical because of much lower air contamination as indicated in Table 1). Noble gases in these fumaroles can therefore reveal little about conditions at depth. In the case of fumaroles K119 and K123 equilibrium with water at a somewhat higher temperature than

that of average recharge (~25°C) suggests that perched aquifers may be causing gases to re-equilibrate at lower than geothermal reservoir temperatures. Higher equilibration temperatures are marked by a tendency towards air-like ratios (though not quantities) for the noble gases (e.g. POTTER and CLYNNE, 1978) which explains the position of the geothermal well OW2 (K110) on the plot. Conversely the carbonatite complex spring (K53) at Bala in the Nyanza rift has a composition suggesting equilibrium with recharge at cooler than normal temperatures. This however receives no support from 0 and H stable isotope ratios (ALLEN et al, 1989). Possibly noble gas ratios have been perturbed in this water by the same factors which have led to the exceptionally high He content (Table 3).

Helium

Amounts of He in crustal gases of the KRV are almost uniformly low (Table 3). There appears to be no particular correlation between concentration of He and other geothermal parameters, as has also been noted in the Ethiopian Rift (CRAIG et al, 1977) and indeed elsewhere (GRIESSHABER et al, 1992; POREDA et al, 1992). Only when 3 He/ 4 He isotope ratios are considered does a pattern emerge. The highest 3 He/ 4 He values, with R/R_A from approximately 5.5 to 8, are generally found in close association with the late-Quaternary volcanic centres of the KRV (Table 3, Fig 1).

For gaseous sources it may be noted that a plot of CO_2 percentage vs neoncorrected ${}^{3}\text{He}/{}^{4}\text{He}$ as R/R_A indicates that highest ratios are only obtained when CO_2 exceeds 50% of the gas phase (Fig 5). Below this figure the presence of air-derived gases appears to perturb the ${}^{3}\text{He}/{}^{4}\text{He}$ ratio to the extent that corrections based on the Ne content cannot alone restore the "true" ${}^{3}\text{He}/{}^{4}\text{He}$

value. While this is difficult to prove conclusively, samples with <50% CO₂ have been largely excluded from further discussion of the helium isotope data.

Examination of the data in Table 3 show that where there is more than one helium isotope analysis for an individual volcanic centre, there is usually fair agreement between the results. For example in the south, four very similar ${}^{3}\text{He}/{}^{4}\text{He}$ values of 5.7 ± 0.1 reported as R/R_{A} have been obtained from the Olkaria geothermal area, while in the north the Silali caldera provided three sites with R/R_{A} values averaging 7.8 ± 0.3. The Olkaria and Eburru ${}^{3}\text{He}/{}^{4}\text{He}$ data apart from demonstrating consistency within individual volcanic centres (and, happily, between laboratories) also show that similar He isotope data can be obtained from surface fumarolic and deep (~2000 m) geothermal well sources, thereby giving confidence that under suitable conditions the results obtained from fumaroles elsewhere in the KRV are genuinely representative of deep fluids.

Table 3 shows that ratios of $C/{}^{3}$ He (effectively $CO_{2}/{}^{3}$ He) for many sites are close to the MORB average of 2 x 10^{9} (MARTY, 1992). The only site with a significantly lower ratio is Bala in the branching Nyanza rift unit, where He concentrations are extremely high. A few sites have significantly higher values, for reasons to be discussed below.

DISCUSSION

The gaseous emanations of the KRV must be derived from one or more of the three principal sources: the atmosphere, the crust and the mantle. For the purposes of considering their origin it is convenient to divide the gases into these subgroups which are described below.

Gases Derived from the Atmosphere

Once the effects of any atmospheric contamination are discounted, it is seen that the amount of original N_2 in fumarolic and borehole gases is almost uniformly low (Table 1). In the absence of any $^{15}N/^{14}N$ data, it is assumed that all N_2 has been ultimately derived from atmospheric sources (although a 'deep' component with a $\delta^{15}N$ of -10 to -15‰ was assumed for Oldoinyo Lengai by JAVOY et al, 1989). The evidence of $^{40}Ar/^{36}Ar$ makes it likely that in virtually all cases argon too has an ultimate atmospheric source. Although the $^{40}Ar/^{36}Ar$ data reported here are all from fluids in the KRV south of the equator, very similar results were obtained from trapped Ar during the dating of volcanic rocks from Silali (Fig 1). These ratios ranged from 275-315 (Smith et al, 1995), and tend to confirm that there is very little radiogenic gas production in the main KRV.

It is also assumed that Ne, Kr and Xe are almost wholly derived from atmospheric sources and therefore that their concentrations may (when uncontaminated) permit tracing of hydrological processes in the subsurface. He isotope results, on the other hand, suggest that only a proportion of helium is atmospherically-derived.

Gases Derived from the Crust

While it has been demonstrated that most Ar is atmospheric in origin, the sample at Bala (K53) in the Nyanza rift contains crustally produced ⁴⁰Ar. A possible interpretation of this is that thermal groundwater at Bala is in residence for significantly longer than similar groundwaters in the main KRV, but differences in mineralogy between the two areas may also contribute. The igneous rocks of the main KRV are predominantly intermediate-peralkaline in type (comendites, trachytes and phonolites) while Bala is situated on the site

of the Homa Mountain carbonatite complex. Carbonatites commonly contain higher concentrations of radiogenic elements than intermediate rocks (MARIANO, 1989). However, some volcanic rocks in the main KRV have higher concentrations of radioelements than others, notably in the southern Rift at Olkaria (CLARKE et al, 1990), without appearing to perturb the atmospheric 40 Ar/ 36 Ar signature in gases and water. The high 40 Ar/ 36 Ar ratio at Bala is therefore probably related to the dominance of mineral alteration over mineral diffusion as a release mechanism for 40 Ar (ANDREWS, 1992) rather than high radioactivity; carbonate minerals would be more susceptible to alteration than the silicates of the main KRV.

Despite the high concentration of He at Bala, the He isotope ratio suggests a balance of sorts between mantle and crustal sources. Conceivably this could be the result of mantle He trapped during the emplacement of the carbonatite being supplemented before release by in-bred ⁴He.

It is inconceivable that the high flux of CO_2 from the KRV and its environs could be derived predominantly from atmospheric or soil zone sources, and this is borne out by the generally consistent $\delta^{13}C-CO_2$ values (Table 1). The average value of -3.6 ‰ is unrepresentative of atmospheric (~-7 ‰) or soil zone (~-16 to -26 ‰) sources, though a few air-contaminated fumaroles such as K159 and K260 have more depleted values which may indicate a proportion of bacterially produced CO_2 from the soil zone.

It is also unlikely that the CO_2 from most sites is crustally derived. Mechanisms such as decarbonation of marine limestones have been postulated as sources of CO_2 with near-zero $\delta^{13}C$ values (e.g. in TRUESDELL and HULSTON, 1980); while no such limestones exist in the KRV, there are carbonate

evaporites in places, and carbonatites are known from the wider region. Nevertheless, the sheer amount of CO_2 outgassing suggests that oxidised carbon must be predominately derived from a mantle reservoir, and this is supported by most of the C/³He ratios in Table 3.

However, there are a few sites where $C/^{3}$ He is significantly higher than MORBlike values. This is illustrated by Fig 6(a), which shows a plot of helium isotope ratios versus $C/^{3}He$ values. Points representing fumaroles at Olkaria (K123) and Ol Kokwe Island (K152), and the Kerita CO₂ well (K237) lie on what appears to be a single trend away from the MORB zone. Fig 6(b) shows this to be a partial coincidence; while in each case there are indications of the influence of crustal He, the CO, well is clearly differentiated from the fumarole sites by its δ^{13} C-CO₂ value. The ¹³C data suggest that there is a minor crustal contribution of organically derived CO_2 at Olkaria and Ol Kokwe. This is not shown by the deep geothermal wells at Olkaria and therefore implies a comparatively near-surface addition, at least in that particular case. The Carbacid Company well at Kerita, however, appears to derive its 'extra' CO₂ from an inorganic crustal source. The well is situated on the rift flanks, almost adjacent to the highest elevation of the rift floor, where carbonate evaporites are unlikely ever to have formed. Possibly the CO₂ is derived from decomposition of carbonatites; though none are exposed in the area, Miocene carbonatites are well developed to the west and south of the region, and may possibly be present at depth in parts of the KRV. The data under consideration here suggest that if present they are very localised.

Unlike most oxidised carbon, reduced carbon probably has a predominantly crustal source in the KRV. A lack of detectable alkene compounds is an indication that methane is unlikely to have been formed by abiogenic synthesis

(GUNTER and MUSGRAVE, 1971); while the presence of H_2 in most hydrothermal systems might be thought to rule out the survival of such unsaturated hydrocarbons, they have been detected in certain geothermal fields elsewhere, e.g. by GIGGENBACH and GLOVER (1992) and CAPACCIONI et al (1993), albeit at low concentrations. On the other hand, the presence of sometimes relatively abundant C_{2+} compounds probably rules out production by bacterial methanogenesis, which tends to produce CH_4 and very little else. A thermogenic (thermocatalytic) decomposition of organic matter seems the most likely source of hydrocarbon production.

Such an origin would tend to be confirmed by the δ^{13} C-CH₄ results (Table 1). The average of -25.2 ‰ is typical of carbon in terrestrial and lacustrine plant matter (e.g. DEINES, 1980) and also of geothermal methane in many other areas. In geothermal fields hosted at least partly in sedimentary rocks, suitable organic precursors have often been identified (for example, coal at Cerro Prieto, Mexico; DES MARAIS et al, 1988). The KRV does not possess sedimentary sequences of great thickness, but lacustrine deposits may provide a source of suitable organic compounds. Either these are invaded episodically in places by hot fluids, or dissolved organic compounds may be drawn into hydrothermal plumes. In each case geothermal heat will cause degradation of the organic compounds into hydrocarbon gases. The spread of δ^{13} C-CH₄ values may reflect the degree of thermal maturity reached locally, or possibly an approach to isotopic equilibrium with CO_2 , though calculated $\Delta^{13}C$ temperatures are nearly always improbably high for the hydrothermal systems concerned. It does not appear to be due to inputs of abiogenic mantle CH_4 (see next section).

A correlation between log (C_1/C_{2+}) and temperature has been observed for the East African Rift System in general (DARLING, in preparation; DARLING and TALBOT, 1991, 1992), and it is concluded that when organic compounds are drawn into hydrothermal plumes, progressive degradation to CH₄ takes place with rising temperature. This suggests that hydrocarbon generation is taking place at shallow levels in the crust where suitable conditions prevail. That the temperature need not be high is confirmed not only by petroleum research literature (e.g. SIMONEIT, 1990) but also by the results from relatively lowtemperature systems such as Bala and Kureswa (K53, K256), with solute geothermometer temperatures of <100 $^{\circ}$ C, and the Kerita CO₂ well on the rift flank (K237). While long heating times would be required at such temperatures, there are indications that KRV hydrothermal systems are in general long-lived. There is for example at Olkaria no evidence for a significant 18 O-shift in the deep thermal waters (DARLING et al, 1990) which suggests that a large amount of water has already passed through the system. Also, the work of STURCHIO et al (1993) on the dating of hydrothermal sinters in the northern KRV testifies to the longevity of hydrothermal activity.

During the thermal cracking of organic matter H_2S may be produced, especially in areas with carbonate evaporite sequences (TISSOT and WELTE, 1984) such as are found in parts of the KRV (ALLEN and DARLING, 1992). While the H_2S in volcanic areas is generally considered to be mantle-derived, a small crustal contribution might therefore be possible in the KRV (though as mentioned earlier, no COS or CS₂ was detected).

Hydrogen where detectable is at low concentrations except in geothermal wells. It is probable that production takes place in the upper part of the crust by dissociation of water buffered by minerals such as chlorite or epidote

(GIGGENBACH, 1980). As stated earlier, stable isotope analyses indicate high temperature equilibrium between H_2 and water, and therefore cannot be used to diagnose ultimate origin.

Gases Derived from the Mantle

The plots in Fig 6 show that, notwithstanding the few exceptions, there is only one significant source of CO_2 , which must be mantle-derived. The occurrence of carbonatite at Bala and south of the KRV at Oldoinyo Lengai demonstrates that CO₂-rich fluids have been ascending from the upper mantle in the region since at least Miocene times. A more negative average with $\delta^{13}\text{C-CO}_2$ of -5 to -8 ‰ is generally associated with such a source, but fractionations between magma and exsolved gas of 1-2% for carbonate (the main dissolved species in melts; OHMOTO AND RYE, 1979) and up to 4 ‰ for graphite put the KRV $\delta^{13}\text{C}$ values well within range of outgassing from MORB-type magmas. A minor problem associated with the assumption that the observed δ^{13} C-CO₂ values are the result of isotopic fractionation of mantle CO_2 is that unless fresh magma were entering volcanic systems in a fairly continuous manner, a decrease in $\delta^{13}\text{C-CO}_2$ would be noted with time (FRIEDMAN et al, 1987). It is highly unlikely that all KRV volcanic centres would be at the same stage in such a cycle and therefore the similarity in δ^{13} C-CO₂ values may not arise solely in this way. However, to the south of the KRV, Oldoinyo Lengai gave average δ^{13} C-CO₂ values of -2.6 ‰ and 3 He/ 4 He values of 7.6 R/R_A, similar to the fumaroles of the northern KRV (JAVOY et al, 1989). The implication of this is that over the timescales involved (i.e. late-Quaternary to present

day) significant differences in the CO_2 fractionation stage between centres do not occur, or are masked by other processes.

For reduced carbon, although a predominantly crustal origin is indicated, inputs from mantle sources cannot wholly be discounted on carbon isotope evidence alone. While the δ^{13} C range of supposed abiogenic mantle CH₄ is not very well constrained, it is believed to be of the order of -15 to -18 ‰ (WELHAN and CRAIG, 1983) and would thus not be easily distinguishable from thermogenic CH₄. However, a plot of δ^{13} C-CH₄ versus ³He/⁴He as R/R_A (Fig 7) shows no well-defined trend that might indicate mixing between crustal and mantle CH₄ reservoirs.

The sulphur in H_2S , an important constituent of geothermal well gases but not normally of surface manifestations as explained above, is assumed here in the absence of S isotope data to be largely derived from magmatic sources and therefore by implication the upper mantle (though see earlier remarks about possible crustal production from evaporitic sources). A relatively low concentration of H_2S was reported even from the active Oldoinyo Lengai volcano by JAVOY et al (1989), suggesting that the KRV in general is a low-S province.

The 3 He/ 4 He results of this study are similar to those obtained from MORB sources (LUPTON, 1983) and undoubtedly indicate an important upper mantle contribution to the He content of fumarolic gases in the KRV. Taken in conjunction with generally lower R/R_A values from the few sites on or towards the rift flanks (usually springs rather than gaseous sources), this suggests that magmatic melts rather than deep normal or listric rift boundary faults are the most important conduit by which mantle He reaches the surface even in an area with relatively thin crust. Similar observations were made in

connection with the continental rifting in western Europe (GRIESSHABER et al, 1992). However, it cannot yet be altogether ruled out that as much or even more mantle He is released via major boundary faults, but is more difficult to identify because of dilution effects.

While there are no correlations between He isotopes and carbon species, there is for fumarole and borehole gases from Longonot to Silali an apparent relationship between ${}^{3}\text{He}/{}^{4}\text{He}$ and the non-isotopic parameter log (CH₄/ Σ C₂₋₄) with a correlation coefficient of $r^2 = 0.75$ (Fig 8). The reason for such a relationship is not immediately clear; a mixing series based on crustal thermogenic CH_4 with a relatively high C_{2+} content with a "pure" abiogenic mantle methane could possibly be invoked to explain the relationship, but would tend to result in a linear rather than logarithmic correlation (i.e. a curve on Fig 8). It would also receive no confirmation from the δ^{13} C-CH₂ results. A relationship between geothermal reservoir temperatures and log $\rm CH_4/\rm C_{2+}$ has already been mentioned, so the correlation may simply arise because ${}^{3}\text{He}/{}^{4}\text{He}$ is a proxy for temperature (crustally produced ${}^{4}\text{He}$ can be ruled out as a cause of variation on the evidence of the $^{40}{\rm Ar}/^{36}{\rm Ar}$ data considered above). It is likely, after all, that sampling points overlying the hottest parts of hydrothermal plumes will tend to have the highest mantle He contents and therefore probably the highest 3 He/ 4 He ratios. This agrees with the link between high ³He and heat flow proposed by MAMYRIN and TOLSTIKHIN (1984), but only because both heat and ³He are magmatically derived in the KRV; in other cases no clear link has emerged (e.g. OXBURGH and O'NIONS, 1987). Nevertheless the consistency of the relationship for many different volcanic centres, plus the Kerita CO_2 well in the eastern rift flank, suggests that there may be more to the relationship than a simple temperature/³He correlation.

Most of the above remarks refer to He in the gas phase from fumarolic outlets situated above active hydrothermal systems. By contrast, He in the dissolved phase can apparently retain its isotope ratio at some distance from the supposed hydrothermal source. A high ${}^{3}\text{He}/{}^{4}\text{He}$ value was for instance found in sub-thermal groundwater of the Elmenteita area (site K124, north of the Eburru volcanic centre, Fig 1) which has been presumed to contain a proportion of outflow from the Eburru hydrothermal plume (ALLEN et al, 1989). In the northern KRV high ³He/⁴He ratios have also been found in thermal water associated with the Namarunu centre (Fig 1). However, this centre is for the most part much older than Eburru and no longer has any surface fumaroles. The springs do not give high solute geothermometer temperatures, although there are some young (<10 ka) basalts in close proximity (DUNKLEY et al, 1993). The Elmenteita area also has prominent basaltic activity of similar age (CLARKE et al, 1990) and it is possible that the high 3 He/ 4 He ratios in both areas are associated with flushing by water of these basalts (as proposed in the context of parts of the Ethiopian rift by CRAIG et al, 1977). The possibility of such leaching of He from basalt glasses raises the question of whether fumarolic He is wholly 'new' or whether at least some is coming by a similar process from previously erupted or intruded volcanic rocks. There is no simple answer to this, but in geological terms all the mantle He must be "recent" because of the Quaternary age of volcanism in the inner trough of the KRV.

The data in Table 3 suggest that there may be a rise in ${}^{3}\text{He}/{}^{4}\text{He}$ peak values from south to north in the KRV. A crude illustration of this is that R/R_{A} values > 7 are only found northwards from Paka (location - Fig 1). (This could simply be an artefact of sampling, but it is likely that at least one of the wells or fumaroles in the southern KRV would have provided a similar

result if equally high R/R_A values were present in the south). Such a rise in ³He/⁴He may have structural and volcanogenic implications (for example it might be related to the northerly crustal thinning commencing at around the latitude of the equator and reaching a minimum in the Silali – Emeruangogolak area according to ACHAUER et al 1992), but it is proposed to consider these in more detail for a greater part of the Eastern Rift in a future paper. At this stage it may simply be noted that peak ³He/⁴He values are typical of an upper mantle source in contrast to the lower mantle source suggested by He isotope data from parts of the Ethiopian Rift, where values of up to 14 R/R_A were measured by CRAIG et al, (1977).

SUMMARY AND CONCLUSIONS

Because of the KRV's position as a thermal province situated on an extensive length of crustal thinning above a domal uplift, outgassing consists of a complex mixture of gases from different sources.

In almost all situations, N_2 and noble gases (apart from He) are derived from atmospheric sources, though their ratios may have been altered by dissolution and boiling processes. The residence time of groundwaters (thermal or otherwise) appears too short to allow the acquisition of significant amounts of radiogenic Ar or He in the main KRV.

Methane and higher hydrocarbons appear to be the main products of the crust itself, and are probably generated relatively close to the surface by the action of hot fluids on organic compounds. Hydrogen is most likely to result from the dissociation of crustal water, though a mantle contribution cannot

be ruled out on isotopic grounds because of rapid re-equilibration between H_2 and meteoric water at hydrothermal temperatures.

Transport of mantle elements such as S and He to the surface is likely to depend on a significant carrier phase, presumably CO_2 as suggested by $C/^3$ He Carbon isotope data indicate a single major source for CO_2 though ratios. original mantle signatures have been overprinted by fractionation during magmatic processes, and there is some $C/^{3}He$ evidence for minor crustal In terms of quantity there is little helium at KRV sampling production. sites, but abundant evidence for MORB-like isotope ratios particularly along the generally axial line of recent volcanic centres. An apparent rise in peak 3 He/ 4 He from south to north along the KRV may be structurally controlled. There is also a correlation with log C_1/C_{2-4} , which may be acting as a proxy for hydrothermal system temperatures, leading to the possibility in this area at least of a relationship between ${}^{3}\text{He}/{}^{4}\text{He}$ and heat flow. In the dissolved phase, high values of ${}^{3}\text{He}/{}^{4}\text{He}$ are found in basalt groundwaters quite far from areas of overt outgassing. Either He can be carried some distance in dissolved form with little or no change in ³He/⁴He ratio, or sub-recent basalts form an effective trap for He which is then leached out relatively slowly to groundwater. By contrast, most He outgassed from fumaroles is likely to be derived more or less directly from underlying melts.

None of the evidence gathered in the KRV conflicts with gas measurements made at the currently active Oldoinyo Lengai carbonatite volcano to the south in Tanzania, and there is no evidence of 'hot spot' He isotope ratios such as those associated with plume-driven updoming in the Main Ethiopian Rift to the north of the KRV.

This paper has shown that the study of gases in the KRV has potentially a broad range of applications ranging from hydrogeological (e.g. groundwater recharge and residence) through geothermal (e.g. identification of heat sources) to geological (e.g. elucidation of gross rift structure). Results so far suggest that future research might profitably concentrate on noble gas isotope systematics, greater knowledge of the role of rift-flank faults as conduits for fluid movement, and comparison with products of outgassing in Tertiary or Quaternary volcanic areas beyond the immediate confines of the KRV (for example in the Mt Kenya, Kilimanjaro and Chyulu areas) which might provide more information on the nature of updoming associated with rifting in Kenya.

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Our co-author John Andrews died in December 1994. We take this opportunity to pay tribute to a colleague whose contributions to the understanding of the

origins and behaviour of crustal fluids were notable for their range and depth of achievement.

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Gas and carbon stable isotope analyses of gas phase samples collected mainly within the KRV (refer to Fig. 1 for sample locations). Table 1.

	Sample No.	Source Source	sampling Temp. C	co ₂ mmole/kg	c02	2 4	0 ₂ + Ar	H ₂ per cent	H ₂ S	сн ₄	c ₂ H ₆	c ₃ H ₈ ppmv	C4H10	^{د 13} رموء	^{د 13} دديد 2018
	K126 K258 K501	նենեն	96 94 92	851 1364 3720	10.2 16.5 97.4	71.3 66.4 0.27	18.5 16.5 20.1	 <0.001 0.001 0.02 	0.01 0.03 0.01	0.0003 0.087 1.40	<pre>~1 0.4 3.4</pre>	~!. ^!.1	<1 0.2 <1	bn 0.5- 3.7	-25.0 nd
ret ¹	K128 K29	لد تب	9 0 86	9382 12561	77.4 95.2	16.2 4.6	4.0 <0.1	1.7 <0.001	0.01 <0.01		1.0		17	-4.0	
04-n ² 04-n ² H-1 F-15	K31 K127	μοοιμ	91(7) na 95 92	118(9) 61 631 ¹	$\begin{array}{c} 84.3(7)\\ 81.0(9)\\ 99.0\\ 17.4 \end{array}$	10.9(7) 0.9(9) <0.1 64.5	2.7(7) <0.1(9) <0.1 18.0	1.54(7) 9.4(9) 0.11 <0.001	$\begin{array}{c} 0.10(3)\\ 7.9(9)\\<0.01\\<0.01\end{array}$	$\left. \begin{array}{c} 0.58(7)\\ 0.76(9)\\ 0.77\\ 0.13\\ 0.13 \end{array} \right.$	18(7) 9.9(9) 29 2.5	2.5(7) 0.4(9) nd <1	0.2(7) <0.1(9) nd <1	-3.8(7) -2.6(2) -2.1 -3.0	-26.5(-27.2 nd
e i non	K119 K502	шo	92 Na	nd 272	78.9 97.4	11.7 0.34	3.1	1.7 0.09	nd 1.18	4.6 0.99	5.0 2.7	<1 0.1	<1 <0.1	-2.3 nd	nd -23.2
Arus Arus 01 Kokwe-Korosi	K260 K257	LL LL	76 95	nd 2561	4.55 99.5	78.3 0.17	17.2 <0.1	<0.001 0.004	nd 10.0>	0.033 0.35	<0.1 6.4	<0.1 1.2	<0.1 0.4	-6.9	nd - 28.1
0K1 KR12 KR18 KR23 KR23 KR23 KR34	K152 K154 K154 K155 K155 K155 K155	لىت ئىت لىت ئىت لىت <u>لى</u> ت	88888888888888888888888888888888888888	1254 753 1178 1494 1420 1580	88.8 962.7 97.24 85.03 85.03	66.8 65.1 1.0 9 65.1	0.10 0.33 2.82 2.82 2.82 2.82	0.79 <0.001 <0.001 <0.001 0.40 0.006	0.23 0.15 0.03 0.01 0.01 0.01	0.32 0.21 1.5 0.015 0.44	20 240 290 88	130 130 16.8	 <0.1 <0.1 43 26 17 2 	444444 444444	-18.3 -24.5 -23.4 -19.7
	K163 K166 K168	14. KL 14.	96 95 94	450 215 684	83.1 91.7 67.0	11.3 2.1 30.2	3.4 0.61 0.61	<0.001 4.1 0.92	0.74 0.19 0.38	1.5 0.85	1.0 1.0 39	<0.1 <0.1	<0.1 <0.1 6	-2.9	-24-9 -27-8 -22-2
k M	K219 K221 K222 K225 K45 K45	ᄕᅚᇆᇿᇝ	812 812 812 812 812 812 812 812 812 812	336 377 377 552 5591 85	97.7 98.2 77.5 69.4 83.6	0.34 0.29 0.22 16.8 13.3	2554000 256400 29465 29655	0.87 0.65 0.93 0.001 0.79	0.70 0.58 0.24 0.08 nd	0.25 0.25 0.24 0.17 0.17	0.550 0.5500 0.5500 0.5500 0.5500 0.5500 0.5500 0.5500 0.5500 0.5500 0.5500000000		0000000 1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	6, 9, 4, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9, 9,	-23.0 -24.3 -25.0 nd -25.1 -28.3
EN9 EM20 Kageinya Namarini	K228 K232 K188	աատ	95 96 68	2272 1545 na	28.8 58.0 <0.1	57.0 32.5 97.5	13.4 7.9 1.1	0.001 0.002 0.003	0.15 1.1 nd	0.64 0.51 1.41	2.0 0.1 280	<0.1 <0.1 120	<0.1 <0.1 33	-4.7 -4.0 nd	-20.7 -22.5 -31.8
	K236	s	95	na	0.62	0.64	0.37	<0.001	pu	0.011	1.1	0.1	<0.1	-2.2 ³	-28.3
KKI Turkana Islands	K235	Ŀ	96	208	17.1	64.8	18.0	0.008	0.02	0.044	0.1	<0.1	<0.1	-3.3	-26.3
	K253 K255	ند لد	96 97	3070 857	89.0 92.5	8.6 0.56	1.2<0.1	0.053 1.85	0.008 4.2	$1.12 \\ 0.89$	80 46	10 9.4	1.1 3.7	-5.4 -3.8	-28.4
	K53 K256	щ	72 62	na na	89.6 2.9	9.86 95.6	<0.1 0.6	0.21 <0.001	pu	0.28 0.82	5.3 16	0.17 0.8	<0.1 0.4	$\frac{-2.0^3}{-7.1^3}$	-26.8 -27.5
Carbacid Co. Meru/Chogoria	K237 K503	υx	amb amb	na Na	98.4 37.5	0.35 nd	<0.1 nd	0.001 <0.001	pu	$1.24 \\ 0.006$	190 <0.1	52 nd	21 nd	-2.4	-20.5 nd

Data for whole gas analysis or specific measurement from ARMANNSSON (1987). OF-n and OW-n refer respectively to averages for typical Olkaria fumaroles and geothermal wells; numbers in brackets refer to the number of samples averaged (full data in DARLING and TALBOT, 1991) Corrected to total inorganic carbon balance.

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Site No.	Locality	Sample Source	Sampling Temp. C	Ne x 10 ⁻⁷	Ar x 10 ⁻⁴	Kr x 10 ⁻⁸	Xe x 10 ⁻⁸	N ₂ /Ar	40Ar/ ³⁶ Ar
<u>Dissolved Phase</u>	l Phase								
K25 K28 K35 K82	Kijabe RVA Mayer's Farm Kariandusi C4178 Naivasha	avva		0444	୰୰ଡ଼୶	<u> </u>	∞ <u>∽ .</u>	37.8 39.9 42.8	94. 95. 95.
K92 K196 K1100 K124	Kanyamwi Farm P65 Kinangop C1404 Ndabibi Nakuru No 7 Soysambu DEL	ന്ന ന ന ന ന ന	221 328 328 328	1.64 1.67 0.87 0.87	2.60 2.83 2.11 2.29 1.05	5.87 6.42 7.03 2.12 2.12 2.12	0.84 0.62 0.62 0.62 0.30	39.3 57.9 35.2 35.2	294.9 296.8 297.0 297.0
<u>Gaseous P</u>	<u>Phase</u>								
K53 K110 K119 K123 K126 K128 K128	Bala Olkaria OW2 Eburru EF2 Olkaria W Suswa F-3 Domes F-15 Longonot F-23	ν σ μ. μ. μ. μ. μ.	72 92 92 90 90	3.65 0.15 0.30 0.21 74.9 61.8 28.4	30.9 0.10 0.35 0.26 34.5 12.0	22.4 0.15 0.75 0.53 43.1 14.0	3.09 - 1 0.10 3.64 1.45	22.5 43.2 35.2 887.8 887.8 887.8 77.8	846.0 304.4 303.4 261.4 293.1 293.3 293.3

Table 2. Noble gas analyses from selected sites in the southern KRV.

Sample sources: B - borehole; F - fumarole; G - geothermal well; S - spring

Gas concentrations in $\rm cm^3$ (STP)/g water or $\rm cm^3/\rm cm^3$ total gas as appropriate.

			ບ	x10 ⁻¹²	×10 ⁻⁶		H.	×10 ⁹
Di ssolved K26 K35 K48 K68 K68 K91 K124 K124 K124 K185 K190 K190	Phase Kijabe RVA Kariandusi Kapedo Bogoria Kanyamwi Farm Soysambu DEL Sv3 Namarunu Logipi	യഗഗതയഗഗഗ	96688277 96688277 966888277 977	0.97 0.49 2.3 0.19 7.7 3.9	0.54 0.12 0.45 0.11 0.65 0.43	24133211-1-43 24133221-1-1-43	0.46.1.3.3.0 6.46.5.3.8900 5.5	
Gaseous K550 K553 K553 K553 K553 K551 K555 K551 K5523 K551 K2533 K551 K2533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533 K551 K5533	Phase Lorusio Clkaria OW2 Olkaria OW2 Olkaria OW2 Olkaria OW2 Olkaria OW2 Olkaria OW2 Olkaria W Suswa F-3 Domes F-15 Longonot F-23 Morosi KR12 Korosi KR12 Silali SL14 Paka PK1 Paka PK1 Paka PK1 Paka PK1 Paka PK1 Silali SL2 Silali SL2 Silali SL2 Emuruangogolak EM20 Barrier KK1 Carbacid Co. Arus	οοαααματικα μαμαματικα ματικα το το το σ	- 999999999999999999999999999999999999	2500 2500	2917 2917 2917 2917 291 291 30074 30074 30074 30074 30075 201 201 201 201 201 201 201 201 201 201	21000000000000000000000000000000000000	๛๚๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

Helium isotope data, ratios with respect to air and carbon dioxide to mantle helium ratios. Table 3.

R/R_A - ³He/⁴He ratio relative to that of air (1.4 x 10⁻⁶; MAMYRIN and TOLSTIKHIN, 1984)) corrected for contamination on the basis of Ne content. * Data of the Unocal Geothermal Division.

- Fig 1 Map of the KRV showing the disposition of late-Quaternary volcanic centres and location of sampling sites (site numbers are given a K prefix in text and tables).
- Fig 2 Plot of 40 Ar/ 36 Ar vs. N₂/Ar for water and gas samples from representative sites in the southern KRV. The 40 Ar/ 36 Ar value for air is shown, together with atmospheric and air-saturated water (ASW) values of N₂/Ar.
- Fig 3 Plot of Xe vs.Kr for wells and springs from representative localities (site numbers as shown) in the southern KRV (data corrected for sampling altitude). ASW ratios corresponding to various temperatures are also shown (data of Wilhelm et al, 1977)
- Fig 4 Log plot of Ne vs. Kr for gas phase samples from representative localities (site numbers as shown) in the southern KRV. Also shown are the air ratio line (AIR) and the ASW ratio lines for 20, 70 and 120°C (ASW 20, 70 and 120) based on the data of WILHELM et al. (1977) and POTTER and CLYNNE (1978).
- Fig 5 Plot of CO_2 percentage vs. He isotope ratio for gaseous sources in the KRV (cutoff line indicates that samples with <50% CO_2 may not be giving a representative ³He/⁴He value).

- Fig 6 (a) Plot of He isotope ratio as R/R_A vs. $C/{}^{3}$ He for gaseous sources in the KRV (samples <50% CO₂ excluded). Most samples plot around the MORB ratio of 2 x 10⁹, but a few sites have values suggesting a crustal contribution of CO₂ (site numbers for these are shown). (b) Plot of δ^{13} C-CO₂ vs. $C/{}^{3}$ He. One outlying site appears to receive a contribution from a different crustal source of CO₂ than the others.
- Fig 7 Plot of δ^{13} C-CH₄ vs He isotope ratio for gaseous sources in the KRV, showing no evidence of a mixing trend involving a mantle methane component (samples <50% CO₂ excluded).
- Fig 8 Plot of log $[CH_4/(C_2H_6 + C_3H_8 + C_4H_{10})]$ vs. He isotope ratio for gaseous sources in the KRV (samples <50% CO₂ excluded). The regression line based on all points except EG is shown. The curved line represents a theoretical mixing relationship between crustal and putative mantle methane. Site abbreviations - A: Arus, C: Carbacid, E: Eburru, EG: Emuruangogolak, K: Korosi, L: Longonot, 0: Olkaria, OK: Ol Kokwe, P: Paka, S: Silali.

FIG 1

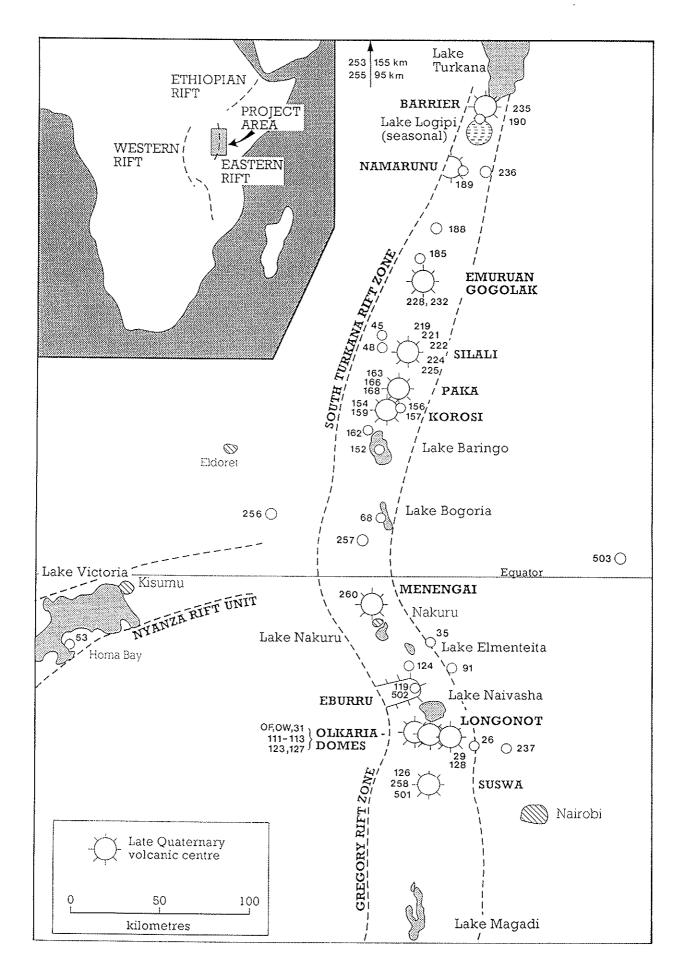
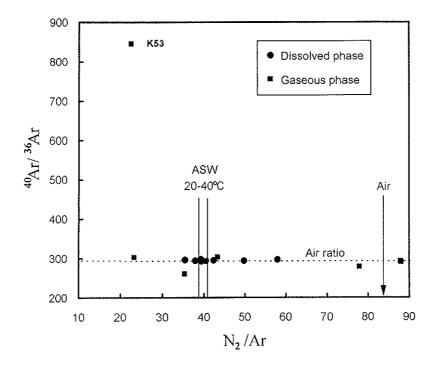
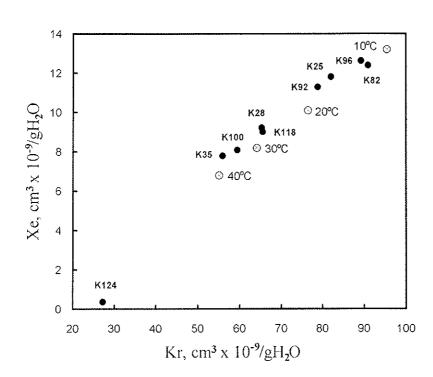
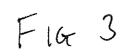
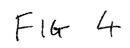


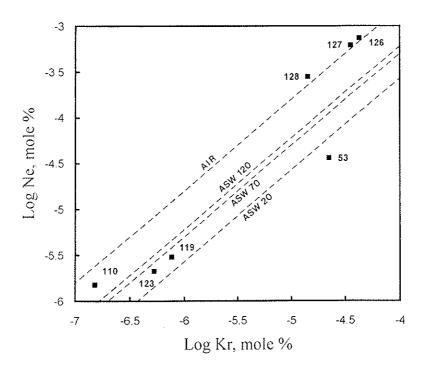
FIG 2

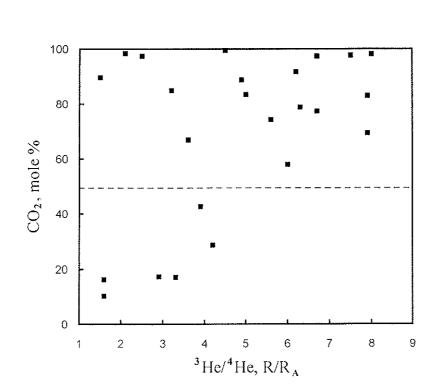






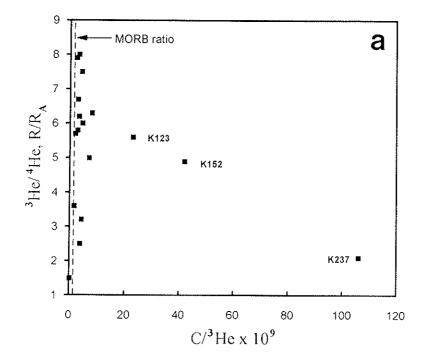




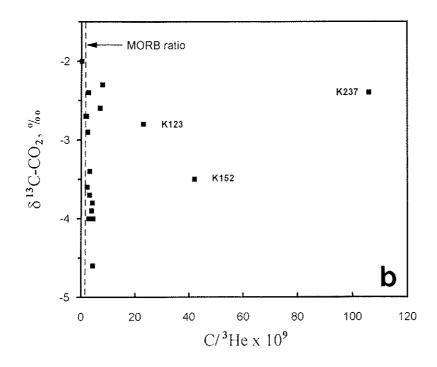


F16 5

F16 6 (a)



F16 6(b)



F16 7

