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Strontium isotopes and rare earth elements as tracers of groundwater–lake water interactions, Lake Naivasha, Kenya

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Abstract

Strontium isotope compositions and rare earth element (REE) concentrations are presented for groundwater and surface water samples collected from the Lake Naivasha watershed in the East African Rift, Kenya. The chief objective of the study is to test the suitability of REEs, in conjunction with Sr isotopes, as tools for investigating groundwater–lake water interactions. In general, the REE concentrations and $^{87}Sr/^{86}Sr$ ratios support the authors' earlier investigations where Cl mass balance, $\delta^{18}O$, δD, and He isotopes were employed to study groundwater–lake water interactions in the Naivasha watershed. The REE data suggest that a significant amount of the groundwater south of Lake Naivasha (i.e., 50–85%) consists of lake water recharge to the aquifer system. Specifically, mixing calculations conducted using REE data of Lake Naivasha water and groundwaters indicate that between 70 and 85% of groundwater directly south of the lake is likely lake water. These values are somewhat higher than the authors' previous estimates determined with conservative stable H isotopes (δD, 50–70%). For both cases, however, the data demonstrate that water originating in Lake Naivasha contributes significantly to the underlying groundwater flow system, hence supporting earlier evidence that the lake's freshness reflects rapid loss of water and dissolved solutes to the local groundwater system. Overall, lake and groundwater Sr isotope compositions support seepage of lake water into the underlying aquifer along the lake's south shore. The $^{87}Sr/^{86}Sr$ data also provide additional insight into the geochemical evolution of waters of the Lake Naivasha watershed indicating that the initial source of Sr to these waters is likely chemical weathering reactions involving basaltic rocks within the recharge zones of the watershed along the Rift Valley flanks. Furthermore, with increasing residence time of groundwaters within the aquifer system and flow down and along the rift valley floor, Sr isotope compositions of groundwaters become more radiogenic, reflecting rock–water interactions with chemically differentiated and radiogenic peralkaline rhyolite volcanic rocks. The importance of the longer aquifer residence times and radiogenic source rocks is especially apparent for geothermal waters of the Olkaria Geothermal Field that have $^{87}Sr/^{86}Sr$ ratios (i.e., 0.70747) similar to local comendites.

1. Introduction

Groundwater inputs to and outflows from lakes are notoriously difficult to quantify using standard hydrological techniques (e.g., Winter, 1981). However,

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understanding these fluxes is important for developing mass balance models for waters and solutes, unraveling biogeochemical cycles of nutrients and heavy metals, and, in the case of closed-basin lakes, understanding the response of water levels to changing climate (Isiorho et al., 1996). Furthermore, under specific hydrologic conditions lakes can contribute significant recharge to groundwater flow systems (Bullen et al., 1996; Katz and Bullen, 1996). Earlier investigations of groundwater–lake water interactions involved examining these fluxes in relatively well characterized aquifers overlain by small lakes (e.g., 0.81 and 0.12 km^2; Krabbenhoft et al., 1990a,b; Katz et al., 1995a,b). These studies focused on aquifers of approximately uniform compositions (i.e., quartz sand, limestone, dolostone), where long-term hydrological and geochemical data bases had previously been assembled. In general, stable O and H isotopes, chlorofluorocarbons, and/or Sr isotopes individually, or in some combination, were employed to investigate groundwater seepage from lakes. It is generally accepted, however, that the ability to characterize groundwater fluxes into and out of lakes accurately using geochemical tools will decrease with increasing lake size (e.g., Ojiambo et al., 2001). Moreover, the majority of groundwater–lake water systems of potential interest are not necessarily well characterized hydrologically, involve monomineralic aquifer compositions, or are associated with long-standing, hydrologic and geochemical data bases. Consequently, the authors submit that application of geochemical tracers that reflect input signals to groundwater–lake water systems (i.e., meteoric waters), and those that derive from water–rock reactions (i.e., chemical weathering) in the aquifer and/or watershed, in conjunction with hydrologic investigations, can provide an improved approach to investigating and cross-validating groundwater–lake water interactions for relatively large lakes overlying complex aquifer systems.

Recently, the authors demonstrated the pertinence of applying different hydrochemical tracers to study groundwater–lake water interactions at Lake Naivasha (surface area ~190 km^2) within the East African Rift zone of Kenya (Fig. 1; Ojiambo and Lyons, 1996; Ojiambo et al., 2001). Initially, conservative tracers (Cl$^-$, δ^{18}O, δD) were employed to verify lake water seepage to the underlying aquifer system (Ojiambo and Lyons, 1996; Ojiambo et al., 2001). Other investigators have argued that the relative freshness of Lake Naivasha waters may reflect loss of lake water to the groundwater system (McCann, 1972, 1974; Åse et al., 1986; Ojiambo, 1992). These studies, including the authors' previous investigations, strongly suggest that Lake Naivasha water is rapidly flushed from the lake into the underlying groundwater system. Furthermore, stable O and H isotopes suggest that much of the groundwater south of the lake (i.e., 50–70%) and in the Olkaria Geothermal Field (40–50%) consists of lake water (Ojiambo and Lyons, 1996; Ojiambo et al., 2001). The chief objective of the current investigation is to test the applicability of Sr isotope compositions and REE concentrations to identify and ultimately quantify groundwater–lake water interactions. Other investigators have employed Sr concentrations and isotopic compositions to this end (e.g., Bullen et al., 1996; Katz and Bullen, 1996). However, to the best of our knowledge, no other study incorporates REEs and Sr isotopes, or REEs alone, to investigate groundwater–lake water interactions. Although the authors believe that the ^{87}Sr/^{86}Sr and REE data are insufficient to conclusively quantify mixing ratios of Lake Naivasha water with local groundwaters, the agreement between the qualitative observations using these tracers and the mixing proportions previously defined with ^{2}H (Ojiambo et al., 2001) is compelling and lends supports to the use of these tracers in future groundwater–lake water studies.

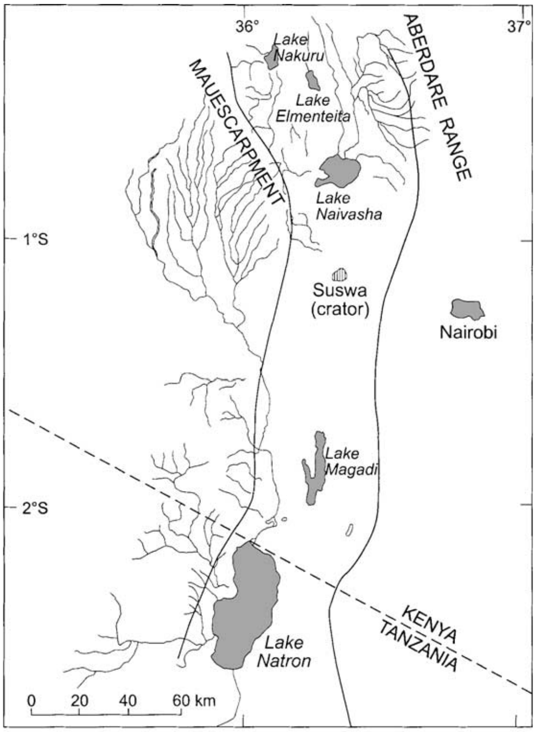

Fig. 1. Location map of Lake Naivasha showing inflow rivers from the north. The two dashed lines on either side of the lake are the approximate locations of the east and west escarpments of the Rift Valley. After Jones et al. (1977) as modified by Ojiambo and Lyons (1996).

2. Hydrogeologic setting

Lake Naivasha is located along the floor (1886 m asl) of the Central Rift Valley of Kenya in the region of the

Kenyan Dome, an elevated portion of the central rift commonly associated with late Quaternary, highly differentiated alkaline volcanism (Fig. 1; Heumann and Davies, 2002). Volcanic rocks of the Naivasha watershed encompass a wide compositional range including tephrites, basalts, trachytes, phonolites and rhyolites, and typically exhibit alkalic characteristics (Thompson and Dodson, 1963; Noble and Ojiambo, 1976; Macdonald et al., 1987; Davies and Macdonald, 1987; Omenda, 1998; Heumann and Davies, 2002). The portion of the East African Rift that contains the Naivasha watershed is also known as the Gregory Rift (Baker et al., 1977). Lake Naivasha is a relatively large (190 km^2), closed-basin freshwater lake with a mean depth of 4.7 m (Åse et al., 1986; Ojiambo, 1992). Surface inflows to Lake Naivasha include the Malewa River (1730 km^2 catchment basin) and the Gilgil River (420 km^2 watershed), with the Malewa River being the chief inflow stream supplying on the order of 90% of the river discharge to the lake (Fig. 1; Gaudet and Melack, 1981). The Karati River, which drains portions of the rift escarpment directly east of Lake Naivasha (Fig. 2), is seasonal and its intermittent flow commonly does not reach the lake (Gaudet and Melack, 1981).

Precipitation in the Lake Naivasha region is seasonal (i.e., monsoonal) with the majority falling from April through May, and a substantially smaller pulse occurring later in November (Gaudet and Melack, 1981). Mean annual precipitation (recorded from 1951 to 1980) is 68 cm with annual evaporation exceeding precipitation by almost a factor of 3 (i.e., 186.5 cm; Ojiambo et al., 2001). The regional groundwater flow is generally from the flanks of the Rift Valley towards the Rift floor, and subsequently southward into and then out of Lake Naivasha (Clarke et al., 1990; Darling et al., 1990; Ojiambo, 1992, 1996; Ojiambo et al., 2001). Aquifers surrounding the lake are composed of lacustrine deposits derived from erosion and redeposition of the local volcanic rocks (Ojiambo, 1992). These lacustrine deposits are characterized by relatively high discharge yields (i.e., > 100 m^3/day and up to 2000 m^3/day) and substantial transmissivities (i.e., > 500 m^2/day, Ojiambo et al., 2001). At greater distances from Lake Naivasha, the aquifers commonly consist of weathered contacts between lava flows (i.e., paleo-weathering surfaces), or highly fractured volcanic rocks (Ojiambo, 1992, 1996). These weathered contacts and fractured volcanic rock aquifers typically exhibit substantially lower discharge yields (<100 m^3/day) than the lacustrine deposits (McCann, 1974; Ojiambo et al., 2001).

3. Methods

3.1. Sampling techniques

Water samples collected from the Lake Naivasha watershed for major solutes and Sr^{2+} were collected in

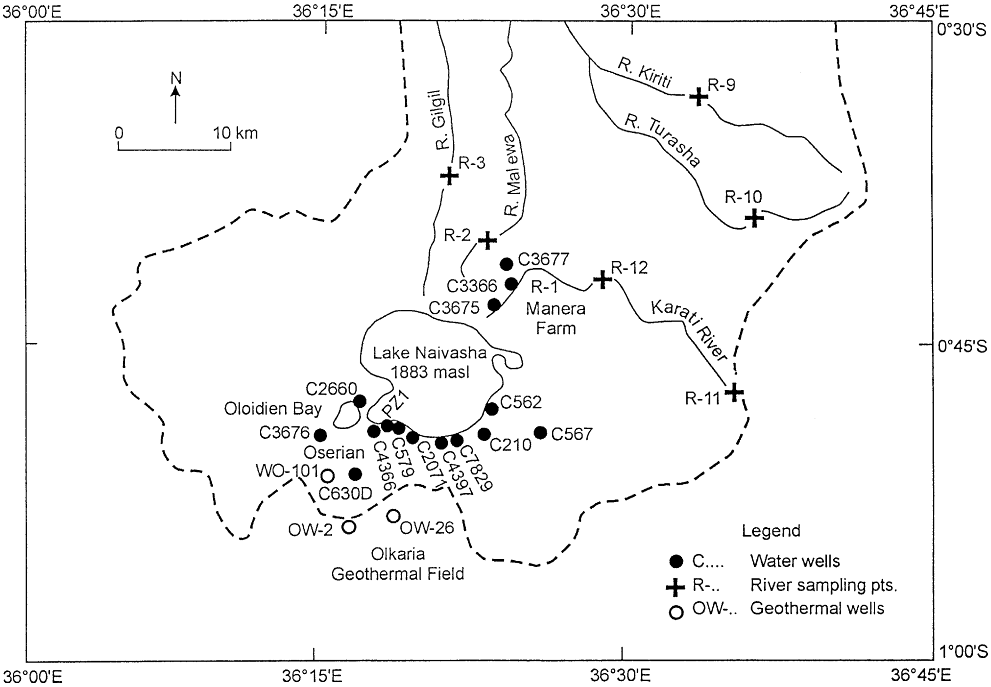

Fig. 2. Enlarged map of the immediate study region showing the sampling locations visited as part of this and the larger study (after Ojiambo et al., 2001). The dashed line indicates the Lake Naivasha watershed boundary.

low-density linear polyethylene (LDPE; Nalgene®) sample bottles that had been previously cleaned by standard acid washing techniques for cations, and using double deionized water with a weak detergent for bottles used to collect anion samples (Ojiambo and Lyons, 1996; Welch et al., 1996). The bottles were subsequently filled with deionized water, and sealed until field sampling. Before collecting water samples for major solutes and Sr^{2+}, the deionized water was decanted from each bottle, and the bottle was subsequently rinsed 3 times with the sample water before being filled with the sample water. Samples were collected using procedures appropriate for ultra-trace element concentration levels (e.g., picomolal) by individuals wearing pre-cleaned, polyethylene gloves (Patterson and Settle, 1976; Gill and Fitzgerald, 1985, 1987). The samples were then transported back to the geochemistry laboratory at the Olkaria Geothermal Project, where they were subsequently emptied into pre-cleaned 1100 ml Quick filter transfer vessels constructed of polyethylene, polycarbonate, and PVC materials, and containing no metals. Using a peristaltic pump, the water samples were filtered through 30-cm^2, 0.45-μm in-line membrane filters (QED Environmental Systems) into new, previously cleaned LDPE sample bottles. Each of these new bottles was rinsed with filtered sample water before filling the new bottle with the filtered sample. The cation and Sr^{2+} samples were subsequently acidified to pH <2 with Ultrex™ HNO_3. The samples were then capped, sealed with an electric, insulating tape, and stored in a refrigerator for approximately 3 weeks until transport back to the USA in cushioned cooler boxes.

Water samples for analysis of $^{87}Sr/^{86}Sr$ ratios were part of the samples collected for ^3H analysis that were discussed previously by Ojiambo et al. (2001). Briefly, double deionized water was processed to establish blank corrections. The samples were collected in 500 ml 1-CHEM quality assured, pre-cleaned glass bottles. These bottles were pre-cleaned using the same procedures as described above for the cations. Groundwater samples from wells were collected as close as possible to the outlet after pumping or purging the well for at least 30 min. The lake water samples were collected approximately 5 m from the shoreline at a depth of roughly 0.5 m. The samples were returned to the geochemistry laboratory at the Olkaria Geothermal Project, where an aliquot of each to be used for $^{87}Sr/^{86}Sr$ measurements was filtered and acidified as described above.

Sample bottles used for collecting waters from the Lake Naivasha watershed for the analysis of REEs were cleaned more rigorously before transport to the study site. Specifically, the cleaning procedure encompassed rinsing high-density linear polyethylene (1 l; HDPE; Nalgene®) sample bottles with distilled–deionized (i.e., 18 MΩ-cm) water. The sample bottles were then soaked in a 10% (v/v) solution of reagent grade HNO_3 for 10 days, followed by a triple rinse with distilled-deionized (18 MΩ-cm) water, and submerged for another 10 days in a second acid bath consisting of a 10% (v/v) trace metal grade HNO_3. The sample bottles were subsequently removed from this acid bath, washed with copious amounts of the distilled–deionized water, filled with distilled–deionized water, and double bagged in similarly cleaned polyethylene bags (Stetzenbach et al., 1994; Johannesson and Hendry, 2000). During sample bottle cleaning, laboratory personnel wore clean polyethylene gloves, and cleaning was conducted in dedicated, laminar-flow hoods.

Two groundwater samples (C3675, C579), 1 geothermal water sample from the Olkaria Geothermal Field (OW-02), a sample of the Malewa River (R-2), and 1 surface water sample from Lake Naivasha (Lk-001) were collected for analysis of the REEs (Fig. 2). These water samples were collected in a similar manner to those collected for major solute and Sr-isotope analysis discussed above. The REE samples were initially collected from the field locations using low-density polyethylene bottles, which were rinsed with the sample water before filling each bottle. These samples were subsequently transported back to the laboratory and were filtered (0.45-μm membrane filters) in the same manner as described above for the major solutes and Sr-isotope samples (the Malewa River sample was not filtered). The filtered water samples for REE analysis were subsequently transferred into the pre-cleaned, 1-l HDPE sample bottles described above, after first rinsing these HDPE bottles with the filtered water sample. After filtration, the samples were acidified to pH <2 with Ultrex™ HNO_3, double bagged in clean polyethylene bags, and shipped back to the USA for analysis.

3.2. Analytical techniques

Major solutes were quantified using ion chromatography (e.g., Welch et al., 1996), whereas Sr^{2+} concentrations were determined by inductively coupled plasma emission spectrometry. Details on the methods used to quantify the $^{87}Sr/^{86}Sr$ ratios are provided in Basu et al. (2001) and references therein. Briefly, $^{87}Sr/^{86}Sr$ ratios were determined using a VG Sector multi-collector mass spectrometer. The isotope ratios were corrected for isotope fractionation using a $^{87}Sr/^{86}Sr$ ratio of 0.1194. Replicate isotope measurements of standard Sr carbonate (NBS987) gave a mean (±standard deviation) $^{87}Sr/^{86}Sr$ ratio of 0.710245 ± 0.00026.

Rare earth element concentrations in Lake Naivasha watershed samples were determined by inductively coupled plasma mass spectrometry (ICP–MS; Perkin-Elmer Elan 5000) with ultrasonic nebulization (Cetac Technologies Model U-5000), following 50-fold preconcentration by cation-exchange chromatography (Stetzenbach et al., 1994; Hodge et al., 1996, 1998). The ultrasonic nebulizer increased the sensitivity of the instrument by roughly 30 times over cross-flow nebulization, and decreased potential interferences from oxide formation (Hodge et al., 1996). The REE isotopes monitored [^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{151}Eu and ^{153}Eu (mean value), ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, and ^{175}Lu] were free of elemental isobaric interferences. Measured REEO$^+$/REE$^+$ ratios were generally $<1\%$, and for those which were $> 1\%$, appropriate corrections were made (Stetzenbach et al., 1994; Johannesson et al., 1997). Interference from BaO$^+$/Ba$^+$ on Eu was avoided by extraction of Ba from separate aliquots of each water sample using diethylhexylphosphoric acid (Cerrai and Ghersini, 1966; Hodge et al., 1998). The ICP–MS was calibrated and the sample concentrations verified using a series of 5 REE standards of known concentrations (10, 50, 100, 500, and 1000 ng/kg). The precision of the REE measurements was generally better than 10% relative standard deviation (RSD) for all the REEs. Exceptions included Sm, Gd, Tb, Dy, and Lu, for which RSD was greater than 10%, but better than 12%.

4. Results

4.1. Strontium and ^{87}Sr/^{86}Sr ratios

Strontium concentrations and ^{87}Sr/^{86}Sr ratios of water samples from the Lake Naivasha watershed are presented in Table 1 and Fig. 3. Groundwaters from wells on the northern side of Lake Naivasha (C3366; C3677; Manera Farms region) have slightly more radiogenic ^{87}Sr/^{86}Sr ratios (0.70575) than Lake Naivasha water (0.70552), whereas the well waters along the southern shore of the lake (C2071; C4397) have ^{87}Sr/^{86}Sr ratios that are similar to lake water. Well waters from SW of Lake Naivasha (UW-1; C3676) have more radiogenic ^{87}Sr/^{86}Sr ratios (0.70639 and 0.70585, respectively) than lake water, Manera Farm groundwaters, and groundwaters along the lake's southern shore. Only one well was sampled from east of the lake (i.e., C567). Groundwater from this well has a radiogenic ^{87}Sr/^{86}Sr ratio of 0.70610. The ^{87}Sr/^{86}Sr ratio of the Olkaria Geothermal water sample from well OW-26 is the most radiogenic of the samples measured (0.70747). Well C567 is a deep well (102 m), and as such, its more radiogenic signature probably reflects a longer flow path and hence, longer aquifer residence time, than other low-temperature groundwaters analyzed from the watershed.

Table 1
Strontium concentrations and isotopic composition of waters from the Lake Naivasha watershed, Kenya

	Sr (μmol/kg)	^{87}Sr/^{86}Sr
C3366	6.129	0.70575
C3677	1.541	0.70575
Lake Naivasha	1.655	0.70552
C567	0.673	0.70610
C4397	3.766	0.70545
C2071	3.538	0.70533
C3676	0.872	0.70585
UW-1	0.708	0.70639
OW-101	0.118	0.70536
OW-26	0.057	0.70747

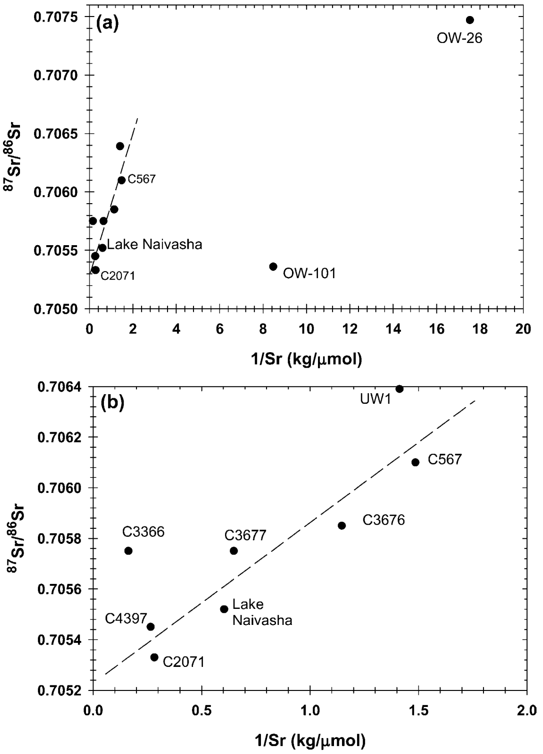

Fig. 3. Plots of ^{87}Sr/^{86}Sr vs. 1/Sr for waters of the Naivasha watershed. Panel (a) shows all of the waters from the study site that were analyzed for Sr isotopes and Sr concentrations, whereas panel (b) does not include the Olkaria geothermal waters.

The 2 geothermal waters sampled from the Olkaria Geothermal field have ^{87}Sr/^{86}Sr ratios that span the range of Sr isotope ratios reported for waters of the Naivasha watershed (Table 1, Fig. 3). Well OW-101 is from the western part of the Olkaria Geothermal Field (Fig. 2). Groundwater from well OW-101 is warm, and is classified as a Na–HCO$_3$–Cl water in contrast to the hot, Na–Cl waters from well OW-26 located in the eastern part of the geothermal field (Fig. 2; Ojiambo, 1992, 1996; Omenda, 1998). Groundwaters from the western part of the geothermal field are more dilute, and are thought to contain higher proportions of shallow, Na-HCO$_3$ groundwaters than the eastern wells of the

Olkaria field (Ojiambo, 1996). In other words, the western groundwaters of the Olkaria Geothermal Field are transitional between the shallow, low-temperature Na-HCO_3 groundwaters, and the deeper, hot Na–Cl waters from the eastern portion of the geothermal field (Ojiambo, 1996). It should be noted that well OW-101 is also located near a fault and the water sampled from this well could represent a mixture of hot geothermal fluids and young meteoric waters. In any case, both possibilities could explain, in part, the less radiogenic $^{87}Sr/^{86}Sr$ ratio of OW-101 well water (Ojiambo, 1996). Paradoxically, Omenda (1998) argues that the high HCO_3 concentrations of western Olkaria thermal waters reflect mantle sources of CO_2 to the geothermal system.

4.2. REE concentrations

Concentrations of the REEs for selected waters from the Lake Naivasha watershed are presented in Table 2. These samples include 1 from the Malewa River (R-2), 1 from Lake Naivasha, a sample of hydrothermal fluid from the Olkaria Geothermal Field (OW-2), and 2, low-temperature, groundwater samples (Fig. 2). The groundwater samples are from north of Lake Naivasha (well C3675), and from along the southern shore (well C579; Fig. 2).

In general, waters from the Naivasha watershed exhibit high REE concentrations compared to many other natural waters. Again, because the Malewa River sample was not filtered, the very high REE concentrations reported reflects both the dissolved and suspended REE load of the river. Consequently, the Malewa River data cannot be directly compared to the majority of world river water REE studies (e.g., Elderfield et al., 1990; Sholkovitz, 1995) nor to the other Naivasha watershed samples. Lake Naivasha has higher REE concentrations than another east African lake, Lake Tanganyika (e.g., Nd values for 2 Lake Tanganyika samples were 107 and 154.5 pmol/kg; Barrat et al., 2000). Lake Tanganyika has a similar pH to Lake Naivasha (8.6–8.9 vs. 8.6, respectively), although it is slightly more concentrated in dissolved ions ($I = 0.006$ vs. $I = 0.0048$ mol/kg, respectively; Barrat et al., 2000; Gaudet and Melack, 1981). The 2 groundwater samples analyzed from the Lake Naivasha watershed (C3675, C579) have REE concentrations that are similar to, or slightly higher than, the REE concentrations reported for other dilute, circumneutral pH groundwaters (Johannesson et al., 1997, 1999; Leybourne et al., 2000; Yan et al., 2001). Only 1 water sample from the Olkaria Geothermal Field was collected for REE analysis (OW-02; Table 2). The Olkaria thermal water does not have unusual REE concentrations compared to other thermal waters (e.g., see Michard et al., 1987; Sanjuan et al., 1988; Lewis et al., 1997; van Middlesworth and Wood, 1998).

Table 2
Rare earth element concentrations (in pmol/kg) of waters from the Lake Naivasha watershed, Kenya

	Manera Farm[a] (C3675)	South Shore[b] (C579)	Olkaria[c] (OW-02)	Malewa River	Lake Naivasha
La	90	689	840	15,508	814
Ce	212	1296	1424	26,053	1380
Pr	27	136	151	3274	150
Nd	113	491	474	11,685	568
Sm	62	90	70	2081	105
Eu	3	15	7.3	271	21
Gd	39	86	51	1942	114
Tb	7.4	17	5.4	298	16
Dy	51	85	20	1673	94
Ho	16	18	2.7	316	20
Er	57	55	6.5	919	56
Tm	9.7	8.8	0.72	133	8.5
Yb	63	60	4.2	805	47
Lu	13	10	0.67	117	7.2

[a] Manera Farm groundwater sample is from north of Lake Naivasha.

[b] The South Shore groundwater sample was collected from Well C579 directly south of the lake.

[c] The Olkaria samples is a geothermal water from the Olkaria Geothermal Field.

4.3. Normalized REE patterns

The REE data for waters from the Lake Naivasha watershed, including the unfiltered Malewa River sample, are plotted normalized to upper continental crustal values (i.e., UCC; Taylor and McLennan, 1985) in Fig. 4. Rare earth element data for these waters are shown in Fig. 5 normalized to mean values of local

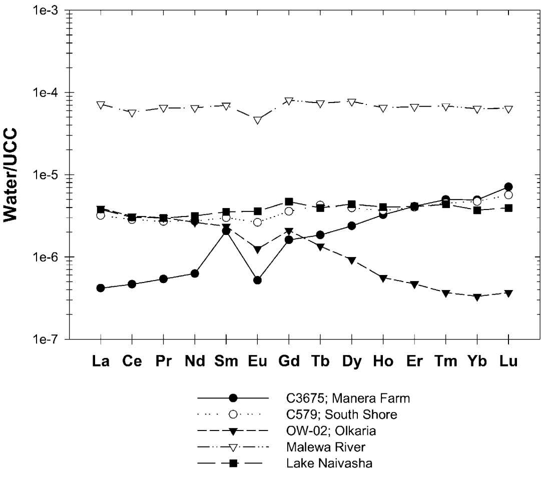

Fig. 4. Upper continental crust (UCC) normalized plot of rare earth element data for waters from the Lake Naivasha watershed. UCC is that of Taylor and McLennan (1985).

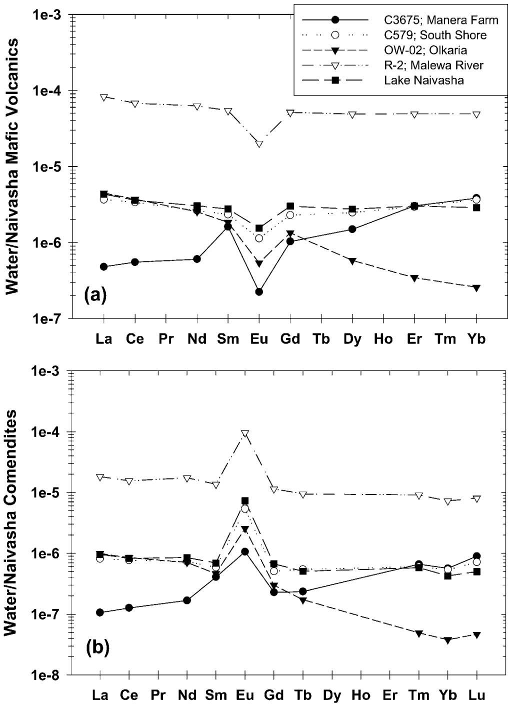

Fig. 5. Rare earth element data for waters from the Lake Naivasha watershed normalized to (a) local basaltic volcanic rocks and (b) peralkaline rhyolites from the Olkaria geothermal field region. Rare earth element data for basalts and rhyolites are from Davies and Macdonald (1987) and Macdonald et al. (1987).

peralkaline rhyolitic volcanics and mafic volcanic rocks (Macdonald et al., 1987; Davies and Macdonald, 1987). The normalized REE pattern of the groundwater sample collected along the southern shore of Lake Naivasha (i.e., C579) is essentially identical to the normalized REE pattern of Lake Naivasha water (Figs. 4 and 5). Both are relatively flat with slight enrichments in the heavy REEs (HREE) when compared to UCC (Fig. 4). On the other hand, the groundwater sample collected from north of the lake (i.e., Manera Farm well C3675) exhibits a substantial enrichment in the HREEs when compared to the light REEs (LREE; Fig. 4). Although concentrations of the heaviest REEs in the northern groundwater sample are similar to those of Lake Naivasha and the south shore groundwater sample, the LREEs are markedly depleted by comparison. The Olkaria geothermal water sample (OW-02) has a different UCC-normalized REE pattern than the other water samples being depleted in the HREEs compared to the LREEs (Fig. 4). It should be noted that the REE distributions in this Olkaria hydrothermal fluid is not unlike other Cl-rich thermal waters (e.g., Michard and Albarède, 1986; Sanjuan et al., 1988; Michard, 1989). Similar relationships are exhibited for the local volcanic rock-normalized plots (Fig. 5). The substantial positive Eu anomalies inherent in all of the water samples when normalized to the local comendites reflects the Eu depletion that characterizes these rocks (Macdonald et al., 1987; Heumann and Davies, 2002).

5. Discussion

5.1. Groundwater–lake water interactions

As mentioned above, Lake Naivasha is the only closed-basin, freshwater lake of substantial size within the East Africa Rift Valley of Ethiopia, Kenya, and Tanzania. All other closed-basin lakes within the rift are either saline or hypersaline (e.g., Eugster, 1970; Jones et al., 1977; Yuretich and Cerling, 1983; Renault and Tiercelin, 1994). Remarkably, Lake Naivasha has no surface water outflow that could explain, via flushing of the lake, the low dissolved solid concentrations that characterize the lake water. Consequently, previous investigators have postulated various processes to explain the freshness of Lake Naivasha waters, including the fact that a large fraction of the water that supplies the lake originates as dilute precipitation either directly on the lake, or indirectly via inflow of dilute river water recharged chiefly along the eastern rift escarpment (Fig. 1; Gaudet and Melack, 1981). The dilute, HCO_3-rich waters of the Malewa River represent the dominant surface water inflow to Lake Naivasha, accounting for approximately 90% of the total river discharge to the lake (Gaudet and Melack, 1981). The chemically similar Gilgil River accounts for much of the remaining surface water inflow to the lake. The Malewa River drains regions underlain by a variety of recent, chiefly alkalic volcanic rocks including trachytes and other highly differentiated tuffaceous rocks, although its headwaters are in the alkaline and olivine basalts of the Kippiri and Aberdares ranges that define the rift valley flanks (Fig. 1; see Gaudet and Melack, 1981; Ojiambo et al., 2001). Lake bottom sediments have also been identified as a major sink for some dissolved solutes in Lake Naivasha including Ca, Mg, K, and HCO_3 (see below), and biochemical sedimentation has been invoked to explain the loss of dissolved silica, as well as Ca and HCO_3, from lake waters (Gaudet and Melack, 1981).

Although input of dilute river water and loss of solutes to sediments can, in part, explain the freshness of Lake Naivasha, the lake is also known to be a seepage lake that loses between 18 and 50×10^6 m^3 of water annually to the groundwater system south of the lake (e.g., McCann, 1972, 1974; Gaudet and Melack, 1981; Åse et al., 1986; Clarke et al., 1990; Darling et al., 1990; Ojiambo, 1992; Ojiambo et al., 2001). Thompson and Dodson (1963) provided water-level data from which Gaudet and Melack (1981) demonstrated seepage of water out of Lake Naivasha along its southern and southeastern shore. In addition, groundwater inflow has been reported to occur along the NE and NW shores of the lake (Gaudet and Melack, 1981). More recently, Ojiambo and coworkers demonstrated, based on the level of the piezometric surface south of the lake, that lake water seepage along the southern shore continues to flow south towards the Olkaria Geothermal Field (Ojiambo, 1992; Ojiambo et al., 2001).

Ojiambo et al. (2001) used stable O and H isotopes, in conjunction with $^3H/^3He$ age dating techniques, to study groundwater–lake water interactions in the Naivasha watershed. They found that deep wells ($\geqslant 91$ m) located to the north of the lake in the Manera Farm region (Fig. 2) have $^3H/^3He$ ages of around 20 a and $\delta^{18}O$ and δD values that resemble those of the Malewa and Gilgil Rivers (Ojiambo et al., 2001). In addition, it was noted that the $\delta^{18}O$ and δD values of these "northern" groundwaters are similar to waters from higher elevations along the eastern rift escarpment (i.e., Aberdare Range), as well as modern precipitation within the region. Consequently, based on the stable isotope data and ^3H levels, groundwaters from north of Lake Naivasha, as well as Malewa and Gilgil River waters, are thought to reflect modern precipitation in the watershed (Ojiambo et al., 2001). Lake Naivasha water is enriched in both $\delta^{18}O$ and δD compared to groundwaters from the Manera Farm to the north of the lake, with water from Oloidien Bay having the highest stable isotope values (Ojiambo et al., 2001). The enriched $\delta^{18}O$ and δD values of Lake Naivasha and Oloidien Bay waters are consistent with evaporative concentration of modern precipitation (i.e., groundwaters of Manera Farm area; Ojiambo et al., 2001). Furthermore, the residence time of Cl in the lake (i.e., 5.4 a), which because of the generally conservative behavior of Cl can be viewed as a measure of the residence time of water in the lake, along with the lake's ^3H concentration and hydrologic considerations indicate that Lake Naivasha water is "young" at around 5 a (Ojiambo and Lyons, 1996; Ojiambo et al., 2001). The short Cl^- residence time of Lake Naivasha water suggests rapid loss of lake water to the local groundwater system as an explanation for the lake water's low salinity (Ojiambo and Lyons, 1996).

Based on ^3H levels, groundwaters collected from wells along the southern shore of the lake are thought to be younger than the northern (i.e., Manera Farm) groundwaters (see Ojiambo et al., 2001). Stable O and H isotope values of the southern groundwaters plot along an evaporative concentration line defined by modern precipitation and the meteoric water-like values of the Manera Farm groundwater to the north, and enriched Lake Naivasha and Oloidien Bay waters (see Fig. 3c of Ojiambo et al., 2001). The fact that the southern groundwaters plot along the evaporative concentration line defined by the lake, indicates that a significant component of southern groundwater consists of seepage water from Lake Naivasha. Indeed, mixing calculations using the δD data suggest that the southern groundwaters consist of between 50 and 70% lake water, with the remainder being deep groundwater similar to Manera Farm well waters (Ojiambo et al., 2001). Perhaps more remarkable is that the stable isotope data for Olkaria geothermal waters also plot on the same lake-defined evaporative concentration/mixing line between modern precipitation and Lake Naivasha water. These relationships suggest that Olkaria geothermal waters consist of between 40 and 55% lake water, and 45–60% deep, circulating groundwater (Ojiambo et al., 2001).

Strontium isotope and concentration data for waters of the Lake Naivasha watershed are presented in Table 1 and Fig. 3. Strontium concentrations range from a high of 6.13 μmol/kg in groundwater from well C3366 in the Manera Farm region north of the lake (Fig. 2), to a low of 0.057 μmol/kg in well OW-26 from the Olkaria Geothermal Field. However, this groundwater sample from the Olkaria Geothermal Field has the most radiogenic Sr isotope composition (i.e., $^{87}Sr/^{86}Sr = 0.70747$) of all waters collected from the Naivasha watershed (Fig. 3a). The Sr isotope data suggest that Lake Naivasha water ($^{87}Sr/^{86}Sr = 0.70552$) is composed of groundwaters from north of the lake (e.g., Manera Farm well waters) and less radiogenic waters exhibiting higher Sr concentrations. The Sr concentrations and $^{87}Sr/^{86}Sr$ composition suggests that this additional source could be groundwater from south of the lake (Fig. 3). However, this possibility seems unlikely in light of the hydrology of the watershed (Thompson and Dodson, 1963; Gaudet and Melack, 1981; Ojiambo and Lyons, 1996; Ojiambo et al., 2001). Although Sr concentrations and isotope compositions of Malewa River water have not been measured, it seems reasonable that the most likely candidate is the river. Major solute mass balance calculations (Gaudet and Melack, 1981; Ojiambo and Lyons, 1996) clearly demonstrate that the Malewa River water is the chief source of water and dissolved solutes to the lake, although contribution from groundwater seepage in the north is also important. The Sr isotope data are consistent with seepage of groundwater into the lake along its northern shore as contributing water and dissolved solutes to Lake Naivasha. Without Malewa River samples, however, the importance of this subterranean flux into the lake cannot be quantified using the existing Sr isotope data.

Groundwaters collected from wells directly south of Lake Naivasha have Sr isotope compositions that are similar to, albeit, slightly less radiogenic than lake water (Table 1, Fig. 3). More specifically, groundwater from well C4397 along the south shore (Fig. 2) has a $^{87}Sr/^{86}Sr$ ratio of 0.70545 which closely resembles the $^{87}Sr/^{86}Sr$ ratio of Lake Naivasha water (0.70552). However, the Sr isotopic composition of groundwater from well C2071, roughly 1 km to the west of well C4397 along the southern lake shore, is less radiogenic than lake water at 0.70533 (Fig. 3). On the other hand, groundwaters from wells to the SW and to the east of Lake Naivasha (i.e., C3676, C567) are more radiogenic than lake water (Table 1). These relatively radiogenic, low-temperature groundwaters also exhibit lower Sr concentrations compared to northern (i.e., Manera Farm) groundwaters, Lake Naivasha, and groundwaters along the lake's southern shore. The southwestern and eastern groundwater samples closely resemble the more radiogenic Olkaria thermal waters in both their Sr isotope compositions and low Sr concentrations (Table 1).

The similar Sr isotope composition of the groundwaters from the lake's southern shore support seepage of lake water into the local groundwater flow system south of the lake. However, the higher Sr concentration of these less radiogenic waters compared to lake water indicate that another, as yet unidentified endmember water, mixes with infiltrating lake water to produce the $^{87}Sr/^{86}Sr$ ratios and Sr concentrations of groundwaters from the lake's southern shore. It is conceivable that this unidentified source is meteoric water. Regardless, it is clear from the Sr isotope data that the southern groundwaters contain a significant component of infiltrated lake water, and further, that the unidentified endmember cannot be waters from the Olkaria geothermal system (Fig. 3).

The nearly identical UCC-normalized REE patterns of Lake Naivasha water and groundwater from the southern shore (i.e., well C579; Fig. 4) are also consistent with the southern groundwaters containing a significant component of Lake Naivasha water. These observations agree well with the previous conclusions based on the $^{3}H/^{3}He$ dating techniques, Cl mass balance, and stable O and H isotope data that southern groundwaters consist of a significant component of lake water (Ojiambo and Lyons, 1996; Ojiambo et al., 2001). Mixing calculations performed with the REE data (i.e., Fig. 6 and Farnham et al., 1999) are in general agreement with the mixing ratios determined using δD (i.e., southern groundwaters consist of between 50 and 70% Lake Naivasha water; Ojiambo et al., 2001). However, the REE data suggest that groundwaters along the south shore of the lake may be composed of even greater proportions of Lake Naivasha water than determined with the ^{2}H data (Fig. 6). In fact, using the REE data for groundwater from well C3675 from the Manera Farm region north of the lake (i.e., "deep groundwater") and the Lake Naivasha data in the mixing calculations, a better fit to the REE data for well C579 water (i.e., south shore groundwater) is found by mixing ~85% lake water with ~15% groundwater from the Manera Farm region (Fig. 6). The mixing ratios of Lake Naivasha water and Manera Farm groundwater suggested by the ^{2}H data to explain the origin of the south shore groundwaters underestimates the LREE concentrations of the southern groundwaters (Fig. 6). The failure to reproduce the LREE concentrations of the south shore groundwater sample (i.e., C579) reflects the substantial depletion of the LREEs in the Manera Farm groundwater sample (C3675), and the significant proportion of deep groundwaters from the Manera Farm region (30–50%) that is required to explain the ^{2}H data of southern groundwaters (Ojiambo et al., 2001). The mixing proportions determined with the REEs, however, should be viewed with caution owing to the general, non-conservative behavior of REEs, and especially the LREEs, in aqueous systems. That is, because the REEs are commonly highly particle reactive for conditions typical of most natural waters, exhibiting strong sorption to some mineral phases (e.g., clays) and/or co-precipiation with others (Fe-Mn oxyhydroxides, carbonates), they are not expected to behave conservatively as, for example, more soluble elements like Na or Cl (Terakado and Masuda, 1988; Koeppenkastrop and DeCarlo, 1992; Zhong and Mucci, 1995; Benedict et al., 1997; Clark et al., 1998; Sinitsyn et al., 2000; Bradbury and Baeyens, 2002; Coppin et al., 2002; Elzinga et al., 2002; Kraemer et al., 2002). It is important to note, however, that in the presence of strong complexing ligands, REEs can exhibit more conservative behavior (e.g., McCarthy et al., 1998; Möller et al., 2000). Nonetheless, it is best to only consider the calculated REE mixing proportions as further supporting evidence that substantial quantities of Lake Naivasha water contribute, via seepage, to the groundwater flow system south of the lake.

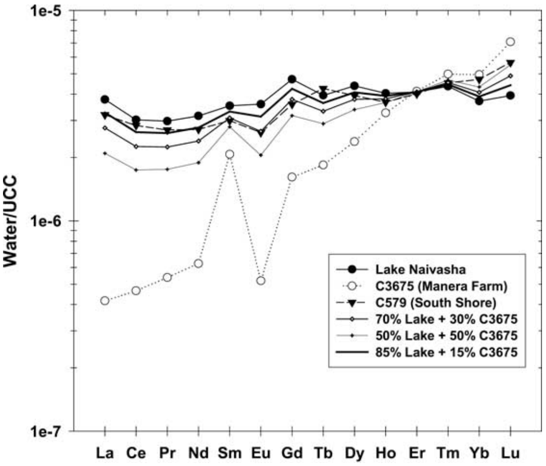

Fig. 6. Results of mixing calculations performed with UCC-normalized REE patterns for waters of the Lake Naivasha watershed, which demonstrates that groundwaters from the south shore of the lake can be explained by a mixture of chiefly lake water with a component of deep groundwater of similar composition to those collected north of the lake within the Manera Farm region (see Fig. 2). See text for details.

The Olkaria thermal waters are characteristically more radiogenic and have lower Sr concentrations than other waters from the Lake Naivasha watershed (Table 1, Fig. 3). The UCC-normalized REE pattern of Olkaria groundwater from well OW-02 is identical to Lake Naivasha water for La, Ce and Pr, but is increasingly depleted in REEs heavier than Nd across the lanthanide series when compared to lake water (Fig. 4). Previously, Ojiambo et al. (2001) demonstrated that waters of the Naivasha watershed consist of 3 general types based on their major solute compositions: (1) dilute, mixed Ca–Na–HCO_3–Cl–SO_4 waters that occur along the eastern escarpment and to the north of the lake; (2) Na–HCO_3 waters, which characterize the low-temperature groundwaters, river waters, and Lake Naivasha waters; and (3) Na–Cl thermal waters of the Olkaria Geothermal Field. The Olkaria Geothermal Field is located within a region dominated by recent ($\leqslant$20 ka) comendites (i.e., peralkaline rhyolites) of the bimodal, Greater Olkaria Volcanic Complex (Heumann and Davies, 2002). Consequently, the LREE-enriched/HREE-depleted, UCC-normalized pattern of the Olkaria thermal water sample (OW-02) could reflect the LREE enrichments that characterize these highly differentiated volcanic rocks (e.g., Davies and Macdonald, 1987; Heumann and Davies, 2002). Inheritance of a rock-like REE signature for Olkaria thermal waters may be expected based on their higher temperatures and longer residence times in the aquifer system compared to the low-temperature groundwaters from the Naivasha watershed (e.g., see Ojiambo et al., 2001 and Michard and Albarède, 1986). The Olkaria geothermal waters lack ^{3}H, indicating that they are older than at least ~50 a (Ojiambo et al., 2001). However, the Olkaria groundwater (OW-02) has a fractionated REE pattern when normalized to either the comendites or basalts of the Greater Olkaria Volcanic Complex (Fig. 5), suggesting that the REE signature of this thermal water sample does not directly reflect a rock-derived REE pattern. Instead, it is suggested that depletion of HREEs in OW-02 compared to Lake Naivasha water, and groundwaters from south of the lake, reflects the differences in the major solute compositions in these waters (i.e., Na–Cl for thermal waters vs. Na–HCO_3 for lake and groundwaters; Gaudet and Melack, 1981; Ojiambo, 1992, 1996; Ojiambo and Lyons, 1996), which strongly controls the solution complexation behavior of REEs (e.g., Cantrell and Byrne, 1987; Wood, 1990; Johannesson and Lyons, 1994; Johannesson et al., 1999; Johannesson and Hendry, 2000). It would be expected that carbonato (i.e., $LnCO_3^+$) and dicarbonato [$Ln(CO_3)_2^-$] solution complexes are the predominant form of dissolved REEs in the moderately alkaline (pH 8.6), HCO_3-rich waters of Lake Naivasha, as well as low-temperature Na–HCO_3 groundwaters and river waters of the watershed (e.g., Johannesson et al., 1996). At the pH value of Lake Naivasha, the very stable dicarbonato complex should be the dominant form of the dissolved HREEs, facilitating their persistence in solution (Johannesson et al., 1996, 1999). However, in the case of the neutral pH, Cl-rich thermal waters of the Olkaria Geothermal Field, REE carbonate complexes will account for substantially lower amounts of each REE, which instead will exist in solution as less stable forms such as the free metal ion (Ln^{3+}), SO_4 complexes ($LnSO_4^+$), and perhaps Cl complexes ($LnCl^{2+}$) depending on the temperature (e.g., Haas et al., 1995). Indeed, in the absence of strong complexing ligands such as the CO_3^{2-} ion, the affinity of the REEs to adsorb to particles and aquifer surface sites will increase with increasing atomic number (Aagaard, 1974; Roaldset, 1974). Therefore, the HREE depletion of OW-02 water compared to Lake Naivasha water, and other waters from the Naivasha watershed, probably reflects the greater tendency of the HREEs, relative to the LREEs, to sorb to surface sites within the aquifer/wall rocks in these Cl-rich, HCO_3-poor thermal waters.

5.2. *Sr isotope systematics*

Although the $\delta^{18}O$ and δD study (Ojiambo et al., 2001), as well as the REE data, indicate that Manera Farm groundwaters contribute to Lake Naivasha, the chief source of surface water to the lake is the Malewa River (Gaudet and Melack, 1981). The Malewa River originates to the north, draining evolved alkalic volcanic rocks (i.e., trachytes, peralkaline rhyolites, rhyolites) within the rift basin, although its headwaters within the Kipipiri Range, and especially the Aberdare Range along the eastern escarpment (Fig. 1), drain olivine basalts and other alkaline volcanic rocks (Gaudet and Melack, 1981). It is likely that groundwater is also recharged in these elevated regions, and that baseflow is a significant component of Malewa River discharge during the dry season (January–February). The concentration of total dissolved solids (TDS) of waters from the Lake Naivasha watershed increases towards the south as is expected from the southerly flow of surface and groundwaters in the region (Ojiambo, 1992). The increase in TDS is especially apparent in groundwater south of Lake Naivasha (e.g., Ojiambo, 1992), which is again consistent with southerly flow of groundwater in this region as suggested by piezometric head levels, stable O and H isotope data, and supported by the Sr isotope and REE data (Figs. 3–6; Ojiambo et al., 2001). The Sr isotope signature of groundwaters increases to the SW and SE of Lake Naivasha, reaching a maximum value for waters from the Olkaria Geothermal Field (i.e., $^{87}Sr/^{86}Sr = 0.70747$; Table 1). It should be noted that the peralkaline rhyolites of the Olkaria Geothermal Field exhibit the most radiogenic Sr isotope signatures of all rocks exposed within the Naivasha watershed ($^{87}Sr/^{86}Sr$ ranges from 0.70607 to 0.711891; Macdonald et al., 1987; Davies and Macdonald, 1987; Heumann and Davies, 2002).

In general, all waters sampled in this study have Sr isotope ratios that fall within the range exhibited by volcanic rocks within the Naivasha watershed indicating that the Sr isotope signatures of these waters reflect the Sr isotope compositions of volcanic rock from the catchment (Fig. 7). For the purpose of shedding light on the evolution of Sr isotope signatures of waters from the Naivasha watershed, the Sr isotope and Sr concentrations of volcanic rocks from the region have been plotted along with the water data. A similar approach has previously been used (e.g., Katz and Bullen, 1996). The rock and water data are plotted together on Fig. 7 in order to *qualitatively* help elucidate possible processes, and thus should not be viewed as a *quantitative* solution. Ideally, a plot of the ^{87}Rb/^{86}Sr vs. ^{87}Sr/^{86}Sr ratios of these waters and rocks from the catchment basin would be employed to derive a quantitative model of water–rock interaction in the watershed. Nonetheless, the data shown in Fig. 7 suggest that the Sr isotope composition of these waters likely evolve from relatively nonradiogenic signatures inherited from chemical weathering of basaltic volcanic rocks on the eastern escarpment and north of Lake Naivasha, towards the radiogenic signatures of the highly differentiated (i.e., comendites) volcanics within the Olkaria Geothermal Field.

Following the arguments of Langmuir et al. (1978), and Faure (1986, 2001), theoretical Sr-isotope "evolution" curves can be calculated for the waters of the Lake Naivasha watershed assuming appropriate endmembers are identified. Based on the conceptual model for Sr isotope evolution of waters from the Naivasha watershed discussed above, it is assumed that the initial source water to the system has a Sr isotope composition identical to the relatively non-radiogenic, basaltic rocks of the catchment basin (Macdonald et al., 1987). Furthermore, it is suggested for the model that the Sr isotope composition of waters from the watershed "evolve" towards the radiogenic, Sr-poor water of Olkaria well OW-26 by chemical reactions with relatively more radiogenic, rhyolitic volcanic rocks of the watershed. In other words, waters recharging the Lake Naivasha

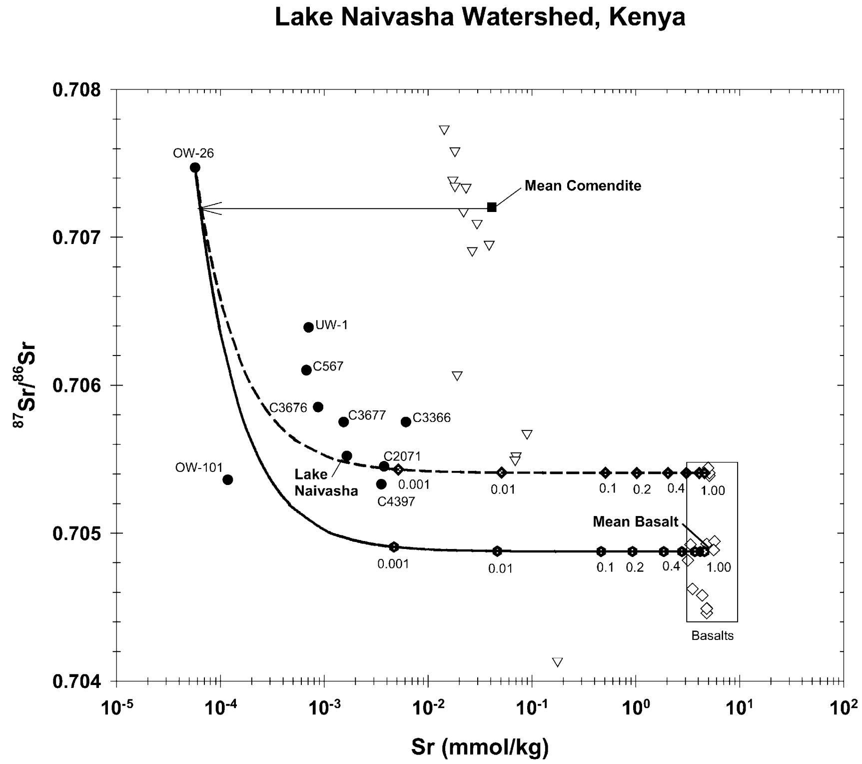

Fig. 7. Strontium isotope ratios (^{87}Sr/^{86}Sr) vs. Sr concentrations (in mmol/kg) of water samples (solid circles) from the Lake Naivasha watershed. Also shown are ^{87}Sr/^{86}Sr and corresponding Sr concentrations of local comendites (i.e., peralkaline rhyolitic volcanics) of the Olkaria geothermal field region (inverted open triangles) and local basaltic rocks (open diamonds) taken from Davies and Macdonald (1987) and Macdonald et al. (1987). Two chemical evolution curves are shown for the Sr isotopes using radiogenic Olkaria geothermal waters from well OW-26 as 1 end member, and hypothetical waters assumed to have only reacted with local basaltic rocks are used as the other end member. Various mixing proportions [i.e., f_{basalt} of Eqs. (1) and (2)] along each calculated curve. See text for details.

watershed inherit Sr isotope compositions from chemical weathering of basalts in the headwaters region (i.e., Aberdare Range of the eastern escarpment), and subsequently become more radiogenic via interaction with differentiated volcanic rocks in the rift basin, and especially the comendites south of the lake within the Olkaria Geothermal Field. The Sr concentration along the Sr "evolution" curves can be calculated using the general mixing equation for Sr:

$$[\mathrm{Sr}]_{\mathrm{Int}} = [\mathrm{Sr}]_{\mathrm{basalt}} f_{\mathrm{basalt}} + [\mathrm{Sr}]_{\mathrm{OW\text{-}26}}(1 - f_{\mathrm{basalt}}) \tag{1}$$

where f_{basalt} is the fraction, between 0 and 1, of the initial source water resulting from chemical weathering of basaltic rocks in the watershed headwaters, and $[\mathrm{Sr}]_{\mathrm{Int}}$ is the Sr concentration of intermediate waters along the flow path. The Sr isotope composition of any intermediate water is related to the Sr concentrations of the initial source water and the final thermal (i.e., OW-26) water, as well as the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of each, as:

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{Int}} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{basalt}} f_{\mathrm{basalt}} \frac{[\mathrm{Sr}]_{\mathrm{basalt}}}{[\mathrm{Sr}]_{\mathrm{Int}}} + \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{OW\text{-}26}} (1 - f_{\mathrm{basalt}}) \frac{[\mathrm{Sr}]_{\mathrm{OW\text{-}26}}}{[\mathrm{Sr}]_{\mathrm{Int}}} \tag{2}$$

where $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{Int}}$ is the Sr isotope ratio of an intermediate water along the Sr isotope "evolution" curve, and the other subscripts are as above for Eq. (1) (Faure, 1986, 2001).

Two hypothetical Sr isotope evolution curves for waters of the Naivasha watershed are plotted on Fig. 7. The lower curve, shown as a solid line, assumes that upon chemical weathering of basalts along the eastern escarpment, the recharge waters inherit Sr concentrations and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios that reflect the mean value of analyzed basaltic volcanic rocks of the Naivasha region (Macdonald et al., 1987). However, because all of the water samples from the Naivasha watershed, except OW-101, plot above this curve, another Sr evolution curve, shown as a dashed line on Fig. 7, has been constructed using a source water with a more radiogenic isotope signature, reflecting chemical weathering of more radiogenic basaltic rocks in the watershed. For this second Sr isotope evolution curve, two water samples (Lake Naivasha and groundwater from well C2071) fall directly on the curve, and another (i.e., C4397) plots slightly below the curve (Fig. 7). All of the other waters, except OW-101, plot above this curve.

In general, the authors interpret these data and the calculated Sr isotope evolution curves (Fig. 7) to indicate that the Sr concentrations and isotopic composition of waters of the Lake Naivasha watershed chiefly reflect chemical weathering of basaltic sources, with additional inputs of more radiogenic Sr from compositionally differentiated volcanic rocks (i.e., trachytes, comendites, pantellerites, rhyolites) that occur along the rift valley and within the catchment basin (e.g., Davies and Macdonald, 1987; Macdonald, 1987; Omenda, 1998; Heumann and Davies, 2002). However, the system is complex with many waters plotting far from each postulated mixing curve, and others (i.e., C2071, C4397) plotting between the lake and the source water. The variation in Sr isotope ratios of waters from the Lake Naivasha watershed may reflect inputs from unidentified sources (e.g., unsampled tributaries, groundwater seeps with $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios reflecting local rock source variations). Indeed, the majority of the Naivasha watershed waters plotting above the calculated Sr isotope evolution curves (Fig. 7) may reflect chemical reaction of individual waters with more silicic and, hence, radiogenic, highly-differentiated alkaline volcanics within the rift valley. For example, groundwater samples from wells C3366 and C3677 in the Manera Farm region north of Lake Naivasha have the same $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio (i.e., 0.70757; Table 1), and plot above both calculated Sr evolution curves (Fig. 7). In the specific case of these Manera Farm groundwaters, it is possible that the higher than expected $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios (i.e., based on the Sr evolution curves) reflect interaction of these waters with the pantelleritic volcanic rocks of the proximal Eburru complex (Macdonald, 1987; Clarke et al., 1990; Heumann and Davies, 2002). However, because the $^{3}\mathrm{H}/^{3}\mathrm{He}$ ages of the Manera Farm groundwaters (~20 a) probably precludes equilibration of these groundwaters with the strongly peralkaline rhyolites of the Eburru complex, these northern groundwaters have not likely had sufficient time in contact with the aquifer rocks to acquire even more radiogenic $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios similar to the pantellerites and local comendites. On the other hand, the longer residence times (i.e. $\geqslant 50$ a based on absence of $^{3}\mathrm{H}$) of groundwaters of the Olkaria Geothermal Field to the south of Lake Naivasha have resulted in more radiogenic Sr isotope ratios for these waters that closely resemble the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of the local comendites (Fig. 7). Consequently, given the greater age of the thermal waters (i.e., based on the absence of $^{3}\mathrm{H}$; Ojiambo et al., 2001), the Sr isotope data indicate that the thermal waters have likely equilibrated isotopically with the more radiogenic comendites of this region. The substantially lower Sr concentrations of the thermal waters (e.g., Olkaria well OW-26) compared to the mean Sr concentration of comendite from the Olkaria region (Fig. 7), may reflect Sr removal during carbonate mineral precipitation in these fluids. The higher temperature of these waters is expected to facilitate carbonate mineral precipitation. However, the precipitation of Sr with carbonate minerals is not expected to change the Sr isotope signature of these waters (e.g., Bullen et al., 1996; McNutt, 1999; Woods et al., 2000). It is critical to stress, however, that the calculations based on the hypothesized Sr evolution curves for the Naivasha watershed are highly speculative owing to the low numbers of samples collected and analyzed. The system is complex and additional sources and sinks suggested by the Sr data (e.g., Fig. 3) remain to be identified. Consequently, more analyses are necessary to adequately test the hypothesized Sr isotope evolution of waters from the Lake Naivasha watershed.

5.3. Neodymium and strontium residence times in Lake Naivasha

The authors chose to estimate Nd residence times in Lake Naivasha because of interest in Sm–Nd isotope dynamics in aquatic systems including the oceans (e.g., Piepgras and Wasserburg, 1980, 1987; Goldstein and Jacobsen, 1987; Jeandel et al., 1995; Albarède et al., 1997). It is important to stress that the calculated residence times for Nd and Sr in Lake Naivasha should be viewed with caution owing to the limited amount of data for both elements in the watershed. Indeed, the results of the residence time calculations are only presented as first approximations of the actual values because of the limited analyses. Nonetheless, it is still instructive to evaluate residences times for these trace elements owing to the fact the calculations may provide insight into the behavior of Nd and Sr in lakes exhibiting leakage to groundwater systems.

The residence time of a solute in a body of water such as Lake Naivasha can be approximated by application of the standard residence time equation (e.g., Yuretich and Cerling, 1983; Barton et al., 1987):

$$t_i = \frac{M_i}{\mathrm{d}M_i/\mathrm{d}t} \tag{3}$$

where t_i is the residence time of solute i, M_i is the total amount of solute i in the water body, and $\mathrm{d}M_i/\mathrm{d}t$ is the annual flux of solute i either into or out of the water body. Based on earlier investigations (i.e., McCann, 1974; Gaudet and Melack, 1981; Åse et al., 1986), Ojiambo and Lyons (1996) presented weighted mean values for river discharge into and groundwater seepage out of Lake Naivasha as 230×10^6 m^3/a and 38×10^6 m^3/a, respectively. The lake has a surface area of approximately 190 km^2, and an average depth of 4.7 m (Ojiambo et al., 2001). Thus, it is estimated that the total mass of Nd in Lake Naivasha, based on the measured Nd concentration of 568 pmol/kg, to be on the order of $\sim$500 moles. Because the Malewa River sample was not filtered, residence times for Nd (and Sr) can only be estimated using the Nd value of groundwater samples from the south shore (i.e., C579 in the case of Nd). Consequently, the calculated residences times for both Nd and Sr may help to elucidate processes occurring within the lake that affect both trace elements, as well as shed some light on those processes occurring within the lake sediments and the groundwater system underlying Lake Naivasha. Using these data leads to an estimated Nd residence time in the lake of roughly 27 a. By comparison, a residence time estimate is calculated for Sr in the lake as approximately 11 a using the mean Sr concentration of the southern groundwater samples C2071 and C4397 (i.e., 3.65 µmol/kg).

The outstanding feature of these calculations is that the residence time of Nd in Lake Naivasha is estimated to be similar to the residence time of Sr in the lake. This result was not expected, and differs from what is observed in the oceans where the estimated residence time of Sr far exceeds that of Nd. For example, Sr has an oceanic residence time on the order of 1 Ma, whereas estimates of oceanic residence time for dissolved Nd range from as low as 20 a to $>10^4$ ka (Goldberg, 1965; Brewer, 1975; Elderfield and Greaves, 1982; Martin and Whitfield, 1983; Goldstein and Jacobsen, 1987, 1988; Bertram and Elderfield, 1993; Jeandel et al., 1995; Byrne and Sholkovitz, 1996; Albarède et al., 1997; Tachikawa et al., 1997; Alibo and Nozaki, 1999, and references therein). Estimates of the oceanic residence time of Nd based on the effective dissolved river flux of Nd to the ocean (i.e., total riverine influx minus the amount of Nd removed in estuaries) produce relatively long residence times (e.g., 4.4–15 ka) depending on, for example, the Nd value of the river flux used in the calculation (Elderfield and Greaves, 1982; Goldstein and Jacobsen, 1988; Byrne and Sholkovitz, 1996). On the other hand, the distinctly different Nd isotopic compositions of the Atlantic, Indian and Pacific Oceans strongly suggests that the residence time of dissolved Nd in the oceans must be in the order of, or shorter than, the oceanic mixing time ($\sim$1 ka; Stordal and Wasserburg, 1986; Bertram and Elderfield, 1993; Jeandel et al., 1995; Byrne and Sholkovitz, 1996; Tachikawa et al., 1997; Alibo and Nozaki, 1999). In either case, it is clear that the oceanic residence time of Sr is substantially longer than for that of Nd.

Although, as mentioned above, it is important to exercise caution when considering the authors' estimated Nd and Sr residence times for Lake Naivasha because they are based on limited measurements of both metals, as well as estimated groundwater fluxes from the lake, it is interesting to speculate as to why the estimated residence time of Nd is similar to that for Sr. One possibility is that compared to Nd, Sr is preferentially taken up by the lake bottom sediments in a similar fashion to Ca and Mg. Gaudet and Melack (1981) demonstrated that roughly 5300 tons of Ca and 1000 tons of Mg are accumulated on the lake bottom on an annual basis. The loss of Ca and Mg to the lake bottom sediments occurs by cation exchange reactions (probably involving K) with the sediments, incorporation into the soft tissues of aquatic plants, biochemical uptake by invertebrates and fish to form shells, exoskeletons, and bones, and possibly calcite precipitation (Gaudet and Melack, 1981). Indeed, these authors argue that geochemical and biochemical sedimentation accounts for much of the Ca, Mg, K and HCO_3 loss from the lake water, and thus contributes significantly to the freshness of Lake Naivasha. However, the high particle reactivity of REEs such as Nd tends to argue against preferential removal of more soluble Sr from the lake waters over that of Nd.

Another possibility is that dissolved Sr is more efficiently transported with flowing water masses in the Lake Naivasha watershed compared to Nd. In this case, Sr would be expected to be more readily transported, along with lake water, via seepage through the lake bottom sediments than Nd, which owing to its greater particle reactivity, would be preferentially sequestered by the lake bottom sediments and/or underlying aquifer materials. The data in fact support this possibility. For example, the Sr concentration in groundwater south of the lake (e.g., well C4397, Sr = 3.8 μmol/kg) is greater than the lake water value (1.7 μmol/kg) suggesting that Sr has been mobilized during sediment–lake water interaction and subsequent seepage of this lake water into the underlying groundwater flow system. However, the Nd value for the southern groundwater sample (well C579, 491 pmol/kg) is lower than that of Lake Naivasha (568 pmol/kg) supporting scavenging of Nd by the lake bottom sediments. Neodymium scavenging by the lake sediments effectively decreases the Nd flux out of the lake bottom and into the groundwater systems (i.e., dM_i/dt), thus resulting in a longer calculated residence time for Nd. Although no evidence currently exists, it is conceivable that Nd experiences additional cycling within the lake (similar to the marine environment; Stordal and Wasserburg, 1986; Albarède et al., 1997, and references therein) owing to particle scavenging and subsequent regeneration that does not similarly affect Sr. Recycling of Nd within the lake itself would be expected to lengthen the effective residence time of Nd in the lake. Lake Naivasha is classified as a warm, polymictic lake that thermally stratifies each morning subsequent to lake overturn later in the day (Verschuren, 1996). Moreover, O depletion in bottom waters of Oloidien Bay, as well as persistent anoxia in the deeper waters of the Crescent Island Crater portion of the lake, have been reported (Melack, 1979; Brierley et al., 1987; Verschuren, 1996). Consequently, daily redox cycling of Fe and Mn in the lake waters could conceivably lead to longer within-lake residence times for Nd compared to Sr. Finally, an additional, as yet unidentified, Sr source may exist within Lake Naivasha which could effectively lead to a shorter residence time for Sr in the lake compared to Nd. Unfortunately, none of these hypotheses can be adequately tested without additional Sr, and especially Nd data, for the Lake Naivasha watershed.

6. Conclusions

Strontium isotope and REE data are consistent with the authors' earlier work using $\delta^{18}O$, δD, and $^{3}H/^{3}He$ analyses that a higher percentage (i.e., 50–85%) of the groundwater south of Lake Naivasha originates from lake recharge. The combination of these data confirms much earlier speculation that the unique freshwater character of Lake Naivasha is chiefly due to the short residence time of water within the lake itself. Hence, Lake Naivasha is a "seepage" lake in a classical sense in that water is rapidly lost from the lake to the groundwater system. The $^{87}Sr/^{86}Sr$ data also provide important new information regarding the chemical evolution of these groundwaters and demonstrates the importance of longer aquifer residence times on the rock–water interactions, especially in the Olkaria geothermal fields.

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