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Received 28 January 2003; revised accepted 23 April 2003

Characterization and origin of silicic and alkali-rich glasses in the Upper mantle-derived spinel peridotite xenoliths from alkali basalts, Deccan Trap, Kutch, northwest India

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Petrological, textural and chemical characters of glasses found as discrete pockets in the spinel lherzolite xenoliths from Kutch region are discussed. These glasses are silica-saturated and alkali-rich in composition and display sharp contacts with the primary mineral assemblage of the spinel lherzolite. In contrast, the basaltic melt infiltrating the xenoliths exhibits reaction textures. We have attempted to compare these glass compositions with worldwide occurrences. In the absence of any trace-element data, we have used the trace-element data of the Cr-diopsides from the same xenoliths and have discussed the mechanisms of glass formation. The glass formation is attributed to the metasomatic fluids, mostly carbonatitic in composition, which is in agreement with our previous work on these xenoliths. The metasomatism has occurred at a shallow level (7–12 kbar), slightly above the carbonatite stability field.

STUDY of mantle xenoliths provides significant information about the composition of the mantle and the processes which impress the mantle composition. The compositions of silicate melts potentially in equilibrium with the earth's mantle have long been of interest to petrologists and geochemists. In recent times, the glasses in the mantle xenoliths have been studied in great detail so as to understand the genesis of silicate melts at mantle depths, and pressure and temperature conditions. Glasses represent such melts, with high silica content (up to 72% SiO_2) occurring as inclusions and discrete pockets within the mantle xenoliths, and have been reported from a variety of settings. Xenolith glasses have a wide range of major element composition; this has been clearly brought out in the compilation of the glass compositions world over by Draper and Green[1].

The formation of glasses has been ascribed to a variety of processes, including infiltration of the host lavas[2], and breakdown of amphibole or phlogopite in response to decompression melting to give rise to silica-undersaturated liquids. These then react with mantle minerals, especially orthopyroxene and crystallize olivine and clinopyroxene, leaving more silica-rich residual liquids[3,4]. The second model includes partial melting of mantle xenoliths at short residence times in crustal magma chambers during ascent to the surface in the host magma[5]. Other models imply formation of silicic melts at mantle depths.

Large group of glasses, however, have remained unexplained by the various processes listed above[1]. These glasses are rich in SiO_2 (> ~ 60 wt%), Al_2O_3 (18–20 wt%) and alkalies ($Na_2O + K_2O$ up to 17 wt%). This prompted several researchers to advocate the hypothesis that such melts could represent a type of metasomatic agent circulating in the upper mantle[6–9]. Experimental investigations have suggested that highly silicic melts could be formed by small degrees of *in situ* partial melting in the upper mantle[10]; such melts are enriched in silica–alumina and alkalis, and depleted in MgO, FeO and CaO. It is also proposed that the silicic, aluminous alkaline melts could be formed by low-degree partial melting of peridotite enriched in alkalis, volatiles and other low melting-temperature components[1]. Recently, on the basis of chemical criteria, the formation of such silica and alkali-rich glasses (with Na_2O content up to 14 wt%) has been ascribed to the process of carbonatite metasomatism[11].

In the Kutch mantle xenoliths, the glasses generally occur as pockets or as discrete grains along with the recrystallization of neoblasts of opx and cpx. Majority of these glasses are spongy, dirty green in colour. Chemically, they are SiO_2–Al_2O–Na_2O–K_2O-rich and TiO_2–FeO–MgO–CaO–P_2O_5- poor types, similar to the set of glasses described from Canary Islands. The Kutch mantle xenoliths which host the silicic glasses are devoid of any hydrous mineral phases; however, they are cryptically metasomatised[12]. The mantle xenoliths are spinel lherzolite in composition; the details of which have been described elsewhere[13]. The silica content of the glasses varies between 55 and 65%. In the light of the various models

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described for the formation of glasses, we aim to discuss the origin of the Kutch glasses.

In the Kutch region, the Deccan Traps are confined to a long strip bordering the Mesozoic highlands from Lakhpat in the northwest to Anjar in the east. Seven flows have been identified[14]; they dip gently southwards and rest disconformably on Mesozoic sediments. The trap flows in Kutch have been considered to be the earliest Deccan eruptions[15]. The alkaline rock in central Kutch occurs as plug, sheet or cone-like intrusions and entrains ultramafic xenoliths of mantle origin[16,17]. These alkaline rocks are considered to be volcanic centres[18] and are situated to the north and northwest of the main Deccan province, within areas once covered by Deccan lavas that are now seen as outliers. The plug-like intrusions occur at Dhrubia, Sayala Devi, Vethon and Dinodhar, while Bhujia hill and Lodlai on the other hand, have sheet-like alkaline bodies. The average xenoliths are between 1 and 2 cm, but xenoliths as large as 4 to 5 cm are common, especially at Bhujia. In the sheet-like bodies, the xenoliths are concentrated in the central portion as against the neck levels in the plugs from Dhrubia and Sayala Devi. The alkaline rocks are mostly represented by alkali olivine basalts and basanites. These basalts are feebly porphyritic with olivine and occasionally, clinopyroxene phenocrysts. In thin sections, some of these phenocrysts show marginal embayment, the groundmass is fine-grained and composed of olivine, clinopyroxene, microlites of plagioclase and opaque oxides with patches of analcite. Nepheline rarely occurs as modal mineral phase. The alkali basalts in Kutch are nowhere in direct contact with the Deccan tholeiite, but several lines of evidence suggest that they can be spatially and temporally correlated to Deccan basalts. ^{40}Ar–^{39}Ar ages for alkali basalts and tholeiite samples from the Kutch region of the Deccan Trap range between 64 and 67 Ma, indicating a close temporal association between these two types of magmatism[19]. These basalts are petrologically similar to those from Reunion Island in the Indian Ocean. The ultramafic xenoliths entrained in the alkaline volcanics hence represent the lithospheric mantle that is spatially and temporally related to the Reunion/ Deccan plume, and may help us to understand the nature of the plume-affected mantle.

Olivine (ol), orthopyroxene (opx), clinopyroxene (cpx) and spinel (sp) in order of abundance dominate the xenoliths. The relatively small size of the xenoliths precludes the determination of precise mineral modes. However, an attempt has been made to determine the average modal abundances by point counting at least 50 samples from different areas. The olivine content varies between 50 and 60%, opx between 15 and 20% and cpx between 2 and 13%. The reddish-brown, aluminous spinel ranges from 0.5 to 4%. The spinel peridotites typically are fine-grained (0.5 to 2 mm) and unfoliated, and are of type-I (Cr-diopside-spinel) lherzolites[20,21]. They exhibit mostly protogranular[22] or xenomorphic granular[23] microstructures. However, a few samples from Sayala Devi locality are coarse-grained with weakly-defined planar fabric. Olivine in all samples displays strain shadows and kink bands and in most samples, olivine contains trails of fluid inclusions. The cpx occurs mostly as discrete grains smaller than the olivines or opx, and shows finely-spaced exsolution lamellae of opx. Spinels in the xenoliths are reddish-brown in colour and occur in close association with opx and cpx. Neoblasts of olivine opx and cpx are sometimes observed armoring the large porphyroclasts of olivine and opx. Such neoblast formation has been ascribed to *in situ* heating and metasomatism during magmatism[9,24] in the xenoliths from Canary Islands. Glass in the xenolith is generally of two types, colourless, and dirty-green to brownish in colour, the details of which are described later in the communication. Volatile bearing phases such as amphibole or phlogopite have not been observed in any of the xenoliths studied.

Glass in the Kutch xenoliths exhibits different modes of occurrence. Minor amount of glass occurs as inclusions in olivine porphyroclasts and at times forms trails, suggesting a secondary origin. Similar inclusions are also observed in some of the opx porphyroclasts along with thin platelets of brown spinel and birefringent acicular crystals of rutile. The glass is coloured or colourless type and both types can occur in one single xenolith. Brownish glass mostly occurs as small isolated pockets in the peridotite. It also occurs as micro-veinlets, sometimes invading into the mineral phases. When it occurs as pockets, the glass contains numerous small grains or microlites of both olivine and cpx. The glass patches are typically connected by thin channels of interstitial glass. Locally, the glass layers expand into continuous films of glass along grain boundaries. These glasses can be referred to as 'jacket glasses', following Edgar *et al.*[25]. These glasses have sharp contacts with the surrounding host minerals, showing no evidence of reaction. This is in stark contrast to the basaltic and basanite melt infiltrating into the xenolith and frequently reacting with the xenolith mineral phases, forming reaction rims. Incidentally, we wish to emphasize that any hydrous mineral phases such as phlogopite or amphibole, as has been reported from many spinel-lherzolite xenoliths in other parts of world, are typically absent in the Kutch xenoliths.

On the basis of compilation of glass compositions in the mantle xenoliths from different parts of the world, certain distinct features have been brought out[1]. These include: (a) glasses have a wide range of major element compositions; (b) many glasses are alkaline ($Na_2O + K_2O$ up to 17 wt%); (c) *mg*-numbers range from 25 to 90, MgO contents show a wide range, from < 1 to > 12 wt%; (d) TiO_2 content correlates negatively with that of SiO_2; (e) highly silicic glasses have generally low TiO_2, i.e. less than 1 wt%; (f) Al_2O_3 content varies between 12 and 25 and does not correlate with SiO_2 or molar N/K; (g) like TiO_2, MgO, FeO and CaO contents exhibit a crude negative relationship with that of SiO_2; (h) most of the silica-rich glasses (> 63 wt% SiO_2) have FeO + MgO < 3 wt% and CaO rarely exceeds 3 wt%; (i) most xenolith glasses have more Na than K; (j) there appears to be no major-element composition features of the glasses that are peculiar to a particular tectonic setting.

The glass compositions in Kutch xenoliths also show wide compositional variation. They are mostly silica-rich where the SiO_2 wt% varies between 58.22 and 65.65%. These glasses are typically alkali-rich, with $Na_2O + K_2O$ varying from 5.02 to 14.45%. Out of the 14 glasses analysed, six have $K_2O > Na_2O$, while the remaining eight have higher Na_2O content. TiO_2 content is typically less than 1 wt% and correlates negatively with that of SiO_2. Similarly, Al_2O_3 content, which is typically high (17.04 to 25.32 wt%), also correlates negatively with that of SiO_2. This is in contrast to the generalizations made above for occurrences in other parts of the world. FeO, MgO as well as CaO contents are low and generally follow the trend observed for glasses the world over. FeO and MgO contents correlate negatively with that of SiO_2. From the major-element values, the CIPW normative composition for the glasses was calculated. Among the 14 glasses, nine are silica-saturated and are qtz-normative, while the remaining are moderately undersaturated with silica and are nepheline-normative.

The composition of the allied mineral phases such as ol, opx, cpx and spinel occurring as microlites within the glass pockets, was also determined so as to understand any mutual relationship, if any. CaO content of the glass correlates positively with that of olivine. Similarly, Al_2O_3, Na_2O and TiO_2 contents of the glass correlate positively with those in the cpx. Al_2O_3 content of the glass exhibits negative correlation with that of the opx, while Na_2O content of the glass shows sympathetic relationship with that of opx. TiO_2 and Na_2O contents of the cpx correlate positively with that of the opx, while the CaO content exhibits a negative correlation. Thus, a consanguineous behaviour is observed among the glass and other allied mineral phases, especially glass and cpx, where the relationship is more pronounced.

In the Na_2O–CaO–K_2O triangular diagram (Figure 1), the glass compositions make two distinct domains; the glasses in the xenoliths from Bhujia plot near the Na_2O side of the triangle, while the remaining plot on the central part of Na_2O–K_2O-side line. In Figure 1, when the composition of the host lava is plotted, it plots separately towards the CaO side of the triangle. When compared to the fields marked for other localities world over, the Kutch glasses plot close to the glasses from Grande Comore. However, xenoliths from Grande Comore have phlogopite as the hydrous phase, which is absent in case of the Kutch xenoliths. The $K_2O + Na_2O$ ratio in the Kutch glasses increases with silica-saturation. The composition of the host lava is however silica undersaturated and closely corresponds with the composition of basanite from Grande Comore. The broken line in Figure 1 represents the boundary between xenoliths containing anhydrous and hydrous phases.

The Kutch xenoliths are devoid of any hydrous mineral phases such as amphibole, apatite or phlogopite. Thus, the formation of glass by decompression of any hydrous minerals[26–28] is completely ruled out. The lack of any hydrous phases would also rule out the *in situ* melting model[4]. Host-magma infiltration in the Kutch xenoliths is generally seen only at the contact between xenoliths and the host-rock basanite. In such cases, however, the individual minerals exhibit reaction rims. The analysed glasses occur as pockets and have sharp contacts with the principal mineral phases from the xenoliths. Contrasting chemical characteristics are observed between the host rock and glass compositions, such as Na_2O content and Na_2O/K_2O ratio. Therefore, the model explaining glass formation due to infiltrating basaltic melts[29–31] is inapplicable to the Kutch glasses. A slight variant of this model is the one given for the La Palma xenoliths[9,32], where glass formation has been ascribed to the processes involving infiltration of basaltic melts into mantle peridotites, followed by reaction and crystallization. In the samples from La Palma, the veined xenoliths show a gradual transition from basaltic to Si-rich melts where TiO_2/Al_2O_3 decreases with increase in the K_2O content, which resembles the basaltic melt. The glasses analysed in the Kutch xenoliths generally are Si–Na–K-rich glasses, where the SiO_2 content has narrow range (58.22 and 65.65%). Besides, TiO_2/Al_2O_3 does not show any relation with K_2O. The ratio of TiO_2/Al_2O_3 should generally decrease in glasses with increasing silica content, if there is reaction between the infiltrating basaltic melt and mantle-wall rocks[33]. In the Kutch glasses, this ratio does not show any relation with SiO_2 and remains constant. Hence, the possibility of glass formation due to reaction between basaltic melt and peridotite-wall rock is ruled out. Draper and Green[1], on the

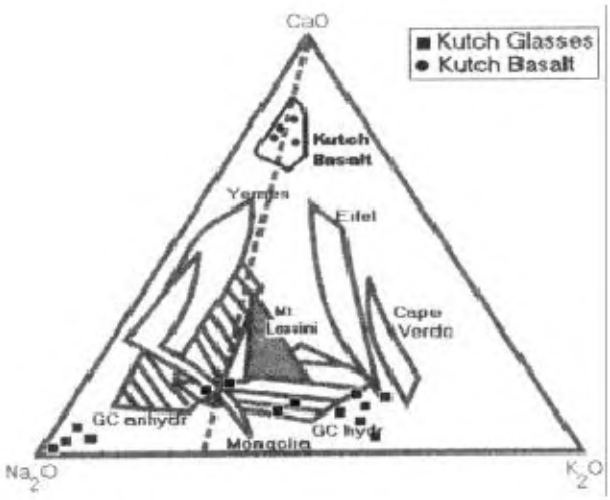

Figure 1. Na_2O–CaO–K_2O triangular plot for Kutch glasses with other world occurrences (after Neumann and Wulff-Pedersen[33]).

basis of experimental work as well as the mass balance calculations, have ruled out the possibility of glass being the product of infiltrating basaltic melt.

The FeO (MgO) content in the Kutch glasses correlates negatively with that of SiO_2. Correlations with other elements are not so well defined. These observations reduce the likelihood of glass formation by any simple crystal fractionation process. The decompression melting model[26,27] has been dismissed as a general mechanism for the formation of highly silicic glasses by Edgar *et al.*[25] and Zinngrebe and Foley[8]. Partial melting of mantle xenoliths during short residence times in shallow magma chambers during ascent, a model suggested for the formation of glass[5], cannot be applied for the Kutch xenoliths on account of the sharp boundaries of the xenoliths with the host basalt.

It is opined that the Si–Na–K-rich glasses possibly represent a type of metasomatic agent circulating in the upper mantle[6,25,34]. Although formation of glass in the mantle xenoliths from both continental and oceanic setting has been ascribed to widely different metasomatic agents ranging from alkali-silicate melts[8,35,36] to carbonatitic melts[36–41], all may result from similar petrogenetic processes. In recent years, carbonatite melts have gained increasing attention as possible metasomatic agents in the upper-mantle peridotites. Physico-chemical characteristics, especially the dihedral angle Φ of alkaline silicate and carbonatite-rich melts facilitate their migration through the mantle matrix with respect to H_2O–CO_2-rich fluids, limiting the range of possible metasomatic agents[11]. Experimental and petrographic studies have indicated that this metasomatic fluid could be silicate or carbonatitic in composition[42,43], and would carry the necessary inventory of incompatible trace-elements. Carbonatite melts have low viscosities, high separation velocities and high diffusivities. Therefore, carbonatite magmas could be effective agents of chemical transport within the upper mantle and thus are important in controlling the incompatible trace-element budget in the lithospheric mantle. It has been argued that the diffusion rates are strongly dependent on melt viscosity, which is several orders of magnitude lower in carbonatite than in the silicate melts[44]. The chemical homogeneity of glasses in the Kutch xenoliths within a single sample does suggest high diffusion rates. Therefore, we strongly favour carbonatite melt as the most promising metasomatic candidate. Another important reason for this is that carbonatitic melt may react with opx in lherzolites to form cpx + carbon dioxide, as has been found in experimental studies[42] of CO_2-bearing peridotite assemblages. Thus, metasomatism-producing wehrlites may be explained invoking percolating carbonatitic melt, especially if there is no strong Fe–Ti enrichment, which is generally assigned to interaction with basaltic melt. Texturally, the highly silicic melts in the Kutch xenoliths are in close to equilibrium with the secondary and primary mineral phases in spinel peridotite in which they are found while the basaltic melt is not. This is also evident from the chemical parameters, which include the observed distribution of Ti between the daughter minerals, cpx, glass and spinel. Similarly, the compositions of daughter minerals in the glass are similar to those in the main mineral phases in peridotites (Fe–Ti-depleted). Melt is morphologically stable (and substantial permeability is possible) when located at Ol–Ol–Ol edges (prismatic shape) or at Ol–Ol–Ol–Ol corner regions (tetrahedron shape). Conversely, melt is not stable in all edges and corners in situations involving at least one cpx or to a lesser extent, opx[45]. As a result, the melt is expected to migrate towards areas having the most stable configurations, and such redistribution will occur over a time span of few weeks[46]. It is generally not possible to maintain clear glass for a long time in the mantle without crystallization or chemical diffusion occurring. This is evident from the presence of both spongy green and brown coloured glasses in the xenoliths under study. Therefore, we strongly believe that the glass pockets in the Kutch xenoliths represent melt acquired at mantle depths, shortly before entrainment in the host basalt and quenched subsequently during transport to the surface, as has been suggested in previous studies[3,11]. Migration of the metasomatic melts in the mantle peridotite is controlled by the value of the dihedral angle Φ, which is an expression of balance between surface tensions of the solid grains and melts[47]. Highly undersaturated silicate and carbonatite magmas present the lowest dihedral angles, confirming the greatest capability to permeate and metasomatise the mantle materials[48,49]. We therefore envisage the composition of the metasomatic fluid being carbonatitic in nature. The alkali-element enrichment, especially Na content in the glasses suggests that the metasomatic agent was an ephemeral alkali-rich carbonatite. This corroborates well with our previous studies on these xenoliths, especially the modelling of cpx trace-element composition[12,13,50], suggesting cryptic metasomatism by carbonatitic melt in the upper mantle. The formation of the Kutch glasses can be explained with a model involving interaction of carbonatite melt and primary mantle assemblage. Incongruent melting of orthopyroxene is restricted to pressures below about 5 kbar, but the pressure limit increases to more than 20 kbar in the presence of H_2O–CO_2-rich fluids[51,52]. The absence of garnet or plagioclase in the Kutch xenoliths constrains the pressure between ~ 10 and ~ 20 kbar. When the temperatures calculated (~ 950°C) referred to geotherms typical for alkali-basalt volcanism[53], the xenoliths have yielded pressure estimates of 9 to 12 kbar. It is of interest to note here that texturally, the opx exhibit corroded borders or embayed margins, indicating incongruent melting. This is also evident from the observed negative relationship between the Al_2O_3 content of the primary opx with that from the secondary cpx. The melting of opx and formation of the daughter phases, viz. ol, cpx, is a major source of SiO_2 enrichment in the melt. The FeO and SiO_2 in glass correlate negatively. It is suggested that the inverse correlation between FeO and SiO_2 can be modelled if the glass is considered as a reaction product between 'primitive' mantle material and metasomatic fluid that caused opx melting and recrystallization of secondary minerals[11]. Considering comparable textural, mineralogical and chemical characters of the Kutch xenoliths with those described from La Grille, Grand Comore[11], we strongly advocate a similar mechanism of glass formation as that of La Grille, Grand Comore. The reaction between the carbonatite melt and the primary mineral phases of the peridotites is as follows

$$\pm x1 \text{ ol1} + x2 \text{ opx} \pm x3 \text{ cpx1} \pm x4 \text{ sp1} \pm x5 \text{ ph} + x6 \text{ carb} = x7 \text{ ol2} + x8 \text{ cpx2} + x9 \text{ sp2} + 1 \text{ GL (ref. 11)},$$

where $x1$ is the mass balance coefficient of the phase 1; ol1, cpx1, sp1, phlogopite (ph) and ol2, cpx2, sp2 are the compositions of the primary and secondary minerals, carb is carbonatite and GL is glass. The mineral phlogopite is used in the reaction to explain the high K_2O content. This is supported by moderate to high values of K_2O and so as the K_2O/Na_2O ratio in the glasses from Kutch xenoliths. Carbonatite melt with Na as dominant alkali was shown experimentally to be in equilibrium with phlogopite lherzolite at 20–25 kbar and 950–1170°C (ref. 54). It is generally observed that there is an increase in the K_2O content with increase in the SiO_2 content. Therefore, consumption of all phlogopite, if considered, would not be far fetched and is keeping in view with the residual mineralogy obtained from the host-rock chemistry. The calculated compositions for glass and secondary minerals for the La Grille, Grand Comore xenoliths[11] are closely comparable to the Kutch glasses and other secondary mineral compositions. Micro-nodules or clusters of wehrlites along with cognate dunite, although reported from Vethon and Dhram, respectively[17] cover relatively low population when compared to the occurrence of spinel lherzolites. Therefore, we envisage limited melting of the opx and low fluid-to-rock ratio. This is evident from the textural observations, where the opx is seen corroded only at the marginal part.

We do not have the trace-element data for the Kutch glasses, and hence we have used the trace-element composition of the cpx (Cr-diopsides) from the xenoliths as an analogue. It is observed that the trace-element content of the cpx from the Kutch xenoliths is closely comparable to those metasomatised xenoliths, especially from Samoa[40], and Mongolia[41], where the metasomatic fluid has been carbonatitic in nature (Figure 2). The cpx from such xenoliths shows greater enrichment in REE and depletion in Zr, Ti and Sr. Carbonatite melts and unaltered magmatic carbonatite rock are highly enriched in CaO and REE, relatively depleted in elements such as Ti and Zr relative to basaltic melts, low in Ti/Eu and have high LREE/HREE ratios[54–57]. CaO–La/Nd and Ti–La/Nd ratios are used to differentiate between metasomatism by carbonatite, alkali basaltic and highly silicic melts[32]. The trends defined by the diopsides from the Kutch xenoliths and

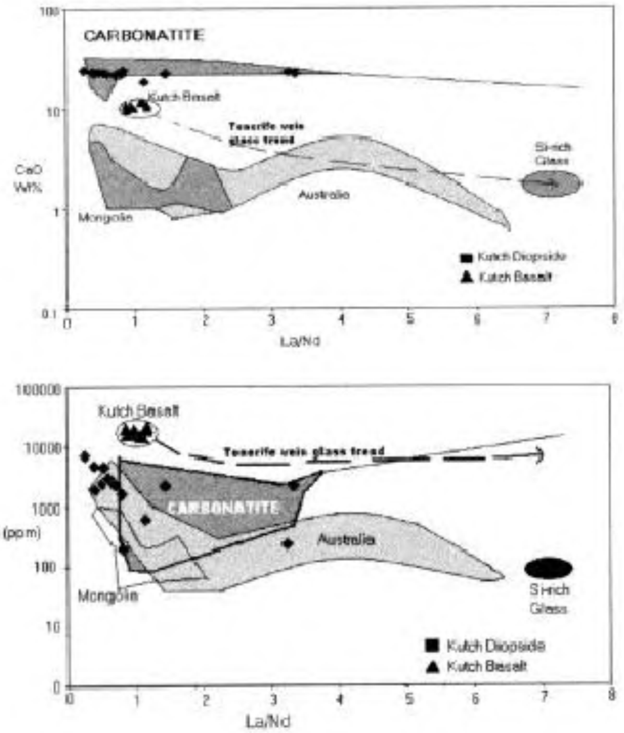

Figure 2. CaO vs La/Nd and Ti vs La/Nd relationship amongst Cr-diopsides from Kutch xenoliths. Also plotted are Australian and Mongolian fields (after Wulff-Pedersen *et al.*[32]).

the host basalts are well in agreement with metasomatism by carbonatite melts. A possible test of this model is to determine whether samples with low Ti/Eu have higher modal cpx content, which would be expected if these geochemical features were related to addition of carbonatite magma[39]. The Ti/Eu ratio does correlate negatively with modal content of cpx, supporting the carbonatite-rich nature of the metasomatising fluid[12]. Such carbonatitic melts have generally been regarded as 'ephemeral'[58] which is consistent with the absence of any carbonatite rocks from this area, similar to the Grand Comore, Indian Ocean. However, there are reports of carbonatite in the Kala Dongar complex from the adjoining area[59].

Calculated temperatures and pressures (~ 950°C; ~ 9–12 kbar) indicate that metasomatism is likely to have occurred within the subcontinental lithospheric plate above the carbonatite field. Although the metasomatism is recorded at the shallowest level (9–12 kbar), the host magmas have been generated at deeper levels (perhaps at depths > 22 kbar) and carbonatite magma generation is anticipated at 21–30 kbar[42]. Hence it is possible that carbonatite genesis and host-magma generation are perhaps two processes associated with same phenomenon, i.e. rising of the deep mantle plume, as has been suggested for the La Palme xenoliths of Grande Comore, Indian Ocean[11].

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ACKNOWLEDGEMENTS. N.R.K. thanks the Head, Department of Geology, University of Pune, for permission to collaborate with GEMOC Macquarie University, Sydney, Australia. We thank Prof. W. L. Griffin and Prof. Suzanne O'Reilly for collaboration as well as for discussions. We are also grateful to Miss Carol Lawson and Dr Norm Pearson for help in the microprobe analysis and Ashwini Sharma for help in the ICPMS microprobe analysis. We thank Dr Mark Norman and the postdoctoral fellows at the Center for fruitful discussions. Review comments from the anonymous referee(s) helped to improve the manuscript.

Received 8 January 2003; revised accepted 25 April 2003

ERRATA

The science and politics of AIDS
[P. Balaram, *Curr. Sci.*, 2003, **85**, 117–118]

Page 118, col. 1, para 1, lines 18–19 should read:

. . . estimates about 3.97 million cases of infection in 2001.

instead of

. . . estimates about 3.97 cases of infection in 2001.

And

Page 118, col. 1, para 2, lines 3–4 should read:

. . . and the disease, an Indian journal provided the forum . . .

instead of

. . . and the disease, *Nature Medicine*, an Indian journal provided the forum . . .

The errors are regretted.