

Zr/Hf IN CARBONATITES AND ALKALINE ROCKS: NEW DATA AND A RE-EVALUATION

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RESUMO *Zr/Hf EM CARBONATITOS E ROCHAS ALCALINAS: NOVOS DADOS E UMA RE-AVALIAÇÃO* Este artigo apresenta novas análises de Zr e Hf em carbonatitos e rochas alcalinas, em conjunto com dados compilados da literatura. As razões Zr/Hf destas rochas têm amplitude de cerca de uma ordem de grandeza, enquanto que as concentrações de Zr variam acima de quatro ordens de grandeza. A maioria das amostras apresenta valores supercondríticos de Zr/Hf. Valores subcondríticos de Zr/Hf são, aparentemente, consequência de problemas analíticos, pois os teores de Hf, e em alguns casos os de Zr, encontram-se próximos ou abaixo dos limites de detecção dos métodos analíticos utilizados. A variação independente de Zr/Hf em relação aos teores de Zr e às razões Y/Ho, e o fato de carbonatitos e rochas alcalinas associadas não apresentarem variações significativas da razão Zr/Hf, sugerem que tais rochas herdaram tais assinaturas de elementos traços de suas fontes mantélicas. O presente artigo discute e reavalia o modelo que considera que os carbonatitos têm tipicamente razões Zr/Hf supercondríticas e que tais razões seriam chaves para interpretar fenômenos de metassomatismo do manto.

Palavras-chaves: zircônio, háfnio, Zr/Hf, carbonatito, metassomatismo do manto

ABSTRACT New analyses for Zr and Hf in carbonatites and alkaline silicate rocks are presented together with corresponding data compiled from the literature. Zr/Hf ratios in these rocks cover a range of about one order of magnitude, whereas Zr concentrations vary over four orders of magnitude. Most samples display chondritic to superchondritic Zr/Hf values. Subchondritic Zr/Hf seems to be analytical artifacts because particularly Hf and sometimes also Zr contents are definitely below detection limits of the applied analytical methods. The uncoupled trends of Zr/Hf vs. both Zr contents and Y/Ho ratios and the fact that carbonatites and associated alkaline silicate rocks do not show markedly different Zr/Hf ratios suggest that carbonatites inherited this signature from their mantle source. The present paper aims to discuss and re-evaluate the common belief that carbonatites have typically superchondritic Zr/Hf, and that this is a clue to interpret some phenomena of mantle metasomatism.

Keywords: zirconium, hafnium, Zr/Hf, carbonatite, mantle metasomatism

INTRODUCTION Carbonatites are the focus of many petrologic and geochemical studies, because their trace element and isotope composition may provide insights into the composition and evolution of the Earth's mantle (Bell & Blenkinsop 1987, 1989, Bell & Simonetti 1996, Tilton & Bell 1987, Toyoda *et al.* 1994, Simonetti *et al.* 1997, Bell *et al.* 1998). Moreover, studies of mantle xenoliths (Green & Wallace 1988, Yaxley *et al.* 1991, Dautria *et al.* 1992, Rudnick *et al.* 1993, Hauri *et al.* 1993, Ionov *et al.* 1993, 1996, Chazot *et al.* 1996, Zinngrebe & Foley 1995, Woodland *et al.* 1996, Wiechert *et al.* 1997), of ocean island basalts (Nelson *et al.* 1988, Dupuy *et al.* 1992, Smellie *et al.* 1995, André *et al.* 1997), and of intracratonic alkali basalts (Furman 1995) suggest that carbonatite melts may play an important role as a metasomatic agent in the upper mantle. In the case of modal metasomatism, there is direct evidence for this connection due to the presence of metasomatic apatite and clinopyroxene in mantle xenoliths (e.g., Yaxley *et al.* 1991, Ionov *et al.* 1993). In those cases where mantle metasomatism is deduced from the trace element composition of alkali basalts, it is suggested that variation in Zr/Hf ratio may help to provide the requested information (Dupuy *et al.* 1992, Furman 1995, Smellie *et al.* 1995).

Zirconium and hafnium are closely coupled during magmatic differentiation because of their very similar partitioning behaviour as both elements are tetravalent and have very similar effective ionic radii (in VI-fold coordination 0.84 and 0.83 Å,

respectively; Shannon 1976). Consequently, basic, intermediate, most of the felsic magmatic rocks, and also clastic sediments (e.g., Goldschmidt 1937, Jochum *et al.* 1986, Bau 1996) show Zr/Hf ratios close to the chondritic ratio of 38 (C1-chondrite from Anders & Grevesse 1989).

In marked contrast to the common rock results, it is assumed that super-chondritic Zr/Hf ratios are typical for carbonatite melts (e.g., Dupuy *et al.* 1992, Rudnick *et al.* 1993, Yaxley *et al.* 1991). Critically screening the relevant literature for reported Zr and Hf analyses in carbonatites and alkaline rocks, however, reveals that this assumption is based exclusively on a single paper by Nelson *et al.* (1988). In their study on the relations between carbonatites and the sources of ocean island basalts, they provided Zr and Hf data for nine carbonatite samples from four continents suggesting a range of Zr/Hf ratios of carbonatites from 6 to 13000. More recent data, however, show that this variation does not occur in such an extent, and the composition of several carbonatites does not corroborate the belief that this rock has Zr/Hf typically above the chondritic value. Recent data for natrocarbonatite lavas erupted from the Oldoinyo Lengai volcano, Tanzania, in 1993 suggest a range from sub- to super-chondritic Zr/Hf and a positive correlation between Zr/Hf and Zr content (Simonetti *et al.* 1997). Two samples from the Araxá carbonatite complex, Brazil, show sub-chondritic Zr/Hf ratio (Toyoda *et al.* 1994). The two Russian carbonatites of Guli (Kogarko *et al.* 1997) and Tomtor (Bagdasarov 1997) have

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sub- as well as super-chondritic Zr/Hf, and lack any correlation between Zr/Hf and Zr content. The Bingo complex (Woolley *et al.* 1995) shows a slightly positive correlation between Zr/Hf and Zr content, in which the carbonatite has the lowest sub-chondritic ratios and the associated ijolite and syenite have sub-as well as super-chondritic ratios. Other alkaline-carbonatite complexes, including Catalão and Tapira, Brazil (Huang *et al.* 1995), Polino and Cupaello, Italy (Stoppa & Woolley 1995), Dalbykha, Russia (Bagdasarov 1997), and Iivaara, Finland (Pearce *et al.* 1997) cluster around the chondritic Zr/Hf ratio, in the range between 26 and 48. Based on the above, it is clear that a re-evaluation of the distribution of Zr and Hf in carbonatites is needed. In order to provide a larger data base on Zr, Hf, Y, and Ho in carbonatites and associated nephelinites and phonolites, an ICP-MS study was conducted on samples from carbonatites and alkaline rocks from South and North America, Europe and Africa.

SAMPLES Namibian complexes A review of the geology of the Namibian carbonatites is given by Verwoerd (1993) and more recently by Bühn & Rankin (1999). In the present study we analyse samples from rocks intruded in the Damara Belt. The Otjisazu complex is the oldest among them and its age is estimated between 550 and 523 Ma based on constraints of the geological setting. Samples from Otjisazu include calcite carbonatites (OS155, OS158), syenites (OS65, OS85) and pyroxenites (OS59, OS69, OS90). The carbonatite-alkaline complexes of Kalkfeld, Ondurakorume and Etaneno all belong to the same magmatic event and have ages constrained to the Early Cretaceous, of around 130 Ma. From the Kalkfeld complex we analysed nephelinites (KF115, KF200, KF201, KF202, KF203, KF208, KF211, KF212) and calcite carbonatites (KF50, KF54, KF94). From the Ondurakorume complex were analysed calcite carbonatites (ON57, ON65, ON76, ON78) as well as dolomite carbonatites (ON58, ON60, ON62a, ON62b). Samples from the Etaneno complex include nephelinites (ET5, ET151, ET152, ET153, ET163, ET169).

Oldoinyo Lengai carbonatite, Tanzania Oldoinyo Lengai is the only known active carbonatite volcano on Earth. Its geological features and petrological significance are discussed in Bell & Keller (1995). The analysed sample (sample OL1) is a natrocarbonatite lava from the 1993 eruption, which is composed by nyerereite, nepheline and fluorite. Detailed mineralogical and geochemical analyses of material from this eruption are given by Simonetti *et al.* (1997) and Bell & Simonetti (1996).

Barra do Itapirapuã carbonatite, Brazil The Cretaceous Barra do Itapirapuã carbonatite complex is composed of magnesio- to ferrocarnatites, and is emplaced in a Proterozoic granitic batholith in southern Brazil (Lapido-Loureiro & Tavares 1984, Andrade *et al.* 1999a, b, Ruberti *et al.* 2002). Fresh samples (1/37,40; 1/33,45; 1/34,90; 2/16,20; 5/13,00) are composed almost exclusively of ankerite, with small amounts of primary pyrochlore. Two samples that show post-magmatic alteration (1/54,70B; 3/37,90) contain quartz, RE-fluorocarbonates, fluorite, apatite and barite as secondary minerals which occur filling in cavities in corroded ankerite.

Oka alkaline complex, Canada The Oka alkaline complex has an age of around 120 Ma and intruded the gneisses and

anorthosites of the Precambrian Grenville province. It consists of rocks of the melteigite-urtite and okaite-jacupirangite series surrounding carbonatite cores (Gold *et al.* 1986). Analysed samples include a phlogopite-sövite (OK 1), a monticellite-sövite (OK 2) with accessory apatite, melilite, magnetite and pyrochlore, an urtite (OK 3) which is predominantly composed by nepheline with smaller amounts of augite, sanidine and chalcopyrite, and an alnöite (OK 4) which is mainly composed by phlogopite with small amounts of apatite.

Mountain Pass carbonatite, USA The Mt. Pass carbonatite has a Pb common age of 1523 Ma (Mitchell & Krouse 1971), and aspects of its geology are given by Olson *et al.* (1954). This complex contains a large REE deposit, where the ore mineral is bastnaesite probably of magmatic origin (Mariano 1989). The two analysed samples include dolomite carbonatite (MP1) and syenite (MP2).

Hegau phonolites, Germany The Tertiary Hegau volcanic field (9.5 to 14 Ma) corresponds to a bimodal sequence of phonolites and melilitites (Staesche *et al.* 1995). Local occurrence of carbonatitic lapilli have been also observed (E. Hegner, personal communication). Samples used in this study are phonolites (AS1, AS5, AS6, AS9, AS22) containing nepheline, sanidine, hornblende, biotite and magnetite.

Kaiserstuhl complex, Germany The Miocene Kaiserstuhl complex (15 to 18 Ma) is situated in the southern part of the Upper Rhine rift valley, in southwestern Germany, and is composed of an association of tephrites, essexites, phonolites and carbonatites (Keller 1981, Hubberten *et al.* 1988, Schleicher *et al.* 1991). Three samples from this complex were analysed, including one calcite carbonatite (KS1), and two phonolites (KS2, KS3) that contain sanidine, nepheline and traces of calcite.

ANALYTICAL METHODS Sample preparation and data acquisition The analytical procedure is described in details by Dulski (1994) and briefly outlined here. The rock samples were routinely digested in a mixed acid (HF/HClO₄) and finally taken up with 0.5 M hydrochloric acid. Prior to analysis by ICP-MS sample solutions were further diluted with 0.5 M HCl, Ru and Re were added as internal standards for correction of instrumental drift and matrix effects, and filled up to 10 ml. Due to the large range of element concentrations within the carbonatite samples, at least two measurements had to be performed for each sample using total dilution factors of 50000 and 5000.

For ICP-MS measurements, an ELAN 5000A quadrupole ICP mass spectrometer (Perkin-Elmer/SCIEX, Canada) was used. Quantitative determination of element concentrations was performed applying external calibration. From replicate analyses of ca. 90 geochemical reference samples the precision and accuracy have been found to be better than $\pm 5\%$ and $\pm 10\%$, respectively (Dulski, in preparation).

Interference corrections are routinely applied to correct analyte isotopes for molecular and isobaric interferences. Most prominent interferences, when analysing common silicate rocks, result from the formation of MO⁺ and MOH⁺ species of Ba and light REE and MCl⁺ species of Ba only. Additional interferences occur for carbonatite samples with complex matrix composition and very high concentrations of REE. The most important

interferences on $^{178}\text{Hf}^+$ and $^{179}\text{Hf}^+$ result from MO^+ species of Dy. Furthermore, MCl^+ species of Ce, Pr and Nd have to be taken into account. The potential interferences on Hf by polyatomic species are summarised in Table 1a. From single element solutions (0.5 M HCl), the yield of interfering polyatomic species have been determined. Calculated interferent equivalent concentrations are given in Table 1b. Interference corrections on Hf up to 100 % may occur for samples with very high concentrations of Ce, Pr, Nd and Dy but low Hf contents. For determination of Hf concentrations ^{178}Hf is generally used because this isotope is less interfered than ^{179}Hf .

EVALUATION OF Zr/Hf RATIOS Most Zr and Hf data in literature are obtained by XRF and INAA, respectively. Both methods are able to analyse solid material, whereas ICP-MS has the disadvantage to work on dissolved material only. Unfortunately, in most of the compiled papers the analytical procedure does not focus on the specific problems of Zr and Hf determination. The most serious aspects will subsequently

be considered.

Zr determination by XRF needs corrections for Sr because the Sr $\text{K}\beta$ -line coincides with the Zr $\text{K}\alpha$ line, which is normally used. Because Zr is low in carbonatites compared to Sr, the interference is significant. Keeping in mind the necessary Sr-correction, Zr contents below 10 ppm should be viewed with suspicion. On the other hand, the extreme value for Zr of 13000 ppm associated with extreme value of 28% Sr (Nelson *et al.* 1988) may also be erroneous and is therefore omitted (Fig. 1). Another aspect is that Zr contents can as low as 1 ppm. Thus, the accuracy may not be as high as the data suggest and the uncertainties drastically increase with decreasing Zr contents in the samples.

Hf determination by INAA is a precise method when properly calibrated. Most Hf data are given by one digit only, which suggests that the values of about 0.1 ppm, which seems to be the detection limit, may be uncertain by at least a factor of 2. One of the problems is the high radioactivity of the abundant REE in the samples, which either leads to long waiting times or enlarged distances between sample and detector, both

Table 1 - Interferences on Hf measurements. a. Potential interferences by polyatomic species. b. Typical interferent equivalent concentrations (IEC) (m/e - mass to charge ratio).

a. Potential interferences by polyatomic species.

	Ce	Pr	Nd	Dy
^{178}Hf		$^{141}\text{Pr}^{37}\text{Cl}$	$^{143}\text{Nd}^{35}\text{Cl}$	$^{162}\text{Dy}^{16}\text{O}$ $^{161}\text{Dy}^{16}\text{O}^{1}\text{H}$
^{179}Hf	$^{142}\text{Ce}^{37}\text{Cl}$		$^{144}\text{Nd}^{35}\text{Cl}$ $^{142}\text{Nd}^{37}\text{Cl}$	$^{163}\text{Dy}^{16}\text{O}$ $^{162}\text{Dy}^{16}\text{O}^{1}\text{H}$

b. Typical interferent equivalent concentrations (IEC) (m/e - mass to charge ratio).

m/e	interfering element	concentration ($\mu\text{g/g}$)	analyte	IEC ($\mu\text{g/g}$)
178	Pr	1000	Hf	0.045
178	Nd	1000	Hf	0.012
178	Dy	1000	Hf	3.3
179	Ce	1000	Hf	0.011
179	Nd	1000	Hf	0.060
179	Dy	1000	Hf	6.4

reducing the intensities of the Hf peak, hence worsening the detection limit.

Hf and Zr determination by ICP-MS yields the results of both elements from the same solution. Here the highest uncertainty is the quantitative dissolution of the mineral zircon. Incomplete dissolution may induce some fractionation if the zircons have a complex history. Our experience is that memory effects in the tubes are also not negligible. Measured intensities are high enough to yield concentrations for Zr but not always for the less abundant Hf. The detection limit for Hf is only better by a factor of 2 than that of Zr, which is not enough to account for the lower abundance of Hf by a factor of about 40. Therefore, those Zr/Hf ratios based on Hf values near the limit of detection are given in italics in Table 2.

In summary, Zr contents lower than 10 ppm measured by XRF in alkaline rocks and particularly in carbonatites should be omitted from a rigorous discussion. Hf values lower than 1 ppm measured by INAA should also be considered to be unreliable. Zr and Hf measurements with ICP-MS seem to yield the most reliable results as long as Zr and Hf exceed 1 ppm and 0.1 ppm, respectively.

Bau (1996) defined a CHARAC field (CHARGE and RADIUS Controlled) in the Y/Ho vs. Zr/Hf ratio diagram by plotting the corresponding ratios of rocks from georeference materials with $\text{SiO}_2 < 60\%$ published by Govindaraju (1994). The observed

spread for Zr/Hf wt ratios was 24 to 45 with a mean corresponding to the chondritic ratio of about 38. Beside the involvement of metasomatised mantle rocks, the above spread also includes analytical uncertainties. The derived spread of Zr/Hf ratios in the CHARAC range is shown in all graphs in order to display data points that distinctively plot outside the chondritic range.

RESULTS All analytical results are compiled in Table 2.

Namibian Complexes The Ondurakorume carbonatite samples have Zr contents from <0.2 to 4.3 ppm, and Hf was below the detection limit of the ICP-MS for this particular matrix. The eight nephelinite samples from the Kalkfeld complex have Zr contents from 65 to 1000 ppm, Hf content from <1.2 to 15.6 ppm, resulting in super-chondritic Zr/Hf ratios ranging between 48 and 78 without any correlation between Zr/Hf ratio and Zr contents. Three carbonatite samples from Kalkfeld have Zr contents between 3.3 and 27.5 ppm, but Hf below the detection limit. The nephelinite samples from the Etaneno complex have Zr contents from 268 to 2100 ppm, Hf contents from 5.1 to 37.9 ppm, and super-chondritic Zr/Hf between 46 and 57. In the Otjisazu, complex the carbonatites have Zr contents from 89 to 980 ppm, Hf contents from <0.15 to 28.1 ppm, and Zr/Hf between 35 and 40. The syenites and

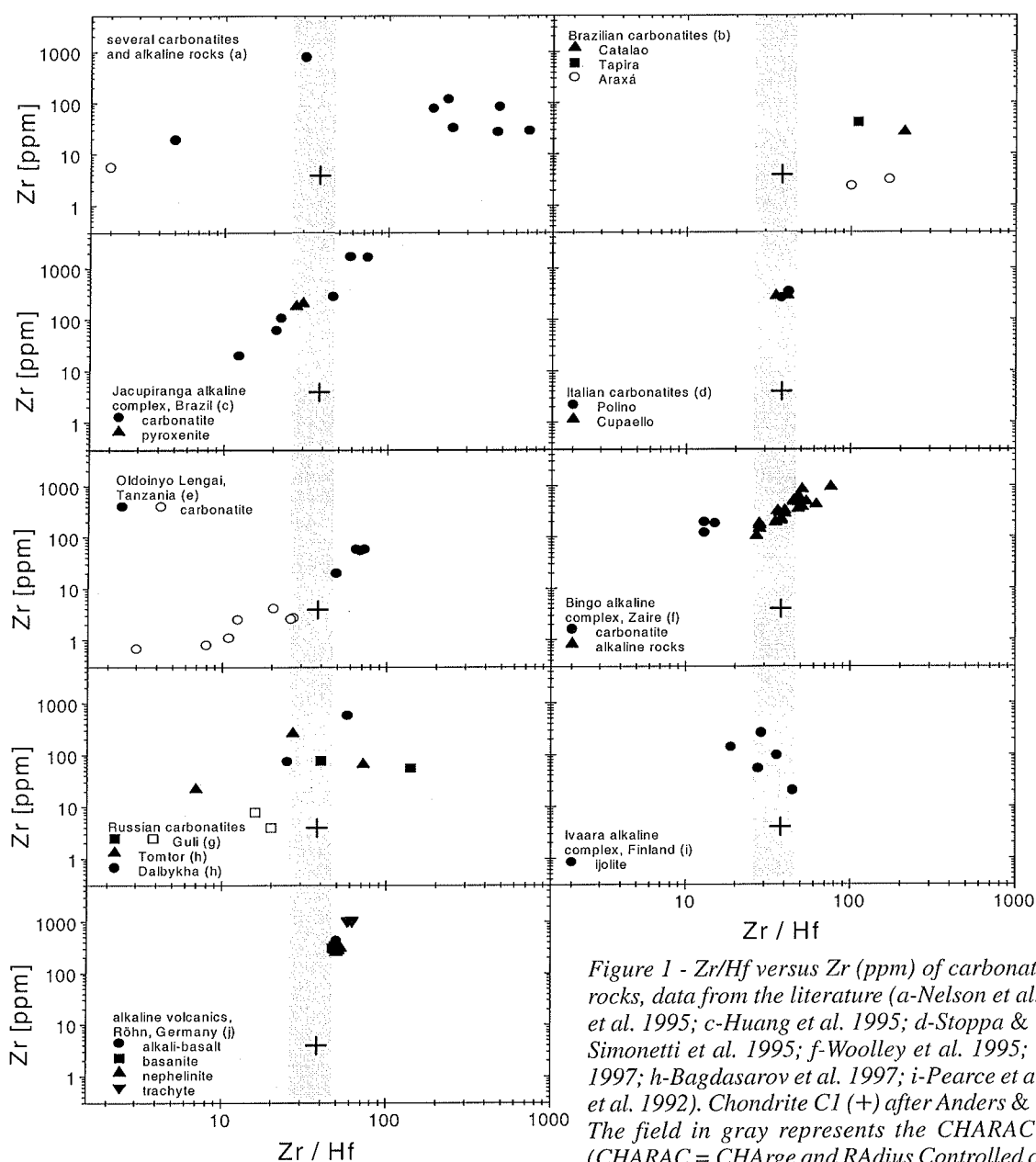


Figure 1 - Zr/Hf versus Zr (ppm) of carbonatites and alkaline rocks, data from the literature (a-Nelson et al. 1988, b-Toyoda et al. 1995; c-Huang et al. 1995; d-Stoppa & Woolley 1995; e-Simonetti et al. 1995; f-Woolley et al. 1995; g-Kogarko et al. 1997; h-Bagdasarov et al. 1997; i-Pearce et al. 1992; j-Enders et al. 1992). Chondrite C1 (+) after Anders & Grevesse (1989). The field in gray represents the CHARAC range of Zr/Hf (CHARAC = CHArge and RAdius Controlled cation behaviour; Bau 1996).

pyroxenites from Otjisazu have Zr contents from 79 to 490 ppm, Hf from 1.9 to 12.5 ppm, and Zr/Hf between 27 and 40.

Oldoinyo Lengai Natrocarbonatite, Tanzania The carbonatite sample from the Oldoinyo Lengai volcano has 3.5 ppm Zr and Hf content below the detection limit (<0.1 ppm).

Barra do Itapirapuã, Brazil The fresh samples from the Barra do Itapirapuã carbonatite have Zr contents from 13 to 48 ppm, Hf contents from 0.2 to 0.64, and Zr/Hf ratios from 49 to 130. Compared to the fresh samples, the two samples that underwent hydrothermal alteration have higher Zr contents (920 and 4970 ppm) and higher Hf contents (78.3 and 131 ppm), with Zr/Hf ratio between 93 and 100, in a range similar to that of the fresh samples.

Oka Complex, Canada The two carbonatite samples from

the Oka complex have Zr contents of 4 and 28 ppm, and Hf below the detection limit. One nephelinite have 12 ppm Zr and 0.15 ppm Hf (Zr/Hf = 79). The alnoite sample have 321 ppm Zr and 8.4 ppm Hf (Zr/Hf = 38).

Mountain Pass Carbonatite, USA The carbonatite sample from Mt. Pass has 213 ppm Zr and 5.6 ppm Hf (Zr/Hf = 38). The syenite sample has 111 ppm Zr and 5.3 ppm Hf (Zr/Hf = 21).

Hegau Alkaline Complex, Germany The five phonolite samples from the Hegau volcanic field have Zr contents ranging between 800 and 1500 ppm, Hf between 9.5 and 19.7 ppm, with a narrow range of Zr/Hf ratios between 77 and 90.

Kaiserstuhl Complex, Germany One carbonatite sample

Table 2 - Zr, Hf, Y, Ho and Sr concentration of carbonatite and alkaline rock samples (carb-carbonatite; pxt-pyroxenite; syen-syenite; neph-nephelinite; phon-phonolite).

Location	Barra do Itapirapuã, Brazil							Otjisazu, Namibia			
sample	1/37,40	1/33,45	2/16,20	5/13,00	1/34,90	3/37,90	1/54,70B	OS59	OS65		
rock type	carb	carb	carb	carb	carb	carb	carb	pxt	syen		
Zr (ppm)	18.6	42.5	4.42	29.8	12.4	922	4971	313	83.2		
Hf uncorrected	0.34	0.62		0.20		9.19	53.9	11.7	3.01		
Hf corrected	0.24	0.53		0.14		8.03	52.6	11.5	2.85		
Y	47.8	34.0	15.1	13.1	18.1	202	533	87.6	66.6		
Ho	1.80	1.29	0.60	0.50	0.62	7.35	17.4	3.29	2.58		
Sr	5510	6550	5770	9920	4780	8290	5330	787	5470		
Zr/Hf corrected	78.5	80.4		211		115	94.6	27.2	29.2		
Y/Ho	26.6	26.4	25.0	26.2	29.2	27.5	30.6	26.6	25.8		
Location	Otjisazu, Namibia							Kalkfeld, Namibia			
sample	OS85	OS90	OS155	OS158	OS67	OS95	OS156	OS159	KF50	KF54	
rock type	syen	pxt	carb	carb	carb	carb	carb	carb	carb	carb	
Zr (ppm)	494	68.9	7.0	107	88.5	5.80	145	976	22.9	11.3	
Hf uncorrected	12.7	1.88	0.23	2.83	2.53	0.34	3.84	28.1			
Hf corrected	12.5	1.72	0.14	2.76	2.42	0.20	3.76	27.5			
Y	87.2	53.0	9.28	85.0	104	140	80.3	802	137	435	
Ho	3.12	2.16	0.34	3.40	3.85	5.24	2.96	33.6	5.07	16.5	
Sr	2170	1080	7080	3410	12900	24000	4940	3720	20000	20000	
Zr/Hf corrected	39.4	40.1	51.5	38.8	36.5	29.4	38.5	35.5			
Y/Ho	27.9	24.5	27.3	25.0	27.0	26.7	27.1	23.9	27.0	26.4	
Location	Kalkfeld, Namibia							Ondurakorume, Namibia			
sample	KF94	KF115	KF200	KF201	KF208	KF60	KF97	KF99	ON57	ON58	
rock type	carb	neph	neph	neph	neph	carb	carb	carb	carb	carb	
Zr (ppm)	9.30	1001	96.6	350	339	4.60	34.4	3.70			
Hf uncorrected		15.8	1.60	4.47	4.28	0.77	0.60	0.33			
Hf corrected		15.7	1.50	4.40	4.21	0.25	0.33	0.17			
Y	504	30.3	7.63	4.02	4.98	474	307	232	141	123	
Ho	19.2	1.05	0.29	0.15	0.20	19.7	11.7	6.08	5.64	5.80	
Sr	6180	2260	1220	963	685	24000	24000	7150	20000	20000	
Zr/Hf corrected		63.9	64.6	79.6	80.6	18.5	105	21.9			
Y/Ho	26.3	28.9	26.4	26.8	24.9	24.1	26.2	38.2	25.0	21.2	
Location	Ondurakorume, Namibia							Etaneno, Namibia			
sample	ON60	ON62a	ON62b	ON65	ON76	ON78	ON50	ET5	ET151	ET152	
rock type	carb	carb	carb	carb	carb	carb	carb	neph	neph	neph	
Zr (ppm)	4.85	1.81	0.81	0.191	2.29	0.70	0.90	389	268	342	
Hf uncorrected	0.30	0.11	0.07	0.29	0.33	0.19	0.35	7.13	5.05	6.00	
Hf corrected	0.16	0.05	0.02	0.01	0.03	0.01	0.13	7.03	4.95	5.90	
Y	82.3	46.2	57.6	230	268	169	137	41.4	35.1	40.5	
Ho	3.23	1.79	1.94	9.27	10.7	6.80	5.81	1.53	1.27	1.47	
Sr	31440	4290	4990	25150	25860	18330	24000	888	816	805	
Zr/Hf corrected	31.1	38.3	43.8	21.5	67.3	124	7	55.3	54.0	58.0	
Y/Ho	25.5	25.8	29.7	24.8	25.0	24.9	23.6	27.1	27.6	27.6	
Location	Etaneno, Namibia			Hegau, Germany					Kaiserstuhl, Germany		
sample	ET153	ET163	ET169	AS1	AS5	AS6	AS9	AS22	KS1	KS2	KS3
rock type	neph	neph	neph	phon	phon	phon	phon	phon	carb.	phon.	phon.
Zr (ppm)	314	1321	2099	1039	1232	811	1530	895	2.40	631	635
Hf uncorrected	5.74	28.5	37.1	13.0	13.5	9.43	19.7	9.73	0.06	9.65	10.1
Hf corrected	5.64	28.3	37.0	13.0	13.4	9.41	19.7	9.72	0.01	9.63	10.0
Y	36.1	120	109	21.9	21.6	18.6	15.2	15.0	81.3	30.1	28.1
Ho	1.24	4.36	4.01	0.81	0.82	0.65	0.57	0.58	2.70	0.99	0.97
Sr	396	405	509	949	1510	883	572	1090	9350	2310	2370
Zr/Hf corrected	55.7	46.6	56.8	79.9	91.7	86.1	77.7	92.1	331	65.5	63.3
Y/Ho	29.1	27.5	27.2	27.0	26.3	28.6	26.7	25.9	30.1	30.4	29.0
Location	Oka, Canada				Mt. Pass, USA			Oldoinyo Lengai, Tanzania			
sample	OK1	OK2	OK3	OK4	AC-DS-1	ASC-5		OL1			
rock type	carb	carb	neph	aln	syen	carb		carb			
Zr (ppm)	3.80	31.5	11.8	330	114	213		3.50			
Hf uncorrected	0.07	0.12	0.16	8.47	5.30	5.78		0.06			
Hf corrected	0.01	0.03	0.15	8.39	5.29	5.75		0.06			
Y	82.8	99.9	13.0	57.0	7.68	30.6		6.63			
Ho	2.84	3.47	0.45	2.51	0.23	1.11		0.16			
Sr	13800	13180	1840	2640	475	5610		10500			
Zr/Hf corrected	397	1043	79.4	39.3	21.5	37.0		58.4			
Y/Ho	29.2	28.8	28.0	22.7	33.4	27.6		41.4			

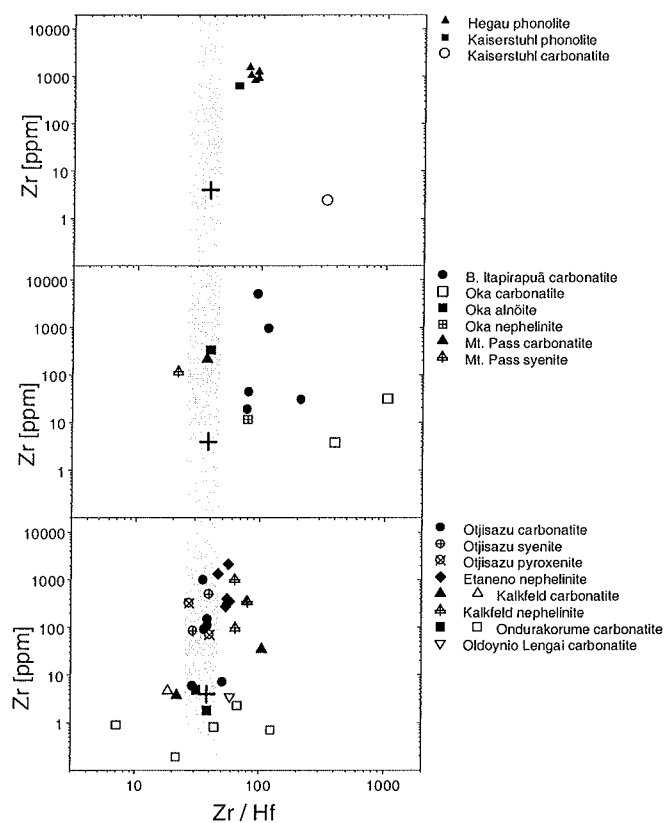


Figure 2 - Zr/Hf versus Zr (ppm) of carbonatites and alkaline rocks, data from this study. Chondrite C1 (+) after Anders & Grevesse (1989). The field in gray represents the CHARAC range of Zr/Hf (CHARAC = CHarge and RADIUS Controlled cation behaviour; Bau 1996).

from the Kaiserstuhl complex have 2.4 ppm Zr and Hf below the detection limits. Two associated phonolites have Zr contents between 625 and 626 ppm, Hf contents between 9.5 and 10 ppm, and Zr/Hf ratios of 66 and 63.

Zr/Hf ratios that fulfil the analytical criteria mentioned above are given by solid symbols in Figs. 2 to 5, whereas the remaining but less reliable ratios (italics in Table 2) are given by open symbols. From the distribution of the solid symbols the following signature can be delineated: all solid symbols fall into and above the indicated chondritic range, which does not exclude that some of those plotting below (open symbols) could also be real, but are questionable for analytical reasons.

The Y/Ho ratio of 57 samples including carbonatites and alkaline silicate rocks shows no significant fractionation, with an average of 27 ± 3 . The only exception is the natrocarbonatite sample from Oldoinyo Lengai, with a Y/Ho ratio of 44. This result is in agreement with previous data of Simonetti *et al.* (1997) for 10 samples of the same eruption, which shows a super-chondritic Y/Ho ratio of 45 ± 9 .

DISCUSSION Carbonatite melts can be generated by partial melting of fertile lherzolites (Wyllie 1987, Wallace & Green 1988, Falloon & Green 1989, 1990, Thibault *et al.* 1992, Dalton & Wood 1993, Kogarko *et al.* 1995). Their superfluid nature enables magma collection at very low degrees of interconnectivity and ascension rates to be very high (Hunter

& McKenzie 1989, Treinman 1989, Genge *et al.* 1995). Evidence from peridotite xenoliths also prove that carbonatite melts may be formed by liquid immiscibility at mantle depths (Amundsen 1987, Chalot-Prat & Arnold 1999). If tectonic conditions are not suitable for these melts to reach the Earth's surface, they undergo decarbonation and overprint the surrounding peridotite with their chemical signature, in a process known as carbonatite mantle metasomatism. This is characterised by the formation of apatite and clinopyroxene that shifts the residual peridotite composition from dunitic-harzburgitic to lherzolitic-wehrlitic (e.g., Wallace & Green 1988). Mineralogical changes are accompanied by the enrichment in Ca, REE (mainly LREE), Th, Nb, Zr, Sr and P (Yaxley *et al.* 1991, Dautria *et al.* 1992, Dupuy *et al.* 1992, Rudnick *et al.* 1993, Hauri *et al.* 1993, Ionov *et al.* 1993, 1996, Smellie *et al.* 1995, Zinngrebe & Foley 1995, Yaxley & Green 1996, Wiechert *et al.* 1997, Coltorti *et al.* 1999).

Super-chondritic Zr/Hf in mantle derived rocks is currently considered as a consequence of carbonatite metasomatism (e.g., Dupuy *et al.* 1992), but we found support for this assumption neither from our own data nor from the data compiled in the literature after screening for analytical artifacts.

The absence of a convincing correlation between Zr contents and Zr/Hf ratio in carbonatites and alkaline silicate rocks in Figs. 1 and 2 precludes a mechanism such as fractional crystallisation during magmatic evolution to explain non-chondritic ratio values, as it would result in a systematic variation of Zr concentration with Zr/Hf ratios. The carbonatite, syenite and pyroxenite from the Oijisazu complex, Namibia, have Zr/Hf varying in a similar, overlapping range (Fig. 3). From the two samples from Mt. Pass, USA, the carbonatite has chondritic Zr/Hf, while the coexisting syenite has a lower ratio of about 20. Published data for the Bingo alkaline complex, Zaire (Woolley *et al.* 1995), indicate lower Zr/Hf of carbonatite compared to coexisting ijolite, which plot around the chondritic ratio (Fig. 1). As the three carbonatite-alkaline rock complexes mentioned above display all possible scenarios in respect to Zr/Hf, liquid immiscibility or any other petrogenetic link between carbonatites and silicate rocks do not influence Zr/Hf in any specific way. If this were the case, an opposite and complementary behaviour of Zr/Hf between carbonatites and coexisting silicate rocks would be present. Additionally, relatively short-lived hydrothermal processes in carbonatites do not cause a shift on Zr/Hf, at least not in the Barra do Itapirapuã carbonatite, in spite of the much higher Zr content of the hydrothermally overprinted carbonatites (Fig. 4). Therefore, our data indicate that the fractionation of Zr/Hf is a not consequence of magmatic evolution or post-magmatic alteration of carbonatites. We are prone to consider that non-chondritic Zr/Hf in carbonatites is a consequence of heterogeneities of their source in the mantle, considering that even slight heterogeneities may become significant due to very low degrees of partial melting and the likely presence of Zr- and Hf-bearing accessory minerals.

Some problems arise when trying to calculate the fractionation of Zr/Hf ratio based on available partition coefficients for mantle minerals (Table 3). The accuracy of the experimental determination of partition coefficients for Hf in carbonatite systems is not very high (Hamilton *et al.* 1989, Klemme *et al.* 1995) and, therefore, calculation of Zr/Hf fractionation based on available partition coefficients between clinopyroxene and

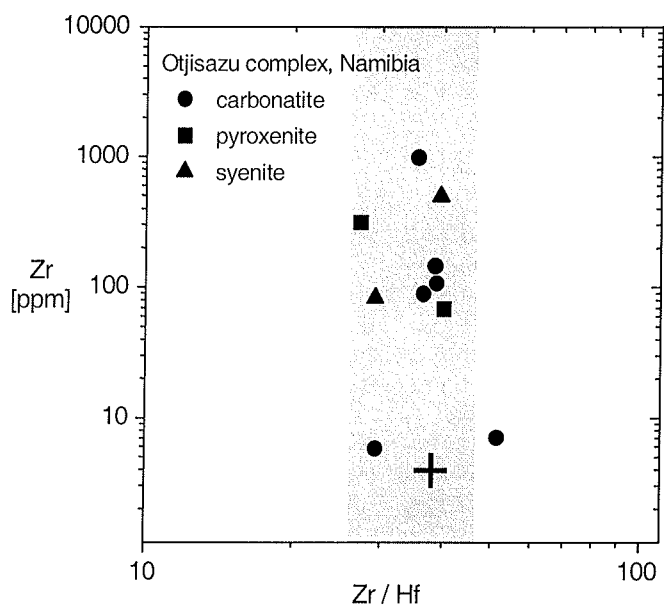


Figure 3 - Zr/Hf versus Zr (ppm) of coexisting carbonatites and alkaline rocks of the Otjisazu complex, Namibia. Chondrite CI (+) after Anders & Grevesse (1989). The field in gray represents the CHARAC range of Zr/Hf (CHARAC = CHARGE and RADIUS Controlled cation behaviour; Bau 1996).

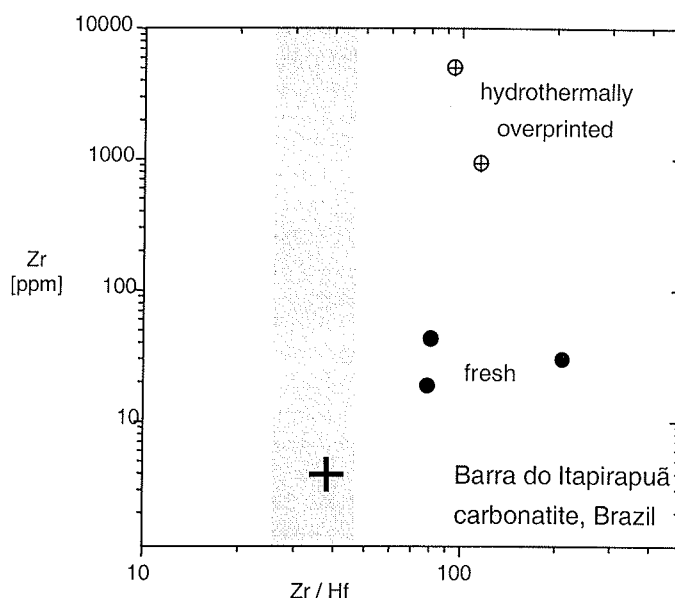


Figure 4 - Zr/Hf versus Zr (ppm) of four coexisting fresh and hydrothermally overprinted carbonatite from Barra do Itapirapuã. Chondrite CI (+) after Anders & Grevesse (1989). The field in gray represents the CHARAC range of Zr/Hf (CHARAC = CHARGE and RADIUS Controlled cation behaviour; Bau 1996).

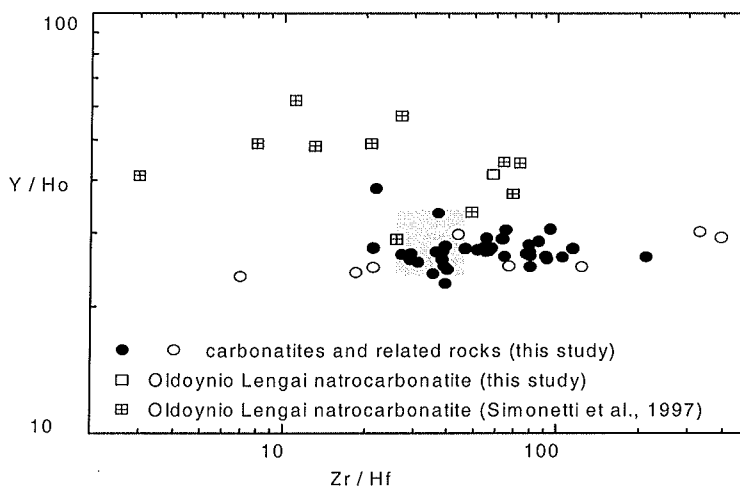


Figure 5 - Zr/Hf versus Y/Ho of carbonatites and alkaline rocks (CHARAC = CHARGE and RADIUS Controlled cation behaviour; Bau 1996).

Table 3 - Partition coefficients of Zr and Hf for melts and minerals of the mantle (1. Hart & Dunn 1993; 2. Klemme et al. 1995; 3. Dalpé et al. 1995; 4. average of literature data up to 1995 by Chazot et al. 1995; 5. Chazot et al. 1995; 6. Fujinawa & Green 1997; * estimated conditions for natural glasses in mantle xenoliths).

Phases	T (°C)	P	D_{Zr}	D_{Hf}	Ref
cpx / basaltic melt	1380	3 GPa	0.1234	0.256	1
cpx / carbonatitic melt	1050-1100	20 – 22 kbar	0.48 ± 0.37	0.16 ± 0.05	2
anf / basaltic melt	1100	1.5 Gpa	0.12 ± 0.01	0.33 ± 0.01	3
cpx / basaltic melt	--	--	0.122	0.256	4
cpx / basaltic melt	1100 *	1.5 Gpa *	0.030 – 0.353	0.085 – 0.246	5
anf / basaltic melt	1100 *	1.5 Gpa *	0.150 – 0.233	0.627 – 0.838	5
ap / cpx	1100 *	1.5 Gpa *	0.066 – 0.132	35.673	5
ap / anf	1100 *	1.5 Gpa *	0.044 – 0.108	2.894 – 14.564	5
anf / basaltic melt	1000-1050	0.5 Gpa	0.45 ± 0.1	0.6 ± 0.2	6
anf / basaltic melt	1000-1050	2.5 Gpa	0.1 ± 0.05	0.18 ± 0.05	6
gr / basaltic melt	1050	2.5 GPa	0.23 ± 0.08	0.1 ± 0.04	6

melt (Hart & Dunn 1993, Klemme *et al.* 1995, Smellie *et al.* 1995, Fujinawa & Green 1997) has to be considered with care. Although clinopyroxene is the most important source for carbonatite compounds in the upper mantle, the presence of accessory minerals such as zircon in the metasomatised mantle would overwhelm the role of clinopyroxene concerning the behaviour of trace element during partial melting (Baker & Wyllie 1992, Haggerty 1994). Experimental data for accessory minerals in mantle systems are not available, and the possible presence and spatial distribution of these minerals are also unknown.

Fractionation between Zr and Hf requires that factors other than charge and ionic radius control the geochemical behaviour of these elements. One of such factors may be alkalinity, which was used to separate Zr from Hf in aqueous solutions through fractional crystallisation of carbonates (De Boer 1927, in Gmelin 1941). In alkaline solutions, Zr is more effective than Hf to form stable complexes, then carbonate precipitation from this solution would fractionate Hf towards solid phase while Zr becomes enriched in solution. Stronger alkalinity of Hf prevents it from staying in an alkaline solution as long as Zr, which is less alkaline and therefore more reactive toward an alkaline medium. In the alkaline medium of carbonatites and related rocks, there is a tendency of Zr to be enriched in respect to Hf, even if this tendency is not so typical as previously believed. In the acidic media of a pegmatite, Hf is enriched in respect to Zr, leading to the crystallisation of hafnon, a Hf-rich mineral isomorph with zircon (Correia-Neves *et al.* 1974) and of cassiterite with Zr/Hf fractionated to values below the chondritic (Möller & Dulski 1983). Wang *et al.* (1996) report the formation of hafnian zircon in a granitic pegmatite, and observed a decrease in Zr/Hf with increasing degree of differentiation of the granite.

The analysed carbonatites and alkaline silicate rocks present chondritic Y/Ho, in spite of the shifts in Zr/Hf from chondritic to superchondritic (Fig. 5). Independent behaviour of the pair Zr-Hf (HFSE) in respect to Y-Ho (REE) should be caused by complexation of Y-REE by carbonate ligands. Olivine-melilitites from the Czech-German border present Zr/Hf higher than chondritic (up to 112; Seifert & Thomas 1995) and near chondritic Y/Ho, and the same is observed in mantle peridotites affected by carbonatite metasomatism (Rudnick *et al.* 1993). The natrocarbonatite lavas from Oldoinyo Lengai (Simonetti *et al.* 1997) fractionate Y/Ho to values higher than chondritic and no correlation is observed between Zr/Hf and Y/Ho. However, the uniqueness of the alkali-rich (Na) composition of Oldoinyo Lengai have to be taken into account. Whatever the process responsible for Zr/Hf fractionation, it has no influence on the Y/Ho systematics.

CONCLUSIONS A critical review of Zr and Hf abundances in carbonatites and associated alkaline rocks has been done in order to organize available knowledge on Zr/Hf ratios. Although Zr concentrations cover a range of four orders of magnitude, Zr/Hf ratios only vary within one order of magnitude, which is due to the chemical similarity of the two elements. A thorough examination of all data with respect to analytical inadequacies reveals that numerous data of Zr and particularly Hf cannot be correct because they are near the detection limits. Excluding these analytical artifacts, it turns out that carbonatites and coexisting alkaline silicate rocks show chondritic to superchondritic ratios only. Not one example for sub-chondritic ratios could be found with certainty. These results corroborate the findings of Nelson *et al.* (1988). However, since superchondritic Zr/Hf ratios are not typical of carbonatites, this element ratio alone cannot be used as conclusive evidence for the metasomatic activity of carbonatite melts in the upper mantle.

The lack of a clear correlation between Zr/Hf and the Zr concentration strongly suggests that the shift of the element ratio is not a consequence of fractional crystallisation of a particular mineral phase carrying a non-chondritic Zr/Hf ratio. Furthermore, the lack of an opposite and complementary behaviour of Zr/Hf between carbonatites and coexisting silicate rocks indicates that liquid immiscibility is not responsible for Zr/Hf fractionation. Therefore, we consider the anomalous Zr/Hf ratio in carbonatites as inherited from their mantle source.

It is also relevant that, although Zr/Hf variation from the chondritic value occurs in several cases, it is not followed by Y/Ho fractionation. Hence, carbonatites do not display a non-CHARAC type behaviour in the sense of Bau (1996), which would imply in fractionation of both element ratios. Our data rather shows that the processes that control the fractionation of HFSE in carbonatites operate through decoupling of Zr-Hf in respect to Y-Ho (REE).

Acknowledgements We are grateful for samples provided by Minerpar S.A. (Barra do Itapirapuã carbonatite), B. Böhn (Namibian samples), K. Bell (Oldoinyo Lengai carbonatite), E. Hegner (Hegau phonolites). To D.P. Gold who guided the excursion to the Oka complex on the MAC/GAC'97 meeting, during which samples for this study were collected. Discussions with B. Böhn and W. Irber strongly improved this manuscript. To W. Kraus Jr. for corrections of the English version of the manuscript, to C. Wiesenberg and X. Zander for the analytical support, to M. Bau for critical comments on various aspects of the study. The first author acknowledges financial support from the Brazilian agency CNPq (Proc. 290051/94-0). To the RBG reviewers for suggestions to the manuscript.

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Manuscrito A-1271

Recebido em 05 de novembro de 2001

Revisão dos autores em 10 de outubro de 2002

Revisão aceita em 12 de outubro de 2002